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Emerging Pollutants Removal in Wastewater Treatment Plants: A review and their implications in a river basin in Uruguay

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Master of Science Thesis
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CHAPTER 1 **Abstract**

The continuous synthesis of new chemical products and the widespread use in all human activities makes the study of the impact of emerging contaminants in the aquatic environment more relevant. By definition in the category of emerging pollutants are compounds that are ubiquitous in water in very small concentrations and there is no complete knowledge about the occurrence in water bodies or exposure of biota to them or the toxic effects they cause, but by their characteristics are presumed to have adverse effects on the environment or human health. This paper compiles studies on emerging pollutants (EP) in water, reviewing the sources of EP and the path they make in the environment, the classes of EP, the occurrence in wastewater treatment plants (WWTP) and in natural water bodies, and their effects on ecosystems. Environmental risk assesses are compiled which allow the identification of EPs that present the greatest risk and which should be directed to greater effort in the research and monitoring programs. The review concludes with the compilation of studies on the behavior of emerging contaminants in WWTP with different technologies used. In addition, it is included a study of environmental risk by emerging contaminants in the Santa Lucía Chico basin of Uruguay. This study identifies compounds that must be studied further to determine if it has pollutant potential.

CHAPTER 2 **Acknowledgements**

Thanks to the public education of my country for giving me opportunities.

CHAPTER 3

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3.4. Abbreviations

AE	Alcohol ethoxylate
AO	Amine oxide
APE	Ethoxylated alkylphenols
BCF	Bioconcentration factor
CAS	Conventional activated sludge
CMC	Critical micellar concentration
CWWTP	Conventional wastewater treatment plant
DBP	Dibutyl phtalate
EC50	Half maximal effective concentration
EP	Emerging pollutant
HRT	Hydraulic retention time
K_d	Coefficient partion water-solid
K_{oc}	Organic carbon-water partitioning coefficient
K_{ow}	Octanol-water coefficient
LC50	Half lethal concentration
LOEL	Lowest observable effect level
LOQ	Limit of quantification
MBR	Membrane biological reactor
NOAEL	No observed adverse effect level
NOEC	No observable effect concentration
NP	Nonylphenol
OP	Octylphenol
PAE	Phthalate ester
PCP	Personal care products
PEC	Predicted environmental concentration
PFC	Perfluorinated compound
PNEC	Predicted non-effect concentration
QAC	Quaternary ammonium compound
RQ	Risk quotient
SRT	Sludge retention time
SSD	Species sensivity distribution
WWTP	Wastewater treatment plant

CHAPTER 4 **Review of Emerging Pollutants**

4.1. Emerging Pollutants

4.1.1. Introduction

The continuous technical and technological development has led to an increase in the synthesis of new chemicals that are continuously incorporated into the environment. These new products are incorporated into the water cycle through: (i) point source discharges such as wastewater treatment plants (WWTP), and industrial discharges; and (ii) through diffuse source discharges such as runoff of pesticides, septic trucks discharges, ship discharges, and natural disasters, among others.

Many of these chemical compounds are found in the water sources at very small concentrations. In spite of this, some of these compounds are toxic and can affect aquatic plants, organisms, humans, and ecosystems. Effects such as immune dysfunction, carcinogenesis, endocrine disruption, and growth disorder can be observed after a medium and long term exposures to these compounds at a very low doses. The bioactive and/or persistent chemical pollutants found in the water bodies in a range of concentrations from pg/L to μg/L are referred to micro-pollutants.

Due to methodological, technological, and economic limitations, there are a large number of chemical substances without a known demonstrated toxicological effect; however, based on their chemical composition, physicochemical properties, and partial toxicological studies it can be inferred that there may be a source of biological risk. These substances are known as emerging pollutants (EPs)[1].

The advance in the analytical determination/detection methods of chemical compounds at trace concentrations is allowing the identification of previously undetected substances in environments where changes in organisms or directly toxic effects are being registered; consequently, new research lines on emerging pollutants have been developing.

4.1.2. Source and pathways of emerging pollutants in the environment

The origin of micro-pollutants and emerging pollutants (EPs) is very varied; they can be found in practically all human activities. EPs can be found in drugs for human and veterinary use, pesticides, herbicides, insecticides, plasticizers, surfactants in detergents, and cosmetic

[1] Definition of Emerging Pollutants: pollutants that are currently not included in routine monitoring programmes at the European level and which may be candidates for future regulation, depending on research on their (eco)toxicity, potential health effects and public perception and on monitoring data regarding their occurrence in the various environmental compartments. (Source http://www.norman-network.net/)

products. This implies that the sources of pollution can be either domestic, industrial, agricultural, or came from the livestock, among others.

The occurrence of emerging pollutants in different matrices will depend both on their properties, as well as on the characteristics of the receptor bodies. Contaminants of diffuse origin will reach the receptor bodies depending both on their physical chemical properties such as volatility, polarity, adsorption, persistence, among others, and on the properties of the matrices with which they interact such as the ability of the soil to adsorb these compounds. The EPs that are of point origin, depending on their properties can be found either dissolved, in the sediments, or in a particulate form.

The EPs can undergo transformation processes or remain unchanged. Biodegradation will depend both on their bioavailability, and on the presence of microorganisms capable of degrading these compounds. The natural or induced degradation of certain compounds can produce sub-products with equal, lesser, or greater toxicity than the original compound.

Micro-pollutants and EPs, once incorporated into the aquatic environment, bio-accumulate within organisms or in trophic chains, accumulate in the sediments, or can follow a degradation process.

The presence of micro-pollutants and EPs exhibit an impact on the environment and compromise the quality of the water resources; particularly for activities involving water reuse such as irrigation, or as a source for drinking water.

The Figure 4-1 shows in a schematic way the sources and pathways of the EPs in the environment.

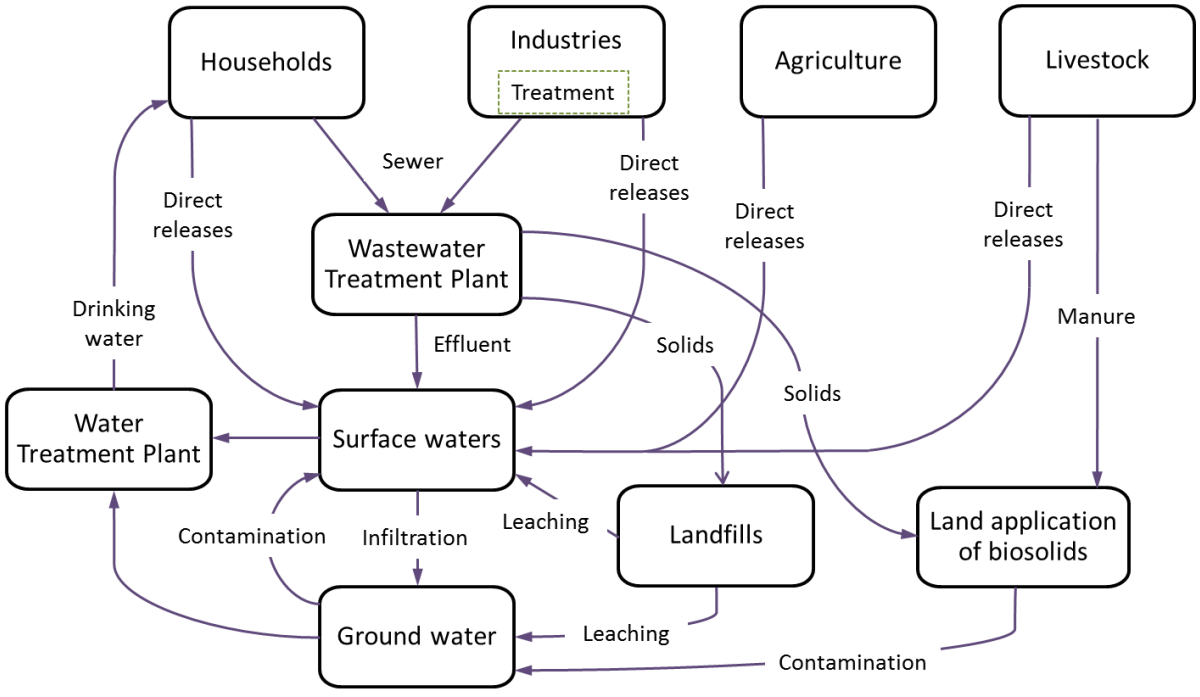


Figure 4-1 *Sources and pathways of Emerging Pollutants. Modified from Petrovic, et al. 2016*

There is a great shortage of knowledge on the behaviour of EPs in ecosystems, including their fate on ecosystems and in the food chains. Moreover, the analytical determination limitations of these compounds, makes extremely challenging conducting studies related to the risk analysis for the aquatic environment as well as for the human health.

4.1.3. Classes of emerging pollutants

According to information collected by Norman Network (Norman), more than 500 EPs have been reported in the aquatic environment in Europe. EPs can be classified by their occurrence, origin, use, molecular similarity, physical chemical characteristics, biochemical activity, and/or environmental and health effects.

Classes according to use

The classification by use groups microcontaminants according to the application they have. This classification allows to associate to an activity a series of pollutants facilitating to focus in a smaller number of substances to investigate and regulate. Table 4-1 shows the classification of EPs commonly used according to their use. Some compounds are overlap under several categories.

Table 4-1 *Common Classes of Emerging Pollutants. Modified from Raghav, et al.2013*

Class of Emerging Pollutants	Example	Definition
Antibiotics	Tetracycline, Erythromycin	Medications that fight bacterial infections, inhibiting or stopping bacterial growth.
Antimicrobials	Triclosan	Biochemicals that kill or inhibit the growth of microorganisms including bacteria and fungi.
Detergent metabolites	Nonylphenol	Chemical compounds formed when detergents are broken down by wastewater treatment or environmental degradation.
Disinfectants	Alcohols, Aldehydes and oxidizing agents	A chemical agent used on non-living surfaces to destroy, neutralize, or inhibit the growth of disease-causing microorganisms.
Disinfection by-products	Chloroform, Nitrosodimethylamine (NDMA)	Chemical substances resulting from the interaction of organic matter in water with disinfection agents such as chlorine.
Estrogenic compounds	Estrone, Estradiol, Nonylphenol, Bisphenol A	Natural or synthetic chemicals that can elicit an estrogenic response.
Fire or flame retardants	Polybrominated Diphenyl Ethers (PBDEs)	Any of several materials or coatings that inhibit or resist the spread of fire.
Fragrances	Galaxolide	Chemical substances that impart a sweet or pleasant odour.

Class of Emerging Pollutants	Example	Definition
Insect repellents	DEET (N,N-diethyl-meta-toluamide)	Chemical substances applied to skin or other surfaces to discourage insects from coming in contact with the surface.
PAHs (poly-aromatic hydrocarbons)	Benzo(a)pyrene, Fluoranthene, Naphthalene	A large group of chemical substances usually found in the environment as a result of incomplete burning of carbon-containing materials like fossil fuels, wood, or garbage.
Personal Care Products	Para-hydroxybenzoate	Chemical substances used in a diverse group of personal items including toiletries and cosmetics.
Pesticides or Insecticides	Permethrin, Fenitrothion, Bacillus thuringiensis israelensis (B.t.i.)	Chemical substances or microbiological agents that kill, incapacitate or otherwise prevent pests from causing damage.
Pharmaceuticals	Fluoxetine (Prozac), Carbamazepine, Diphenhydramine	Chemical substances used in the prevention or treatment of physiological conditions.
Plasticizers	Dioctyl Phthalate (DOP)	Chemical additives that increase the plasticity or fluidity of a material.
Reproductive hormones	Dihydrotestosterone (DHT), Progesterone, Estrone, Estradiol	A group of chemical substances, usually steroids, whose purpose is to stimulate certain reproductive functions.
Solvents	Ethanol, Kerosene	Chemical solutions, other than water, capable of dissolving another substance.
Steroids	Cholesterol, Coprostanol, Estrone, Progesterone	A large group of fat-soluble organic compounds with a characteristic molecular structure, which includes many natural and synthetic hormones.
Surfactants	Sodium Lauryl Sulfate	Chemical substances that affect the surface of a liquid.

Classes according to simplifying criteria

There is a great effort to find relationships that links physico-chemical properties of the substances with the most suitable removal technology for them. For example, it is sought to predict the behavior of substances that have a certain neutral charge, or molecular structure in processes such as adsorption and filtration. One difficulty to generalize this type of relationships is that it is often worked with affluents that are complex mixtures in environments less controlled than in a laboratory and can generate different reactions expected in the processes designed. In this sense, there are several simplifying criteria for EP classification. These criteria should not be taken as general, each criterion has substances that are exceptions.

Verlicchi, et al. 2012 mentions the following simplifying classification criteria:

1- According biological trasformation rate (k_{biol}) or half - live

$k_{biol} < 0.1$ L/(gSS d)	poor degradability
$0.1 < k_{biol} < 10$ L/(gSS d)	quite good biodegradability
$k_{biol} > 10$ L/(gSS d)	very good degradability

This parameter indicates how much time it takes to biodegrade a compound in half. The rate of degradation can indicate how much hydraulic retention time (HRT) is required for degradation to occur within the plant or the degree of persistence. Also given an HRT what is the charge of the compound that will end its biodegradation process in the body of water where it was discharged.

2- According to partition coefficient octanol-water (K_{ow})

$\text{Log } K_{ow} < 2.5$	high hydrophilic compound
$2.5 < \text{Log } K_{ow} < 4$	moderate hydrophilic compound
$\text{Log } K_{ow} > 4$	high lipophilic compound

This parameter allows to predict the potentiality of the substances to be incorporated to the biomass by their easiness to be adsorbed or not to organic matter among other phenomena.

3- According partition coefficient (K_d)

$\text{Log } K_d < 2.7$	low adsorption potential
$\text{Log } K_d > 2.7$	high adsorption potential

From the determination of K_d of a substance can be predicted the amount of this that will be sorbed by sludge, sediments and soils. Ternes, et al. 2004, determined the partition coefficient in primary and secondary sludge in a German WWTP for a significant number of drugs and polycyclic fragrances. The study shows that the sorption removal of compounds with K_d less than 500 L/kgSS ($\text{Log } K_d < 2.7$) is negligible compared to the total mass of the compound and, that the rate of removal by sorption to the sludge in a WWTP of a compound can be reasonably predicted through estimating K_d.

At steady state the sorbed concentration and the soluble concentration are related through the following expression:

$$C_{sorbed} = K_d \times SS \times C_{soluble}$$

Estimating the amount of a compound sorbed in the sludge of a reactor is done by taking into account the amount of sludge generated per unit of treated water instead of the SS concentration of the reactor. It is estimated that the SRT is sufficiently long that the recirculated sludge is in equilibrium with the aqueous phase and is not able to adsorb the continuous incoming compounds. Only newly generated sludge is capable of supporting incoming loads.

The study found different K_d for the same compound in the primary sludge than for the secondary sludge. The difference in composition and pH between the sludge influences the sorption mechanisms. In the secondary sludge, the biomass represent the largest proportion of suspended solids, while the primary sludge contains fewer microorganisms and higher inorganic fraction.

The absortion is due to hydrophobic interactions of the aliphatic and aromatic groups of a compound with the lipophilic cell membrane of the microorganisms and the lipid fractions of the sludge. Adsorption is the electrostatic interactions of positively charged groups of chemicals with negatively charged surfaces of microorganisms.

Non-ionic compounds (neutral pH) tend to be absorbed into the lipid fractions or absorbed in the organic matter at environmental pH values via van der Waals interactions. The pH of the sludge determines the adsorption capacity of compounds containing functional groups which can be protonated and deprotonated. The pH difference between primary and secondary sludge for certain compounds (eg diclofenac and cyclophosphamide) determines significant differences in the K_d of each sludge.

4.1.4. Occurrence of emerging pollutants

Introduction

The occurrence of emerging pollutants in influent and effluent streams at WWTP, as well as in natural bodies can be pbserved both in the liquid and solid matrices. The compounds may be either dissolved or adsorbed on suspended particles or in sediments.

This chapter compiles available information on the presence of emerging pollutants in influent and effluent streams of conventional WWTP with emphasis in (but not limited to) Europe.

Most of the available information refers to the presence of EPs in the aqueous phase. Based on their physicochemical properties, some compounds are likely to be dissolved in water, not justifying the efforts of determining/analysing the occurrence of these compounds in the solid phase. However, there are other compounds more likely to be fully or partially adsorbed in the solid phase; for the later compounds there is not much information available on the literature regarding their occurrence in terms of presence and concentrations/loads. The lack of information often leads to an underestimation of the burden of emerging pollutants present in solid matrices, which will be later assimilated by plants with the potential subsequent toxicological and epidemiological effects.

The concentration of a particular compound in the influent to a WWTP can vary appreciably from one plant to another. Firstly, it depends on the type of wastewater discharging into the sewer; type of wastewater (from different activities) may include: domestic wastewater, industrial wastewater, infiltrations, runoff, among others. Local regulations and variations in the costs of certain compounds may discourage the use of particular substances and promote

the use of other alternatives. Moreover, the climate may influence the seasonal variation of the concentrations of some of these compounds including antiallergics, repellents, sun protectors, among others. Population habits such as frequency at which laundry is done, or for instance the use of social illicit drugs may also influence the different patterns of occurrence of emerging pollutants observed at WWTP.

In addition, the concentrations of emerging pollutants observed at different effluents from conventional WWTP depend on their ability to be removed, and the avility of the plant to remove then; this is discuss in detail in section 4.2.1 Removal of emerging pollutants in conventional wastewater treatment plant4.2.1.

The presence of emerging pollutants in a water body will depend both on the point and diffuse sources, and on the characteristics of the receiving body. The effects of pollution by these contaminants are observed primarily when there is a need for either direct reusing the treated wastewater, or for reusing the sludge.

Occurrence of pharmaceutical compounds

The sources of pharmaceuticals compounds in the water came from drugs for human or veterinary use, and from the pharmaceutical industries. These compounds can reach the WWTP from residences, hospitals, industries, or by an improper disposal of drugs from stocks. The loads of these compounds have shown seasonal variations.

Verlicchi et al. 2012 compiled the presence of pharmaceutical compounds in influent and effluent streams of 224 conventional activated sludge (CAS) WWTP and 20 WWTP equipped with biological membrane reactors (MBR)s. The processes involved in these plants consisted in pre-treatment (screening and grit removal), primary settling, and biological treatment CAS with different configurations provided with either secondary clarifier or membranes (as in MBRs).

Most of the evaluated WWTPs (68% of the plants) were located in Europe (Spain, Germany, Italy, Switzerland, Sweden, Austria, UK, Finland, France, Greece and Denmark), 14% in America (USA, Canada and Brazil), 14% in Asia (China, Japan, Israel, South Korea and North Korea), and 4% in Australia.

This review compiles the presence of 118 pharmaceutical substances divided into 17 therapeutic classes. Table 4-2 shows the reported contaminants grouped according to the therapeutic class in the influent and effluent streams of the conventional WWTPs. A detailed description of the composition, structure and properties of the detected compounds is presented in the Appendix A.

The compounds to be evaluated in the project LIFE EMPORE are highlighted in light grey colour in the Table 4-2 below.

Table 4-2 *Occurrence of Pharmaceutical compounds in raw influent and effluent streams of conventional WWTPs. Modified from Verlicchi, et al. 2012*

Therapeutic class	Pharmaceutical compound	Number of papers reported	Average concentration raw influent µg/L	Average concentration effluent µg/L
Analgesics / anti-inflammatories	5-Aminosalicylic acid	1	14	0,64
	Acetaminophen	15	38	0,89
	Acetylsalicylic acid	2	3,1	0,36
	Aminopyrine	2	no available	1
	Codeine	5	6,9	1,7
	Dextropropoxyphene	1	0,03	0,1
	Diclofenac	36	1	0,8
	Dipyrone	1	14	4,9
	Fenoprofen	6	0,05	0,02
	Flurbiprofen	2	no available	0,34
	Hydrocodone	1	0,12	0,01
	Ibuprofen	43	37	3,6
	Indomethacin	8	0,47	0,21
	Ketoprofen	21	1,1	0,36
	Ketorolac	1	1,1	0,42
	Meclofenamic acid	1	no available	0,03
	Mefenamic acid	9	1,1	0,63
	Naproxen	30	6	1
	Phenazone	3	0,04	0,16
	Propyphenazone	3	0,05	0,04
	Salicylic acid	4	17	0,17
	Tolfenamic acid	1	no available	0,03
	Tramadol	2	32	20
Antibiotics	Amoxicillin	1	0,24	0,01
	Azithromycin	4	0,4	0,16
	Cefaclor	1	0,74	0,01
	Cefalexin	4	3,2	0,13
	Cefotaxime	2	0,014	0,02
	Chloramphenicol	3	1	0,05
	Chlortetracycline	2	0,005	0,005
	Ciprofloxacin	15	1,6	0,86
	Clarithromycin	7	1,3	0,29
	Clindamycin	1	0,004	0,01
	Cloxacillin	1	0,16	0,001
	Doxycycline	2	0,066	0,04
	Enoxacin	1	no available	0,03
	Enrofloxacin	3	0,05	0,01
	Erythromycin	19	1,8	0,7

Therapeutic class	Pharmaceutical compound	Number of papers reported	Average concentration raw influent µg/L	Average concentration effluent µg/L
	Lincomycin	3	0,07	0,06
	Lomefloxacin	1	no available	0,28
	Metronidazole	2	0,36	0,25
	Norfloxacin	12	0,23	0,06
	Ofloxacin	12	5,1	0,45
	Oxytetracycline	2	0,003	0,01
	Penicillin G	2	0,004	0,004
	Penicillin V	1	0,01	0,03
	Roxithromycin	12	1,5	0,5
	Spiramycin	1	no available	no available
	Sulfachloropyridazine	1	0,19	0,06
	Sulfadiazine	3	5,1	0,04
	Sulfadimethoxine	3	0,07	0,09
	Sulfamethazine	4	0,16	no available
	Sulfamethoxazole	31	0,92	0,28
	Sulfapyridine	4	3,3	0,33
	Sulfasalazine	2	0,031	0,005
	Sulfathiazole	3	0,11	0,01
	Tetracycline	5	0,33	0,14
	Trimethoprim	25	0,76	0,36
	Tylosin	1	0,055	no available
Antidiabetics	Glibenclamide	1	8,7	no available
Antifungals	Clotrimazole	1	0,03	0,02
	Diltiazem	3	0,7	0,12
Antihypertensives	Enalapril	1	no available	no available
	Hydrochlorothiazide	5	3,9	3,3
Barbiturates	Phenobarbital	1	0,07	no available
Beta-blockers	Acebutolol	2	no available	0,05
	Atenolol	14	4,5	3,7
	Betaxolol	3	0,008	0,12
	Bisoprolol	2	0,3	0,23
	Carazolol	1	no available	0,07
	Celiprolol	2	0,13	0,19
	Metoprolol	12	0,24	0,32
	Nadolol	1	no available	0,04
	Oxprenolol	1	no available	0,02
	Propranolol	12	0,32	0,17
	Sotalol	6	0,6	0,75

Therapeutic class	Pharmaceutical compound	Number of papers reported	Average concentration raw influent µg/L	Average concentration effluent µg/L
	Timolol	1	no available	0,04
Diuretics	Bendroflumethiazide	1	0,05	0,004
	Furosemide	3	2,4	0,66
Lipid regulators	Bezafibrate	15	3,5	0,9
	Clofibrate	2	no available	0,3
	Clofibric acid	16	0,22	0,21
	Etofibrate	1	no available	0,05
	Fenofibrate	3	no available	0,11
	Fenofibric acid	5	0,21	11
	Gemfibrozil	14	2,4	0,93
	Pravastatin	4	0,49	0,02
	Simvastatin	1	0,004	0,002
Psychiatric drugs	Amitriptyline	1	3,1	0,14
	Carbamazepine	31	1,2	1,04
	Diazepam	6	22	9,1
	Fluoxetine	8	0,54	0,24
	Gabapentin	2	13	2,6
	Lorazepam	1	no available	0,2
	Norfluoxetine	2	0,012	0,01
	Oxcarbazepine	1	0,03	no available
	Paroxetine	2	0,016	0,007
	Valproic acid	1	0,14	no available
Receptor antagonists	Cimetidine	2	4,1	3,5
	Famotidine	1	0,08	no available
	Loratadine	1	0,03	no available
	Omeprazole	1	0,85	0,63
	Ranitidine	6	2,7	0,51
	Valsartan	1	2,5	0,33
Hormones	Estradiol	11	0,25	0,01
	Estriol	4	0,17	0,016
	Estrone	12	0,08	0,03
	Ethinylestradiol	10	0,02	0,003
Beta-agonists	Clenbuterol	1	no available	0,052
	Fenoterol	1	no available	0,04
	Salbutamol	4	0,1	0,06
	Terbutaline	1	no available	0,07
Antineoplastics	Cyclophosphamide	1	no available	0,012
	Ifosfamide	3	0,14	0,97

Therapeutic class	Pharmaceutical compound	Number of papers reported	Average concentration raw influent µg/L	Average concentration effluent µg/L
	Tamoxifen	2	0,17	0,34
Topical products	Crotamiton	1	1,5	0,66
Antiseptics	Triclosan	13	1,9	0,32
Contrast media	Iopromide	5	2,2	2,5

Within the group of analgesics and anti-inflammatories the most studied compounds are ibuprofen, diclofenac, and naproxen. The compounds that register the highest average concentrations in the influent are acetaminophen, ibuprofen, and tramadol; while in the effluent are tramadol, dipyrone, and ibuprofen.

In the group of antibiotics the most studied compounds are sulfamethoxazole, trimethoprim, and erythromycin. The compounds that record the highest average concentrations in the influent are ofloxacin, sulfadiazine, and sulfapyridine, while in the effluent ciprofloxacin, erythromycin, and roxithromycin.

The most studied psychiatric drugs are carbamazepine, fluoxetine, and diazepam. The compounds that register the highest average concentrations in the influent are diazepam, gabapentin, and amitriptyline; while in the effluent are fenofibirc acid, diazepam, and gabapentin.

Within the group of hormones the compounds most studied are estrone, estadiol, and ethinylestradiol. The compounds that register the highest average concentrations in the influent are estradiol, estriol and estrone; while in the effluent the hormones were found at extremely low concentrations, always lower than 0.11 µg/L.

The data presented so far refer to studies evaluated analysing the aqueous phase. To complete the presence of pharmaceutical compounds in the influent to the treatment plants it is necessary to analyse the compounds that arrive with the solid phase. Such studies are less frequent. According to Petrie, et al. 2015 the compounds amitriptyline, EMDP, dosulepin, fluoxetine, norfluoxetine, triclosan, ofloxacin, and ciprofloxacin exhibited concentrations in the solid phase concentrations higher than 20% of the total amount found un the total samples (liquid and solid).

Occurrence of pesticides

The presence of pesticides in conventional WWTP is not usual since the main source comes from agricultural activities associated with diffuse sources such as runoff and soil erosion.

Pesticides presence at WWTP come from industries that manufacture these type of products, from domestic use, and from runoff on green areas treated with these substances which they may end up in the sewage system.

In the work carried out by Köck-Schulmeyer, et al. 2013 the presence of 22 pesticides was evaluated. The selection was based on the degree of their use, the current regulations, and analytical capabilities using, liquid chromatography tandem mass spectometry (LC-MC / MS). The evaluation was carried out at three WWTP in Catalonia, Spain.

Table 4-3 shows the evaluated pesticides grouped according to families in the influent and effluent samples of the conventional WWTPs.

Table 4-3 *Frequency of detection and mean concentration of the individual pesticides in the influent (n=24) and effluent (n=24) wastewater samples collected from the three WWTP. Modified from Köck-Schulmeyer, et al. 2013*

Family	**Pesticide**	**Detection Frequency** %	**Average concentration influent** ng/L	**Detection Frequency** %	**Average concentration effluent** ng/L
Acids	2,4D	33	32,1	50	42,9
	Bentazone	0	---	4	12,2
	MCPA	25	7,64	8	15,1
	Mecoprop	25	106	38	17,3
Anilides	Alachlor	4	2,59	0	---
	Metolachlor	0	---	0	---
	Propanil	33	8,98	46	9,42
organophosphates	Diazinon	96	133	88	281
	Dimethoate	25	4	21	49,1
	Fenitrothion	0	---	0	---
	Malathion	0	---	4	0,48
Phenylureas	Chlortoluron	13	3,94	8	98,2
	Diuron	88	93	88	127
	Isoproturon	0	---	8	13,2
	Linuron	0	---	0	---
Thiocarbamate	Molinate	0	---	0	---
Triazines	Atrazine	17	1,24	63	124
	Cyanazine	0	---	0	---
	Desethylatrazine	13	24,1	4	22,7
	Deisopropylatrazine	38	13,7	21	38,8
	Simazine	29	7,27	54	169
	Terbuthylazine	46	20,6	5	

Most of the compounds were found at concentrations below 1 μg/L in the influent. The removal of these compounds at the WWTP was insignificant with even negative removal cases reported.

The pesticides reported at the larger frequency were diazinon and diuron ata frequency greater than 88%. On the other hand, cyanazine, fenitrothion, linuron, metolachlor and molinate were not even observed at the evaluated samples. Alchlor was observed only in one influent sample; while bentazone, isoproturon, and malathion were detected only in some effluent samples. Substances such as 2,4D, Diazinon, Dimethoate, Diuron, and Simazine present a large gap between the observed mean and maximum concentrations (ratios maximum to mean ranging from 5 to 74). These peaks may be due to rain events or illegal discharges of these substances.

Occurrence of personal care products

Personal care products (PCPs) are chemical compounds commonly found in personal hygiene products such as lotions, shampoos, soaps, cosmetics, sunscreens, and repellents, among others.
Most of these products use fragrances. Fragrances are also PCPs that can be grouped according to their physicochemical properties in four different families:

- Nitro musk: musk ketone, musk ambrette, musk xylene, musk Tibetan, and musk moskene
- Polycyclic musk: galaxolide, tonalide, celestolide, phantolide, cashmeran and fundoside
- Macrocyclic musk: ambrettolide, muscone, ethylene brassilate, and globalide
- Alicyclic musk: romandolide and helvetolide

The most interesting groups of compounds are polycyclic and nitro musk, since it has been found that they are lipophilic synthetic compounds that bioaccumulate in sediments and biota; in addition, they are biomagnified through the food chain. Within this group tonalide and galaxolide are the most widely used compounds in EU and USA (Clara, et al., 2011).

The industrial sector of PCP is continuously producing and launching new compounds into the market; these causes continuously a new source of emerging pollutants in the wastewater.

Table 4-4 below shows the PCPs commonly found in conventional WWTP.

Table 4-4 *Frequency of detection and mean concentration of the PCP in WWTPs*

Family	**Personal care product (PCP)**	**Detection Frequency** %	**Average concentration influent** µg/L	**Detection Frequency** %	**Average concentration effluent** µg/L	
Insect repellent	N, N-diethyl-meta-toluamide (DEET)		0,066		0,040	(a)
	Bayrepel		0,6 – 1,4		< LOD	(b)
Polycyclic musk	Celestolide (ADBI)	72	0,0372	28	0,025	(c)
	Phantolide (AHMI)	19	0,0420	0	< 0,018	(c)
	Traseolide (ATII)	81	0,168	67	0,045	(c)
	Galaxolide (HHCB)	100	2,031	100	0,751	(c)

Family	Personal care product	Detection	Average	Detection	Average	
	Tonalide (AHTM)	100	0,804	97	0,274	(c)
	Cashmeran		0,21 – 0,69		0,08	(b)
UV filters	3-(4-methylbenzylidene) camphor (4-MBC)		0,960		0,070	(b)
	Octyl-methoxycinnamate (OMC)		20,070		0,030	(b)
	Octocrylene (OC)		1680		< LOQ	(b)
	Octyl-triazone (OT)		720		< LOQ	(b)
	1-benzophenone	100	258	58	12	(d)
	2-benzophenone	100	194	42	4	(d)
	3-benzophenone	64	1195	8	22	(d)
	4-benzophenone	100	4152	75	3370	(d)
Preservative	Methylparaben	100	11601	50	9	(d)
	Ethylparaben	100	2002	8	4	(d)
	Propylparaben	100	3090	67	26	(d)
	Butylparaben	100	723	8	0	(d)

Sources: (a) Wang, D., et al. (2014) (b) Barceló, D., et al. (2008) (c) Lishman, L., et al. (2006) (d) Kasprzyk-Hordern, B., et al. (2009)

Occurrence of surfactants

Surfactants are chemicals widely used for their properties as detergents, emulsifiers, humectants, or solubilizes. They are commonly found in personal, domestic, and industrial cleaning products. Moreover, they can be found in paints, in the industrial paper and cellulose processes, in biotechnological industries, as well as in microelectronics, among others.

At WWTPs their concentrations varies from micrograms to milligrams per litter. Concentrations as high as grams per litter were found in the sludge becoming a great environmental problem. The consumption of surfactants is constantly increasing.

The surfactants consist of amphipathic molecules with one hydrophilic polar extreme and one hydrophobic extreme. The hydrophobic part may be composed by either one or up to four chains; while the hydrophilic end may be composed by a charged or by an uncharged polar group. Depending on the nature of the latter extreme, the surfactants can be classified as anionic, cationic, non-ionic, or amphoteric (Barceló, et al. 2008).

Table 4-5 *Names and abbreviations of the most common classes of surfactants. Source: (Ivankovic and Hrenovic 2010)*

Class	Abbreviation	Common name
Anionic	LAS	Linear alkylbenzene sulphonic acid
	SDS	Sodium dodecyl sulphate
	AS	Alkyl sulphate
	SLS	Sodium lauryl sulphate
	AES	Alkyl ethoxysulphate

Class	Abbreviation	Common name
Cationic	QAC	Quaternary ammonium compound
	BAC	Benzalkonium chloride
	CPB	Cetylpyridinium bromide
	CPC	Cetylpyridinium chloride
	HDTMA	Hexadecyltrimethylammonium bromide
Amphoteric	AO	Amine oxide
Non-ionic	APE	Alkylphenol ethoxylate
	AE	Alcohol ethoxylate
	FAE	Fatty acid ethoxylate

When the surfactants get dissolved in water at low concentrations, the molecules are found as monomers. At high concentrations, the surfactant molecules are aggregated in micelles; therefore, reducing the free energy of the system. The threshold concentration at which this occurs is called the critical micellar concentration (CMC).

Non-ionic surfactants have lower CMC levels than ionic and cationic surfactants. The capacity to form micelles is what gives the surfactant its detergent and solubility properties. At concentrations above the CMC the surfactants solubilize hydrophobic organic compounds and also have antibacterial properties. However, the surfactants are below the CMC levels at environmentally relevant concentration. Therefore, that feature of the surfactants are not commonly observed (Ivankovic and Hrenovic 2010).

A higher consumption of non-ionic surfactants followed by anionic and in a smaller quantity the cationic and amphoteric compounds have been found in Western Europe. Many surfactants are biodegradable; however, due to their high consumption, they have been found in water bodies, sludge, and soil (Jardak et al. 2016).

Anionic surfactants

Anionic surfactants are used in biotechnological processes, in the cosmetic industry, in the pharmaceutical industry, and for the removal of petrochemical products, among others. The hydrophobic part of the molecule is generally composed by an alky chain of various lengths, and the hydrophilic part is composed of carboxyl, sulphate, sulphonate, or phosphate.

Cationic surfactants

The most commonly used as cationic surfactant are quaternary ammonium compounds (QAC). These molecules contain at least one hydrophobic hydrocarbon chain attached to a positively charged nitrogen atom; in addition, they may have other alkyl groups such as methyl or benzyl groups which act as substituents. They are widely used in detergents, softeners, and hair conditioners. Long chain QACs are also used as disinfectants, because of their antibacterial activity against Gram-negative and Gram-positive bacteria, as well as against some pathogenic species of fungi and protozoa.

Amphoteric surfactants

Amphoteric surfactants have the capacity to change their properties with pH. The molecules change the cationic to anionic net charge from a low pH to a high one, with zwitterion behaviour at intermediate pH. The best known and studied amphoteric surfactants are amine oxides (AOs). AOs firstly are used as substituents for traditional fatty alkanolamides as foam reinforces in dishwashing. AOs are also used in the textile industry as antistatic agents, in the rubber industry as foam stabilizers as a polymerization catalysts, and in deodorant bars as antibacterial agents. Due to their zwitterion nature, they are compatible with anionic surfactants and can produce synergistic effects (Ivankovic and Hrenovic 2010).

Non-ionic surfactants

Non-ionic surfactants are considered amphiphilic compounds. They do not ionize in aqueous solution because they have a non-dissociable hydrophilic group (e.g., alcohol, phenol, ester, ether or amide) and are less sensitive to electrolytes than ionic surfactants. Therefore, non-ionic surfactants are compatible with other types of surfactants and are excellent components for use in complex mixing. They are commonly found in a large number of domestic and industrial applications; they are good detergents, humectant agents and emulsifiers and some have good antifoaming properties. The most commonly used non-ionic surfactants are alcohol ethoxylates (AE) and ethoxylated alkylphenols (APE). The chemical structure of different non-ionic surfactants is presented in Figure 4-2.

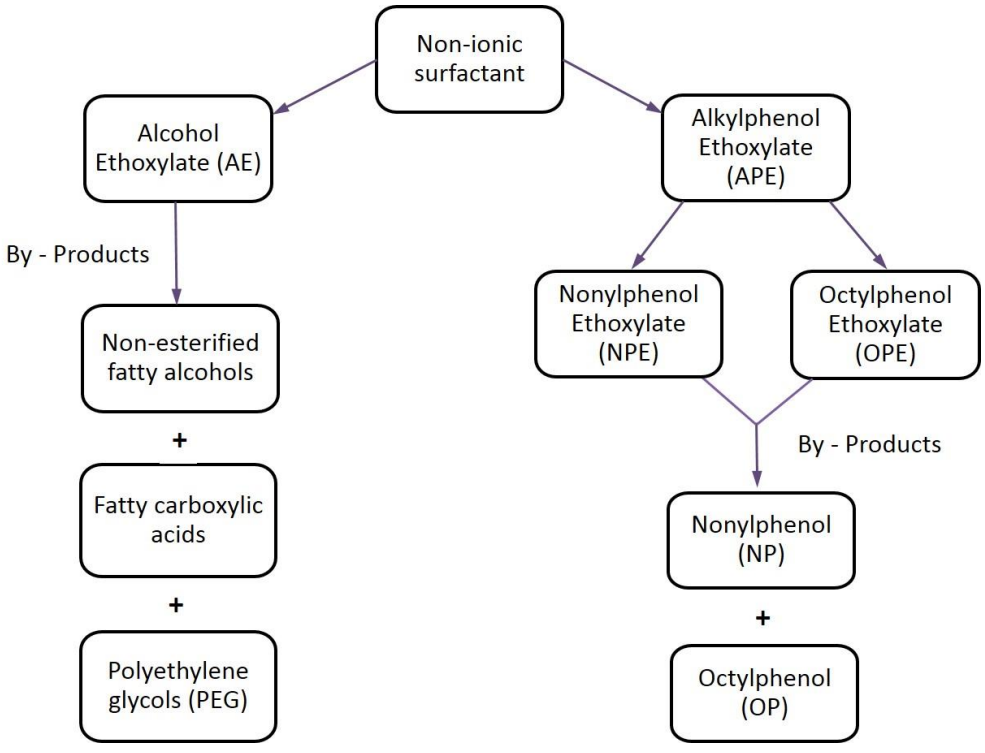


Figure 4-2 *Chemical structure of different non-ionic surfactant. Source: Modified Jardak, et al. 2016*

The use of APE has been restricted because they are partially degraded and their decomposition products, nonylphenol (NP) and octylphenol (OP), are more toxic and more persistent in the environment than the APEs themselves. APE metabolites usually formed

during the degradation process show the highest concentrations in aquatic environments where they can persist for decades due to their low biodegradability in the sediments. One of the surfactants most used since the restrictions imposed on the APE has been the AE that is more biodegradable. AEs are used in industrial and household detergents, as well as in agriculture, cosmetics, textiles, paper, and petroleum products. Because of their hydrophobic character, AEs can adsorb onto solid particles and accumulate in sediments and soils. As a consequence, aquatic and terrestrial organisms are continuously exposed to AE (Jardak, et al. 2016).

Table 4-6 shows the occurrence of the different surfactants in conventional WWTP.

Table 4-6 *Influent, effluent and removal of surfactants in CAS WWTP*

Group	Surfactant	Total Influent	Influent dissolved	Influent Sorbed	Total Effluent	Effluent dissolved	Effluent Sorbed	
Anionic	LAS (Linear alkylbemzene sulfates)	4,233,333 ng/L	2,166,667 ng/L	2,066,666 ng/L	13,277 ng/L	13,277 ng/L	--	(a)
	AES (Alkyl ether sulfates)		400 – 4,500 µg/L			< 1 µg/L		(b)
	AS (Alkyl sulfates)		< 20 – 620 µg/l			< 1 µg/L		(b)
Cationic	BAC - C12 (alkyl benzyl ammonium chlorides)	55,111 ng/L			175 ng/L			(a)
	BAC - C14	39,278 ng/L			177 ng/L			(a)
	BAC - C16	6,901 ng/L			74 ng/L			(a)
	BAC - C18	4,233 ng/L			85 ng/L			(a)
	DDAC - C10 (dialkyl ammonium chlorides)	68,444 ng/L			378 ng/L			(a)
	DDAC – C12	563 ng/L			12 ng/L			(a)
	DDAC – C14	240 ng/L			---			(a)
	DDAC – C16	4,046 ng/L			163 ng/L			(a)
	DDAC - C18	18,100 ng/L			647 ng/L			(a)
	ATAC – C12 (Trialkyl ammonium chlorides)	2,400 ng/L			17 ng/L			(a)
	ATAC – C14	1,601 ng/L			10 ng/L			(a)
	ATAC – C16	16,967 ng/L			216 ng/L			(a)
	QAC (Quaternary ammonium compound)				62 µg/L			(d)
Non-ionic	NPEO (Nonylphenol ethoxylates)		< 30 – 2,120 µg/L			< LOD – 49 µg/L		(b)
	NPEC (Nonylphenoxy carboxylates)		< 0.2 – 219 µg/L			0.6 – 113 µg/L		(b)
	NP (Nonylphenol)	4,541	2,933 ng/L	1,608	742	724 ng/L	22 ng/L	(a)

Group	Surfactant	Total Influent	Influent dissolved	Influent Sorbed	Total Effluent	Effluent dissolved	Effluent Sorbed	
		ng/L		ng/L	ng/L			
	OP (octylphenol)	363 ng/L	302 ng/L	69 ng/L	104 ng/L	104 ng/L	---	(a)
	4-Tetr-octylphenol		745 ng/L			68 ng/L		(c)
	NP_1EO (-diethoxylates)	13,468 ng/L	9,167 ng/L	4,301 ng/L	740 ng/L	641 ng/L	99 ng/L	(a)
	NP_2EO (nonylphenolmono-)	2,831 ng/L	2,300 ng/L	531 ng/L	406 ng/L	380 ng/L	26 ng/L	(a)
	AE (Alcohol ethoxylate)		125 – 3,600 µg/L			< 0.1 – 509 µg/L		(b)
	PEG (Polyethylene glycols)		85 – 3,720 µg/L					(b)
	MCPEG (Monocarboxylated polyethylene gycol)		22 – 85 µg/L			0.5 – 7.7 µg/L		(b)
	DCPEG (Dicarboxylated metabolites)		10 -100 µg/L			< 0.2 – 5.8 µg/L		(b)
	CDEAs (coconut diethanolamides)		111 – 124 µg/L			14 µg/L		(b)
	AG (Alky glucamides)		26 – 45 µg/L			< LOD – 0.2 µg/L		(b)
	APG (Alky polyglucosides)		7 – 13 µg/L			Not detected		(b)

Source: (a) Clara, M., et al. (2007) (b) Barceló, D., et al. (2008) (c) Höhne, C. and W. Püttmann (2008); (d) Versteeg D., et al. (1997)

Occurrence of plasticizers (phthalate esters)

Phthalate esters (PAEs) are used as additives in the manufacture of polyvinylchloride (PVC). They give flexibility to the PVC. PAEs can also be found as additives in paints, lubricants, adhesives, insecticides, packaging industry, and cosmetics. Bis(2-ethylbenzyl) phthalate (DEHP) is one of the phthalates with the highest volume of production being one third of the total PAEs produced in the EU and 80% of the produced in China. Dibutyl phthalate (DBP) is also one of the most widely used phthalates and global consumption is growing rapidly (Gao and Wen 2016).

PAEs are gradually released by products containing PAEs during their manufacture, storage, use, and final disposal. Once released to the environment PAEs can be adsorbed to particles. Urbanization has increased the discharge of PAEs in atmospheric and aquatic environments, and the use of agricultural plastics has increased their presence in soil in rural areas.

Phthalate esters are one of the most frequently encountered persistent pollutants in the environment. They have been detected in all the environmental compartments. Figure 4-3 shows the displacement of the PAE between different phases.

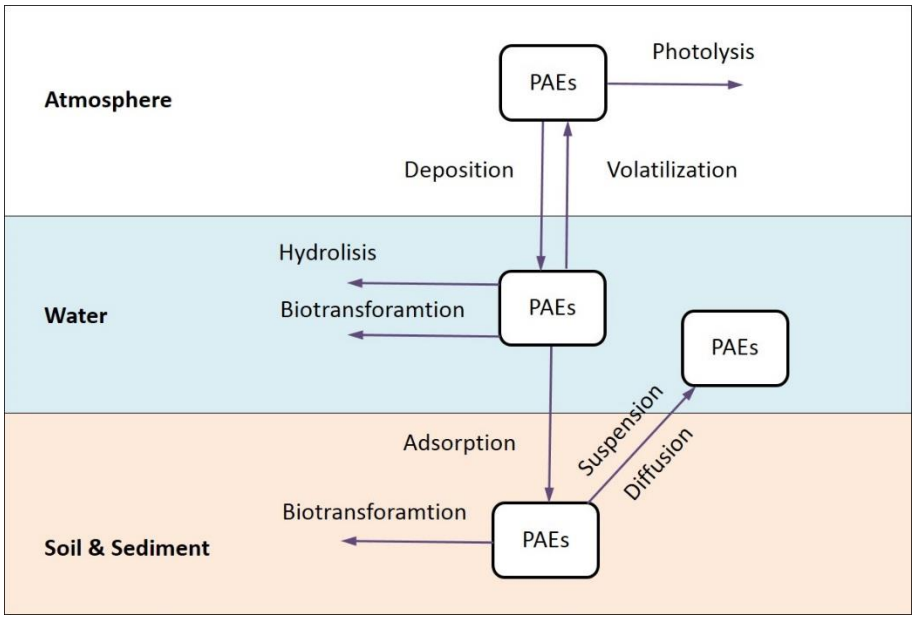


Figure 4-3 *Occurrence and biodegradation of phthalate esters (PAEs) in environment. Modified from (Gao and Wen 2016).*

Clara, et al. 2010, evaluated the presence of six phthalates in the aqueous and solid phases in conventional WWTP. To analyse the aqueous phase 15 influent and effluent samples were taken at 15 Austrian WWTP; the results are shown in the Table 4-7.

Table 4-7 *Occurrence of the six analysed phthalates in raw and treated wastewater (n=15) Modified form (Clara, et al. 2010)*

Phthalate	**Detection Frequency** %	**Mean concentration Influent** ng/L	**Detection Frequency** %	**Mean concentration effluent** ng/L
Dimethyl phthalate (DMP)	87	0,95	60	0,062
Diethyl phthalate (DEP)	100	4,1	80	0,20
Dibutyl phthalate (DBP)	53	2,2	53	0,54
Butylbenzyl phthalate (BBP)	100	0,95	100	0,36
Bis(2-ethylbenzyl) phthalate (DEHP)	100	18	100	1,6
Dioctyl phthalate (DOP)	80	0,49	7	0,017

DEP, BBP and DEHP were found in all influent samples. DBP was the compound with the lowest occurrence frequency (53%). BBP and DEHP were found in all the effluent samples. DOP recorded the lowest effluent frequency of 7%. DEHP is the compound exhibiting the largest influent and effluent concentrations at the WWTPs with a significant removal.

The presence of phtalates in the sludge was evaluated at 2 Austrian WWTPs as observed in Table 4-8. WWTPs 1 and 2 include the nitrification-denitrification process and operate with solid retention times (SRTs) of 17 days and 12 days respectively.

Table 4-8 *Measured phthalix esters concentration in untreated and treated wastewater (µg/l) and in the sludge samples (µg/kg dry weight) of the two mass balances subjected WWTPs. Modified from Clara, et al. 2010*

Phthalate	**Influent 1** µg/L	**Effluent 1** µg/L	Influent 2 µg/L	**Effluent 2** µg/L	**Primary sludge 1** µg/kg	**Excess sludge 1** µg/kg	**Primary sludge 2** µg/kg	**Excess sludge 2** µg/kg
DMP	0,26 – 0,41	n.d.	0,43 – 0,81	n.d.	74 - 89	< 4 0- 56	n.d.	n.d.
DEP	1,2 - 2	n.d. - < 0,1	2,2 – 2,7	n.d.	85 - 85	61 - 70	44 - 55	130 - < 40
DBP	< 0,1 – 0,47	n.d.	0,15 – 0,41	n.d.	270 - 290	810 - 1200	310 - 850	640
BBP	n.d. - 0,11	n.d.	0,11 – 0,26	n.d.	140 - 140	120 - 130	180 - 380	250 - 200
DEHP	4,4 – 8,8	< 0,2 – 0,28	4,1 - 13	< 0,2 – 1,3	24000 - 25000	22000 - 27000	20000 - 27000	27000 - 29000
DOP	n.d.	n.d.	n.d. - < 0,1	n.d.	130 - 180	58 - 96	140 - 260	89 - 120

Occurrence of perfluorinated compounds (PFCs)

Perfluorinated compounds (PFCs) are a group of persistent organic emergent pollutants consisting of a fully fluorinated hydrophobic alkyl chain attached to a hydrophilic end group.

PFCs are employed in a wide range of commercial and industrial applications such as polymers, metal plating, surfactants, lubricants, pesticides, coating formulations, inks, varnishes, firefighting foam, stain/water repellents for leather, paper, and textiles.

PFCs are persistent, bioaccumulative, and potentially dangerous compounds for humans and wildlife. Long chain PFCs and perfluorooctanesulfonate (PFOS) are more toxic than perfluorooctanoic acid (PFOA) and short chain homologs.

PFOS and PFOA are the most commonly detected PFCs. Arvaniti and Stasinakis, 2015, compiles studies documenting the occurrence of short and long chain PCF in WWTP. Most studies focus on PFOS and PFOA on the aqueous phase, with little information about other compounds and about PFCs in sludge, which may lead to underestimation of the amount of PFCs.

Studies that have analyzed the seasonal variation of PFCs have not observed significant variations. Perfluorododecanoic acid (PFDoA), perfluorotetradecanoic acid (PFTeDA), perfluoroheptanesulfonate (PFHpS), perfluorodecanesulfonate (PFDS), and perfluorooctane sulfonamide (PFOSA) were found in the solid phase, whereas perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), and perfluorohexanesulfonate (PFHxS) were detected mainly in the dissolved phase. These findings indicate the importance of the analysis of both the dissolved phase and the particulate phase in raw sewage, in order to avoid underestimation of the PFC levels in WWTP.

The dominant compound in the sludge is PFOS since it has been detected in concentrations up to 7304.9 ng/g dry weigth.

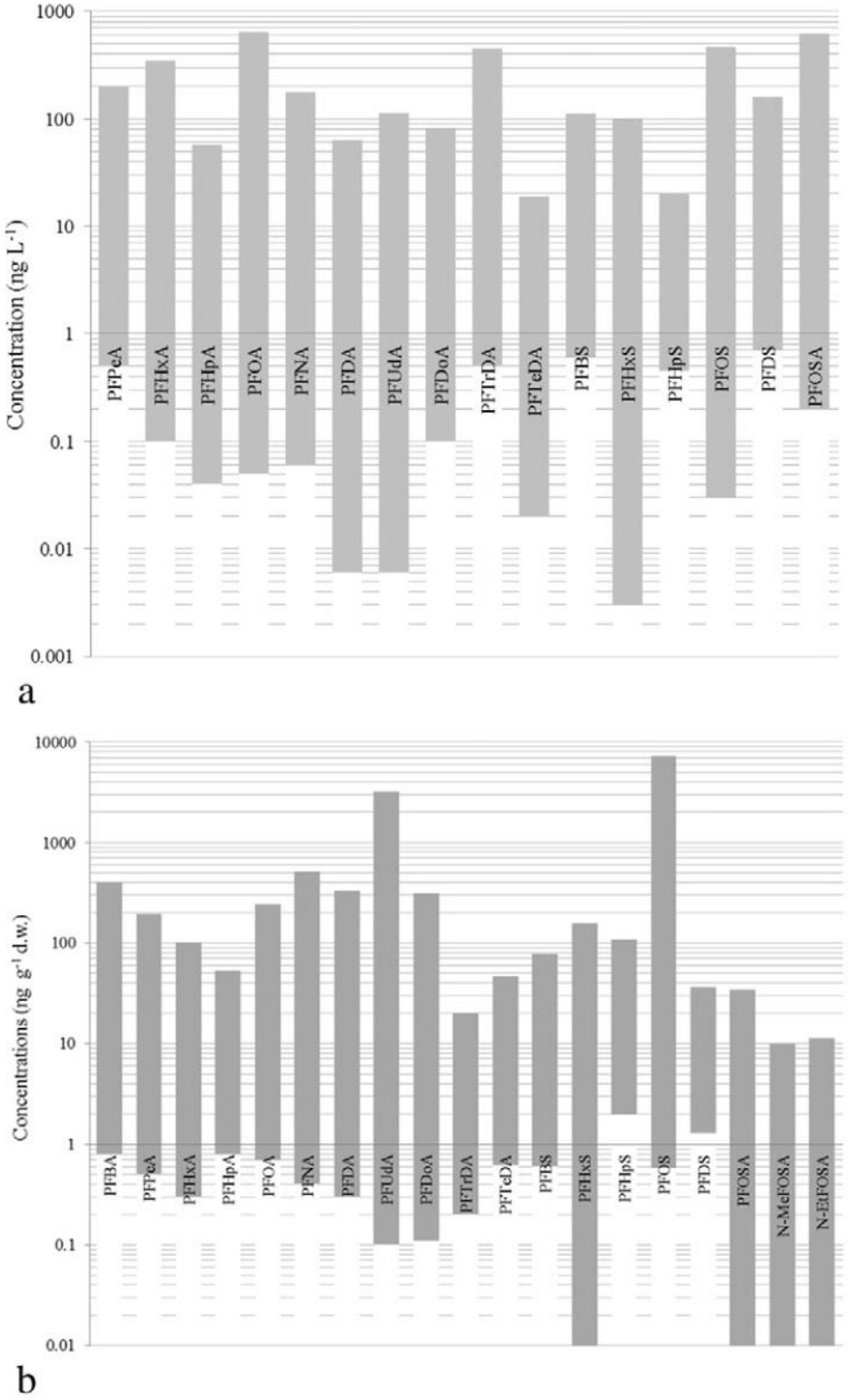


Figure 4-4 *Range of PFCs concentrations in influent wastewater (a) and sewage sludge (b), worldwide. Source: (Arvaniti, and Stasinakis2015)*

The Figure 4-4 shows the presence of PFC reported in several studies conducted in USA, Canada, Europe, Asia, and Australia.

Concentrations of PFOS and PFOA of 449 ng/L and 513 ng/L, respectively were reported in raw sewage from European cities in Germany, Switzerland, Denmark, Spain, and Greece.

PFOSA was found in an influent of a Spanish WWTP at a concentration of 615 ng/L. It has also found cases with high concentrations of short chain PFC in effluents. More specifically, perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA) and perfluorobutanesulfonate (PFBS) were detected at concentrations of 209.4 ng/L, 57.4 ng/L and 57.9 ng/L, respectively (Arvaniti, and Stasinakis 2015).

In the sludge, concentrations of PFOS and PFOA of up to 2440 ng/g and 29 ng/g, respectively, have been reported. Among the other PFCs examined, perfluoroundecanoic acid (PFUdA) was found at a maximum concentration of 3209 ng/g, while other compounds were detected in concentrations lower than 399 ng/g (as for perfluorobutanoic acid (PFBA)).

4.1.5. Occurrence mapping

This chapter presents the ocurrence of emerging pollutants in both surface and groundwater in European countries through sampling information collected from the Norman database network (Norman). The database contains environmental monitoring data from government agencies, institutes and universities.More than 90 laboratories reporting results. The main countries contributing information to this database are France, the Netherlands and Germany.

The registered emergent contaminants are 532 and the database has approximately 9,640,000 samples of bodies of water. This base also has samples in sediments but they are about 1% of total records.

The information on the presence of emergent contaminants in Eupora is presented in the form of a matrix where by country and contaminate emergents is reported if the compound has been detected in concentrations greater than LOQ (red box), if the compound was searched but the reported concentration is less than LOQ (green box) and finally the empty boxes correspond to unreported samples.

The samples contain information of the country where it was carried out and a description of the location. The reported description does not allow the sampling to be refer to a river basin. Watershed mapping instead of per country would allow for an analysis of the level of monitoring of the environment.

In the Appendix B it is possible to observe the matrix that represents the mapping of emergent contaminates based on the data collected in Network Norman.

4.1.6. Effects of emerging pollutants

The effects of emerging pollutants in the environment are partially known. As it is also little known the pathways of EP having into an ecosystem and the transformation process that suffer. The effects on human health are still unknown.
In the following table examples of effects associated with the different types of EP are exposed. As it can see the impacts can be quite varied.

Table 4-9 *Examples of Emerging Pollutants Categories and Associated Effects. Modified from Raghav, et al.2013*

Use Category	Suspected health effects from environmental exposure
Antibiotics	Antibiotic resistance in disease causing bacteria complicating treatment of infections
Disinfectants	Genotoxicity, cytotoxicity, carcinogenicity
Fire retardants	Endocrine disruption, indications of increased risk for cancer
Industrial additives	Can be toxic to animals, ecosystems, and humans
Life-style products (Caffeine, Nicotine)	Can cause cellular stress, negative effects on reproductive activity in animals
Nonprescription drugs	Unknown health effects
Other prescription drugs	Increased cancer rates, organ damage
Personal care products	Bacterial resistance, endocrine disruption
Pesticides	Endocrine disruption
Plasticizers	Endocrine disruption, increased risk of cancer
Reproductive hormones	Endocrine disruption
Solvents	Endocrine disruption, liver and kidney damage, respiratory impairment, cancer
Steroids	Endocrine disruption

Endocrine disrupter

According to WHO (2012). State of the Science of Endocrine Disrupting Chemicals 2012, endocrine disrupter (ED) is "an exogenous substance or mixture that possesses properties that might be expected to lead to endocrine disruption in an intact organism, or its progeny, or (sub)populations." And the potential ED is the same definition for ED but inside the causes adverse effects, it is might be expected to lead to endocrine disruption.

The effects can be register in human and wildlife. Endocrine disruption is a functional change that may lead to adverse effects, non-always toxic effects. EDCs covers a wide range of chemical classes, including natural and synthetic hormones, plant constituents, pesticides,

compounds used in the plastics industry and in consumer products, and other industrial products.
Some EDC are persistent, and can therefore be transported long distances finding worldwide. Others are rapidly degraded in the environment or the human body or may be present only for short periods of time, but in critical periods of development.

The mechanisms of action of EDCs are receptor-mediated, in the synthesis processes, transport and metabolism disorders, among others. There is no unique relationship between exposure to an agent and the effects it produces. For example exposure of an organism in the development stage may have different effects in adulthood, while at an early age can have permanent effects, in adulthood the organism can trigger compensatory mechanisms and not be affected. The different reactions that have the organisms to compounds depending on what stage of the life cycle is, exposure time, other environmental factors that affect the endocrine system, etc. makes it very difficult to determine dose-response.

The effects of EDCs can be seen in humans, wildlife species and populations. Effects on reproductive and immune function of mammals, effects on reproductive and immune function of birds, effects on reproductive endocrine function of fish, are examples of damages caused by EDC in wildlife. Despite the difficulties that exist to determine the relation between EDC exposure and effects in humans, it has been found adverse effects on neurodevelopment, neuroendocrine function, and behavior.

4.1.7. Risk evaluation

Introduction

The risk analyses methodology presented in this chapter are based on the method described in the Thechnical Guidance Document on Risk Assessment Part 2 EC, (2003) and will focus both on the aquatic compartment which includes the sediments, and on the local geographical scope. There are other relevant guides such as the EPA or the OECD (not presented in this report) which can also be used as reference guides.

The Guideline EC (2003) establishes the principles for assessing environmental risks caused by individual substances in the environment whose means of exposure is through emissions of compounds and the effects analysed are on the structure and functions of the ecosystems.

The proposed methodologies lead to the identification of risks as either acceptable, or not acceptable through environmental risk indicators. This type of evaluation allows to support regulatory decisions. However, the evaluation of the levels of uncertainty at which each step is carried out needs to be assessed to better determine the validity of the conclusions.

There are several environmental risk indicators to assess the quality of the aquatic environment. Risk indicators are fundamental tools for the management of water resources. Indicators based on the concept of the relation between toxicity and exposure are extensively used (Köck-Schulmeyer et al. 2012).

The risk indicators are used as part of the risk assessment methodology. The risk assessment methodology consists of: (i) identifying the risks, (ii) evaluating the dose-response (effects), (iii) assessing the exposure, and (iv) characterizing the risk.

The emerging contaminants may come from active sources or from sources that were active and are now closed. It may happen that although the emission of a particular compound has been interrupted, if the compound is persistent, it can still be found in the environment. The identification of the sources is relevant to implement actions either to minimize exposures, or minimize sources.

Emerging pollutants act on individual organisms, communities, or on ecosystem functioning together with various other (both biotic and abiotic) stressors. The evaluation of the effects of multiple stressors acting and interacting simultaneously is difficult to assess; however, there has been an increase in the number of publications analysing more than one factor simultaneously mostly at laboratory scale. In addition, some field studies were carried out to correlate the effects of organisms to multivariable stressors (Petrovic et al. 2016).

The effects may range from extreme effects such as death to physiological or pathological changes. The risk assessments utilize toxic results from all the available sources (studies). The studies that usually provide more information evaluate the response at different doses.

The duration of the exposure, as well as the dosage can vary significantly; however, special attention is given to studies where chronic exposures are evaluated at low doses. Particularly, these experiments allow to reveal the effects of the accumulation of toxic compounds (toxicity) in the evaluated organisms.

The risk characterization is the final process in the risk assessment methodology. The risk characterization consists in analysing all the experimental evidence, analysing the uncertainty of the procedures, and obtaining a no-observed-adverse-effect-level (NOAEL) based primarily on the dose-response data. The risk characterization along with additional factors such as efficiency, timeliness, equity, consistency, public acceptability, technological feasibility, and administrative capacity can strengthen regulatory and control decisions (Barnes and Dourson 1988).

Assessment of environmental exposure

In order to evaluate the environmental exposure of a compound, the entire life cycle of that compound needs to be assessed including production, transportation, use, and disposal. The present methodology for assessing the environmental exposure does not contemplate substances that are originated naturally; the guide EC (2003) treats them as unintentional sources; however, their effect must be analysed.

During the life cycle assessment of the compounds, the degradation pathway (biotically or abiotically) needs to be determined. In addition, the potential for by-products formation and their stability needs to be assessed. If the by-products exhibit toxicity, a risk study should be

perform also for them. The exposure can occur in different environmental compartments including air, soil, water, and sediments.

The concentration of a substance in the environment can be measured or estimated using a model. In the case that the concentrations of a compound present in the environment are through direct measurements must be taken into account that may have high levels of uncertainty due to technical limitations or spatial and seasonal variations of the compound. In spite of having the information through direct means of concentration, the realization of the model of prediction of concentrations (PEC) can contribute a more profound knowledge of the sources and behavior of a compound. Just as the PEC complements the direct measurements, the direct measurements allow to calibrate and to understand the models of estimation of the PEC.

In order to measure the presence of a compound in water, the presence in both the aqueous and sediment phases must be measured. Concentrations measured in water may correspond to the total concentrations of a compound or to the concentrations dissolved in accordance with the sampling procedure employed.

Concentrations that are lower than Limit of Quantification (LOQ) should be analysed how they are incorporated into the statistical analysis. There are several models for this, having to be analysed in each case which is best adapted.

The number of samples should be such as to be representative of the site concentration and the site should be capable of being representative of the selected local or regional area.

In the case of estimating the PEC through a model, the emission rate of the compound must be estimated based on the usage pattern of that compound. All potential sources of emissions and emissions should be identified and analysed. In addition, it is necessary to identify the environmental compartments that may receive that compound. In addition, the route of exposure and the biotic and abiotic processes of transformation must be traced. The quantification of the distribution and degradation of the compound leads to the calculation of the PEC.

In modelling it is important to know the properties of the substances. For ionizing substances it is necessary to know the dependence of the partition coefficient (K_d) with both the pH and the solubility in water; therefore, the partition coefficients can be corrected at the environmental pH. Adjustment considering the temperature may be also necessary.

Calculation of the PECs

For the calculation of the PEC at the local level in the aquatic compartment the determinations need to be carried out after the effluent discharge is completely mixed with the main stream. The dilution process should be completely consider. The dilution process occurs in a very short time; therefore, removal by either degradation, volatilization, or sedimentation can be considered negligible. Dilution can be considered as the main mechanism for reducing the discharge concentration. Adsorption may contribute to the observed reduced concentration of the contaminants depending both on the effluent and the receiving body characteristics.

Dilution factors may vary according to the discharged flows and the flow of the receiving body; that is, the dilution factor have seasonal, climatic, and geographical variation. In the discharge zone, higher concentrations of the contaminants are commonly observed compare to the concentrations observed after the complete mixing occurs. At each point, the contaminant concentration should be assessed to evaluate compliance with local standards. Particularly, in cases where the mixing zone is very long the area with higher levels of concentration may be relevant. The guide CE (2003) states that the dilution coefficients should not exceed a value of 1000.

The adsorbed fraction is estimated from the partition coefficient between suspended matter and water. If the measured partition coefficient is not available for the local conditions the partition coefficient organic carbon-water (Koc) of the substance for sorbents as the sediment can be used. It is necessary to analyze case by case if it is possible to use this type of coefficients.

The local concentration in the surface water is calculated through the following expression:

$$C_{local-water} = \frac{C_{local-eff}}{\left(1 + Kp_{susp} \cdot Susp_{water} \cdot 10^{-6}\right) \cdot Dilution}$$

Where:

$C_{local\text{-}eff}$	concentration of the substance in the sewage treatment plant effluent (mg/L)
Kp_{susp}	solids-water partitioning coefficient of suspended matter (L/kg)
$Susp_{water}$	concentration of suspended matter in the river (mg/L)
Dilution	dilution factor
$C_{local\text{-}water}$	local concentration in surface water during emission episode (mg/L)

The dilution factor in the case of variable flows should be estimated with the low flows (percentile 10). If the average flow data is available, the factor should be estimated at one third of the average. These criteria apply to rivers; this is not suitable for estuaries or lakes. The dilution factor calculation is accordin the next expression:

$$Dilution = \frac{Effluent_{stp} + Flow}{Effluent_{stp}}$$

Where:

$Effluent_{stp}$	effluent discharge rate of sewage treatment plant (STP) (L/d)
Flow	flow rate of the river (L/d)
Dilution	dilution factor at the point of complete mixing (max. =1000)
$C_{local\text{-}water}$	local concentration in surface water during emission episode (mg/L)

The mean annual concentration in water is calculated by the following expression:

$$C_{local-water,anv} = C_{local-water} \cdot \frac{T_{emission}}{365}$$

Where:

$C_{local\text{-}water,anv}$	annual average local concentration in surface water (mg/L)
$T_{emission}$	number of days per year that the emission takes place (d/year)
$C_{local\text{-}water}$	local concentration in surface water during emission episode (mg/L)

The PEC estimate for sediment in local scope can be calculate through next expression:

$$PEC_{local-sed} = \frac{K_{susp-water}}{RHO_{susp}} \cdot PEC_{local-water} \cdot 1000$$

Where:

$PEC_{local\text{-}water}$	concentration in surface water during emission episode (mg/L)
$K_{susp\text{-}water}$	suspended matter-water partitioning coefficient (m^3/m^3)
RHO_{susp}	bulk density of suspended matter (kg/m^3)
$PEC_{local\text{-}sed}$	predicted environmental concentration in sediment (mg/kg)

Highly adsorbent substances can be poorly estimated by this method because they are not in equilibrium between the adsorbed phase and the aqueous phase.

Concentration used for risk characterization

Once the measured environmental concentration and the estimated PECs are obtained, they should be compared. In the case that the measured and calculated PECs are of the same order, it can be inferred that the main sources of exposure were taken into account. To calculate the risk, the environmental concentration value with the greatest confidence should be selected.

Instead, if the measured environmental concentration is lower than the PEC estimated, it may mean that the model or processes that were assumed are not correct to describe the real concentration. There may also be errors in the analytical determinations, and/or on the sampling procedures. If the sampling campaign and analytical determinations were carried out correctly, the measured environmental concentration shall be adopted for the estimation, otherwise the calculated PEC should be chosen.

Finally, if the measured environmental concentration is greater than the calculated PEC it may mean that some sources were omitted in the estimation. There may also be errors in the model such as overestimating degradation or otherwise extraordinary spills leading to non-representative sampling. If the sampling is reliable and representative the measured environmental concentration is the one to be taken. Measurements and estimates of the PEC must be performed in all compartments to give greater confidence to the values adopted since it allows to do a balance and detect inconsistencies.

Evaluation of the effect

The risk assessment methodology requires to evaluate the effects of the substance in the environment and human health; therefore, it is necessary to identify the hazards and to evaluate the dose-response. The guide CE (2003) proposes to determine the predicted non-effect concentration (PNEC) for each compartment. The PNEC is the concentration under which it is very probable that unacceptable effects will not occur.

The effects assessment is often done through testing the effects of substances on non-standardized organisms or methods; therefore, it is essential to analyse the quality and relevance of the data to be incorporated into the risk assessments.

It is recommended to begin the evaluation process with the available toxicological data. In principle, the PNEC is calculated through the short-term parameter LC50, EC50 or the long-term parameter No Observable Effect Concentration (NOEC) to which a safety factor should be applied reflecting the uncertainty involved in the extrapolation of the laboratory test to the medium environment.These ecotoxicological tests give information on the direct toxic effects of a substance. There are other types of effects such as endocrine disruption, carcinogenesis, among others. There are not that much availability of these tests; however, when the tests are available, these effects must be taken into account for estimating the PNEC. The current state-of-the-art does not yet permit the standardization of these methods, although great advances have been made in the last decade on this regards. One of the greatest contributions of these methods is that they have proved and identified new substances exhibiting additional toxicological effects.

On the other hand the ecotoxicity tests do not take into account effects of bioaccumulation and biomagnification. These phenomena should be analyzed for the substance that have potential to bioaccumulate and is done by secondary poisoning study.

The basic set of tests for the ecotoxicological evaluation in the aquatic compartment includes tests for algae, Daphnia and fish, which may include bacterial respiration inhibition tests. This last test is used to evaluate the effects on microbial activity in effluent treatment plants.

Calculation of the PNEC using evaluation factors

The main assumptions for the determination of the PNEC in the aquatic compartment include the following: (i) the sensitivity of the ecosystem depends on the most sensitive species; and (ii) the protection of the ecosystem structure protects the community's function. It is generally accepted that the protection of the weaker species leads to the protection of the entire ecosystem; and hence, their functions.

Very limited data is available to assess the effects of a particular substance on an ecosystem. Most of the available data considers the short-term toxicity whose validity is limited; therefore evaluation factors are developed in different guides such as the EU, EPA or OECD to assess the effects of substances on ecosystems.

These factors often come from empirical assessments. Their goal is to predict the concentrations under which an unacceptable effect most probably will not occur (since it is not possible to establish levels at which below those levels a substance can be considered safe). The evaluation factors seek to cover the uncertainty of extrapolating laboratory scale tests using single species to multi-species ecosystems; the uncertainties include doubts intrinsic to the trials, and phenomena of synergies or antagonisms between substances, among others.

The guide (CE 2003) proposes the evaluation factors for obtaining PNEC shown in the next Table 4-10. The evaluation factor decreases as more data are available, such as toxicity data on organisms at different trophic levels, taxonomic groups, and different feeding strategies, among others.

Table 4-10 *Assessment factors to derive a PNECaquatic Source: (CE 2003)*

Available data	Assessment factor
At least one short-term L(E)C50 from each of three trophic levels of the (fish, *Daphnia* and algae) baseset	1000 [a)]
One long-term NOEC (either fish or *Daphnia*)	100 [b)]
Two long-term NOECs from species representing two trophic levels (fish and/or *Daphnia* and/or algae)	50 [c)]
Long-term NOECs from at least three species (normally fish, *Daphnia* and algae) representing three trophic levels	10 [d)]
Species sensitivity distribution (SSD) method	5-1 (to be fully justified case by case) [e)]
Field data or model ecosystems	Reviewed on a case by case basis [f)]

a) The use of a factor of 1000 on short-term toxicity data is a conservative and protective factor and is designed to ensure that substances with the potential to cause adverse effects are identified in the effects assessment. It assumes that each of the uncertainties identified above makes a significant contribution to the overall uncertainty. For any given substance there may be evidence that this is not so, or that one particular component of the uncertainty is more important than any other. In these circumstances it may be necessary to vary this factor. This variation may lead to a raised or lowered assessment factor depending on the available evidence. A factor lower than 100 should not be used in deriving a PNECwater from short-term toxicity data except for substances with intermittent release (see Section 3.3.2).
There are cases where the base-set is not complete: e.g. for substances that are produced at <1 t/a (notifications according to Annex VII B of Directive 92/32). At the most the acute toxicity for Daphnia is determined. In these exceptional cases, the PNEC should be calculated with a factor of 1000.
Variation from a factor of 1000 should not be regarded as normal and should be fully supported by accompanying evidence.
b) An assessment factor of 100 applies to a single long-term NOEC (fish or Daphnia) if this NOEC was generated for the trophic level showing the lowest L(E)C50 in the short-term tests.
If the only available long-term NOEC is from a species (standard or non-standard organism) which does not have the lowest L(E)C50 from the short-term tests, it cannot be regarded as protective of other more sensitive species using the assessment factors available. Thus the effects assessment is based on the short-term data with an assessment factor of 1000. However, the resulting PNEC based on short-term data may not be higher than the PNEC based on the long-term NOEC available.
An assessment factor of 100 applies also to the lowest of two long-term NOECs covering two trophic levels when such NOECs have not been generated from that showing the lowest L(E)C50 of the short-term tests. This should, however, not apply in cases where the acutely most sensitive species has an L(E)C50 value lower than the lowest NOEC value. In such cases the PNEC might be derived by using an assessment factor of 100 to the lowest L(E)C50 of the short-term tests.

c) An assessment factor of 50 applies to the lowest of two NOECs covering two trophic levels when such NOECs have been generated covering that level showing the lowest L(E)C50 in the short-term tests. It also applies to the lowest of three NOECs covering three trophic levels when such NOECs have not been generated from that trophic level showing the lowest L(E)C50 in the short-term tests. This should however not apply in cases where the acutely most sensitive species has an L(E)C50 value lower than the lowest NOEC value. In such cases the PNEC might be derived by using an assessment factor of 100 to the lowest L(E)C50 of the short-term tests.
d) An assessment factor of 10 will normally only be applied when long-term toxicity NOECs are available from at least three species across three trophic levels (e.g. fish, Daphnia, and algae or a non-standard organism instead of a standard organism). When examining the results of long-term toxicity studies, the PNECwater should be calculated from the lowest available NOEC. Extrapolation to the ecosystem effects can be made with much greater confidence, and thus a reduction of the assessment factor to 10 is possible. This is only sufficient, however, if the species tested can be considered to represent one of the more sensitive groups. This would normally only be possible to determine if data were available on at least three species across three trophic levels. It may sometimes be possible to determine with high probability that the most sensitive species has been examined, i.e. that a further long-term NOEC from a different taxonomic group would not be lower than the data already available. In those circumstances, a factor of 10 applied to the lowest NOEC from only two species would also be appropriate. This is particularly important if the substance does not have a potential to bioaccumulate. If it is not possible to make this judgement, then an assessment factor of 50 should be applied to take into account any interspecies variation in sensitivity. A factor of 10 cannot be decreased on the basis of laboratory studies.
e) Basic considerations and minimum requirements as outlined in Section 3.3.1.2.
f) The assessment factor to be used on mesocosm studies or (semi-) field data will need to be reviewed on a case-by-case basis.

If short-term toxicity data are available, an evaluation factor of 1000 will be applied to the lowest LC50 available whether or not it is referred to a standard species. If NOEC data derived from long-term trials on relevant species are available, the evaluation factor may be lowered.

The general evaluation factors proposed by the guide (CE, 2003) can be modified either whenever data on additional taxonomic groups are available, or, the mode of action of the substance (such as endocrine disruption) or data on structurally similar substances are known. The approach to reduce the assessment factors by adding more data is justified with respect to the true uncertainty. However, the uncertainty in defining the problem (as for example the environment) is subject to either multiple stressors, or to the variability of the strain sensitivity for the same evaluated species are not incorporated into current approaches of risk assessment (von der Ohe, et al. 2011).

Short-term toxicity tests can not be used for substances with high octanol-water partition coefficient (log K_{ow}). It may be the case that even long-term tests are not suitable for this type of compound since steady state would never be reached.
If a substance exhibited log K_{ow}> 3, the substance does not exhibit toxicity in short-term trials and the local PEC/PECregional > 1/100th of the water solubility a long-term test, generally *Daphnia*, should be performed.

Calculation of PNEC using statistical extrapolation techniques

The evaluation of the effect performed through the use of evaluation factors can be also determined by applying a statistical extrapolation method. To apply that method, the database on species sensitivity distributions (SSDs) must be large and comprehensive enough. If a

comprehensive set of long-term test data is available for different taxonomic groups, statistical extrapolation methods can be used to obtain a PNEC. The main assumptions of this method are both that the distribution of the sensitivities of the species follows a theoretical distribution function, and that the group of species tested in the laboratory is a random sample of this distribution (CE, 2003). The statistical extrapolation approach is still under discussion and needs further validation.

Assessment of secondary poisoning

The bioconcetration factor (BCF) can be determined to evaluate of effects that can be produced by the bioaccumulation of substances. These studies are of particular interest for lipophilic organic substances and for metal compounds.

Another indicator of the bioaccumulation potential of a substance is the octanol / water partition coefficient (log K_{ow}). A high log K_{ow} calue can be associated with a high tendency to bioaccumulate; however, there may be substances with a high log K_{ow} that do not tend to bioaccumulate and the other way around. Other factor that influence the bioaccumulation properties of a substance is the ability to adsorb. An adsorption coefficient (log K_p) < 3 may indicate a high bioaccumulation potential.

If a substance is rapidly degraded by hydrolysis, it is less likely to be bioaccumulated. When the half-life of a substance at environmental relevant pH and temperature is less than 12 hours, it can be assumed that the rate of adsorption to exposed organisms is less than the rate of degradation of the compound; therefore, not producing bioaccumulation.

Certain classes of substances with a molecular mass greater than 700 daltons are not easily captured by fish because of possible steric hindrance in the passage through the cell membranes. It is unlikely that these substances significantly bioaccumulate regardless log K_{ow} value.

Characterization of environmental risk

Based both on the exposure assessment, and on the dose-response assessment in all environmental compartments, a quantitative or qualitative risk characterization can be performed.

The quantitative risk characterization is done by comparing the PEC with the PNEC for each compartment. When it is not possible to obtain PEC or PNEC values with acceptable levels of confidence, a qualitative characterization can be done.

If the PEC/PNEC ratio (known as the ratio quatient RQ) is greater than one, the substance should be considered as a substance of concern; therefore, measures such as additional studies and/or palliative actions should be applied.

Risk of pharmaceutical compounds in effluents

Verlicchi et al. (2012) compiled the threshold toxicity values determined in several studies carried out on a single compound and on a single organism. Many of these studies refer only to acute effects not contemplating chronic effects.

The Table 4-11 shows the PNEC values reported applying a assessment reducing factor of 1000 according to the guide CE (2003) to contemplate the potential effects on species more sensitive than the ones used in the standard tests.

Table 4-11 *PNEC for the pharmaceutical compounds (PhCs) and corresponding assayed species. From Verlicchi, et al. 2012*

Therapeutic class	**Pharmaceutical compound**	**Species assayed**	**Test (endpoint)**	**Toxicity** µg/L	**PNEC** µg/L	
Analgesics / anti-inflammatories	Acetaminophen	*Daphnia*	EC50 (24h)	136	1	(1)
		Daphnia	EC50 (48h)	9.2		(1)
		S.proboscideu	LC50 (24h)	29.6		(1)
		Fish	EC50 ECOSAR	1		(2)
		Daphnia	EC50 ECOSAR	42		(2)
		Algae	EC50 ECOSAR	2549		(2)
		Invertebrates	EC50	300		(3)
		Algae	EC50	105		(3)
		Fish	EC50	900		(3)
		Daphnia	EC50 (48h-immobility)	9.2		(4)
	Acetylsalicylic acid	*Fish*	EC50 ECOSAR	796	61	(2)
		Daphnia	EC50 ECOSAR	8858		(2)
		Algae	EC50 ECOSAR	61		(2)
		Daphnia	EC50 ECOSAR	61		(5)
	Aminopyrine	*Fish*	EC50 ECOSAR	3.7	1.3	(2)
		Daphnia	EC50 ECOSAR	8.3		(2)
		Algae	EC50 ECOSAR	1.3		(2)
	Codeine	*Fish*	EC50 ECOSAR	238	16	(2)
		Daphnia	EC50 ECOSAR	16		(2)
		Algae	EC50 ECOSAR	23		(2)
	Dextropropoxyphene	*Fish*	EC50 ECOSAR	13	1	(2)
		Daphnia	EC50 ECOSAR	24		(2)
		Algae	EC50 ECOSAR	1		(2)
	Diclofenac	*Fish*	EC50 ECOSAR	532	9.7	(2)
		Daphnia	EC50 ECOSAR	5057		(2)
		Algae	EC50 ECOSAR	2911		(2)
		Daphnia	EC50 (48h-mortality)	22.4		(6)

Therapeutic class	Pharmaceutical compound	Species assayed	Test (endpoint)	Toxicity µg/L	PNEC µg/L	
		Algae	EC50 (96h-growth)	16.3		(6)
		Bacteria	EC50 (30min-luminescence)	11.4		(6)
		Bacteria	EC50 (15min-inhibition)	9.7		(7)
		Microtox	EC50 (30min)	11.45		(8)
		Daphnia	EC50 (48h)	22.43		(8)
		C. dubia	EC50 (48h)	22.7		(8)
		Algae	EC50 (96h-growth)	14.5		(6)
		Invertebrates	EC50	90		(3)
		Algae	EC50-inhibition	72		(9)
		Daphnia	EC50-immobilisation	68		(9)
	Ibuprofen	*Fish*	EC50 ECOSAR	5	1.65	(2)
		Daphnia	EC50 ECOSAR	38		(2)
		Algae	EC50 ECOSAR	26		(2)
		Bacteria	EC50 (15min-inhibition)	37.5		(7)
		Bacteria	EC50 (15min)	12.1		(10)
		Daphnia	EC50 (48h)	9.06		(11)
		Invertebrates	EC50 (96h)	1.65		(12)
		Invertebrates	EC50	100		(3)
		Algae	EC50	500		(3)
		Fish	EC50	110		(3)
		Algae	EC50-inhibition	342.2		(9)
		Daphnia	EC50-immobilisation	101.2		(9)
	Indomethacin	*Fish*	EC50 ECOSAR	3.9	3.9	(2)
		Daphnia	EC50 ECOSAR	26		(2)
		Algae	EC50 ECOSAR	18		(2)
	Ketoprofen	*Fish*	EC50 ECOSAR	32	15.6	(2)
		Daphnia	EC50 ECOSAR	248		(2)
		Algae	EC50 ECOSAR	164		(2)
		Bacteria	EC50 (15min)	15.6		(10)
	Mefenamic acid		EC50 ECOSAR	0.43	0.43	(13)
	Naproxen	*Fish*	EC50 ECOSAR	34	2.62	(2)
		Daphnia	EC50 ECOSAR	15		(2)
		Algae	EC50 ECOSAR	22		(2)
		Algae	EC50-inhibition	626		(9)
		Invertebrates	EC50 (96h)	22.4		(12)
		Bacteria	EC50 (15min)	21.2		(10)

Therapeutic class	Pharmaceutical compound	Species assayed	Test (endpoint)	Toxicity µg/L	PNEC µg/L	
		Invertebrates	EC50 (96h)	2.62		(12)
		Invertebrates	EC50	150		(3)
		Fish	EC50	600		(3)
		Daphnia	EC50-immobilisation	166.3		(9)
	Phenazone	*Fish*	EC50 ECOSAR	3	1.1	(2)
		Daphnia	EC50 ECOSAR	6.7		(2)
		Algae	EC50 ECOSAR	1.1		(2)
	Propyphenazone	*Fish*	EC50 ECOSAR	0.8	0.8	(2)
		Daphnia	EC50 ECOSAR	3.5		(2)
		Algae	EC50 ECOSAR	1		(2)
	Salicylic acid	*Fish*	EC50 ECOSAR	1.28	1.28	(2)
		Daphnia	EC50 ECOSAR	59		(2)
		Algae	EC50 ECOSAR	48		(2)
		Invertebrates	EC50 (48h)	1147		(14)
		Invertebrates	LC50 (48h)	112		(15)
		Algae	EC50 (48h)	>100		(16)
		Bacteria	EC50 (15min)	43.1		(10)
	Tolfenamic acid	*Fish*	EC50 ECOSAR	0.4	0.4	(2)
		Daphnia	EC50 ECOSAR	1.7		(2)
		Algae	EC50 ECOSAR	1.3		(2)
Antibiotics	Amoxicillin			0.1	0.0037	(17)
		Algae	EC50	0.0037		(18)
	Azithromycin			0.15	0.15	(17)
	Cefaclor	*Algae*	EC50 ECOSAR	734.05	687.42	(19)
		Daphnia	EC50 ECOSAR	687.42		(19)
		Fish	EC50 ECOSAR	11524		(19)
	Cefalexin			2.5	2.5	(17)
	Cefotaxime			0.04	0.04	(17)
	Chloramphenicol			1.6	1.6	(17)
	Ciprofloxacin	*Fish*	EC50 ECOSAR	246000	938	(2)
		Daphnia	EC50 ECOSAR	991		(2)
		Algae	EC50 ECOSAR	938		(2)
	Clarithromycin	*Invertebrates*	EC50	20	0.07	(3)
		Algae	EC50	0.07		(3)
	Clindamycin			0.5	0.5	(17)
	Doxycycline			0.3	0.3	(17)
				316		(20)
	Enoxacin			0.15	0.15	(17)
	Erythromycin	*Fish*	EC50 ECOSAR	61	0.02	(2)
		Daphnia	EC50 ECOSAR	7.8		(2)

Therapeutic class	Pharmaceutical compound	Species assayed	Test (endpoint)	Toxicity µg/L	PNEC µg/L	
		Algae	EC50 ECOSAR	4.3		(2)
		Invertebrates	EC50	15		(3)
		Algae	EC50	0.02		(3)
		Fish	EC50	900		(3)
	Lincomycin	*Fish*	EC50 ECOSAR	1391	82	(2)
		Daphnia	EC50 ECOSAR	82		(2)
		Algae	EC50 ECOSAR	86		(2)
	Metronidazole			2.5	2.5	(17)
		Algae	EC50	39.1		(18)
		Algae	EC50	40.4		(18)
	Norfloxacin	*Algae*	EC50	15	15	(3)
	Ofloxacin	*Algae*	EC50 (96h-growth)	0.016	0.016	(6)
		Invertebrates	EC50	30		(3)
		Algae	EC50	1.5		(3)
		Fish	EC50	10		(3)
	Oxytetracycline	*Algae*	EC50	0.207	0.207	(18)
		Fish	EC50 ECOSAR	166000		(2)
		Daphnia	EC50 ECOSAR	2432		(2)
		Algae	EC50 ECOSAR	2294		(2)
		Invertebrates	EC50 (96h)	40.13		(12)
	Penicillin G	*Algae*	EC50	0.006	0.006	(18)
	Penicillin V	*Daphnia*	EC50	177	177	(13)
	Roxithromycin	*Fish*	EC50 ECOSAR	50	4	(2)
		Daphnia	EC50 ECOSAR	6		(2)
		Algae	EC50 ECOSAR	4		(2)
	Sulfachloropyridazine	*Bacteria*	EC50 (15min-florescence)	26.4	26.4	(21)
	Sulfadiazine			5	0.135	(17)
		Algae	EC50	0.135		(18)
	Sulfadimethoxine	*Fish*	EC50 ECOSAR	226	3.5	(2)
		Daphnia	EC50 ECOSAR	3.5		(2)
		Algae	EC50 ECOSAR	24		(2)
	Sulfamethoxazole	*Fish*	EC50 ECOSAR	890	0.027	(2)
		Daphnia	EC50 ECOSAR	4.5		(2)
		Algae	EC50 ECOSAR	51		(2)
		Fish	EC50 (96h)	563		(21)
		Daphnia	EC50 (48h-mortality)	>100		(6)
		Bacteria	EC50 (15min)	78.1		(21)
		Algae	EC50 (96h-growth)	0.15		(6)

Therapeutic class	Pharmaceutical compound	Species assayed	Test (endpoint)	Toxicity µg/L	PNEC µg/L	
		Algae	EC50 (96h-growth)	0.027		(6)
	Sulfapyridine	*Invertebrates*	EC50 (96h)	21.61	21.61	(12)
	Sulfathiazole	*Daphnia*	EC50 (96h-immobility)	85.4	85.4	(21)
	Tetracycline			0.3	0.09	(17)
		Algae	EC50	0.09		(18)
	Trimethoprim	*Fish*	EC50 ECOSAR	795	2.6	(2)
		Daphnia	EC50 ECOSAR	4.8		(2)
		Algae	EC50 ECOSAR	2.6		(2)
		Bacteria	EC50 (15min)	177		(21)
		Daphnia	EC50 (96h-immobility)	121		(21)
		Invertebrates	LC50 (96h)	>100		(12)
		Fish	EC50 (48h)	>100		(21)
		Invertebrates	EC50	110		(3)
		Algae	EC50	90		(3)
		Fish	EC50	100		(3)
Antihypertensives	Diltiazem	*Daphnia*	EC50 (96h-immobility)	8.2	1.9	(21)
		Fish	EC50 ECOSAR	23		(2)
		Daphnia	EC50 ECOSAR	2.9		(2)
		Algae	EC50 ECOSAR	1.9		(2)
Beta-blockers	Atenolol	*Invertebrates*	EC50 ECOSAR	30	30	(3)
	Metoprolol	*Fish*	EC50 ECOSAR	116	8	(2)
		Daphnia	EC50 ECOSAR	8		(2)
		Algae	EC50 ECOSAR	14		(2)
		Invertebrates	LC50 (48h)	>100		(22)
		Invertebrates	LC50 (48h)	8.8		(22)
		Invertebrates	LC50 (48h)	63.9		(22)
		Fish	LC50 (48h)	>100		(22)
	Nadolol	*Invertebrates*	EC50	110	110	(3)
	Propranolol	*Fish*	EC50 ECOSAR	29.5	0.244	(2)
		Daphnia	EC50 ECOSAR	2.3		(2)
		Algae	EC50 ECOSAR	5.5		(2)
		Bacteria	EC50 (30min-luminescence)	61		(6)
		Algae	EC50 (48h)	0.7		(23)
		Diatoms	EC50 (96h-growth)	0.244		(6)
		Invertebrates	LC50 (48h)	29.8		(22)
		Invertebrates	LC50 (48h)	0.8		(22)
		Invertebrates	LC50 (48h)	1.6		(22)

Therapeutic class	Pharmaceutical compound	Species assayed	Test (endpoint)	Toxicity µg/L	PNEC µg/L	
		Fish	LC50 (48h)	24.3		(22)
		Invertebrates	EC50	11		(3)
		Algae	EC50	0.8		(3)
		Fish	EC50	20		(3)
	Timolol	*Fish*	EC50 ECOSAR	126	9	(2)
		Daphnia	EC50 ECOSAR	9		(2)
		Algae	EC50 ECOSAR	15.5		(2)
Lipid regulators	Bezafibrate	*Fish*	EC50 ECOSAR	5.3	5.3	(2)
		Daphnia	EC50 ECOSAR	25		(2)
		Algae	EC50 ECOSAR	18		(2)
		Invertebrates	EC50	50		(3)
	Clofibrate	*Fish*	EC50 ECOSAR	5	0.5	(2)
		Daphnia	EC50 ECOSAR	6.5		(2)
		Algae	EC50 ECOSAR	0.5		(2)
	Clofibric acid	*Fish*	EC50 ECOSAR	53	40.2	(2)
		Daphnia	EC50 ECOSAR	293		(2)
		Algae	EC50 ECOSAR	192		(2)
		Algae	EC50 (96h-growth)	94		(6)
		Bacteria	EC50 (30min)	91.8		(8)
		Invertebrates	EC50 (48h)	83.5		(24)
		Invertebrates	EC50 (48h)	72		(9)
		Microtox	EC50 (30min)	91.8		(8)
		Algae	EC50 (96h-growth)	40.2		(6)
	Fenofibrate	*Fish*	EC50 ECOSAR	0.8	0.1	(2)
		Daphnia	EC50 ECOSAR	0.35		(2)
		Algae	EC50 ECOSAR	0.1		(2)
	Fenofibric acid	*Fish*	EC50 ECOSAR	7.6	7.6	(2)
		Daphnia	EC50 ECOSAR	38		(2)
		Algae	EC50 ECOSAR	26		(2)
	Gemfibrozil	*Fish*	EC50 ECOSAR	0.9	0.9	(2)
		Daphnia	EC50 ECOSAR	6		(2)
		Algae	EC50 ECOSAR	4		(2)
		Bacteria	EC50 (15min)	35.3		(24)
		Bacteria	EC50 (15min)	18.8		(10)
		Invertebrates	EC50 (48h)	10.4		(15)
		Invertebrates	EC50 (96h)	1.18		(12)
	Pravastatin	*Fish*	EC50	1.8	1.8	(25)
Psychiatric drugs	Carbamazepine	*Fish*	EC50 ECOSAR	101	13.8	(2)
		Daphnia	EC50 ECOSAR	111		(2)
		Algae	EC50 ECOSAR	70		(2)

Therapeutic class	Pharmaceutical compound	Species assayed	Test (endpoint)	Toxicity µg/L	PNEC µg/L	
		Algae	EC50 (3d)	74		(9)
		Bacteria	EC50 (15min)	52.2		(21)
		Fish	EC (48h)	35.4		(21)
		Daphnia	EC (48h-mortality)	13.8		(6)
		Diatoms	EC (96h-growth)	31.6		(6)
		C. dubia	EC50 (48h)	77.7		(8)
	Diazepam	*Fish*	EC50 ECOSAR	28	2	(2)
		Daphnia	EC50 ECOSAR	2		(2)
		Algae	EC50 ECOSAR	5.5		(2)
		Fish	EC50	11		(3)
		Invertebrates	EC50	90		(3)
		Algae	EC50	12		(3)
	Fluoxetine	*Fish*	EC50 ECOSAR	1.7	0.05	(2)
		Daphnia	EC50 ECOSAR	0.17		(2)
		Algae	EC50 ECOSAR	0.8		(2)
		Fish	EC50	2		(3)
		Invertebrates	EC50	0.9		(3)
		Algae	EC50	0.05		(3)
Receptor antagonists	Cimetidine	*Fish*	EC50 ECOSAR	571	35	(2)
		Daphnia	EC50 ECOSAR	35		(2)
		Algae	EC50 ECOSAR	40		(2)
		Daphnia	EC50 (96h-immobility)	271.3		(21)
	Ranitidine	*Fish*	EC50 ECOSAR	1076	63	(2)
		Daphnia	EC50 ECOSAR	63		(2)
		Algae	EC50 ECOSAR	66		(2)
Beta-agonists	Clenbuterol	*Fish*	EC50 ECOSAR	30	2	(2)
		Daphnia	EC50 ECOSAR	2		(2)
		Algae	EC50 ECOSAR	10		(2)
	Fenoterol	*Fish*	EC50 ECOSAR	20	17.5	(2)
		Daphnia	EC50 ECOSAR	17.5		(2)
		Algae	EC50 ECOSAR	25		(2)
	Terbutaline	*Fish*	EC50 ECOSAR	1.05	1.05	(2)
		Daphnia	EC50 ECOSAR	27		(2)
		Algae	EC50 ECOSAR	32		(2)
Antineoplastics	Cyclophosphamide	*Fish*	EC50 ECOSAR	70	11	(2)
		Daphnia	EC50 ECOSAR	1795		(2)
		Algae	EC50 ECOSAR	11		(2)
	Ifosfamide	*Fish*	EC50 ECOSAR	140	11	(2)
		Daphnia	EC50 ECOSAR	1795		(2)

Therapeutic class	Pharmaceutical compound	Species assayed	Test (endpoint)	Toxicity µg/L	PNEC µg/L	
Contrast media	Iopromide	*Algae*	EC50 ECOSAR	11		(2)
		Fish	EC50 ECOSAR	865,000	370,000	(2)
		Daphnia	EC50 ECOSAR	766,000		(2)
		Algae	EC50 ECOSAR	370,000		(2)

(1) Stuer-Lauridsen et al. (2000); (2) Sanderson et al. (2003); (3) Boillot (2008); (4) Kühn (1989); (5) US EPA (1999); (6) Ferrari et al. (2004); (7) Ra et al. (2008); (8) Ferrari et al. (2003); (9) Cleuvers (2004); (10) Farré et al. (2001); (11) Halling-Sorensen et al. (1998); (12) Quinn et al. (2008); (13) Jones et al. (2002); (14) Marques et al. (2004); (15) Han et al. (2006); (16) Henschel et al. (1997); (17) Kümmerer and Henninger (2003); (18) Halling-Sorensen (2000); (19) Lee et al. (2008); (20) Brain et al. (2004); (21) Kim et al. (2007); (22) Huggett et al. (2002); (23) Cleuvers (2005); (24) Rosal et al. (2009); (25) Ginebreda et al. (2010)

The environmental risk assessment performed through the risk quotient (RQ) PEC / PNEC for the pharmaceutical compounds presented in the Table 4-11 and whose presence in the effluent from wastewater treatment plants is shown in the Table 4-2 are summarized in the **Figure 4-5** Risk of Pharmaceuticals compounds in conventiona WWTP effluent. Source: Verlicchi, et al. 2012**Figure 4-5** Risk of Pharmaceuticals compounds in conventiona WWTP effluent. Source: Verlicchi, et al. 2012.

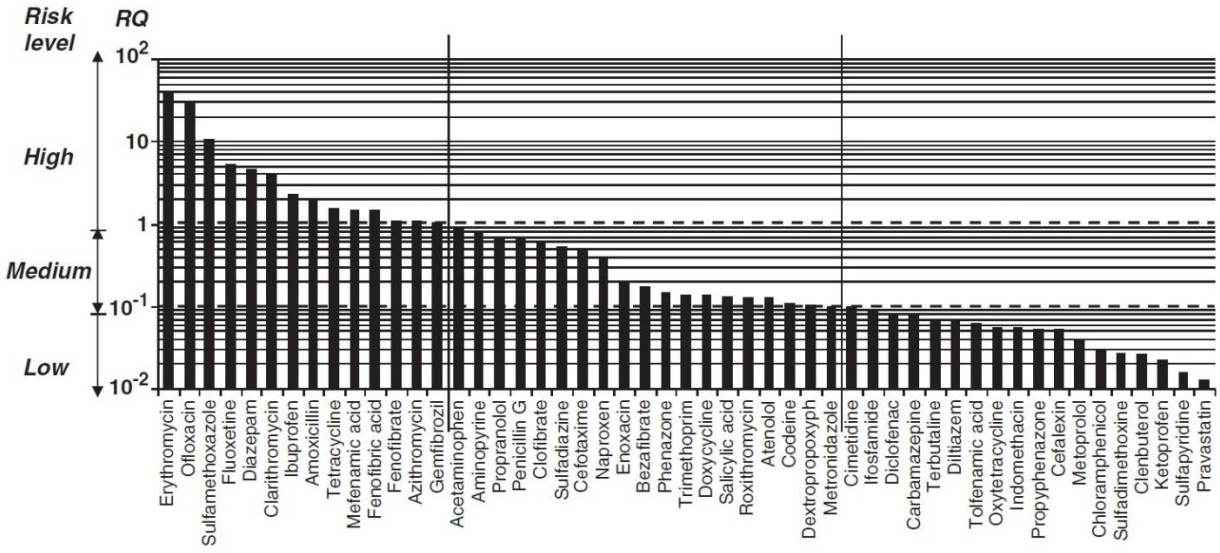


Figure 4-5 *Risk of Pharmaceuticals compounds in conventiona WWTP effluent. Source: Verlicchi, et al. 2012*

Fourteen compounds present high risk (RQ ratios higher than one) of which seven are antibiotics (erythromycin, ofloxacin, sulfamethoxazole, clarithromycin, amoxicillin, tetracycline, and azithromycin), tow psychiatric drugs (fluoxetine, and diazepam), two analgesics-anti/inflammatories (ibuprofen, and mefenamic acid), and three are lipid regulators (fenofibric acid, fenofibrate, and gemfibrozil).

Nineteen compounds present medium risk (RQ ratios between 0.1 and 1) of which seven are analgesic-anti/inflammatories (acetaminophene, aminopyrine, naproxen, phenazone, codeine, and dextropropoxyphene), eight antibiotics (penicillin G, sulfadiazine, cefotaxime, enoxacin,

trimethoprim, doxycycline, roxithromycin, and metronidazole), two beta-blockers (propranolol, and atenolol), and two lipid regulators (clofibrate, and bezafibrate). The rest of the compounds present a low environmental risk (RQ ration lower than 0.1).

The measurement of the estrogenic activity of the effluents has a great variability. The variability depends on the method due to the high variability of the chemical species in the effluents and the synergistic effects between the estrogens and the water matrix.

Fernandez, et al. 2007, measured the estrogenic activity in WWTP effluent. Their study observed that 17α-Ethynylestradiol (EE2), BPA, NP, 17β-Estradiol E2), Estrone (E1) are responsible for most of the estrogenicity in all samples analyzed.

The same study also analyzed the sexual reversal or intersexuality of Chinook salmon (*Oncorhynchus shawytscha*) without finding evidence of adverse effects.

The Table **4-12** shows the lowest observable effects levels (LOEL) in fish for 17α-Ethynylestradiol (EE2), 17β-Estradiol (E2) and Estrone (E1).

Table 4-12 *Reported levels for adverse endocrine effects in fish. Source: Fernandez, et al. 2007*

Compound	Lowest observable effects level (LOEL)	Reported effect(s)	Mean effluent level
17α-Ethynylestradiol (EE2)	1 ng/L[a]	↑Vitellogenin	< 1 ng/L⋆
17β-Estradiol (E2)	1–10 ng/L[c]	↑Vitellogenin	5.5 ng/L
Estrone (E1)	25–50 ng/L[c]	↑Vitellogenin	41 ng/L

⋆Excluding extreme value of 131 ng/L for this substance found in the week 8 effluent. [a]Jobling et al. (2003); [c]Routledge et al. (1998).

The mean concentration of the hormones Ethynylestradiol (EE2), 17β-Estradiol (E2), and Estrone in the effluents of the conventional treatment plants shown in the Chapter 4.1.4 are 3 ng /L, 10 ng/L and 30 ng/L respectively.

If there was no dilution capacity of the effluent receiving body and the species studied were relevant, they would present an environmental risk for causing endocrine Vitellogenin-like effects in fish.

Risk of pesticides in effluents

The analysis of the removal of pesticides by conventional WWTP allows to identify the level of persistence of this type of compounds.

Many pesticides have formulations that make them toxic to certain organisms and non-toxic to others, so the presence of a compound can mean different levels of risk depending on the different species. The Table 4-13 show the critical toxicological end point concentrations for the standard tests EC50, and LC50 for algae, *Daphnia* and fish.

Following the same environmental risk classification methodology described above, the RQ was calculated considering the predicted non effect environmental concentrations given from the toxicity tests exhibited in the Table 4-13 and the mean concentrations of the effluents from the conventional treatment plants discussed in the Chapter 4.1.4. The risk is estimated considering the RQ ratio; a reduced factor of 1000 was applied to the PNEC as shown in Table **4-14** (Köck-Schulmeyer, et al. 2012).

Table 4-13 *EC50 / LC50 of the target pesticides for algae,* Daphnia *and fish, and Log K_{ow} of each pesticide. From Köck-Schulmeyer, et al. 2012*

	Algae EC50[a] (mg/L)	*Daphni* EC50[b] (mg/L)	Fish LC50[c] (mg/L)	$LogK_{ow}$[8]
Triazines				
atrazine	0.059[1]	6.9[7]	4.5[1]	2.7
cyanazine	0.2[3]	49[5]	10[6]	2.1
desethylatrazine	0.1[3]	6.9[e]	4.5[e]	1.51
deisopropylatrazine	0.050[d]	3.795[d]	47.25[d]	1.15
simazine	0.04[1]	1.1[1]	90[1]	2.3
terbuthylazine	0.012[2]	21.2[5]	2.2[2]	3.4
Phenylureas				
chlortoluron	0.024[2]	67[2]	20[2]	2.5
diuron	0.0027[3]	12[7]	4.3[5]	2.87
isoproturon	0.013[2]	507[7]	37[7]	2.5
linuron	0.016[2]	0.12[7]	3.15[7]	3
Organophosphates				
diazinon	6.4[2]	0.001[2]	3.1[2]	3.69
dimethoate	90.4[2]	2[2]	30.2[2]	0.704
fenitrothion	1.3[2]	0.0086[2]	1.3[2]	3.32
malathion	13[1]	0.0007[2]	0.1[7]	2.75
Anilides and Chloroacetanilides				
alachlor	0.966[3]	10[3]	1.8[1]	3.09
metolachlor	57.1[3]	23.5[4]	3.9[4]	3.4
propanil	0.05[9]	4.8[7]	2.3[5]	2.29
Thiocarbamate				
molinate	0.5[2]	14.9[2]	16[2]	2.86
Acids				
2,4D	24.2[2]	100[2]	100[7]	-0.83

bentazone	10.1[(2)]	125[(7)]	100[(2)]	-0.46
MCPA	79.8[(2)]	190[(2)]	50[(2)]	-0.81
mecoprop	237[(2)]	420[(7)]	150[(7)]	-0.19

a) 72 hrs; b) 48 hrs; c) 96 hrs; d) average of ATR with SIM; e) the same as ATR

(1) UK PSD ACP Evaluation Documents / and other DEFRA (UK) documents (See http://www.pesticides.gov.uk/publications.asp?id=202)

(2) EU Regulatory & Evaluation Data as published by EC and EFSA (DAR & Conclusion dossiers) / EU Annex III PIC DGD / EU MRL Database (See http://ec.europa.eu/sanco_pesticides/public/index.cfm)

(3) U.S. EPA ECOTOX Database (see http://cfpub.epa.gov/ecotox/) / U.S. EPA Pesticide Fate Database (See http://cfpub.epa.gov/pfate/home.cfm) / Miscellaneous WHO documents.

(4) Extension Toxicology network Database EXTOXNET (See http://extoxnet.orst.edu/ghindex.html)

(5) Pesticide Action Network Database (See http://www.pesticideinfo.org/)

(6) U.S. Department of Interior, Fish and Wildlife Service. Handbook of Acute Toxicity of Chemicals to Fish and Aquatic Invertebrates. Resource Publication No. 137. Washington, DC: U.S. Government Printing Office, 1980, p. 23.

(7) Book: The pesticide Manual. Editor: Clive Tomlin, Editorial: Crop protection publications, Tenth edition

(8) Agriculture & Environment Research Unit (AERU), 2011. The PPDB, Pesticide Properties Database. University of Herfordshire, UK (see)http://sitem.herts.ac.uk/aeru/footprint/

(9) French database provided by ARVALIS-Institut du Végétal.

Table 4-14 *Risk of pesticides in conventional WWTP effluent.*

	PEC ng/L	PNEC Algae ng/L	PNEC *Daphnia* ng/L	PNEC Fish ng/L	RQ Algae	RQ *Daphnia*	RQ Fish
Triazines							
atrazine	124	59	6900	4500	**2,1**	0,02	0,03
cyanazine	---	200	49000	10000	---	---	---
desethylatrazine	22,7	100	6900	4500	0,2	0,00	0,01
deisopropylatrazine	38,8	50	3765	47250	0,8	0,01	0,00
simazine	169	40	1100	90000	**4,2**	0,15	0,00
terbuthylazine	20	12	21200	2200	**1,7**	0,00	0,01
Phenylureas							
chlortoluron	98,2	24	67000	20000	**4,1**	0,00	0,0
diuron	127	2,7	12000	4300	**47,0**	0,01	0,0
isoproturon	13,2	13	507000	37000	**1,0**	0,00	0,0
linuron	---	16	120	3150	---	---	---
Organophosphates							
diazinon	281	6400	1	3100	0,0	**281,00**	0,1
dimethoate	49,1	90400	2000	30200	0,0	0,02	0,0
fenitrothion	---	1300	8,6	1300	---	---	---
malathion	0,48	13000	0,7	100	0,0	0,69	0,0
Anilides and Chloroacetanilides							
alachlor	---	966	10000	1800	---	---	---

metolachlor	---	57100	23500	3900	---	---	---
propanil	9,42	50	4800	2300	0,2	0,00	0,0
Thiocarbamate							
molinate	---	500	14900	16000	---	---	---
Acids							
2,4D	42,9	24200	100000	100000	0,0	0,00	0,0
bentazone	12,2	10100	125000	100000	0,0	0,00	0,0
MCPA	15,1	79800	190000	50000	0,0	0,00	0,0
mecoprop	17,3	237000	420000	150000	0,0	0,00	0,0

The results show that there is a greater ecotoxicological risk for algae and invertebrates than for fish. The organophosphate compounds (diazinon, phenylurea chlortoluron, and diuron), the isoproturon compounds, and the triazines (atrazine, simazine, and terbuthylazine) are the main contributors to the overall toxicity; therefore, the most problematic compounds.

Risk of personal care products (PCP)s in effluents

Personal care products are substances used in large quantities and many of them have been classified as environmentally persistent, bioactive, or biocumulative.

Brausch and Rand (2011), compiled the acute and chronic toxicity data for PCPs and determined a set of substances on which further investigation is needed. The Table 4-15 shows the results for acute toxicity test, while the Table 4-16 shows the results for chronic toxicity.

From the toxicity tests available on disinfectants, the triclosan and triclocarban compounds exhibit the larger toxicity values. The presence of the methyl triclosan derivative (M-TCS) has also been identified; this compound is stable and lipophilic, so it would be necessary to study the possible bioaccumulation potential for this substance. Algae and invertebrates are more sensitive in the acute toxicity and long-term exposure tests to the collected disinfectants. Algae are especially sensitive to triclosan and triclocarban.

Fragrances are ubiquitous substances. Nitro musks are being phased out due to their persistence and potential toxicity to the aquatic compartment. The most widely used musks are the polycyclics. The high octanol-water coefficients (log Kow = 5.4 to 5.9 for poliycyclic musks) indicate a high bioaccumulation potential. Nitro musks exhibit low acute toxicity, but they are potentially toxic to aquatic organisms under long term exposures. Polycyclic musks, in addition to being potentially toxic in the long term, exhibit more acute toxicity than nitro musks. The musks had no toxic effects on amphibians, and they have not significant effects on invertebrates.

DEET is the most common active compound within the insect repellents. DEET is a persistent compound in the aquatic environment, and it exhibits a low bioconcentration factor (BCF). Therefore, it might probably not bioaccumulate. This compound exhibit a slightly acute toxicity. Chronic exposures evaluations did not show specific adverse effects; howver, these

studies are not comprehensively sufficient to conclude, since there are still many effects not yet investigated.

There are seven types of parabens (used as preservatives) mostly used as follows: benzyl, butyl, ethyl, isobutyl, isopropyl, methyl, and propyl. Of these compounds benzylparaben appears to be the most toxic. Several acute toxicity studies and a few chronic exposure studies, recopilated in (Brausch and Rand, 2011) performed on these compunds showed that benzyl-, butyl- and propylparaben compounds could cause limited adverse effects in aquatic organisms. The reported environmental concentrations mostly suggests minimal risk for these compounds.

UV filters substances are potentially bioaccumulating compounds. Chronic exposure evaluations have shown potential estrogenic activity.

Brausch and Rand (2011) performed a preliminary environmental risk assessment for each of the PCPs previously described. The PEC of the surface water is taken rather than the PECs of the effluents from the treatment plants. From this analysis it can be seen that only triclosan and triclocarban present a potential of causing chronic toxicity effects having a PEC/PNEC ratio greater than one.

Using the PNECs of this study but applied to the PECs of the conventional WWTP effluents collected in Table 4-4, the following environmental risk coefficients are obtained (Table 4-14). The risk coefficients, correspond to the situation where the receiving body does not have the capacity to dilute the effluent.
Traseolide (ATII), Phantolide (AHMI), Cachmeran (DPMI) Propylparaben, and Benzophenone-4 exhibit some risk, so they should be analyzed with more attention.

Table 4-15 *Acute toxicity data for personal care products. Source: Brausch, and Rand 2011.*

Compound	Category	Species	Trophic group	Endpoint /duration	LC50 (mg/L)	Additional tox. Values	
Biphenylol	Antimicrobial	*Daphnia magna*	Invert.	48 h Mobility	3.66		(1)
		D. magna	Invert.	48 h Survival	3.66		(2)
		Tetrahymena pyriformis	Invert.	48 h Survival	5.7–8.26		(3)
		T. pyriformis	Invert.	60 h Survival	0.7–8.26		(4)
		Cyprinus carpio	Fish	44 h Survival	157–292		(5)
Triclosan	Antimicrobial	*D. magna*	Invert.	48 h	0.39		(6)
		Ceriodaphnia dubia	Invert.	24, 48 h (pH=7.0)	0.2,~125		(6)
		Pimephales promelas	Fish	24, 48, 72, 96 h	0.36, 0.27, 0.27, 0.26		(6)
		Lepomis macrochirus	Fish	24, 48, 96 h	0.44, 0.41, 0.37		(6)
		Oryzias latipes	Fish	96 h	0.602 (larvae),		(7)

Compound	Category	Species	Trophic group	Endpoint /duration	LC50 (mg/L)	Additional tox. Values	
					0.399 (embryos)		
		Xenopus laevis	Amphibian	96 h	0.259		(8)
		Acris blanchardii	Amphibian	96 h	0.367		(8)
		Bufo woodhousii	Amphibian	96 h	0.152		(8)
		Rana sphenocephala	Amphibian	96 h	0.562		(8)
		Pseudokirch-neriella subcapitata	Algae	72 h Growth	0.53 (µg/L)		(9)
Triclocarban	Antimicrobial	*D. magna*	Invert.	48 h	0.01		(10)
		C. dubia	Invert.	48 h	0.0031		(10)
		Mysidopsis bahia	Invert.	48, 96 h	0.015, .01		(10)
		Salmo gairdneri	Fish	96 h	0.120		(10)
		L. macrochirus	Fish	96 h	0.097		(10)
		Scenedesmus subspicatus	Algae	72 h Growth	0.02		(10)
		P. subcapitata	Algae	72 h Growth	0.017 (µg/L)		89)
Benzophenone	Fixative	*Caenorahbditis elegans*	Nematode	24 h	56.8		(11)
		P. promelas	Fish	96 h	10.89		(12)
1,4-dichlorobenzene[a]	Insect repellant	*D. magna*	Invert.	24, 48 h Immobilization	1.6, 0.7		(13), (14)
		Artemia salina	Invert.	24 h	14		(15)
		Palaemonetes pugio	Invert.	96 h	60		(16)
		M. bahia	Invert.	96 h	1.99		(17)
		Danio rerio	Fish	24 h, 96 h	4.25, 2.1		(18), (19)
		Jordanella floridae	Fish	96 h	2.05		(20)
		P. promelas	Fish	96 h	4.2		(21)
		O. mykiss	Fish	24 h	1.18		(19)
		L. macrochirus	Fish	96 h	4.3		(22)
		Cyprinodon variegatus	Fish	96 h	7.4		(23)
		Selenastrum capricornutum	Algae	96 h Growth	0.57		(14)
		Scenedesmus pannonicus	Algae	72 h Growth	31		(13)
		S. subspicatus	Algae	48 h Growth, Biomass	38, 28		(22)

Compound	Category	Species	Trophic group	Endpoint /duration	LC50 (mg/L)	Additional tox. Values	
		Skeletonema costatum	Algae	96 h Growth	59.1		(17)
N,N-diethyl-m-toluamide (DEET)b	Insect repellant	*D. magna*	Invert.	48 h, 96 h	160, 108		(25)
		Gammarus fasciatus	Invert.	96 h	100		(26)
		P. promelas	Fish	96 h	110		(27)
		Gambusia affinis	Fish	24–48 h	235		(28)
		Oncorhynchus mykiss	Fish	96 h	71.3		(29)
		Chlorella protothecoides	Algae	4 h Photosynthesis	388		(30)
Musk ambrette (MA)	Nitro musk	*Vibrio fischeri*	Bacteria	Microtox	>Sol.[c]		(31)
		Pseudokirch-neriella subcapitata	Algae	72 h	>Sol.		(31)
Musk ketone (MK)	Nitro musk	*V. fischeri*	Bacteria	Microtox	>Sol.		(31)
		Nitocra spinipes	Invert.	96 h	>1.0		(32)
		Acartia tonsa	Invert.	48 h	1.32	LC10=0.40	(33)
		D. magna	Invert.	24, 48 h	>Sol., 5.6		(28)
		D. magna	Invert.	48 h	>0.46		(31)
		D. rerio	Fish	96 h Survival, Hatching	>0.4		(28)
		P. subcapitata	Algae	72 h	>Sol.		(31)
Musk moskene (MM)	Nitro musk	*V. fischeri*	Bacteria	Microtox	>Sol.		(31)
		D. magna	Invert.	24 h	>Sol.		(31)
		Danio rerio	Fish	96 h Survival, Hatching	>0.4		(34)
		P. subcapitata	Algae	72 h	>Sol.		(31)
Musk Tibetene (MT)	Nitro musk	*V. fischeri*	Bacteria	Microtox	>Sol.		(31)
		P. subcapitata	Algae	72 h	>Sol.		(31)
Musk xylene (MX)	Nitro musk	*V. fischeri*	Bacteria	Microtox	>Sol.		(31)
		D. magna	Invert.	24, 48 h Mobility	EC50≤Sol.		(35)
		Oncorhynchus. mykiss	Fish	96 h	>1000		(36)
		L. macrochirus	Fish	96 h	1.2		(37)
		D. rerio	Fish	96 h Survival, Hatching	>0.4		(34)

Compound	Category	Species	Trophic group	Endpoint /duration	LC50 (mg/L)	Additional tox. Values	
		P. subcapitata	Algae	72 h	>Sol.		(31)
Celestolide (ADBI)	Polycyclic musk	*N. spinipes*	Invert.	96 h	>2.0		(38)
		A. tonsa	Invert.	48 h	>2.0	LC10>2.0	(39)
		D. rerio	Fish	96 h Survival, Hatching	>1.0		(38)
		D. rerio	Fish	96 h Malformation	LOEC~0.65		(39)
		O. latipes	Fish	96 h Survival	1.97		(40)
Galaxolide (HHCB)	Polycyclic musk	*N. spinipes*	Invert.	96 h	1.90		(28)
		A. tonsa	Invert.	48 h	0.47	LC10=0.12	(39)
		Lampsilis cardium	Benthic invert.	24, 48 h	1.0, 0.99		(41)
		D. rerio	Fish	Fish 96 h Survival, Hatching	>0.67		(39)
		D. rerio	Fish	96 h Malformations	LOEC~0.45		(39)
		O. latipes	Fish	96 h Survival	0.95		(40)
Tonalide (AHTN)	Polycyclic musk	*N. spinipes*	Invert.	96 h	0.61		(31)
		A. tonsa	Invert.	48 h	0.71	LC10=0.45	(32)
		L. cardium	Benthic invert.	24, 48 h	0.45, 0.28		(41)
		D. rerio	Fish	96 h Malformation	LOEC~0.1		(39)
		D. rerio	Fish	96 h Survival, Hatching	>0.67		(38)
		O. latipes	Fish		1.00		(40)
Traseolide (ATII)		*O. latipes*	Fish	96 h Survival	0.95		(40)
Phantolide (AHMI)		*O. latipes*	Fish	96 h Survival	1.22		(40)
Cachmeran (DPMI)		*O. latipes*	Fish	96 h Survival	11.6		(40)
Benzylparaben	Preservative	*T. thermophila*	Protozoa	24 h, 28 h	4.3, 5.7	LOEC=0.48	(42)
		V. fisheri	Bacteria	15 min, 30 min Illuminescence	0.11, 0.11	LOEC=0.02	(42)
		Photobacterium leiognathi	Bacteria	15 min, 30 min Illuminescence	1.3, 1.6	LOEC=0.25	(42)
		D. magna	Invert.	48 h	4.0		(43)
		D. magna	Invert.	24 h, 48 h Mobility	5.2, 6	LOEC=1.2	(42)
		P. promelas	Fish	48 h	3.3		(43)
Butylparaben	Preservative	*T. thermophila*	Protozoa	24 h, 28 h	5.3, 7.3	LOEC=2.5	(42)
		V. fisheri	Bacteria	15 min, 30 min	2.5, 2.8	LOEC=0.7	(42)

Compound	Category	Species	Trophic group	Endpoint /duration	LC50 (mg/L)	Additional tox. Values	
				Illuminescence			
		P. leognathi	Bacteria	15 min, 30 min Illuminescence	3.7, 4.3	LOEC=1.12	(42)
		D. magna	Invert.	48 h	5.3		(43)
		D. magna	Invert.	24 h, 48 h Mobility	6.2, 6	LOEC=3.2	(42)
		P. promelas	Fish	48 h	4.2		(43)
Ethylparaben	Preservative	*T. thermophila*	Protozoa	24 h, 28 h	25, 30	LOEC=10.7	(42)
		V. fisheri	Bacteria	15 min, 30 min Illuminescence	2.5, 2.7	LOEC=0.55	(42)
		P. leognathi	Bacteria	15 min, 30 min Illuminescence	19, 24	LOEC=5.5	(42)
		D. magna	Invert.	48 h	18.7		(43)
		D. magna	Invert.	24 h, 48 h Mobility	25,23	LOEC=12	(42)
		P. promelas	Fish	48 h	34.3		(43)
Isobutylparaben	Preservative	*D. magna*	Invert.	48 h	7.6		(43)
		P. promelas	Fish	48 h	6.9		(43)
Isopropylparaben	Preservative	*D. magna*	Invert.	48 h	8.5		(43)
		P. promelas	Fish	48 h	17.5		(43)
Methylparaben	Preservative	*T. thermophila*	Protozoa	24 h, 28 h	54, 58	LOEC=11.5	(42)
		V. fisheri	Bacteria	15 min, 30 min Illuminescence	9.6, 10	LOEC=2.9	(42)
		P. leognathi	Bacteria	15 min, 30 min Illuminescence	31,35	LOEC=8.5	(42)
		D. magna	Invert.	48 h	24.6		(42)
		D. magna	Invert.	24 h, 48 h Mobility	32, 21	LOEC=15	(42)
		P. promelas	Fish	48 h	>Sol.		(43)
Propylparaben	Preservative	T. thermophila	Protozoa	24 h, 28 h	9.7, 12.5	LOEC=2.6	(42)
		V. fisheri	Bacteria	15 min, 30 min Illuminescence	2.5, 2.6	LOEC=0.9	(42)
		P. leognathi	Bacteria	15 min, 30 min Illuminescence	21, 25	LOEC=4.5	(42)
		D. magna	Invert.	48 h	12.3		(43)
		D. magna	Invert.	24 h, 48 h Mobility	13, 7	LOEC=6	(42)
		P. promelas	Fish	48 h	9.7		(43)
Benzophenone-3	UV filter	D. magna	Invert.	48 h Immobility	1.9		(44)
Benzophenone-4	UV filter	D. magna	Invert.	48 h Immobility	50		(44)
4-Methylbenzy-lidene camphor	UV filter	D. magna	Invert.	48 h Immobility	0.56		(44)
2-Ethyl-hexyl-4-	UV filter	D. magna	Invert.	48 h	0.29		(44)

Compound	Category	Species	Trophic group	Endpoint /duration	LC50 (mg/L)	Additional tox. Values
trimethoxy-cinnamate				Immobility		

(1) Kopperman et al. (1974), (2) Carlson and Caple (1977), (3) Schultz et al. (1989), (4) Schultz and Riggin (1985), (5) Loeb and Kelly (1963), (6) Orvos et al. (2002), (7) Ishibashi et al. (2004), (8) Palenske et al. (2010), (9) Yang et al. (2008), (10) TCC Consortium (2002), (11) Ura et al. (2002), (12) Marchini et al. (1992), (13) Canton et al. (1985), (14) Calamari et al. (1982), (15) Abernathy et al. (1986), (16) Curtis and Ward (1981), (17) USEPA (1978), (18) Roederer (1990), (19) Calamari et al. (1983), (20) Smith et al. (1990), (21) Carlson and Kosian (1987), (22) Buccafusco et al. (1981), (23) Heitmuller et al. (1981), (24) Kuhn and Pattard (1990), (25) Seo et al. (2005), (26) Mayer and Ellersieck (1986), (27) Brooke et al. (1984), (28) Michael and Grant (1974), (29) Office of Pesticides Program (2000), (30) Costanzo et al. (2007), (31) Schramm et al. (1996), (32) Breitholtz et al. (2003), (33) Wollenberger et al. (2003), (34) Tas et al. (1997), (35) Hughes and Krishnaswami (1985), (36) MITI (1992), (37) Adema and Langerwerf (1985a,b), (38) Van der Plassche and Balk (1997), (39) Dietrich and Chou (2001), (40) Yamauchi et al. (2008), (41) Gooding et al. (2006), (42) Bazin et al. (2010), (43) Dobbins et al. (2009), (44) Fent et al., 2009.

a 1,4-dichlorobenzene table is modified from Boutonnet et al. (2004).

b DEET information is modified from Table presented by Costanzo et al. (2007).

c No effects found at concentrations exceeding water solubility.

Table 4-16 *Chronic toxicity data for personal care products. Brausch, and Rand 2011.*

Compound	**Category**	**Species**	**Trophic level**	**Endpoint/duration**	**LOEC (µg L^{-1})**	**NOEC (µg L^{-1})**	
Triclosan	Antimicrobial	D. magna	Invert.	21 d Survival, Reproduction	Repro.=200 (LOEC)	Surv.=200 (NOEC)	(1)
		C. dubia	Invert.	7 d Survival, Reproduction		50,6	(1)
		C. dubia	Invert.	7 d Survival, Reproduction	IC25=170		(2)
		Chironomus riparius	Invert.	28 d Survival, Emergence		440	(3)
		Chironomus tentans	Invert.	10 d Survival, Growth	LC25=100		(4)
		Hyalella azteca	Invert.	10 d Survival, Growth	LC25=60		(4)
		O. mykiss	Fish	96 d ELS[c] Hatching, Survival	No Effect, 71.3		(1)
		O. latipes	Fish	14 d Hatching	213		(5)
		O. latipes	Fish	21 d Growth, Fecundity, HSI and GSI[d], VTG[e]	200, No Effect, 200, 20		(5)
		O. latipes	Fish	14 d Hatchability	IC25=290		(2)
		Gambusia affinis	Fish	35 d Sperm Count, VTG	101.3		(6)
		Danio rerio	Fish	9 d Hatchability	IC25=160		(2)
		Xenopus laevis	Amphibian	21 d Metamorphosis	No effect (200)		(7)
		Rana catesbeiana	Amphibian	18 d Development	300		(8)

Compound	Category	Species	Trophic level	Endpoint/duration	LOEC (µg L^{-1})	NOEC (µg L^{-1})	
		Rana pipiens	Amphibian	24 d Survival, Growth	230, 2.3		(9)
		Bufo americanus	Amphibian	14 d Survival, Growth	No effect (230)		(10)
		S. capricornutum	Algae	96 h Growth	EC50=4.46	EC25=2.44	(1)
		S. subspicatus	Algae	96 h Biomass, Growth Rate	EC50=1.2, 1.4	EC50=0.5, 0.69	(1)
		S. costatum	Algae	96 h Growth Rate	EC50≥66	EC25 > 66	(1)
		A. flos-aquae	Algae	96 h Biomass	EC50 = 0.97	EC25 = 0.67	(1)
		P. subcapitata	Algae	72 h Growth	EC25 = 3.4	0.2	(2),(11)
		N. pelliculosa	Algae	96 h Growth Rate	EC50 = 19.1	EC25 = 10.7	(1)
		Natural algal assemblage	Algae	96 h Biomass	0.12		(12)
		Closterium ehrenbergii	Algae	96 h Growth		250	(13)
		Dunaliella tertiolecta	Algae	96 h Growth		1.6	(14)
		L. gibba	Plant	7 d Growth	EC50≥62.5	EC25≥62.5	(1)
		S. herbacea	Plant	28 d Seed Germination, Morphology	100 germination, 10 morphology		(15)
		E. prostrata	Plant	28 d Seed Germination, Morphology	No effect, 1000		(15)
		B. frondosa	Plant	28 d Seed Germination, Morphology	100,1		(15)
Triclocarban	Antimicrobial	D. magna	Invert.	21 d Growth	4.7	2.9	(16)
		M. bahia	Invert.	28 d Reproduction	0.13	0.06	(16)
		P. subcapitata	Algae	14 d Growth	10 000	EC50=36000	(16)
Benzophenone	Fixative	Pimephales promelas	Fish	7 d Survival, Growth	9240, 3100	5860, 2100	(17)
		P. promelas	Fish	7 d ELS (Survival, Growth)	6400, 1800	3300, 1000	(17)
1,4-dichlorobenzene	Insect repellant	D. magna	Invert.	28 d Growth		0.22	(18)
		D. magna	Invert.	21 d Reproduction		0.3	(19)
		Jordanella floridae	Fish	28 d Growth		>0.35	(20)
		O. mykiss	Fish	60 d Growth		>0.122	(18)
		P. promelas	Fish	33 d Growth		0.57	(21)
		D. rerio	Fish	28 d Growth		1.0	(22)
Musk ketone (MK)	Nitro musk	D. magna	Invert.	21 d Development, Reproduction	340		(23)
		D. magna	Invert.	21 d Survival	LC50 = 338–		(24)

Compound	Category	Species	Trophic level	Endpoint/duration	LOEC (µg L^{-1})	NOEC (µg L^{-1})	
					675		
		A. tonsa	Invert.	5 d Developmental Rate	EC50 = 66	EC10=10	(25)
		A. tonsa	Invert.	5 d Juvenile Survival	2000	800	(25)
		N. spinipes	Invert.	7 d Developmental Rate, Survival	30		(23)
		N. spinipes	Invert.	26 d Population Growth Rate	100		(23)
		D. rerio	Fish	ELS 24–48 h Tail Extension, Coagulated Eggs, Edema, Circulation	1000	330	(26)
		D. rerio	Fish	ELS 24–48 h Movement, Tail Extension	330	100	(26)
		D. rerio	Fish	ELS 48 h Heart Rate	10	3.3	(26)
		D. rerio	Fish	ELS 48 h Survival	33	10	(26)
		O. mykiss	Fish	21 d Reproduction	EC50 = 169–338		(27)
		L. macrochirus	Fish	21 d Survival	LC50≥500		(28)
		D. rerio	Fish	8w Reproduction	33		28
		P. promelas	Fish	96 h Teratogenesis	EC50≥400		28
		X. laevis	Amphibian	96 h FETAX[b]	>4000		29
		P. subcapitata	Algae	72 h Growth, Biomass	EC50 = 244, 118		30
Musk moskene (MM)	Nitro musk	D. magna	Invert.	21 d Survival	LC50≥Sol.		31
		O. mykiss	Fish	21 d Reproduction	EC50≥Sol.		29
		X. laevis	Amphibian	96 h FETAX	EC50≥400		30
Musk xylene (MX)	Nitro musk	D. magna	Invert.	21 d Survival	LC50 = 680		32
		D. rerio	Fish	ELS 24–48 h Tail Extension, Coagulated Eggs, Edema, Circulation	1000	330	27
		D. rerio	Fish	Circulation, Movement ELS 48 h Heart Rate, Survival	330	10	27
		D. rerio	Fish	14 d Survival	LC50 = 400		33
		X. laevis	Amphibian	96 h FETAX[b]	>400		30
		P. subcapitata	Algae	72 h Growth, Biomass	EC50≥Sol.[a]		34
		M. aeruginosa	Algae	5 d Cell Count	>10 000		34
Celestolide	Polycyclic	N. spinipes	Invert.	7 d Developmental	100		24

Compound	Category	Species	Trophic level	Endpoint/duration	LOEC (µg L^{-1})	NOEC (µg L^{-1})	
(ADBI)	musk			Rate, Survival			
		A. tonsa	Invert.	5 d Developmental Rate	EC50 = 160	EC10=36	28
		A. tonsa	Invert.	5 d Juvenile Survival	600	240	28
		X. laevis	Amphibian	96 h FETAX	EC50≥1000		30
Galaxolide (HHCB)	Polycyclic musk	D. magna	Invert.	21 d Development, Reproduction	282 (EC50)		24
		D. magna	Invert.	21 d Growth, Survival	205	11	35
		D. magna	Invert.	21 d Survival	LC50 = 293		36
		A. tonsa	Invert.	5 d Developmental Rate	EC50 = 59	EC10=37	26
		A. tonsa	Invert.	5 d Juvenile Survival		300	26
		N. spinipes	Invert.	7 d Developmental Rate, Survival	20		24
		L. cardium	Benthic invert.	96 h Growth	EC50 = 153–563		36
		Capitella sp.	Benthic invert.	119 d Survival, Growth, Development	123 mg kg^{-1}, No effect, 168 mg kg^{-1}		37
		Potamopyrgus antipodarum	Benthic invert.	94 d Adult and Juvenile Survival, Growth, Reproduction	100 Time to 1st reproduction, 10 number of offspring		38
		L. macrochirus	Fish	21 d Growth, Survival 182	LC50 = 452	182	39
		P. promelas	Fish	36 d Hatch, Survival, Growth, Development 140	>140, 68, 68, 68	>140, 140, 140, 140	40
		O. mykiss	Fish	21 d Reproduction	EC50 = 282		36
		D. rerio	Fish	21 d Survival	LC50 = 452		36
		O. latipes	Fish	72 h VTG, ERα[f]	500		41
		X. laevis	Amphibian	96 h FETAX	EC50≥100		30
		X. laevis	Amphibian	32 d Survival	LC50≥140		30
		P. subcapitata	Algae	72 h Growth, Biomass	466	201	42
		P. subcapitata	Algae	72 h Growth, Biomass	EC50≥854, 723		43
Tonalide (AHTN)	Polycyclic musk	D. magna	Invert.	21 d Growth, Survival	184–401	89–196	39
		D. magna	Invert.	21 d Development, Reproduction	244 (EC50)		24
		A. tonsa	Invert.	5 d Developmental Rate	EC50 = 26	EC10=7.2	26
		A. tonsa	Invert.	5 d Juvenile	160	60	26

Compound	Category	Species	Trophic level	Endpoint/duration	LOEC (µg L^{-1})	NOEC (µg L^{-1})	
				Survival			
		N. spinipes	Invert.	7 d Developmental Rate, Survival	>60		24
		L. cardium	Benthic invert.	96 h Growth	EC50 = 108–708		36
		D. rerio	Fish	ELS 24–48 h Heart Rate	33	10	27
		L. macrochirus	Fish	21 d Growth, Survival	184 LC50 = 314	89	36
		P. promelas	Fish	36 d Hatch, Survival, Growth, Development	>140, 140, 67, 67	>140, 67, 35, 35	40
		O. mykiss	Fish	21 d Reproduction	EC50 = 244		36
		D. rerio	Fish	21 d Survival	LC50 = 314		36
		O. latipes	Fish	72 h VTG, ERα[f]	500		43
		X. laevis	Amphibian	96 h FETAX	EC50≥1000		30
		X. laevis	Amphibian	96 h FETAX	EC50≥1000		30
		P. subcapitata	Algae	72 h Growth, Biomass	797–835	204–438	42
		P. subcapitata	Algae	72 h Growth, Biomass	EC50≥797, 468		43
Benzylparaben	Preservative	D. magna	Invert.	7 d Growth, Reproduction	200, 2600		44
		P. promelas	Fish	7 d Growth	1700		44
Butylparaben	Preservative	D. magna	Invert.	7 d Growth, Reproduction	200, 2600		44
		P. promelas	Fish	7 d Growth	1000		44
		S. trutta	Fish	10 d VTG	134	76	45
Ethylparaben	Preservative	D. magna	Invert.	7 d Growth, Reproduction	9000, 2300		44
		P. promelas	Fish	7 d Growth	17 000		44
Isobutylparaben	Preservative	D. magna	Invert.	7 d Growth, Reproduction	300, 2000		44
		P. promelas	Fish	7 d Growth	3500		44
Isopropylparaben	Preservative	D. magna	Invert.	7 d Growth, Reproduction	4000, 2000		44
		P. promelas	Fish	7 d Growth	9000		44
Methylparaben	Preservative	D. magna	Invert.	7 d Growth, Reproduction	6000, 1500		44
		P. promelas	Fish	7 d Growth	25 000		44
Propylparaben	Preservative	D. magna	Invert.	7 d Growth, Reproduction	400, 6000		44
		P. promelas	Fish	7 d Growth	2500		44
		O. latipes	Fish	7 d VTG	99 00[g]		46
Benzophenone-1	UV filter	P. promelas	Fish	14 d VTG	4919.4		46
		O. mykiss	Fish	14 d VTG, Growth	4919		47

Compound	Category	Species	Trophic level	Endpoint/duration	LOEC (µg L^{-1})	NOEC (µg L^{-1})	
Benzophenone-2	UV filter	P. promelas	Fish	14 d VTG	8782.9		48
		O. mykiss	Fish	14 d VTG, Growth	8783		47
Benzophenone-3	UV filter	O. mykiss	Fish	14 d Growth	3900		47
Benzophenone-4	UV filter	O. mykiss	Fish	14 d Growth	4897		47
3-benzylidene camphor	UV filter	Potamopyrgus antipodarum	Benthic invert.	56 d Reproduction	0.28 mg kg^{-1} sediment		48
		Lumbriculus variegatus	Benthic invert.	28 d Reproduction	6.47 mg kg^{-1} sediment		48
		P. promelas	Fish	14 d VTG, Reproduction, Gonad Histology	434.6, 74, 74		49
		P. promelas	Fish	14, 21 d VTG	435,74		50,51
		O. mykiss	Fish	14 d VTG, Growth	453		47
		O. mykiss	Fish	10 d Injection	68 mg kg^{-1}		51
		X. laevis	Amphibian	35 d Metamorphosis	No effect		52
3-(4'-methylbenzy-lidene camphor)	UV filter	Potamopyrgus antipodarum	Benthic invert.	56 d Reproduction	1.71 mg kg^{-1} sediment		48
		Lumbriculus variegatus	Benthic invert.	28 d Reproduction	22.3 mg kg^{-1} sediment		48
		O. mykiss	Fish	14 d Growth	415		47
Oxybenzone	UV filter	O. mykiss	Fish	14 d VTG	749		54
		O. latipes	Fish	21 d VTG, Hatching	620		54
Ethyl-4-aminobenzoate	UV filter	P. promelas	Fish	14 d VTG	4394		49

References: (1) Orvos et al. (2002), (2) Tatarazako et al. (2004), (3) Memmert (2006), (4) Dussault et al. (2008), (5) Ishibashi et al. (2004), (6) Raut and Angus (2010), (7) Fort et al. (2010), (8) Veldhoen et al. (2006), (9) Fraker and Smith (2004), (10) Smith and Burgett (2005), (11) Yang et al. (2008), (12) Wilson et al. (2003), (13) Ciniglia et al. (2005), (14) DeLorenzo and Fleming (2008), (15) Stevens et al. (2009), (16) TCC Consortium (2002), (17) Marchini et al. (1992), (18) Calamari et al. (1982), (19) Kuehn et al. (1989), (20) Smith et al. (1990), (21) Carlson and Kosian (1987), (22) Adema and de Ruiter (1987), (23) Breitholtz et al. (2003), (24) Grutzner (1995b), (25) Wollenberger et al. (2003), (26) Carlsson and Norrgren (2004), (27) Grutzner (1995c), (28) Tas et al. (1997), (29) Chou and Dietrich (1999), (30) Grutzner (1995a), (31) Schramm et al. (1996), (32) Adema and Langerwerf (1985a,b), (33) Sousa and Suprenant (1984), (34) Payne and Hall (1979), (35) Wuthrich (1996a), (36) Gooding et al. (2006), (37) Ramskov et al. (2009), (38) Pedersen et al. (2009), (39) Wuthrich (1996b), (40) Croudace et al. (1997), (41) Yamauchi et al. (2008), (42) Van der Plassche and Balk (1997)), (43) Van Dijk (1997), (44) Dobbins et al. (2009), (45) Bjerregaard et al. (2008), (46) Inui et al. (2003), (47) Kunz et al. (2006c), (48) Schmitt et al. (2008), (49) Fent et al. (2008), (50) Kunz et al. (2006a), (51) Kunz et al. (2006b), (52) Holbech et al. (2002), (53) Kunz et al. (2004), (54) Coronado et al. (2008).

a No effects found at concentrations exceeding water solubility. b Frog Embryo Teratogenesis Assay – Xenopus.

c Early Life Stage.

d Hepatosomatic Index and Gonadosomatic Index.

e Vitellogenin.

f Estrogen receptor.

g Only concentration tested.

Table 4-17 *Effluent Risk of personal care products*

Compound	Category	PNEC µg/L	PNEC µg/L	PNEC µg/L	PNEC µg/L	Average concentration effluent µg/L	Risk
		Factor 1000	Factor 100	Factor 50	Factor 10		PEC/PNEC
Biphenylol	Antimicrobial	3,66					n/d
Triclosan	Antimicrobial				0,012		n/d
Triclocarban	Antimicrobial			0,0026			n/d
Benzophenone	Fixative		1,8				n/d
1,4-dichlorobenzene	Insect repellant			0,00244			n/d
N,N-diethyl-m-toluamide (DEET)	Insect repellant	71,3				0,04	0,0
Musk ambrette (MA)	Nitro musk	--					n/d
Musk ketone (MK)	Nitro musk				0,33		n/d
Musk moskene (MM)	Nitro musk	--					n/d
Musk Tibetene (MT)	Nitro musk	--					n/d
Musk xylene (MX)	Nitro musk				1		n/d
Celestolide (ADBI)	Polycyclic musk		0,36			0,025	0,1
Galaxolide (HHCB)	Polycyclic musk				1,1	0,751	0,7
Tonalide (AHTN)	Polycyclic musk				0,72	0,274	0,4
Traseolide (ATII)		0,00095				0,045	**47,4**
Phantolide (AHMI)		0,00122				< 0,018	**7,0**
Cachmeran (DPMI)		0,0116				0,08	**6,9**
Benzylparaben	Preservative			4			n/d
Butylparaben	Preservative			2,68		0	0,0
Ethylparaben	Preservative			46		4	0,1
Isobutylparaben	Preservative			6			n/d
Isopropylparaben	Preservative			40			n/d
Methylparaben	Preservative			30		9	0,3
Propylparaben	Preservative			8		26	**3,3**
Benzophenone-1		--	49,19			12	0,2
Benzophenone-2		--	87,83			4	0,0
Benzophenone-3	UV filter		39			22	0,6
Benzophenone-4	UV filter		48,97			3370	**68,8**
3-benzylidene camphor		--		1,48			n/d
3-(40-methylbenzy-lidene camphor)		--		8,3		0,07	0,0

Compound	Category	PNEC µg/L	PNEC µg/L	PNEC µg/L	PNEC µg/L	Average concentration effluent µg/L	Risk
Oxybenzone		--	6,2				n/d
Ethyl-4-aminobenzoate		--	43,94				n/d
4-Methylbenzy-lidene camphor	UV filter	0,56					n/d
2-Ethyl-hexyl-4-trimethoxy-cinnamate	UV filter	0,29					n/d

Risk of surfactants in effluents

Surfactants are bioactive compounds. Anionic surfactants can bind to macromolecules such as peptides, enzymes, DNA and proteins. They are able to modify the folding of proteins and peptides and modifying their biological functions. Cationic surfactants are incorporated into the cytoplasmic membranes of bacteria affecting their functions. Non-ionic surfactants bind to various phospholipid proteins and membranes having antimicrobial effects.
Conventional WWTPs are able to remove a high percentage of these compounds. But being massively used and continuously discharged into water bodies, the ecosystems are exposed to a great variety of these compounds that a potential risk.

The Table 4-18 shows the toxicity levels of certain surfactants for different aquatic organisms (Ivankovic, and Hrenovic 2010).

Table 4-18 *Toxicicity of different types of surfactants against various oragnisms. Modified form Ivankovic and Hrenovic, 2010.*

Group	**Surfactant**	**Species assayed**		**Test (endpoint)**	**Concentration** mg/L	
Anionic	SDS (Sodium dodecyl sulphate)	*Bacteria*	*Vibrio fischeri*	EC50 (Luminescence 15min)	2.6	(1)
		Algae	*Raphidocelis subcapitata*	IC50 (Cell density 72h)	36.58	(2)
		Crustaceans	*Artemia salina*	LC50 (Larvae mortality 24h)	41.04	(2)
		Gastropod	*Physa acuta*	LC50 (Mortality 24h)	27.2	(2)
		Sea Urchin	*Paracentrotus lividus*	EC50 (Fertilization rate)	3.2	(1)
		Fish	*Gammbusia affinis*	EC50 (Immobilization 48h)	40.15	(3)
	LAS (Linear alkylbemzene	*Bacteria*	*Vibrio fischeri*	EC50 (Luminescence	109.7	(4)

Group	Surfactant	Species assayed		Test (endpoint)	Concentration mg/L	
	sulfates)			30min)		
		Bacteria	*Pseudomonas putida*	EC50 (Growth Inhibition 16h)	33.4	(4)
		Algae	*Dunaliella sp.*	EC50 (24h)	3.5	(3)
		Crustaceans	*Ceriodaphnia dubia*	EC50 (Immobilization 48h)	5.96	(5)
		Fish	*Carassius auratus*	EC50 (Immobilization 48h)	5.1	(3)
	AES (Alkyl ether sulfates)	*Algae*	*Pseudokirchneriella subcapitata*	EC50 - Cell density 72 h	3.5	(6)
		Algae	*Raphidocelis subcapitata*	IC50 - Cell density 72 h	2.18	(2)
		Crustaceans	*Artemia franciscana*	LC50 - Nauplii mortality 72 h	23.92	(7)
		Fish	*Salmo gairdneri*	EC50 - Immobilization 48 h	10.84	(3)
		Amphibian	*Xenopus laevis*	LC50 (72h)	6750	(7)
	AS (Alkyl sulfates)					
Cationic	QAC (Quaternary ammonium compound)	*Bacteria*	*Vibrio fischeri*	EC50 (Luminescence 30min)	0.5	(4)
		Bacteria	*Pseudomonas putida*	EC50 (Growth Inhibition 16h)	6.9	(4)
		Algae	*Dunaliella sp.*	EC50 (24h)	0.79	(3)
		Crustaceans	*Daphnia magna*	EC50 (Immobilization 24h)	0.38	(8)
		Fish	*Salmo gairdneri*	EC50 (Immobilization 48h)	1.21	(3)
	ATAC – C14					
	ATAC – C16					
Amphoteric	AO (Amine oxide)	*Bacteria*	*Phosphobacterium phosphoreum*	EC50 (Luminescence 15min)	2.4	(8)
		Crustaceans	*Daphnia magna*	EC50 (Immobilization 48h)	6.8	(8)
Non-ionic	AE (Alcohol ethoxylate)	*Bacteria*	*Microcystis aeruginosa*	Estimated EC10 - Cell density	0.154	(9)
		Algae	*Lemna minor*	Estimated EC10 -	0.101	(9)

Group	Surfactant	Species assayed		Test (endpoint)	Concentration mg/L	
				Frond count		
		Algae	*Navicula pelliculosa*	Estimated EC10 - Cell density	0.140	(9)
		Algae	*Scenedesmus*	EC20 (growth rate 72h)	0.646	(10)
		Crustaceans	*Ceriodaphnia dubia*	EC50 - Immobilization 48 h	0.39	(5)
		Invertebrates	*Carbicula flumine*	56d EC50 (length gain)	0.050	(10)
		Invertebrates	*Daphnia magna*	EC50	0.36 – 50.5	(11)
		Fish	*Pimephales promelas*	NOEC - Survival	4.35	(9)
		Fish	*Rainbow trout*	56d EC20 (dry weight)	0.135	(10)

(1) Mariani L., et al. (2006); (2) Liwarska-Bizukojc E., et al. (2005); (3) Ying GG, (2006); (4) Sütterlin H., et al. (2008); (5) Warne MStJ., et al. (1999); (6) Pavlic Z., et al. (2005); (7) Sibila M,. et al. (2008); (8) Garcia M., et al. (2007); (9) Belanger S., et al. (2006); (10) Environnement Canada (1999); (11) Boejeije et al. (2005);

HERA (2009) study determined that the ecological risk of LAS, AES and AS is low for surface waters, sediments, wastewater treatment plants and soil.
The PECs for LAS, AES and AE are approximately 50 to 100 times lower than the PNEC.

The QACs are used as disinfectants. There are several studies on microbial toxicity. There is concern about the generation of resistance to these compounds when using at sub-lethal concentrations of these substances.
QACs may also affect the biological process in conventional WWTPs, particularly, negative effects on nitrifying bacteria have been found at concentrations of 2mg/L (Jardak, et al. 2016).

Risk of emerging pollutants in the environment

The study of von der Ohe, et al. 2011, assessed the environmental risk of 500 organic substances in four European basins Elbe, Scheldt, Danube and Llobregat.

About each substance there are different knowledge about its toxic effects as well as there are different analytical capacities to measure its presence in the environment.
These limitations make it impossible for some compounds to determine the PNEC and PEC, and when it is possible determine, the value have different degrees of uncertainty.
From the PNEC and PEC of a compound they obtained the environmental risk of the same, not being possible to be estimated for all the compounds by lack of parameters.

The study managed to classify the substances into six categories according to the environmental risk and the uncertainty associated with the data used to estimate them. For

each category, different actions were identified, such as completing missing information or management actions among others.

Within each category the substances are prioritized according to the Frequency of Exceedance and the Extent of Exceedance of PNECs. The Frequency of Exceedance is calculated on the basis of maximum environmental concentrations (MEC) instead statistical averages such as the PEC. So the methodology is different from the one proposed in the guide (CE, 2003).

The first division by category is between substances that have sufficient data on exposure and those that do not have sufficient evidence.

The group that has sufficient exposure evidence is then divided among those who have sufficient data to estimate the Environmental Quality Standards (EQS) defined in Eupean legislation (Directive 2008/105/EC).

Compounds that do not have sufficient data to estimate the EQS but exist the evidence of exposure has associated actions such as rigorous effects assessments sufficient to underpin management measures.

Then the compounds that if it has enough data to estimate the EQS and there is evidence of exposure are subdivided according to the risk. If the percentile 95th of a compound divided its lower PNEC is greater than 1 should be included in the prioriy substance list of Water Framework Directive (WFD), if not it is concluded that exposure to the compound does not damage ecosystems or human health in the observed concentrations.

By following this procedure all the compounds are assigned a category. Within each category the substances are prioritized according to the exposure rate and the amount that exceeds the PNEC.

Of the 500 compounds analyzed, 40% come from industrial processes, 33% come from the pesticide group and its metabolites, 5% from biocides and 4% from pharmaceuticals, eleven substances from natural sources and five combustion compounds.

Caffeine was the compound most frequently detected 97%, followed by DEHP of industrial origin and bisphenol A at 95% and 94% respectively. Diclofenac and ibuprofen drugs exhibited a detection frequency of95% and 94%, respectively. The most commonly detected biocide was triclosan at 94%.

Fifty six percent of the analyzed compounds have PNEC mostly from toxicity evaluations with low evaluation factors, and the rest of the compounds have PNEC from standard acute toxicity studies on *Daphnia magna*, *Pimephales promelas* and *Selenastrum capricornutum*.

The Appendix C showas the list of 500 compounds classified according to categories and within each hierarchy.

Category 1 contains compounds with sufficient toxicity and exposure data to derive an EQS. In this table it can be observed that there are 15 compounds that exceed the PNEC with a

factor greater than 100. The five substances with higher priority were the pesticides diazinon, azoxystrobin, terbutylazine, heptachlor and endosulfan I which is a priority substance. These 5 compounds should be entered into a monitoring program.

Category 2 comprises compounds for which sufficient information is available to characterize its toxicity but there is insufficient evidence to determine exposure levels. From the prioritization analysis within this category it emerges that the three compounds with the highest priority are the pesticides endosulfan sulfate, propachlor and desmetryn. Campaigns should be conducted to detect these compounds in order to determine exposure levels.

In category 3 are substances with PNEC based on predictions and that were detected in more than 20 sites with values greater than LOQ. Substances presenting a risk in this category should be evaluated in a more exhaustive way. The three substances with the highest priority are the transformation product 2-hydroxy-atrazine, the industrial compounds perfluorononanoate and HHCB.

In Category 4 are substances whose PNEC is generally below the LOQ but this is greater than the safety thresholds therefore it is necessary to improve the detection methods. Tolclofos-methyl, dichlorvos and chlorpyrifos pesticides are the three compounds on which these actions must be prioritized.

In category 5, are compounds whose PNEC are based on predicted toxicities and few observations in the environment. The three compounds with the highest priority were nonylphenol-1-ethoxylate, nonylphenol-2-ethoxylate and benzo[e]pyrene. For these substances, effects and exposure studies should be further studied.

At last in category 6 are compounds for which there is enough information to derive an EQS and they do not present risk. Within this category are 44 compounds that are detailed in the Appendix C. These substances could be monitored to a minimum level.

4.1.8. UE Guidelines and Directives about micro-pollutants

The regulatory framework that has incidence on the EP in the EU are the directives about the use, emission and trade of chemical substances and those that regulating their presence in the environment and drinking water.

EU – Micro-pollutan

Directive 2000/60/EU explicit the general framework for water policy. With it seeks sustainable management and gradually reduces the discharge of pollutants to mean a risk for the aquatic environment or sources of drinking water.

For this purpose was made a list of pollutants, called priority substances (PS), with its maximum allowable concentrations to be met into water bodies. Within this list is defined the priority hazardous substances (PHS) for which the policy is to cease or phase out discharges

by the significant risk posed. Also there is a list of emerging pollutants to which must be followed up and are under study to be eventually included in the PS list.

EU – Emission regulations

Through Directive 2010/75/EU, the Community lays down rules for the prevention and control of pollution from industrial activities.
View the gap between industrial emissions in the Community, best practice guidelines for each industrial branch were prepared to obtain the expected results in emission levels.

The directive states that the substances or mixtures whose content of volatile organic compounds are classified as toxic must be replaced if possible by less toxic substances or mixtures. Finally states which are pollutants and discharge limits. Among the pollutants are the priority substances established in the general water framework described above.

As for the domestic effluents, the EU set the goal that all agglomerations with more than 2000 equivalent inhabitants have collecting systems and treatment plant with secondary treatment. Directive 91/271/EEC lay down the treatment of wastewater that must be implemented depending on your geographic location and the receiving body. The requirements for discharge of the treatment plants imposes limit values of the parameters BOD_5, COD, TSS, total phosphorus and total nitrogen.

EU – Reuse water

Direct reuse of treated wastewater is an installed practice in areas with water shortages. This practice provides economic and environmental benefits compared to other practices such as desalination.

The EU has no regulations governing this activity which difficulty agricultural products trade and deprive tools for managing health and environment risks arising from this practice. Most of the reuse water is for irrigation. That is why control of chemical pollution in this activity is very important.

In the EU Guidelines on Integrating Water Reuse into Water Planning and Management in the context of the WFD (EU, 2016), can be found a compendium of reuse regulations for some member countries of the EU and other normative that are referent the topic outside the EU.

EU –Others regulation

EU (2006) Regulation No1907/2006 Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), establishing a European Chemicals Agency

EU Directive 2009/128/EC Framework for Community action to achieve the sustainable use of pesticides.

EU (2006) Regulation No 166/2006 European Pollutant Release and Transfer Register and amending Council Directives 91/689/EEC and 96/61/EC.

EU (2009) Regulation No 1107/2009 Placing of plant protection products on the market and repealing Council Directives 79/117/EEC and 91/414/EEC.

Directive 2008/105/EC Environmental quality standards in the field of water policy.

4.1.9. Conclusion

The emerging pollutants are compounds about which there is ignorance about some aspect of them, such as ignorance about its long-term toxic effects, presence in the environment, processes of transformation that suffer, among others.

Through the risk assessement it is possible to distinguish those compounds that present greater environmental risk. Taking into account the studies carried out in surface waters it can be observed that the compounds of high environmental risk come from diffuse sources as a result of the agricultural and livestock activity and some industrial compounds are identified, on which the presence and the relationship exposure - effect must be better studied.

On the other hand, if the compounds that have the greatest environmental risk in the effluents of the treatment plants are analyzed, there are other types of compounds such as pharmaceuticals and personal care products as well as pesticides. This fact makes effluent treatment plants relevant as sources of emerging pollutants when water is reused or the recipient body has very low dilution capacity.

As for the reported concentrations, it is necessary to incorporate the sediments into the samples. The sediments can through different sorption mechanisms accumulate compounds that are then released to the aqueous phase. In addition to accumulating these compounds in the solid phase may be toxic to non-aquatic organisms but incorporated into aquatic trophic chains.

It is essential that the approach of emerging pollutants be managed locally, taking into account the economic activities that are developed, the environmental support that exists and the uses of the water resource. The studies concerning emerging contaminants are expensive and require high specialization from various scientific disciplines and on the other hand require management measures that cross horizontally practically all administrative levels. The multidisciplinarity of the approach is fundamental to know if the emerging contaminants are or are not polluting.

4.2. Removal technologies of Emerging Pollutants

4.2.1. Removal of emerging pollutants in conventional wastewater treatment plant

Introduction

Conventional WWTPs are designed to reduce organic loads and eliminate pathogens from wastewater before being discharged into the receiving body. The different processes involved in WWTPs have very different emergent pollutant removal efficiencies as they are not designed or operated for this purpose. Some micro-pollutants are removed together with the sludge, while others are transformed or volatilized. There is an important fraction of micropollutants remaining unchanged in the treatment. The main mechanisms for the removal of emerging pollutants in secondary wastewater treatment proesses are photolysis, volatilization, sorption and desorption, and biotransformation as described in Figure 4-6 (Clouzot et al., 2013).

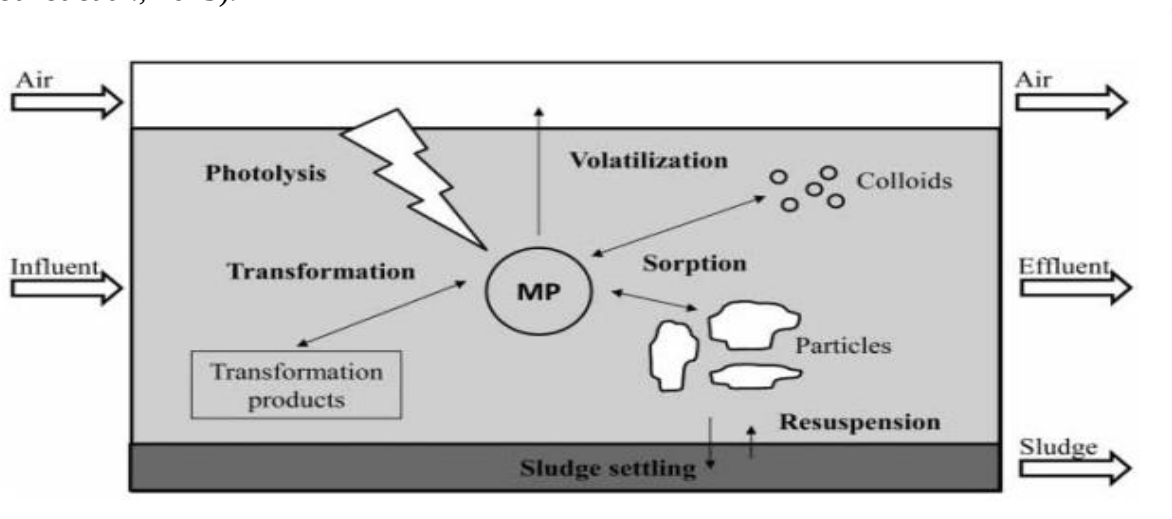


Figure 4-6 *Processes controlling the fate of MPs during wastewater treatments Source: Clouzot, et al. 2013.*

Biotransformation

Biotransformation involves a series of catabolic processes either transforming the original compounds into metabolites (byproducts), or completely mineralizing the original parent compound to carbon dioxide fand water. The by-product formation is unknown for many emerging pollutants. The effects of the biodegradation can be observed as an alteration of the chemical structure of the parent compound. This modification of the chemical structure of the parent compund may cause either the lost of some specific property of the parent compound (in such a way that the contaminating effects may disappear), or the total decomposition in completely oxidized substances or in simple molecules.

Since the amounts of micro-pollutants are generally too low to be used as a growth substrate, co-metabolism is the main route of biodegradation in activated sludge. However, given the complexity of the matrix and the biological communities present, it is most likely that the direct metabolism and co-metabolism coexist at different speeds depending on the operating parameters of the facility and the characteristics of the incoming wastewater (Petrovic, et al. 2016).

Micro-pollutants are distributed among four compartments depending on their specific equilibrium partition coefficients. That is, they can be observed in the gaseous state, in the aqueous phase, in the colloidal matter, or sorbed into particles. Figure 4-7 shows a schematic describing the distribution between the four compartments (Delgadillo-Mirquez et al., 2011).

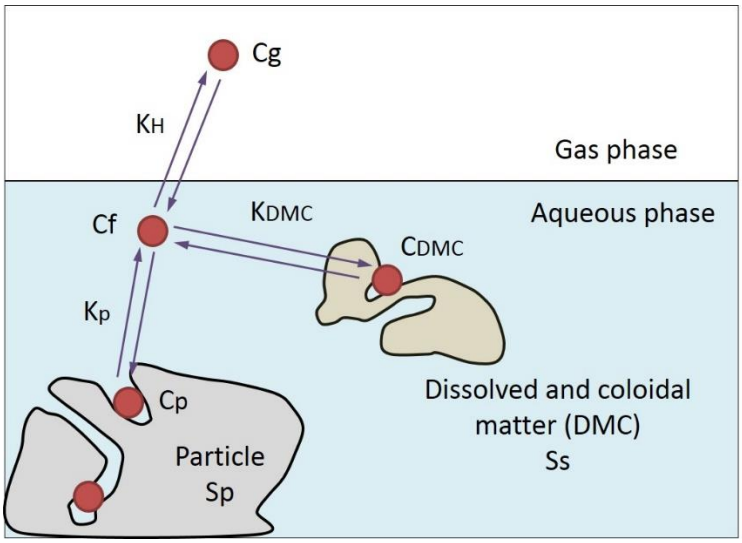


Figure 4-7 *Representation of the four –compartment model of an organic micro-pollutant. Modified from Delgadillo-Mirquez, et al. 2011.*

The bioavailability of the micro-pollutants distributed in the three aqueous compartments depends on multiple factors Delgadillo-Mirquez et al., (2011) listed three of these factors as follows: (i) sorption-desorption processes that could outcompete for biodegradation, (ii) irreversibility phenomena such as chemical reactions with other compounds, or sequestration in a solid phase, and (iii) the presence of other compounds that could physically compete for the sorption sites decreasing the bioavailability of the micro-pollutants.

Sorption and desorption

The exchange of contaminants between the aqueous phase and the solid phase (such as suspended particles and colloids' in a biological wastewater treatment process, is continuous and in both directions. The mechanism of sorption and desorption is complex and not well known for many of these compounds.

The sorption capacity depends both on the characteristics of the media, and on the characteristics of each particular contaminant. A single coefficient of sorption (K_d) usually is considered for describing the bahviour of several substances (Petrovic et al., 2016).

The sorption process is commonly describe using several coefficients: (i) The soild adsorption coefficient (K_d) = concentration of chemical in soil/concentration of chemical substance in water; (ii) The organic mater adsorption coefficient (K_{oc}) = concentration of chemical in organic matter/concentration of chemical in water (also reffered as the organic carbon-water partition coefficient); and (iii) The octanol-water partition coefficient (K_{ow}).

The K_d of many neutral hydrophobic organic compounds depends on the carbon content of the sorbent; therefore, a standard K_{oc} sorption coefficient is defined for this type of compound. In addition, a relationship has been established between K_{oc} and K_{ow} (octanol-water coefficient). Because of the ease of measurement offered by the K_{ow} versus the other coefficients, the use of K_{ow} as a measure of sorption is widely used. The K_{oc} coefficient does not take into account the non-hydrophobic interactions or other sorption mechanisms (also not considered by the K_{ow}), which can lead to considerable under or over estimations (Tolls, 2001). The K_d for a particular compound can vary over a wide range between different WWTP depending on the characteristics of the sludge, pH, among others.

Photolysis

Photolysis in a WWTP can be produced by the adsorption of light directly by the contaminant or by intermediate compounds. The photolysis process will depend on the light absorption properties of the contaminant, the availability of light, and the presence and concentration of suspended solids in the matrxi (Petrovic et al., 2016).

Volatilization

The transfer of a compound dissolved to gas by volatilization depends on the physicochemical properties of the compound (H, Henry's law constant) and on the operating characteristics of the plant as the aeration system, agitation, temperature, atmospheric pressure etc. The transfer can be given by stripping where the aeration is fundamental or by the volatilization on the surface (Pomies, et al. 2013).

Removal efficiencies

The removal efficiencies of conventional WWTPs depends: (i) on the physic-chemical properties and biological persistence of the compounds; (ii) on the microbial community of the biomass; and (iii) on the technologies applied in each particular WWTP and the operational parameters.

During the operation of the treatment plants, certain parameters such as the pH, dissolved oxygen, hydraulic retention time (HRT), and sludge retention time (SRT) are well control and monitor. These parameters (together with the temperature) influence both the type and kinetics of the chemical reactions mostly carried out by the active biomass. Therofre, these

parameters will have a great impact on the removal efficiencies of substances such as micro-pollutants.

The hydraulic and sludge retention times determine the the contact time of the effluent with the biomass and the time that the sludge remains in the reactor, respectively. High SRTs favour greater diversity of microorganisms and influence the total concentration of suspended solids and the amount of total sludge produced. That is, the SRT influences the bioactivity and the amount of compounds potentially absorbed onto the sludge (Petrovic et al. 2009).

As co-metabolism is one of the major routes for removal of contaminants, the SRT should be adequate to primarily maintain a good degradation of the primary substrate and thus achieve an active and large biomass concentration capable of co-metabolism.

Larger biomass concentrations in the aerobic rector promotes a better contact between the microorganisms and pollutants increasing the chances for the biological degradation. In addition, as the larger the biomass concentration, the larger the concentration of enzymes which may promot cometabolic processes. Moreover, higher biomass concentrations decreases the food to microorganism's ratio, favouring the metabolism and co-metabolism of less biodegradable substances.

An incomplete degradation of a compound in a conventional WWTP may be either due to the persistence or the compound, or due to operational conditions such as the establishment of a shorter than needed hydraulic retention time for the degradation to occur. In the latter case there is the possibility that the degradation is completed in the body of natural water where the treated wastewater is discharged.

The removal of biodegradable substances (that is, substances exhibiting a high biological degradation constant k_{biol}) with a low tendency to be adsorbed by sludge (that is, low Log K_d) are more influenced by HRT. On the other hand, substances with low k_{biol} and high Log K_d are more influenced by the SRT (Gros, et al. 2010).

Under different pH conditions, a particular substance may be neutral, cationic, anionic or bipolar; therefore, the physical, chemical, and biological characteristics (sorption, photoreactivity, antibiotic activity, and toxicity) may tremendously differ (Kümmerer, 2009). Conventioanl WWTPs generally operate in a controlledand well monitored pH range, so the predominant characteristic of the substances can be predicted.

Biological reactions are greatly affected by temperature; lower efficiency have been observed during winter seasons in colder climates compared to during summer seasons (Vieno, et al. 2005).

The sorption of a compound by the sludge depends on many factors such as the pH, redox potential, stereochemical structure, and chemical nature of the sorbent and the sorbate. Sorption can occur through absorption processes due to the hydrophobic interactions of the aliphatic and aromatic groups of a compound with the lipophilic cell membrane of the microorganism or the lipid fractions of the suspended solids. Another mechanism of adsorption is due to the electrostatic interactions of the positively charged groups of a

compound with the negative charges of the microorganisms (Verlicchi, et al. 2012). This is why sorption is the most important process for removing lipophilic compounds and some hydrophilic compounds (e.g. surfactants) rather than biodegradation process. The retention time needed for the biodegradation of these compounds is usualy much higher that the retention time provided in conventional biological processes (Barceló, et al. 2008).

The main processes for the removal of polar pollutants (for example pharmaceutical compounds) consists of biological transformation or the mineralization by microorganisms (Petrovic, et al. 2016).

The molecular structure of the compounds can provide relevant information about the biodegradability of the compounds. Compounds such as esters, nitriles, and aromatic alcohols have functional groups which can increase the biodegradability, while aromatic amines, iodide, nitro and azo groups may increase the persistence of the compound (Tunkel, et al. 2000).

The presence of long and highly branched side chains (e.g. omeprazole and ranitidine) as well as structures with complex aromatic rings (e.g. nrofluxetine and diazepam) or halogenated groups (e.g. iopromide and diazepam), make a compound less biodegradable; therefore, more persistent (Jones et al. 2005).

Removal of pharmaceutic compounds

The pharmaceutic compounds (drugs) are intentionally designed to have some bioactive function and different degrees of persistence. More over, they commonly exhibit lipophilic properties to be able to cross cellular membranes and be assimilated by organisms.

The review conducted by Verlicchi et al., (2012) (described in Chapter 6 summarizes both the occurrence of drugs in conventional WWTPs andtheir removal efficiencies. In cases where the removal efficiencies were not reported on the original work, the values were estimated by the authors. Table 4-19 shows the average removal efficiencies reported at the different evaluated WWTPc. The determination of the removal efficiencies was calculated based on the average influent and effluent concentration to and from the WWTPs. Therefore, this efficiency is referred to the entire processes that occur within a conventional WWTP. These processes include pre-treatment, primary sedimentation, and conventional activated sludge (CAS) or membrane bioreactor (MBR). The plants with CAS were operated at HRTs between 2 and 24 hours and SRTs from 2 to 20 days. The MBRs were operated at HRTs from 7 to 25 hours, and the SRTs from 15 to 80 days. Most of the samples were taken as 24 hours composite samples to obtain daily average concentrations.

Table 4-19 *Removal efficiencies of Pharmaceutical compounds in Conventional WWTP. Modified from Verlicchi, et al., 2012*

Therapeutic class	Pharmaceutical Compound	Average removal efficiencies CAS (%)	Average removal efficiencies MBR (%)	Negative removal efficiencies CAS (%)	Negative removal efficiencies MBR (%)
Analgesics / anti-inflammatories	5-Aminosalicylic acid	94	no available		
	Acetaminophen	93	99		
	Acetylsalicylic acid	90	no available		
	Aminopyrine	38	no available		
	Codeine	68	no available		
	Dextropropoxyphene	no available	no available		
	Diclofenac	29	60	-12, -11, -111	-8, -7
	Dipyrone	65	no available		
	Fenoprofen	82	no available		
	Flurbiprofen	no available	no available		
	Hydrocodone	no available	96		
	Ibuprofen	87	98	-4.4, -4.3, -13	
	Indomethacin	37	43		
	Ketoprofen	56	70		
	Ketorolac	44	no available		
	Meclofenamic acid	no available	no available		
	Mefenamic acid	38	64		
	Naproxen	73	91		
	Phenazone	56	no available		
	Propyphenazone	45	63		
	Salicylic acid	99	no available		
	Tolfenamic acid	no available	no available		
	Tramadol	23	no available		
Antibiotics	Amoxicillin	96	no available		
	Azithromycin	44	15		
	Cefaclor	98	no available		
	Cefalexin	82	no available		
	Cefotaxime	63	no available		
	Chloramphenicol	95	no available		
	Chlortetracycline	84	no available		
	Ciprofloxacin	70	73	-44	
	Clarithromycin	40	70		
	Clindamycin	no available	no available	-150	
	Cloxacillin	no available	no available		
	Doxycycline	71	no available		
	Enoxacin	no available	no available		

Therapeutic class	Pharmaceutical Compound	Average removal efficiencies CAS (%)	Average removal efficiencies MBR (%)	Negative removal efficiencies CAS (%)	Negative removal efficiencies MBR (%)
	Enrofloxacin	54	56		
	Erythromycin	26	61	-109	
	Lincomycin	27	no available		
	Lomefloxacin	no available	no available		
	Metronidazole	38	no available		
	Norfloxacin	68	no available	-6	
	Ofloxacin	60	94		
	Oxytetracycline	44	no available		
	Penicillin G	no available	no available		
	Penicillin V	60	no available		
	Roxithromycin	32	57	-4, -80, -32	
	Spiramycin	0	no available		
	Sulfachloropyridazine	62	no available		
	Sulfadiazine	93	no available		
	Sulfadimethoxine	84	no available		
	Sulfamethazine	83	no available		
	Sulfamethoxazole	52	54	-44	
	Sulfapyridine	51	56		
	Sulfasalazine	no available	no available	-50	
	Sulfathiazole	88	no available		
	Tetracycline	56	no available	-88	
	Trimethoprim	40	61	-11, -17, -34, -106, -2, -88, -56	
	Tylosin	no available	no available		
Antidiabetics	Glibenclamide	45	75		
Antifungals	Clotrimazole	31	no available		
Antihypertensives	Diltiazem	67	no available		
	Enalapril	69	no available		
	Hydrochlorothiazide	45	25		
Barbiturates	Phenobarbital	99	no available		
Beta-blockers	Acebutolol	60	no available		
	Atenolol	38	71		
	Betaxolol	no available	no available		
	Bisoprolol	0	no available		
	Carazolol	no available	no available		
	Celiprolol	no available	no available		

Therapeutic class	Pharmaceutical Compound	Average removal efficiencies CAS (%)	Average removal efficiencies MBR (%)	Negative removal efficiencies CAS (%)	Negative removal efficiencies MBR (%)
	Metoprolol	24	44		
	Nadolol	no available	no available		
	Oxprenolol	no available	no available		
	Propranolol	39	72		
	Sotalol	29	42		
	Timolol	no available	no available		
Diuretics	Bendroflumethiazide	91	no available		
	Furosemide	51	no available		
Lipid regulators	Bezafibrate	61	90		
	Clofibrate	no available	no available		
	Clofibric acid	40	65		
	Etofibrate	no available	no available		
	Fenofibrate	64	no available		
	Fenofibric acid	23	no available		
	Gemfibrozil	54	66		
	Pravastatin	61	87		
	Simvastatin	57	no available		
Psychiatric drugs	Amitriptyline	96	no available		
	Carbamazepine	18	15	-122, -3, -47, -43, -35, -4, -67, -11, -3, -43, -12	-13
	Diazepam	14	29		
	Fluoxetine	56	95		
	Gabapentin	93	no available		
	Lorazepam	no available	no available		
	Norfluoxetine	48	no available		
	Oxcarbazepine	no available	no available		
	Paroxetine	91	90		
	Valproic acid	99	no available		
Receptor antagonists	Cimetidine	52	no available		
	Famotidine	60	56		
	Loratadine	15	19		
	Omeprazole	9	no available		
	Ranitidine	52	56		
	Valsartan	84	no available		
Hormones	Estradiol	80	99		

Therapeutic class	Pharmaceutical Compound	Average removal efficiencies CAS (%)	Average removal efficiencies MBR (%)	Negative removal efficiencies CAS (%)	Negative removal efficiencies MBR (%)
	Estriol	67	no available		
	Estrone	76	96	-112, -35, -83, -40	
	Ethinylestradiol	78	60		
Beta-agonists	Clenbuterol	no available	no available		
	Fenoterol	no available	no available		
	Salbutamol	61	no available		
	Terbutaline	no available	no avalaible		
Antineoplastics	Cyclophosphamide	no available	no avalaible		
	Ifosfamide	no available	no avalaible		
	Tamoxifen	no available	no avalaible		
Topical products	Crotamiton	41	no available	-33	
Antiseptics	Triclosan	76	99		
Contrast media	Iopromide	50	no available	-41, -32	

Pharmaceutical compounds within the same therapeutic class have different chemical and physical properties resulting in very varied removal rates within each class.

By considering the K_d, K_{ow} and K_{biol} coefficients for each compound the potential adsorption to particles, the hydrophilic or lipophilic characteristics, and thebiodegradability can be predicted, respectively. However, it is very difficult to correlate the physical-chemical properties of the compounds with their removal efficiencies. The removal efficiencies involve many other factors such as the concentration of biomass in the system, the SRT, the HRT, pH, temperature, type of technologies used, among others.

Carballa et al., (2004) reported a negligible removal efficiency in the pre-treatment and primary sedimentation processes for ibuprofen and naproxen. These compounds have an acidic structure (negative charge of the molecule at pH 7) and low partition coefficients K_d (Log K_d < 2.7 very low sorption in the sludge); therefore, the compound have a high tendency to be present mainly in the aqueous phase.The same study reported a higher estrone concentration after the primary settler compared to the estrone concentration in the raw wastewater to the WWTP (that is, before the primary settler). This reported negative removal is due to a by-product formation from the oxidation of estradiol to estrone. This also indicates that the positive removal of estradiol does not necesarilly mean a decrease in the risk or toxicity since it is being transformed into a different compound. In general the removal of drugs in preliminary and primary treatment is relatively low; even in some cases some transformation by-products can be released.

In the biological reactor/basin of a conventional WWTP the main removal mechanisms are sorption and biotransformation, the latter being the main reported mechanism. Removal by volatilization can be considered negligible since generally the drugs exhibit low volatility.

The list of drugs previously mentioned together with their K_d and k_{biol} coefficients are presented in the Appendix A. These values can indicate the path for a particular compound in a WWTP. Howver, the removal processes are generally complex making extremely difficult to predict the potential removal mechanismby just knowing these coefficients (Verlicchi, et al. 2012).

The Table 4-19 shows the removal efficiencies collected from 224 conventional WWTPs provided with CAS and from 20 plants provided with the MBR technology. The lack of a greater number of studies on the removal efficiencies of the MBR technology does not allow for a comparison of these two systems (CAS vs MBR). Differences between CAS and MBR include: (i) the separation mechanism between the liquid and the sludge; (ii) the operational SRT; and (iii) the concentration of biomass (8 to 10 kg/m^3 in the MBR and 3 to 5 kg/m^3 in the CAS); among others

The same table showscompounds exhibiting a negative removal efficiencies in conventional WWTPs. This phenomenon can be explained by: (i) the presence of large concentraton of particualte compounds in the raw wastewater not determined since only dissolved compounds are measred; (ii) the release of compounds sorbed into the particles; (iii) analytical measurement errors cause by the very low concentrations exhibited by these compounds; and (iv) incorrect correlation between influent and effluent concentrations for not considering the HRT of the WWTPs; among others (Verlicchi, et al. 2012).

Analgesics removal of the aqueous phase

The Table 4-19 with the different analgesic removal efficiencies reported at the different WWTPs. There are substances exhibiting a largerate of removal; others, showing a low removal rate. Moreover, there are compounds (e.g. diclofenac) showing removal rates ranging from from 0 to 90%.

Negative removal efficiencies for diclofenac can be explained by the deconjugation of glucuronidated or the sulphated diclofenac into diclofenac, or by the desorption of diclofenac from particles at the raw wastewater (Zorita, et al. 2009).

The negative removal efficiencies for ibuprofen may be due to the fact that this compound is largely transformed into its hydroxyl and carboxy derivatives which can be later hydrolyzed and converted to the original compounds (Ziylan, and Ince 2011).

Antibiotics removal of the aqueous phase

Average removal efficiencies of antibiotics range from 0% (spiramycin) to 98% (cefachlor) in CAS and from 15% (azithromycin) to 94% (ofloxacin) in the MBR.

The average removal efficiencies for antibiotics range from 0% (spiramycin) to 98% (cefachlor) in CAS systems, and from 15% (azithromycin) to 94% (ofloxacin) in MBRs. Antibiotic release was reported for nine compounds. Negative removal efficiencies for clindamycin were due to analytical measurement errors. Negative removal efficiencis for sulfamethoxazole and sulfasalazine were explained due to the main metabolites of these compounds are biologically inactive (acetylated products-N4) and can be transformed back into the original compound (Gobel, et al. 2007). Negative removal efficiencies of erythromycin and roxithromycin can be explained since they are present in the raw wastewater adsorbed into particles and arereleased at the WWTP. Similar trends were observed for iprofloxacin, tetracycline and norfloxacin.

Psychiatric Drugs removal of the aqueous phase

The removal efficacy of psychiatric drug exhibited great variability except for carbamazepine. This compound is very persistent. Negative removal efficiencies were also reported for this compound. A possible cause of this phenomenon is the enzymatic cleavage of its glucuronic conjugate (reaching the WWTP with the raw wastewater together with carbamazepine) into carbamazepine and the release of the original compound in the treated effluent (Radjenovic, et al. 2007).

Hormones removal of the aqueous phase

Hormone removal efficiencies are generally high in CAS (67% to 80%) and in MBRs (60% to 99%). Despite this, there were negative removals for estrone. Research shows that one cause may be the oxidation of estradiol to estrone and another cause partial deconjugation of other estrogens in the water.

Pharmaceutical compounds removal through the sludge

To complete the analysis of the removal capacity of pharmaceutical compounds from a WWTP the fate of the compounds to the sludge need to be analyzed. There are fewer studies on the removal of emerging pollutants in the sludge than in the aqueous phase. The Table 4-20 shows the fraction of the compounds that are removed on the sludge through the sludge wastage (Verlicchi et al., 2012).

Table 4-20 *Fractions with respect to the influent mass load of selected PhCs removed during secondary biological treatment, sorbed to sludge and discharged with secondary effluent. Data with asterisk as apex refer to MBR systems. Modified from (Verlicchi, et al. 2012).*

Therapeutic class	Compound	SRT (days)	Biotransform (%)	Sorption onto sludge (%)	Effluent (%)
Analgesic and anti-inflammatories	Diclofenac	4–60	5–45	< 5	55–95
		6	25	< 5	70–75
		16	10	5	85
		< 20	5	0	95
		> 50	10–30	0	70–90

Therapeutic class	Compound	SRT (days)	Biotransform (%)	Sorption onto sludge (%)	Effluent (%)
	Ibuprofen	4–60	90–100	< 5	0–10
		2	< 5	< 5	95–100
		10–55*	95–100	< 5	0–5
		< 20	35–40	0	60–65
		> 50	95	0	5
	Indomethacin	6	27	0	73
		16	40	< 5	58–60
	Ketoprofen	6	70	0	30
		16	< 95		5–10
	Mefenamic acid	6	65	7	28
		16	55–58	< 30	< 20
	Naproxen	10–30	55–85	< 5	15–45
		6	77	0	23
		16	95–98	0	< 5
		< 20	5	0	95
		> 50	85–90		10–15
Antibiotics	Azithromycin	10–30	< 40	< 10	60–90
	Chloramphenicol	6	0	0	100
	Ciprofloxacin	10–12	< 10	70–80	≤ 30
		20	< 10	77	< 4
	Clarithromycin	< 20	< 10	< 5	75–90
		> 50	90	< 5	10
		< 20	< 10	≤ 10	> 90
		6	0	18	82
		16	0	< 45	55–60
	Enrofloxacin	20–25	19	65	17
	Erythromycin	< 20	20		80
	Lomefloxacin	20–25		60	40
	Metronidazole	6	15–18		100
		16			82–85
	Norfloxacin	10–12	< 10	80–90	≤ 20
		20	< 10	72	< 4
	Ofloxacin	20–25		60	40
	Roxithromycin	4–30	< 60	< 5	> 35
		< 20	18	2	80
	Sulfamethazine	6	< 85	0	< 20
		16	15–18	20	60–65
	Sulfamethoxazole	4–12	50–90	< 5	10–50
		< 20	20	0	80

Therapeutic class	Compound	SRT (days)	Biotransform (%)	Sorption onto sludge (%)	Effluent (%)
	Sulfapyridine	10–30	≤ 70	< 10	≥ 30
	Trimethoprim	<50	~ 90	≤ 5	~ 10
		<20	< 10	≤ 5	> 90
		6	40	< 5	< 60
		16	38–40	5–10	50–55
		< 20	18		72
Antidiabetics	Glibenclamide	6		< 10	90–95
		16		60	40
Antihypertensives	Enalapril	6	95–98		2–5
		16	95–98		2–5
	Hydrochlorothiazide	6		100	
		16		100	
Beta-blockers	Atenolol	6	< 70	< 5	< 35
	Metoprolol	6	~ 35	0	~ 65
		16	0	0	100
	Nadolol	6	35–40	< 5	60
		16	70	30	
	Sotalol	6	10	< 5	< 90
		16	< 50	< 5	50
	Timolol	6	< 40	< 5	< 65
		16	40–45	0	55–60
Diuretics	Furosemide	6	35–40	< 5	60–65
		16	75–80	2–5	20
Lipid regulators	Bezafibrate	6	12	2	86
		16	< 80	< 5	20–25
		2	45–50	< 5	50
	Fenofibrate	6	0	100	0
		16	25–30	65–70	
	Gemfibrozil	6	0	3	97
		16	90	< 5	5–10
	Pravastatin	6	45	0	55
		16	62	2	< 40
Psychiatric drugs	Carbamazepine	4–60	< 40	< 5	> 60
		6	22	3	75
		16	0	5	95
	Diazepam	6	0	42	58
		16		65	35
	Fluoxetine	<20	80	0	20
		>50	90	0	10

Therapeutic class	Compound	SRT (days)	Biotransform (%)	Sorption onto sludge (%)	Effluent (%)
Receptor antagonists	Lorazepam	6	30	< 5	65–70
		16	30	5–8	65
	Cimetidine	6	42	4	54
		16	60	5-8	32-35
	Famotidine	6	< 10	10	85
		16	80	20	0
	Ranitidine	6	< 20	< 5	80
		16	75	< 5	20-25
Hormones	Estradiol	10–30	85–99	< 5	< 15
	Estrone	10–30	35–97	≤ 5	5–60
	Ethinylestradiol	10–30	45–95	≤ 5	5–50
		<20	25	5	70
		>50	80–90	0	10–20
Beta-agonist	Salbutamol	6	< 60	< 5	< 45
		16	40–42	2	55-60
Contrast agent	Iopromide	10–30	20–95	< 5	5–80

As can be observed, the influence of sorption as a removal mechanisms within the sludge is little compare to other mechanisms. Appendix A shows that most of the compounds have a Log K_d < 2.7 or have hydrophilic properties with a tendency to be little adsorbed.

Effects of biomass concentration and SRT

SRT larger than 10 days are usually needed to biodegrade bezafibrate. SRT of 5 days are needed for ibuprofen and some hormones. Moreover, there is not a clear relationship between the SRT and degradation for other compounds such as carbamazepine, ciprofloxacin, ofloxacin, and norfloxacin (Clara, et al. 2005), (Joss, et al. 2004).

The higher concentrations of biomass observed in MBR compare to CAS favours adsorption processes. Higher concentrations of hydrochlorothiazide, azithromycin, carbamazepine, and ketoprofen were found in MBR sludge than in CAS sludge.

pH effects

The removal of ionisable compounds such as sulfamethoxazole, diclofenac, ibuprofen, and ketoprofen was found to be strongly pH-dependent. At lower pH, higher rate of elimination were observe since these compounds become more hydrophobic; therefore, more adsorbed by the activated sludge. The removal efficiency of the non-ionisable carbamazepine showed no pH dependence on the mixed liquor (Tadkaew, et al. 2010).

Effects of temperature

Tthe effect of the temperature on drug removal on a laboratory-scale MBR reportedthat most of the hydrophobic compounds (such as estrone, ethinyl estradiol, estradiol, and triclosan) were stable by varying the temperature over a range of 10 to 35 °C.

On the other hand, the less hydrophobic compounds (salicylic acid, ketoprofen, naproxen, metronidazole, ibuprofen, paracetamol, diclofenac, gemfibrozil, carbamazepine, and estriol) exhibited a large variation in the absorption levels at the lower temperatures (Hai, et al. 2011).

Removal of pesticides

Pesticides are used in order to protect plants against harmful organisms preventing the actions of these harmful organisms. Pesticides are composed of herbicides, insecticides and fungicides, acaricides, nematicides, molluscicides, and rodenticides, among others.

Köck-Schulmeyer et al., (2013), (as already described in section 4.1.4) reported the removal of 22 pesticides in 3 conventional WWTPs. The plants operate at HRTs between 26 and 40 hours. The first plant was provided with a biological treatment followed by tertiary treatment consisting of coagulation, flocculation, chlorination, and microfiltration. T second evaluated WWTP was just provided withbiological treatment. The third WWTP was provided with biological treatment incorporating a nutrient removal process. This WWTP receives both domestic and industrial wastewater.

Figure 4-8 describes the average removals of 17 compounds at the above mentioned WWTPs.

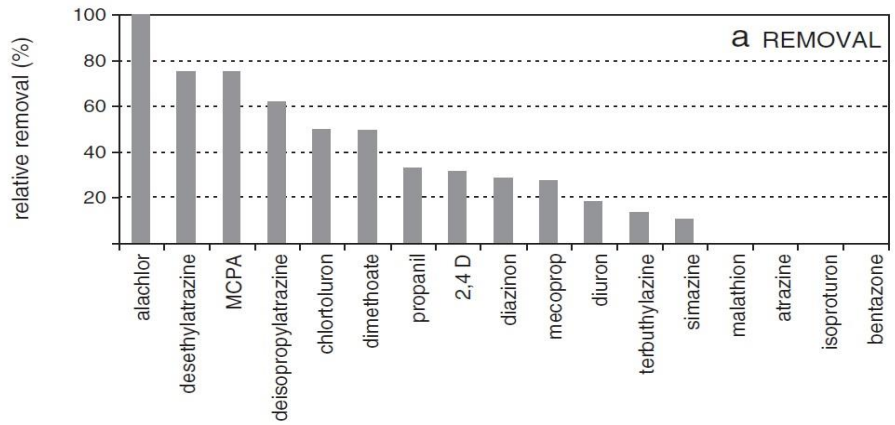


Figure 4-8 *Average relative removal of the detected pesticides in the three WWTPs Source: Köck-Schulmeyer, et al. 2013*

The Figure 4-9 shows the total concentrations of pesticides at the influent and effluent streams of each evaluated WWTPs grouped by families of compounds.

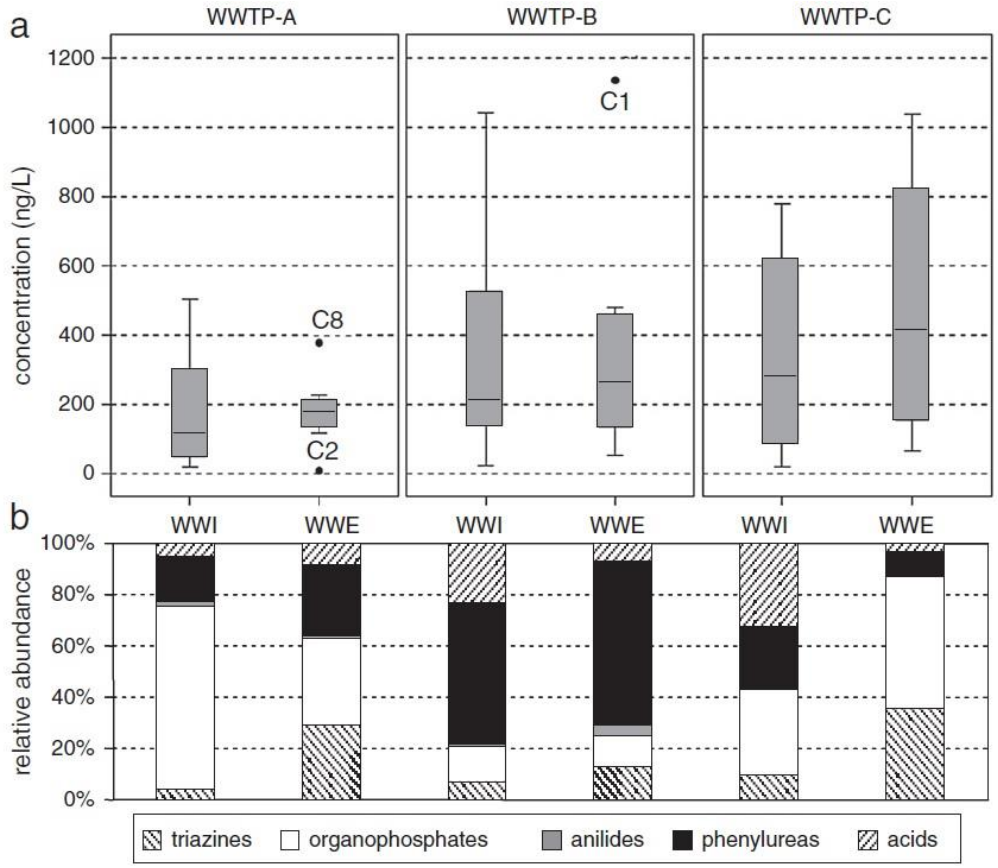


Figure 4-9 *(a) levels of total pesticides in influent (WWI) and effluent (WWE) of each plant; (b) relative abundance of pesticides families in the different samples. Source: Köck-Schulmeyer, et al. 2013.*

As can be observed, the three WWTPs exhibited a very low removal performance. The WWTP provided with tertiary treatment exhibited the best performance. Different compositions at the influent and effluent streams were observed at the different plants. The relative abundance of pesticedies families at the different WWTPs did not follow a similar pattern except the triazines whose concentration where higher at the effluent streat compared to at the influent stream reaching the plant.

A more detailed analysis revealed that the concentrations found on the treated effluent for atrazine, malathion, isoproturon, and bentazone where higher than those of the influent. Triazines, simazine, and tertbutylazine were not removed at all.

The pesticides with the highest removal rates were alachlor, DEA, MCPA and DIA.

Removal of PCP

Table 4-21 shows the PCP removals obtained in conventional WWTPs from different studies.

Table 4-21 *Removal and mean concentration of the PCP in CWWTP*

Family	Personal care product (PCP)	Average concentration influent µg/L	Average concentration effluent µg/L	Removal CAS %	
Insect repellent	N, N-diethyl-meta-toluamide (DEET)	0,066	0.040	39	(a)
	Bayrepel	0.6 – 1.4	< LOD	100	(b)
Polycyclic musk	Celestolide (ADBI)	0.0372	0.025	39	(c)
	Phantolide (AHMI)	0.0420	< 0.018	--	(c)
	Traseolide (ATII)	0.168	0.045	65	(c)
	Galaxolide (HHCB)	2.031	0.751	43	(c)
	Tonalide (AHTM)	0.804	0.274	37	(c)
	Cashmeran	0.21 – 0.69	0.08	82	(b)
UV filters	3-(4-methylbenzylidene)camphor (4-MBC)	0.960	0.070	93	(b)
	Octyl-methoxycinnamate (OMC)	20.070	0.030	99	(b)
	Octocrylene (OC)	1680	< LOQ	100	(b)
	Octyl-triazone (OT)	720	< LOQ	100	(b)
	1-benzophenone	258	12	95	(d)
	2-benzophenone	194	4	98	(d)
	3-benzophenone	1195	22	98	(d)
	4-benzophenone	4152	3370	19	(d)
Preservative	Methylparaben	11601	9	99,9	(d)
	Ethylparaben	2002	4	99,8	(d)
	Propylparaben	3090	26	99,2	(d)
	Butylparaben	723	0	100	(d)

Source: (a) Wang, D., et al. (2014) (b) Barceló, D., et al. (2008) (c) Lishman, L., et al. (2006) (d) Kasprzyk-Hordern, B., et al. (2009)

Wang, et al. (2014), analysed the removal of N, N-diethyl-meta-toluamide (DEET), (a repellent), in a conventional WWTP plant located in Shanghai, China. The WWTP was also provided with a UV disinfection process as a tertiary treatment. A removal of approximately 39% was reported. The SRT and HRT of the plant were set at 20 days and 13-15 hours, respectively. The samples were taken during the winter months. The use of repellents is more noticeable during the summer. The biological reactor temperature was approximately 9.6°C.

After primary treatment a negative removal of the compound was reported at approximately 25%. At the biological treatment a removal a removal of approximately 43% was reported. The WWTP was provded with an anaerobic-anoxic-aerobic process as the biological reactor. Most of the removal was observed in the anaerobic tank and just a little removal at the aerobic basin. Negative removal rates were reported at the anoxic tank. That could be explained etiher by the deconjugation of conjugated metabolites, or by changes in the adsorption conditions of the compound.

Salgado et al., (2010) evaluated the presence of five polycyclic musks at five Portuguese WWTPs. As part of this evaluationgalaxolide, tonalide, and cashmeran were reported in all the influent and effluent samples. The effluent samples exhibited lower concentrations compared to the influent samples. These compounds were also found in the sludge samples at a high frequency which suggests the importance of adsorption as a mechanism for the removal of these compounds. This can be explained by the high hydrophobicity exhibited by the musks. Celestolide was detected in the influent, but it was not observed in the effluent or in the sludge. Moreover, traseolide, and phantolide were not detected. Traseolide exhibits the lowest S_w and the highest K_{ow} of all the polycyclic musks and tends to be adsorbed to the sludge. On the other hand, cashmeram exhibits the highest solubitily and has lowest $K_{oc.}$. That is, higher concentrations of this compoundare found in the effluent than in the sludge. In addition to the adsorption cashmeram is also biotransformated in the reactor (Clara, et al. 2011). HHCB and AHTN presented removal efficiencies of 99 and 98%, respectively in lagoons systems (Lishman, et al. 2006). Laggons performed better than CAS systems on the removal of these two compounds. A removal efficiencies between 93 and 100% were observed for the sunscreens except for benzophenone-4. A removal as low as 19% was reported for this compound possibly because the high polar behaviour exhibited by this compound. More than 50% of octocrylene and octyl-triazone were adsorbed onto the sludge. On the other hand, biological degradation was the main mechanism for the removal of 4-MBC (Barceló, et al. 2008).

Removal of surfactants

WWTPs provided with CAS systems reports a high removal efficiency of surfactants. The compounds are not completely mineralized due to either the lower than necessary hydraulic retention times (HRT)s set at the CAS systems, or if the surfactants are present at high concentrations. Moreover, these compounds can be removed by adsorption into the sludge. The main problem in the biological degradation process is the potential formation of recalcitrant metabolites (byproducts) such as the situation reported with alkylphenol ethoxylate (APE). The biotransformation of this compound produces metabolites more resistant to degradation and more toxic (Jardak, et al. 2016).

Table 4-22 summarizes the removal efficiencies of several surfactants evaluated at different conventional WWTPs.

Table 4-22 *Removal and mean concentration of the surfactant and their metabolites in CWWTP*

Group	**Surfactant**	**Influent dissolved** µg/L	**Effluent dissolved** µg/L	**Removal CAS** %	
Anionic	LAS (Linear alkylbemzene sulfates)	2166	13.277	> 99	(a)
	AES (Alkyl ether sulfates)	400 - 4500	< 1	99,9	(b)
	AS (Alkyl sulfates)	< 20 – 620	< 1	99,9	(b)
Cationic	BAC - C12 (alkyl benzyl ammonium chlorides)			96,9 - > 99	(a)
	BAC - C14			94,8 - > 99	(a)

Group	Surfactant	Influent	Effluent	Removal	
	BAC - C16			93,3 - > 99	(a)
	BAC - C18			92,8 - > 99	(a)
	DDAC - C10 (dialkyl ammonium chlorides)			95,1 - > 99	(a)
	DDAC – C12			17,6 – 98,3	(a)
	DDAC – C14			88,9 - > 99	(a)
	DDAC – C16			93,5 – 98,4	(a)
	DDAC - C18			94,0 - > 99	(a)
	ATAC – C12 (Trialkyl ammonium chlorides)			97,5 - > 99	(a)
	ATAC – C14			90,9 - > 99	(a)
	ATAC – C16			95,2 - > 99	(a)
Non-ionic	NPEO (Nonylphenol ethoxylates)	< 30 – 2120	< LOD – 49	81 – 99,5	(b)
	NPEC (Nonylphenoxy carboxylates)	< 0.2 – 219	0.6 – 113		(b)
	NP (Nonylphenol) + NP_1EO (-diethoxylates) + NP_2EO (nonylphenolmono-)			80,7 – 96,6	(a)
	OP (octylphenol)	0.302	0.104	0 – 92,2	(a)
	4-Tetr-octylphenol	0,75	0,07	73 - 100	(c)
	Alcohol ethoxylate	125 – 3600	< 0.1 – 509	98 – 99,9	(b)
	PEG (Polyethylene glycols)	85 – 3720		81 - 98	(b)
	MCPEG (Monocarboxylated polyethylene gycol)	22 – 85	0.5 – 7.7		(b)
	DCPEG (Dicarboxylated metabolites)	10 -100	< 0.2 – 5.8		(b)
	CDEAs (coconut diethanolamides)	111 – 124	14	~ 90	(b)
	AG (Alky glucamides)	26 – 45	< LOD – 0.2		(b)
	APG (Alky polyglucosides)	7 – 13	Not detected	~ 100	(b)

Source: (a) Clara, M., et al. (2007) (b) Barceló, D., et al. (2008) (c) Höhne, C. and W. Püttmann (2008)

In the case of anionic surfactants, a high removal efficiency of the linear alkylbenzene sulphonic acid (LAS) was reported. This phenomenon occurs primarily due to the biological degradation of this compound starting at the oxidation of the terminal carbon at the alkyl chain. As a part of this process sulfophenylcarboxylic acids (SPCs) are formed as intermediate products. Then, the process continues with the desulfonation and breakage of the aromatic rings. The absence of SPC indicates that the biodegradation of LAS has been fully completed. The influx of a high amount of LAS can impede complete removal within the plant (Jardak, et al. 2016).

The degradation of the non-ionic surfactant APE in conventional WWTPs occurs by shortening the ethoxylate chains generating as intermediates products short chain APE containing one or two units of ethoxylates. APE metabolites are more easily degraded under aerobic than anaerobic conditions. Nonylphenol (NP) is one of the most important metabolites of APE (Jardak, et al. 2016).

Alcohol ethoxylate (AE) are the non-ionic surfactants used to replace APEs. They are generally found as a complex mixture with more than hundred homologous compounds with different lengths of the alkyl chains and with different number of ethylene oxide units. The aerobic biological degradation of these compounds begins with the central cleavage of the molecule forming polyethylene glycols (PEG) and free fatty alcohol (FFA). Then, the N- or H- oxidation of the terminal carbon of the alkyl chain is observed, and the hydrolytic shorting of the terminal carbon of the polyethoxylic chain. On the other hand, in the anaerobic biological degradation the microorganisms act on the ethoxy end units, releasing acetaldehyde. The ehtoxy chain is shortened until reaching the lipophilic half (Jardak, et al. 2016).

The removal of cationic (QAC) and non-ionic surfactants (APEO) by anaerobic processes is not effective.

The presence of surfactants in biological WWTPs interferes with primary sedimentation and the generation of foams decreases the ability to transfer oxygen; thus reducing the efficiency of the biodegradation process. Decreasing the degradation capacity limits the overall treatment capacity of the plant.

High concentrations of surfactants are commonly found both in the particulate (solid phase) influent wastewater, as well as in the untreated sludge from the treatment plants. Approximately 10 to 35% of anionic surfactants such as LAS are mostly adsorbed in the sludge in conventional WWTPs. LAS has been found to be highly biodegradable under aerobic conditions. However, dissolved oxygen concentrations higher than 1 mg/L need to be provided (citation). Aerobic digestion processes showed positive removal of LAS from the sludge, while anaerobic digestion processes were not effective on removal LAS from the sludge (Jardak, et al. 2016).

Cationic surfactants (positivily charged surfactants) favour the adsorption to negatively charged particles on the sludge. Several studies reported adsorption levels from 20 to 95% (citation). The initial oxidation of the cationic surfactants begins at the presence of molecular oxygen. Cationic surfactants cannot be anaerobically biodegradable because either the lack of an adequate metabolic pathway, or possible toxic effects. However, studies show that some QAC are anaerobically converted into methane at relatively low concentrations (low enough not to inhibit the activity of methanogenic microorganisms) (Jardak, et al. 2016).

Non-ionic surfactants adsorbed to the sludge are readily biodegradable under aerobic conditions (aerobic digestion), whereas under anaerobic conditions they are not biologically degreded (citation). Anaerobic biotransformation of nonylphenol ethoxylate (NPEO) promotes the formation of nonylphenol (NP), nonylphenol monoethoxylate (NP1EO), and nonylphenol diethoxylate (NP2EO). Anaerobic digestion of these two latter also produces NP. In general, NPEO is less biodegradable and only partial mineralization occurs during biological treatment. The biodegradation of nonylphenol polyethoxylate produces metabolites such as NPE2, NPE1, NPEC1, and NPEC2 which are not fully removed. Consequently, the persistence of nonylphenol ethoxylate by-products in the sludge could alter microbial and enzymatic activities, since the biosolids are contaminated in the soil after treatment (Jardak, et al. 2016).

Removal of Plasticizers (Phthalate esters)

Clara et al., (2010) evaluated the trajectory of six types of phthalate esters acid (PEAs) in two conventional WWTPs provided with primary clarifier and CAS systems. The plants are provided with nitrification and denitrification capacities and operates at SRTs of 17 and 12 days respectively.

Figure 4-10 shows the mass balances for the six selected phthalates, dimethyl phthalate (DMB), diethyl phthalate (DEP), dibutyl phthalate (DBP), butylbenzyl phthalate (BBP), bis(2-ethylbenzyl) phthalate (DEHP), and dioctyl phthalate (DOP). Moreover, the figures shows the mass balance for the total phosphorus (TP). The TP served as a quality indicator for the mass balances since the mass of incoming TP must be equal to the mass of the outcoming TP. The TP balance shows that plant 2 has a better performance than 1.

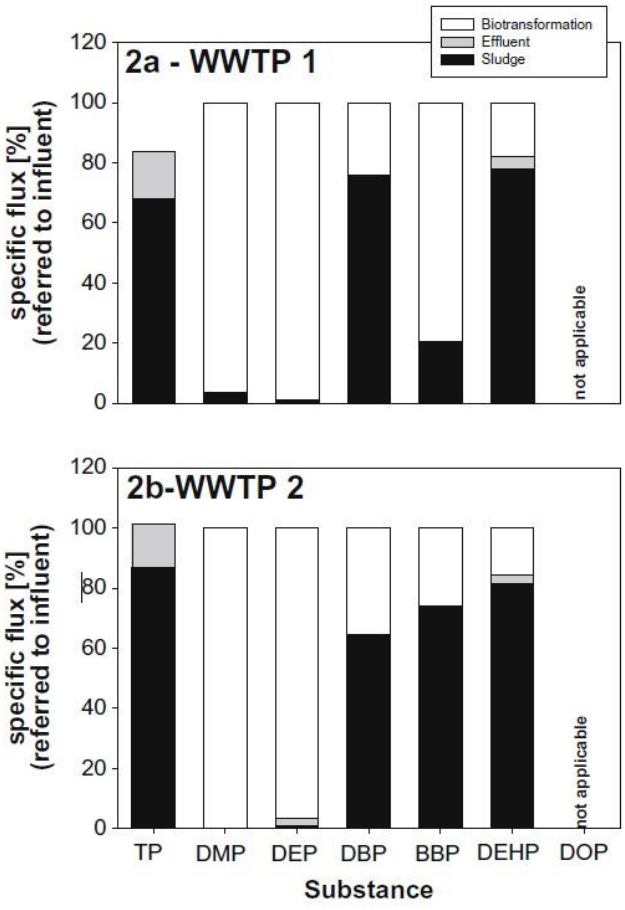


Figure 4-10 *Mass balance for the investigated phthalate in two WWTPs ((a) WWTP 1 and (b) WWTP 2. Source: Clara, et al. 2010.*

The removal of the six compounds by adsorption and biotransformation is greater than 95%.

Only DEP and DEHP were detected in the effluent. The mass fraction detected in the sludge at the treatment plants 1 and 2 were as follows: for DMP 3.4% and 0%, respectively; for DEP 1.0% and 0.7%; for DBP 76% and 64%; for BBP 21 % and 74%; and for DEHP 78% and 81%. The higher the molecular weight of the substance and its lipophilic character (higher log K_{ow}), the higher the chances for adsorption processes.

The removal of DEHP due to biotransformation was approximately 14%, and 68% due to adsorption to the primary sludge and wasted sludge.

Phthalates exhibit a high tendency to accumulate in the sludge; therefore, are no longer available for biodegradation processes. A high removal efficiencie for these compounds have reported at sludge treatment plants (Clara et al., 2010).

Removal of Perfluorinated compounds (PFC)

Perfluorinated compounds (PFC)s have been recognized as persistent and recalcitrant pollutants under natural environmental conditions due to their extremely strong carbon-fluorine bonds at the molecular level. Several studies reported that conventional WWTPs are not able to remove PCFs. Moreover, negative removals for these compounds were observed. Biodegradation processes forms precursor compounds (Arvaniti, and Stasinakis 2015).

Studies of the biotransformation of PCFs in activated sludge processes at laboratory-scale showed that perfluorooctanoic acid (PFOA) is the main transformation product of 8:2 fluorotelomer alcohol (8:2 FTOH) and that 6:2 fluorotelomer alcohol (FTOH 6:2) and 6:2 fluorotelomer sulfonate (FTS 6:2) can be biotransformed to short chain perfluoroalkyl carboxylate acids (PFCAs), including perfluoropentanoic acid (PFPeA) and perfluorohexanoic acid (PFHxA). Perfluorooctanesulfonate (PFOS) is a microbiologically inert compound under aerobic and anaerobic conditions. However, it was reported that it was possible to decompose up to 67% of this compound by the specific microorganism *Pseudomonas aeruginosa*, with perfluorobutanesulfonate (PFBS) and perfluorohexanesulfonate (PFHxS) being detected as by-products. The PFC sorption to the sludge could be an important mechanism for the removal of these compounds by conventional WWTPs. Most of the available studies focus on PFOS and PFOA. These compounds have a higher sorption capacity than short chain PFCs. Since PFCs have a strong hydrophobic perfluorinated chain, hydrophobic interactions is the main sorption mechanism. The hydrophobic property of the PFCs increases with the increase in the length of the perfluorocarbon chain. In addition, PFOS has higher sorption capacity than PFOA due to the presence of more carbon in the chain and the existence of different functional groups with higher acidity in its molecule (Arvaniti, and Stasinakis 2015).

4.2.2. Removal of emerging pollutants by Advance Oxidation

Ozonation

In ozonation processes two different mechanisms usually take place: (i) ozone reacts directly with the organic compounds (with the micropollutatn) through a molecular reaction with

ozone that is slow and selective; and (ii) ozone reacts with other substances (or physical agents) forming hydroxyl radicals which are highly reactive oxidizing compounds.

The chemical reactions that occur in the treatment with ozone can generate sub toxic products. One example is the generation of bromate from the bromide present in the wastewater or the generation of nitrosamines from the degradation of fungicides.Wastewater matrices are complex and may contain compounds that consume hydroxyl radicals reducing the removal efficiency of micro pollutants.Ozone can eliminate most PPCPs with elimination efficiency greater than 90% (Wang, and Wang, 2016).

Table 4-23 *Removal by Ozone oxidation of PPCPs. Wang, and Wang, 2016.*

	Initial concentration	**Source water**	**Ozonation conditions**	**Removal efficiency (%)**	
Hormone					
Estriol	100 mg/L	Ultrapure water	30 mL/min for 0-90 min, pH 3-4	100	(1)
Estrone	100 mg/L	Ultrapure water	30 mL/min for 0-90 min, pH 3-4	100	(1)
	5-20 mg/L	Water	0.38 mg/min for 12 min, pH 6.5	>95	(2)
	5 mg/L	Ultrapure water	1.31 mg/min for 60 min, pH 6.5	100	(3)
17-b Estradiol	5-20 mg/l	Water	0.38 mg/min for 8 min, pH 6.5	100	(2)
Antibiotics					
Sulfamethoxazole	0.15 mM	Ultrapure water	0.2 mM for 10 min, pH 2 and 8	100	(4)
	0.05 - 5mg/L	Water	2 mg/L for 60 min, pH 7	>95	(5)
	60 mg/L	Ultrapure water/	83 mg/L, pH 7.1, 17 °C	100	(6)
	100 µg/L	Wastewater	14 mg/L, pH 7.1, 17 °C	100	
	1 mg/L	Deionized water	1.3-3.6 mg/L for 180 min, pH 2, 22 °C	>99	(7)
Trimethoprim	50 µM	Ultrapure water	3.5 mg/L, pH 7	100	(8)
Erythromycin	0.68 µM	Ultrapure water	3.4 µM, 6.8 µM for 2 min, 20 °C	>70	(9)
Ofloxacin	15 mg/l	Water	290 ml/min, pH 2,7,12, 25 °C	100	(10)
	22 mg/L	Ultrapure water/wastewater	390 mL/min, pH 7.4, 25 °C	100	(11)
Ciprofloxacin	200 µg/L	Wastewater	7.5 mg/min for 30 min, pH 9	100	(12)
	45.27 µM	Deionized water	2.5 g/L for 90 min, pH 7,27.5 °C, H2O2 concentration of 10 µmol/L	>95	(13)
	15 mg/L		2.5 g/L for 75 min, pH 7, 27.5 °C, H2O2 concentration of 10 µmol/L	95	(14)
Sulfadiazine	1 mg/L	Deionized water	1.1-3.1 mg/L for 180 min, pH 2, 22 °C	>90	(7)
Sulfamethazine	10-40 mg/L	Deionized water	10-20 mg/l for 120 min,pH 3-11, catalyst 0.1-0.4 g/l	100	(15)
Tetracycline	2.08 mmol/L	Deionized water	0.53-1.13 mmol/L for 90 min, pH 7.8,	>90	(16)

	Initial concentration	Source water	Ozonation conditions	Removal efficiency (%)	
	0.5 mM	Deionized water	10 mg/min for 30 min, pH 7.0, 20 °C	100	(17)
Lipid regulator					
Bezafibrate	426 µg/L	Drinking water	2 mg/L for 10 min, pH 7.3	>89	(18)
Clorfibric acid	1 mg/L	Ultrapure water	160 mg/L for 20 min, pH 9, 25°C	99	(19)
Nonsteroidal anti-inflammatory drugs					
Ibuprofen	1 mg/L	Ultrapure water	12 g/L for 20 min, pH 9, 25 °C	99	(19)
	0.1-10 mg/L	Ultrapure water	160 mg/L for 20 min, pH 9, 25°C	99	(20)
Diclofenac	8 mg/L	Ultrapure water	0.8-80 mg/L for 40 min, pH 7.0, 20 °C	100	(21)
	30 mg/L	Ultrapure water	20 mg/L for 20 min, pH 7.0, 20°C	100	(22)
Paracetamol	1 µM	Ultrapure water	0-6.8 µM for 24 h, pH 7.2, 20 °C	100	(23)
	5 mM	Ultrapure water	9.8 mg/L for 90 min, pH 9.0, 25 °C	53	(24)
Naproxen	15 mg/L	Water	0.22 mM, pH 3-7, 25 °C	100	(25)
Phenazone	0.16 mM	Ultrapure water	0.167 mM for 7 min, pH 7.9, 20 °C	100	(26)
Ketoprofen	0.1 mM	Ultrapure water	4.94 mM for 60 min, pH 7.0, 25 °C	100	(27)
	50 µM	Natural water/ultrapure water	80 µM for 20 min, pH 3,9, 20 °C	>90	(28)
Beta-blocker					
Atenolol	100 mg/L	Ultrapure water	0.7 g/h for 20 min, pH 2,7,9, 25 °C	N.A	(29)
Metoprolol	100 mg/L	Ultrapure water	0.7 g/h, pH 8.3, 25 °C	N.A	(30)
Acebutolol	100 mg/L	Ultrapure water	0.7 g/h, pH 2,7,12, 25 °C	N.A	(31)
Propanolol	10 µM	Wastewater	30-120 µM, pH 8.4,	N.A	(32)
	0.38 mM	Ultrapure water	0.47 mM for 8 min, pH 4, 25 °C	100	(33)
Antidepressant					
Fluxetine	50 mg/L	Ultrapure water	30 mg/l for 20 min, 0.02 mM H2O2	86	(34)
Anticonvulsants					
Carbamazepine	278 µg/L	Drinking water	2 mg/L for 10 min, pH 7.3,	100	(18)
	15 mg/L	Water	0.22 mM, pH 3-7, 25 °C	100	(25)
	10 mg/L	Ultrapure water	3.5 mg/L for 60 min, pH 6,7,8,15 °C	100	(34)
	11 mg/L	Ultrapure water	1.2 g/L for 30 min, pH 7.0	100	(35)
Primidone	50 µM	Natural water/ultrapure water	80 µM for 20 min, pH 3,9, 20 °C	20-30	(28)
Antineoplastics					

	Initial concentration	Source water	Ozonation conditions	Removal efficiency (%)	
Ifosfamide	20 mg/L	Deionized water	3 g/h for 15 min, Ph 9, 11, 20 °C	100	(36)
Methotrexate	100 ng/L	Drinking Water	10 mg/L for 2 h, Ph 8.1, 20 °C	96	(37)
Cyclophosphamide	20 mg/L	Deionized water	3 g/h for 15 min, pH 9, 11, 20 °C	100	(36)
	200 ng/L	Drinking Water	10 mg/L for 2 h, pH 8.1, 20 C	>90	(37)
Diagnostic Contrast Media					
Iopromide	114 µg/L	River water	0.5-2.0 mg/L for 15 min, pH 7.4, 25 °C	47-92	(38)
	1 µg/L	WTPs effluents/synthetic water	1-3 mg/L for 10 min, pH 8	20-70	(39)
	10 mg/L	Ultrapure water	16 mg/L for 30 min, pH 7.5, 21 °C	~60	(40)
Iomeprol	10 mg/L	Ultrapure water	16 mg/L for 30 min, pH 7.5, 21 °C	55	(40)
Diatrizoate	50 µM	Natural water/ultrapure water	80 µM for 20 min, pH 3,9, 20 °C	100	(41)
	10 mg/L	Ultrapure water	16 mg/L for 30 min, pH 7.5, 21 °C	26	(42)
Fragrances					
Musk xylene	200-400 µg/L	Tap water	5 mg/L for 120 min, 28 °C	no removal	(43)
Musk ketone	200-400 µg/L	Tap water	5 mg/L for 120 min, 28 °C	no removal	(43)
Preservatives					
Methylparaben	100 µM	Ultrapure water	0.67 g/h for 12 min, pH 6.9, 25 °C	99	(44)
Disinfectants					
Triclosan	1.4-4.5 mg/L	Water	1.1-1.7 mg/L, pH 7, room temperature	94-99.9	(45)

The experiments presented in the table were conducted in the laboratory.
N.A: not available.
Water means that type of water used in the study was not explicitly stated.
(1) Ogata et al., 2011; (2) Lin et al., 2009; (3) Sarkar et al., 2014; (4) del Mar Gómez-Ramos et al., 2011; (5) Gao et al., 2014; (6) Rodayan et al., 2010; (7) Garoma et al., 2010; (8) Kuang et al., 2013; (9) Luiz et al., 2010; (10) Tay and Madehi 2015; (11) Carbajo et al., 2015; (12) Vasconcelos et al., 2009; (13) De Witte et al., 2009; (14) Dewitte et al., 2008; (15) Bai et al., 2016a; (16) Wang et al., 2011; (17) Khan et al., 2010; (18) Tootchi et al., 2013; (19) Quero-Pastor et al., 2014b; (20) Quero-Pastor et al., 2014ª; (21) Sein et al., 2009; (22) Beltrán et al., 2009; (23) El Najjar et al., 2014; (24) Neamt¸u et al., 2013; (25) Rosal et al., 2008;(26) Miao et al., 2015;(27) Illés et al., 2014;(28) Real et al., 2009; (29) Tay et al., 2011; (30) Tay et al., 2013; (31) Tay and Madehi 2014; (32) Benner and Ternes 2009; (33) Dantas et al., 2011; (34) Antoniou and Andersen 2012; (35) Palo et al., 2012; (36) Lin et al., 2015ª; (37) Garcia-Ac et al., 2010; (38) Ahn et al., 2015; (39) Seitz et al., 2008; (40) Ning and Graham 2008; (41) Real et al., 2009; (42) Ning and Graham 2008; (43) Janzen et al., 2011; (44) Tay et al., 2010; (45) Chen et al., 2012

To evaluate the situation regardin the generation of oxidation by-products toxicity through ozonation Ashauer (2016) carried out and compiled studies on the toxicity of municipal wastewater before and after treatment consisting of ozonation and sand filtrationas an additional treatment to the conventional WWTP.
Several in vitro bioassays demonstrated that ozonation reduced the effluent toxicity measured through non-specific toxicity in Vibrio fischeri bacteria and Pseudokirchneriella subcapitata algae, inhibition of photosystem II in algae, estrogenicity, inhibition of acetylcholinesterase, and complete elimination of genotoxicity. Moreover, an evaluation based on toxicity tests on the first stages of life on fish (FELTS) found that ozonation led to reduced growth and development of FELTS, but sand filtration eliminates these toxic effects. Finally, a study was carried out on the receiving water body of a real WWTP in Switzerland provided with ozonation and sand filtration. The impact on macroinvertebrates was evaluated used as a risk species indicator (SPEAR). The study found favorable impacts on the composition of the macroinvertebrate community and the water quality in the receiving water body.

Advanced oxidation process

The UV treatment consists of applying UV light and destroying the chemical bonds of the compounds by photolysis. Photolysis has shown very different efficiencies on the removal of different emerging pollutants. Therefore, combing UV treatment with other alternatives for the removal of emerging contaminants may be beneffitial.

Several studies evaluated the removal of emerging contaminants by combining UV with hydrogen peroxide (advanced oxidation process). This process consists of the generation of hydroxil radicals by the reaction between the UV light and the supplied hydrogen peroxide. There are other alternatives for generating hydroxyl radicals (that is, other advanced oxidation processes) such as combining ozone with UV, or ozone with hydrogen peroxide.

Table 4-24 *Removal by UV/hydrogen peroxide treatment of PPCPs (Wang, and Wang 2016).*

Compounds	Initial concentration	Source water	Conditions	Removal efficiency (%)	
Hormone					
Estriol	N.A.	River water	1000 mJ/cm2, 15 mg/L H2O2, pH 7.0	>95	(1)
Estrone	50 µg/L	Deionized water	350 µW/cm2, 25 °C, 50 min, H2O2 = 15 mg/L	>60	(2)
17-b Estradiol	50 µg/L	Deionized water	350 µW/cm2, 25 °C, 120 min, H2O2 = 15 mg/L	>90	(2)
Antibiotics					
Sulfamethoxazole	120 ng/L	Wastewater	2768 mJ/cm2; room temperature, pH 6.5 ,H2O2 = 1.72 g/L, 15 min	100	(3)
	578 ng/L	Wastewater	550 w/m2, 17 °C, pH 2.5, H2O2 = 50 mg/L, 30 min	100	(4)

Compounds	Initial concentration	Source water	Conditions	Removal efficiency (%)	
	1.0 µg/L	Ultrapure water	200 mJ/cm2; pH 6.5, H2O2 = 10 mg/L	>99	(5)
Trimethoprim	~95 ng/L	Wastewater	2768 mJ/cm2; room temperature, pH 6.5, H2O2 = 1.72 g/L, 15 min	100	(3)
	10 uM	Synthetic fresh and hydrolyzed human urines	2.57x10-6 E L-1 s-1, pH 9, H2O2 = 294 uM	>99	(6)
	131 ng/L	Wastewater	550 w/m2, 17 °C, pH 2.5, H2O2 = 50 mg/L, 30 min	100	(4)
	68.9 uM	Ultrapure water	2000 mJ/cm2, room temperature, pH 7.4, H2O2 = 10 mg/L, 30 min	>99	(7)
Amoxicillin	25 mg/L	Distilled water	2.3 w/cm2, 40 °C, pH 7.0, H2O2 = 588 mg/L, 67 min, 10 rpm	~90	(8)
Erythromycin	110 ng/L	Wastewater	2768 mJ/cm2; room temperature, pH 6.5,H2O2 = 1.72 g/l, 15 min	~98	(3)
	2.48 µg/L	Ultrapure water	500 mJ/cm2; pH 6.5, H2O2 = 10 mg/L,	>99	(5)
Ofloxacin	41 ng/L	Wastewater	550 w/m2, 17 °C, pH 2.5, H2O2 = 50 mg/L, 30 min	100	(4)
Ciprofloxacin	129 ng/L	Wastewater	550 w/m2, 17 °C, pH 2.5, H2O2 = 50 mg/L, 30 min	100	(4)
	6.04 uM	Ultrapure water	2000 mJ/cm2, room temperature, pH 7.4, H2O2 = 10 mg/L, 30 min	>99	(7)
Penicillin	29.9 uM	Ultrapure Water	2000 mJ/cm2, room temperature, pH 7.4, H2O2 = 10 mg/L, 30 min	>99	(7)
Tylosin	65 uM	Nanopure water	7.2x10-5 E s-1, 25 °C, pH 3.0, H2O2 = 3 mM, 3 min	100	(9)
Enoxacin	0.06 mM	Ultrapure water	2 x106 photon s-1, H2O2 = 0.05 mM, 30 min	100	(10)
Tetracycline	~70 ng/L	Wastewater	2768 mJ/cm2; room temperature, pH 6.5, H2O2 = 1.72 g/L. 15 min	~99	(3)
Lipid regulator					
Bezafibrate	120 ng/L	Wastewater	2768 mJ/cm2; room temperature, pH 6.5, H2O2 = 1.72 g/L, 15 min	100	(3)
	426 ng/L	Wastewater	550 w/m2, 17 °C, pH 2.5, H2O2 = 50 mg/L, 30 min	100	(4)
	1 µg/L	Ultrapure water	500 mJ/cm2; pH 6.5, H2O2 = 10 mg/L	>90	(5)
Clorfibric acid	1 mg/L	Distilled-deionized water	UV 254 nm, 25 °C, pH 5, 30 min, H2O2 = 11 mM	>60	(11)
	~10 ng/L	Wastewater	2768 mJ/cm2; room temperature, pH 6.5, H2O2 = 1.72 g/L. 15 min	>90	(3)
	1.0 µg/L	Ultrapure Water	500 mJ/cm2; pH 6.5, H2O2 = 10 mg/L	>99	(5)
	10 mg/L	Ultrapure Water	2.09x10-5 Einstein cm-2s-1, 30°C, pH 7.1, H2O2 = 100 mg/L, 15 min	99.6	
	46.7 mM	Deionized water	2.12 w/cm2, H2O2 = 1 mM, 60 min	100	(12)

Compounds	Initial concentration	Source water	Conditions	Removal efficiency (%)	
Gemfibrozil	25 ng/L	Wastewater	550 w/m2, 17 °C, pH 2.5, H2O2 = 50 mg/L, 30 min	>100	(4)
	1.0 µg/L	Ultrapure water	500 mJ/cm2; pH 6.5, H2O2 = 10 mg/L	>99	(5)
Nonsteroidal anti-inflammatory drugs					
Ibuprofen	112 ng/L	Wastewater	550 w/m2, 17 °C, pH 2.5, H2O2 = 50 mg/L, 30 min	100	(4)
	95.82 µM	Nanopure water	7.2x10-5 E s-1, 25 °C, pH 7.0, H2O2 = 1 mM, 3 min	100	(9)
Diclofenac	1 mg/L	Distilled-deionized water	UV 254 nm, 25 °C, pH 5, 30 min, H2O2 = 11 mM	100	(11)
	~90 ng/L	Wastewater	2768 mJ/cm2; room temperature, pH 6.5, H2O2 = 1.72 g/L, 15 min	100	(3)
	518 ng/L	Wastewater	550 w/m2, 17 °C, pH 2.5, H2O2 = 50 mg/L, 30 min	100	(4)
	31.4 µM	Deionized water	2.12 w/cm2, H2O2 = 1 mM, 60 min	100	(12)
Naproxen	~5 ng/L	Wastewater	2768 mJ/cm2; room temperature, pH 6.5 ,H2O2 = 1.72 g/L. 15 min	100	(3)
	178 ng/L	Wastewater	550 w/m2, 17 °C, pH 2.5, H2O2 = 50 mg/L, 30 min	100	(4)
Acetaminophen	~9 ng/L	Wastewater	2768 mJ/cm2; room temperature, pH 6.5, H2O2 = 1.72 g/L. 15 min	~90	(3)
Ketoprofen	100 ng/L	Wastewater	2768 mJ/cm2; room temperature, pH 6.5, H2O2 = 1.72 g/l. 15 min	100	(3)
	123 ng/L	Wastewater	550 w/m2, 17 °C, pH 2.5, H2O2 = 50 mg/L, 30 min	100	(4)
Beta blocker					
Atenolol	~90 ng/L	Wastewater	2768 mJ/cm2; room temperature, pH 6.5,H2O2 = 1.72 g/L. 15 min	100	(3)
	669 ng/L	Wastewater	550 w/m2, 17 °C, pH 2.5, H2O2 = 50 mg/L, 30 min	100	(4)
	1.0 µg/L	Ultrapure water	500 mJ/cm2; pH 6.5, H2O2 = 10 mg/L,	>90	(5)
Metoprolol	~85 ng/L	Wastewater	2768 mJ/cm2; room temperature, pH 6.5, H2O2 ¼ 1.72 g/L.15 min	100	(3)
	179 ng/L	Wastewater	550 w/m2, 17 °C, pH 2.5, H2O2 = 50 mg/L, 30 min	100	(4)
	1.0 µg/L	Ultrapure water	500 mJ/cm2; pH 6.5, H2O2 = 10 mg/L	>99	(5)
Propanolol	~70 ng/L	Wastewater	2768 mJ/cm2; room temperature, pH 6.5, H2O2 = 1.72 g/L. 15 min	100	(3)
Sotalol	260 ng/L	Wastewater	550 w/m2, 17 °C, pH 2.5, H2O2 = 50 mg/L, 30 min	100	(4)
Antidepressant					
Diazepam	~90 ng/L	Wastewater	2768 mJ/cm2; room temperature, pH 6.5, H2O2 = 1.72 g/L. 15 min	100	(3)
Anticonvulsants					

Compounds	Initial concentration	Source water	Conditions	Removal efficiency (%)	
Carbamazepine	5 mg/L	Ultrapure water	1.0 g BiPO4, pH 0.5, 200 °C, 60 min,	72.4	(13)
	1 mg/L	Distilleddeionized water	UV 254 nm, 25 °C, pH 5, 30 min, H2O2 = 11 mM	>40	(11)
	~95 ng/L	Wastewater	2768 mJ/cm2; room temperature, pH 6.5, H2O2 = 1.72 g/L. 15 min	100	(3)
	263 ng/l	Wastewater	550 w/m2, 17 °C, pH 2.5, H2O2 = 50 mg/l, 30 min	100	(4)
	21.16 µM	Deionized water	153 mM/cm2, 25 °C, pH 3.0, H2O2 = 5 mM, 45 min	>95	(14)
	1.0 µg/L	Ultrapure water	500 mJ/cm2; pH 6.5, H2O2 = 10 mg/L	>99	(5)
Primidone	~80 ng/L	Wastewater	2768 mJ/cm2; room temperature, pH 6.5, H2O2 = 1.72 g/L. 15 min	100	(3)
	49 ng/L	Wastewater	550 w/m2, 17 °C, pH 2.5, H2O2 = 50 mg/L, 30 min	100	(4)
Diagnostic Contrast Media					
Lopamidol	1716 ng/L	Wastewater	550 w/m2, 17 °C, pH 2.5, H2O2 = 50 mg/L, 30 min	100	(4)
Diatrizoate	25 mg/L	Ultrapure water	300 w/m2, room temperature, pH 7.0, H2O2 = 200 mg/L pH 2.8, 240min	100	(15)
Preservatives					
Butylparaben	8x10-5 M	Distilled water	22°C, 29.6 w/cm2, 0.01 M H2O2, pH 7.0, 20 min	>95	(16)
Disinfectants					
Triclosan	135 ng/L	Wastewater	550 w/m2, 17 °C, pH 2.5, H2O2 = 50 mg/L, 30 min	100	(4)

(1) Rosenfeldt and Linden 2004; (2) Ma et al., 2015a,b; (3) Kim et al., 2009; (4) De la Cruz et al., 2012; (5) Wols et al., 2014; (6) Zhang et al., 2015; (7) Keen and Linden 2013; (8) Dogan and Kidak 2015; (9) He Y. 2013; (10) Santoke et al., 2015; (11) Giri et al., 2010; (12) Kim et al., 2014; (13) Xu et al., 2013; (14) Deng et al., 2013; (15) Polo et al., 2016; (16) BŁe˛dzka et al., 2010

The experiments presented in the table were conducted in the laboratory.

N.A: not available.

4.2.3. Removal of emerging pollutants by Membrane Technology

Membrane filtration such as microfiltration (MF) and ultrafiltration membranes (UF) are commonly used technologies for the treatment of municipal effluents. The process operates by the passing the effluent through a membrane filter driven by the pressure difference between the two sides.

The rejection of chemical compounds by a membrane is the result of physical interactions between the solute, the solution, and the membrane. The rejection processes are by sieving, steric effects, adsorption on the membrane and repulsion of charges. An evaluation carried out by Bellona et al., (2004) proposed a guide to estimate the rejection of a membrane of a

specific organic pollutant. The guide is illustrated in Figure 4-11. The predictions introduced by this guide were contrastedwith laboratory evaluations showing a good fit with various compounds; however, limitations were observed such as their applicability to full-scale plants or complex waters.

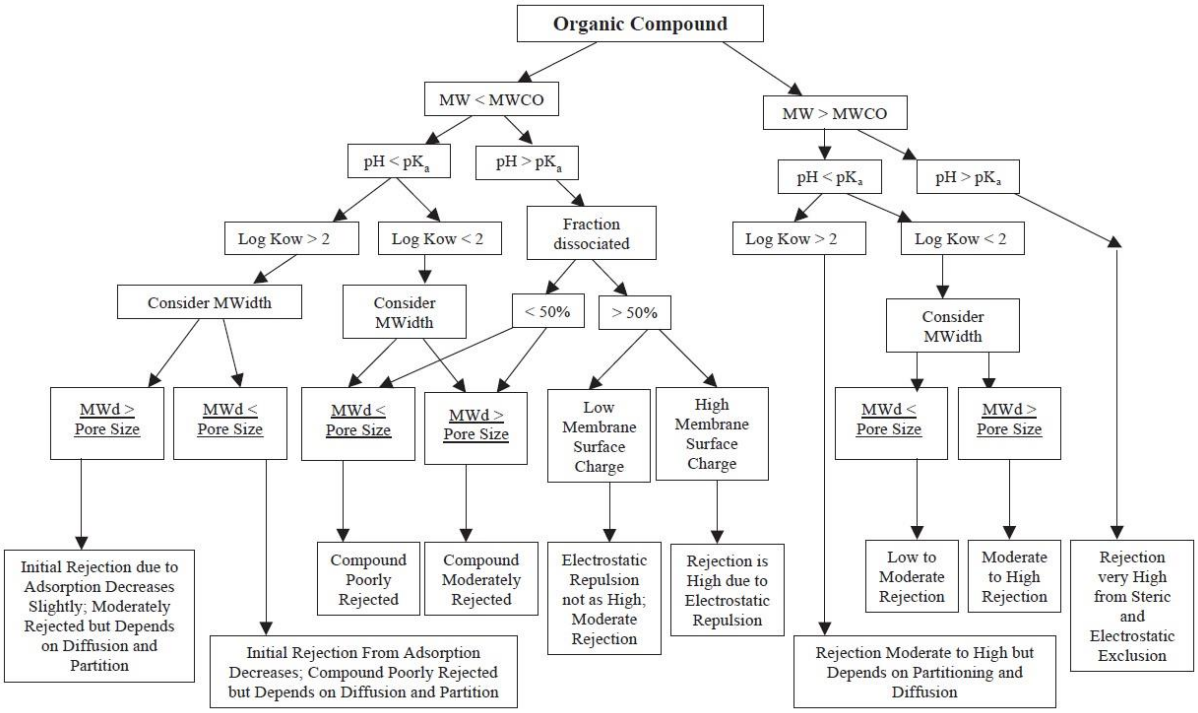


Figure 4-11 *Rejection diagram for organic micropollutants during membrane treatment based on solute and membrane properties. MW: molecular weight; MWCO: molecular weight cut-off; MWd: molecular width. Source: Bellona, et al., 2004.*

MBR

The MBR technology combine a biological reactor with membrane filtration. MBRs are widely used in wastewater treatment systems as a good technology in order to promote water reuse of the treated effluents. The incorporation of the filtration process by a microfiltration or ultrafiltration membrane improves the removal of some emerging pollutants. The WWTPs can be operated at higher SRT compared to conventional systems; therefore, there is more variety of microorganisms, and the adsorption processes can be more noticeable (since high biomass concentrations are possible to achieve). The main drawbacks of this technology include high energy cost, and high costs of membrane replacements.

Radjenovic et al., (2009) evaluated the removal of pharmaceutical compounds both in full-scale conventional activated sludge (CAS) systems, and in pilot-scale membrane bioreactors.The evaluation reported better removal efficiencies in the MBR system compared to CAS systems for the following compounds: glibenclamide, fluoxetine, mefenamic acid, indomethacin, diclofenac, propyphenazone, pravastatin, gemfibrozil, and naproxen. Regardin the removal of b-blockers, ranitidine, famotidine, erythromycin, the opposite situation was observed. For the evaluated compounds mefenamic acid, indomethacin, and diclofenac, it was observed that the CAS system did not remove any of these compounds; on the other hand, the

MBR achieved limited removals of mefenamic acid and indomethacin, and high removals for diclofenac.

Ketoprofen removal was slightly lower in MBR systems compared to CAS system. The almost complete removal of the anti-inflammatory drugs ibuprofen and acetaminophen from the aqueous phase was observed regardless of the type of treatment applied. The anti-epileptic drug carbamazepine and diuretic hydrochlorothiazide compounds were not affected by either type of biological reactor.

Table 4-25 summarizes the performance of flat-sheet (FS) and hollow-fiber (HF) MBR regarding pharmaceutical compounds removal efficiencies.

Table 4-25 *Removal with flat-sheet (FS) and hollow-fibre (HF) MBR of pharmaceutical compounds (Radjenovic, et al., 2009)*

Compound	**MQL, ng/L**	**c (Primary effluent), µg/L**		**Elimination from the aqueous phase (%)**		
		Range	Mean	CAS	FS MBR	HF MBR
Analgesics and anti-inflammatory drugs						
Ibuprofen	115.3	14.6–31.3	21.7	99.1 ± 1.8	99.2 ± 1.8	99.5 ± 1.6
Naproxen	65.1	0.13–0.67	0.463	71.8 ± 14.3	90.7 ± 3.2	91.6 ± 8.1
Ketoprofen	139.0	0.70–1.2	1.08	54.6 ± 19.7	43.9 ± 27.7	44.0 ± 20.6
Diclofenac	96.2	1.0–1.6	1.32	21.8 ± 28.5	65.8 ± 13.1	62.6 ± 18.3
Mefenamic acid	5.3	0.80–1.2	1.07	n.e.	40.5 ± 23.7	35.5 ± 28.3
Propyphenazone	4.8	0.046–0.097	0.065	37.6 ± 10.8	64.5 ± 16.0	60.7 ± 18.7
Acetaminophen	75.3	7.1–11.4	9.90	99.9 ± 0.1	99.8 ± 0.2	99.9 ± 0.1
Indomethacin	134.7	0.66–1.0	0.875	n.e.	41.4 ± 20.6	39.7 ± 26.2
Anti-histamines						
Ranitidine	8.2	0.072–0.54	0.347	24.7 ± 44.9	44.2 ± 29.6	29.5 ± 47.9
Loratidine	12.7	0.015–0.043	0.028	15.0 ± 43.9	n.e.	33.5 ± 52.2
Famotidine	1.2	0.027–0.14	0.080	60.1 ± 22.3	64.6 ± 24.5	47.4 ± 63.0
Anti-epileptic drug						
Carbamazepine	15.8	0.054–0.22	0.156	n.e.	n.e.	n.e.
Psychiatric drugs						
Fluoxetine	32.5	0.12–2.3	0.573	33.1 ± 28.9	98.0 ± 1.9	98.0 ± 1.6
Antibiotics						
Erythromycin	12.8	0.32–2.7	0.82	35.4 ± 50.5	43.0 ± 51.5	25.2 ± 108.9
Sulfamethoxazole	1.7	0.25–1.3	0.093	73.8 ± 12.7	80.8 ± 12.2	78.3 ± 13.9
Ofloxacin	21.5	0.89–31.7	10.5	75.8 ± 13.8	95.2 ± 2.8	91.3 ± 10.8
Trimethoprim	5.5	0.15–0.43	0.204	40.4 ± 25.4	66.7 ± 20.6	47.5 ± 22.5
ß-blockers						
Atenolol	8.2	0.84–2.8	2.0	61.2 ± 18.6	76.7 ± 12.6	69.5 ± 12.5
Sotalol	9.2	0.17–0.85	0.509	21.4 ± 31.5	53.1 ± 24.1	30.4 ± 25.3
Metoprolol	2.3	0.026–0.063	0.039	24.7 ± 44.9	44.2 ± 29.6	29.5 ± 47.9

Compound	MQL, ng/L	c (Primary effluent), µg/L		Elimination from the aqueous phase (%)		
Propranolol	8.6	0.108–1.13	0.292	58.8 ± 24.5	77.6 ± 12.2	65.5 ± 22.4
Hypoglycaemic agents						
Glibenclamide	25.8	0.12–15.9	9.89	46.1 ± 40.8	95.6 ± 4.4	82.2 ± 28.6
Lipid regulator and cholesterol lowering statin drugs						
Gemfibrozil	11.5	2.0–5.9	3.08	n.e.	42.2 ± 36.7	32.5 ± 49.3
Bezafibrate	15.6	1.9–29.8	14.9	80.8 ± 20.9	90.3 ± 10.1	88.2 ± 15.3
Pravastatin	47.3	0.46–1.5	0.886	59.4 ± 16.2	86.1 ± 9.1	83.1 ± 12.5
Diuretics						
Hydrochlorothiazide	17.3	2.3–4.8	2.74	n.e.	n.e.	n.e.

FS: flat-sheet
HF: hollow-fibre
n.e.: no elimination, defined for the mean elimination efficiency less than 10%.

The study also estimated the K_d for the sludge generated in the primary clarifier, for the sludge of the CAS biological process, and for the sludge at the FS MBR and HF MBR. The values are estimates calculated based on non-homogeneous samples; therefore, they and could not be at equilibrium. Most of the compounds have K_d lower than 500 L/kg, so sorption is not a significant way to remove the compounds. Acetaminophen presented a high K_d in the CAS biological process sludge which can be attributed to a high rate of degradation. Therefore, low concentrations of this compound were measured in the aqueous phase.
Loratadine was the only analysed compound exhibiting a high K_d at both the CAS and MBR biological system; there, the sorption mechanisms represented a significant path for the removal of these compounds.

Nanofiltration and Reverse Osmosis

The removal efficiency of emerging contaminants by nanofiltration (NF) strongly depends strongly on the specific properties of the compounds. The hydrophobicity of the compounds has a strong incidence in the rejection processes of the membranes; the more hydrophobic the compound, the greater the rejection. The removal efficiencies for emerging contaminants by NF and reverse osmosis (RO) are comparable as shown in several studies (citation)
Reverse osmosis generates in the process a concentrated effluent which is rich in organic matter and microcontaminants that need to be further treated.
From the data presented, it can be concluded that the use of membranes of MF or UF alone is not sufficient for the elimination of microcontaminants. Combination with other processes is necessary for achieving a better removal compared to conventional treatment.

4.2.4. Removal of emerging pollutants by Adsorption

The main adsorbent used is activated carbon due to primarily economical reasons. Activated carbon processes are usually implemetned after the biological treatment processes. The biological processes remove substances that can compete with the microcontaminats for the sorbent.

It can also be used in times of low flows and reduced capacity of the receiving body to dilute. Activated carbon processes use either powder activated carbon (PAC) or granular activated carbon (GAC). The type of activated carbon and the contact time provided may give different removal efficiencies. Usually smaller doses of PAC than GAC are required to obtain equal removal efficiencies. Longer contact times favour the removal of these compounds. Other factors influencing the removal efficiency for these compounds are both the adsorbent properties such as the surface area, porosity, surface polarity, and physical form of the material, as well as the characteristics of the compound such as the shape, size, charge, and hydrophobicity. It was found that the removal of molecules with high molecular weight it may be adsorbed on the particulate organic matter rather than on the activated carbon (Wang, and Wang, 2016).

Table 4-26 *Removal of PPCPs by activated carbo (Wang, and Wang, 2016).*

Compounds	Adsorbent	Initial concentration	Source water	qm (mg/g)	Removal efficiency (%)	
Hormone						
Estriol	PAC (5 mg/L)	100 ng/L	Surface water	n.a.	~60	(1)
Estrone	PAC (5 mg/L)	100 ng/L	Surface water	n.a.	~72	(1)
Estradiol	PAC (5 mg/L)	100 ng/L	Surface water	n.a.	~80	(1)
Antibiotics						
Sulfamethoxazole	PAC (5 mg/L)	100 ng/L	Surface water	n.a.	~35	(1)
	PAC (50 mg/L)	600 ng/L	WWTPs effluents	n.a.	~60	(2)
	PAC (20 mg/L)	100 ng/L	Synthetic water	n.a.	~95	(3)
	PAC (0.6 g/L)	0.5 µmol/L	Synthetic water 98 mmol/kg	n.a.	98 mmol/kg	
Trimethoprim	PAC (5 mg/L)	100 ng/L	Surface water	n.a.	~75	(1)
Tylosin	PAC (0.6 g/L)	0.13 mmol/L	Synthetic water	197.6 mmol/kg	n.a.	(4)
Tetracycline	PAC (0.6 g/L)	0.19 mmol/L	Synthetic water	213.9 mmol/kg	n.a.	(4)
Lipid regulator						
Bezafibrate	PAC (50 mg/L)	1.3 µg/L	WWTPs effluents	n.a.	~90	(2)
Gemfibrozil	PAC (5 mg/L)	100 ng/L	Surface water	n.a.	~37	(1)
Nonsteroidal anti-inflammatory drugs						
Ibuprofen	PAC (5 mg/L)	100 ng/L	Surface water	n.a.	~15	(1)
	PAC (10 mg/15 cm3)	40 mg/L	Synthetic water	57.1 mg/g	95.3	(5)
Diclofenac	PAC (5 mg/L)	100 ng/L	Surface water	n.a.	~40	(1)
	PAC (50 mg/L)	5.8 mg/L	WWTPs effluents	n.a.	~80	(2)
	PAC (20 mg/L)	100 ng/L	Synthetic water	n.a.	~100	(3)
Paracetamol	PAC (5 mg/L)	100 ng/L	Surface water	n.a.	~70	(1)
	PAC (20 mg/L)	100 ng/L	Synthetic water	n.a.	~85	(3)
Naproxen	PAC (5 mg/L)	100 ng/L	Surface water	n.a.	~50	(1)
	GAC (500ng/L)	500 ng/L	Synthetic water	3.2 mg/g	100	(6)

Compounds	Adsorbent	Initial concentration	Source water	qm (mg/g)	Removal efficiency (%)	
	PAC (20 mg/L)	100 ng/L	Synthetic water	n.a.	~95	(3)
Antidepressant						
Diazepam	PAC (5 mg/L)	100 ng/L	Surface water	n.a.	~65	(1)
Anticonvulsants						
Carbamazepine	PAC (5 mg/L)	100 ng/L	Surface water	n.a.	~70	(1)
	GAC (10 mg/L)	500 ng/L	Synthetic water	3.2 mg/g	100	(6)
	PAC (50 mg/L)	2.5 µg/L	WWTPs effluents	n.a.	90	(2)
Primidone	PAC (50 mg/L)	900 ng/L	WWTPs effluents	n.a.	92	(2)
Diagnostic Contrast Media						
Iopromide	PAC (5 mg/L)	100 ng/L	Surface water	n.a.	~30	(1)
	PAC (50 mg/L)	15.4 µg/L	WWTPs effluents	n.a.	~40	(2)
Fragrances						
Musk ketone	PAC (5 mg/L)	100 ng/L	Surface water	n.a.	~60	(1)
Sunscreen agents						
Octylphenol	PAC (5 mg/L)	100 ng/L	Surface water	n.a.	~65	(1)
Oxybenzone	PAC (5 mg/L)	100 ng/L	Surface water	n.a.	~90	(1)

(1) Snyder et al., 2007; (2) Altmann et al., 2014; (3) Nam et al., 2014; (4) Ji et al., 2010; (5) Mestre et al., 2007; (6) Yu et al., 2008

N.A. represents not available.

The adsorption mechanisms consist both on the chemical (electrostatic interaction) and on the physical interaction bewteen the molecules of the compounds to be adsorbed and the surface of the adsorbent. The latter is often more important because of the ability to form multiple layers. The ability of the activated carbon to adsorb a particular compound can be predicted on the basis of the hydrophilic or hydrophobic nature of the chemical compounds.

The hydrophobic (non-polar) or hydrophilic (polar) properties of the antibiotics can be determined from their Log K_d values. Non-polar antibiotics with Log K_{ow}> 2, can be efficiently removed by activated carbon processes by hydrophobic interaction. However, the adsorption of more polar or charged compounds to the activated carbon is much more difficult to predict due to polar interactions and ion exchange (Le-Minh, et al., 2010).

4.3. Project Life

4.3.1. Life Project objective

1- To demonstrate that the selected combination of technologies is able to reduce the concentration below Directive 2013/39/UE threshold of the following priority emerging pollutants:

Name of priority substance	CAS	Identified as priority	Anual Average-EQS	Maximum Allowable

	number	hazardous substance (*)	Inland surface waters (*)	Concentration Inland surface waters (*)
			µg/l	µg/l
Chlorpyrifos	2921-88-2		0,03	0,1
Trifluralin	1582–09 -8	X	0,03	Not applicable
Di(2-ethylhexyl)phthalate (DEHP)	117-81-7	X	1,3	Not applicable
4-t-OctylPhenol	140-66-9		0,1	Not applicable

(*) Directive 2013/39/UE

2- To demonstrate that the selected combination of technologies is able to reduce the concentration in a 99% of their original concentration of the following emerging pollutants:

Name of substance	CAS number	Maximum acceptable method detection limit (**)
		ng/l
Diclofenac	15307-86-5	10
17-alfa-ethinylestradiol	57-63-6	0,035
17-Beta-Estadiol	50-28-2	0,4

(**) Directive 2015/495/UE

3- To demonstrate that the selected combination of technologies is able to reduce the concentration of the following pharmaceutical emerging pollutants in 99% of their original concentration.

Name of substance	CAS number
Carbamazepine	298-46-4
2-(4-isobutylphenyl)propionic Acid	51146-56-6
Fluoxetine	54910-89-3
Chloramphenicol	56-75-7

Name of substance	CAS number	Maximum acceptable method detection limit (**)
		ng/l
Estrone	53-16-7	0,4

(**) Directive 2015/495/UE

Expected results

Name of substance	CAS number	Final concentration
		µg/l
Chlorpyrifos	2921-88-2	0,0 – 0,00069
Trifluralin	1582 – 09 -8	0,0005 – 0,0006
Di(2-ethylhexyl)phthalate (DEHP)	117-81-7	0,09 – 0,26
4-t-OctylPhenol	140-66-9	0,0 – 0,005
17-alfa-ethinylestradiol	57-63-6	0,00045 – 0,006
17-Beta-Estadiol	50-28-2	0,205 – 2,4
Chloramphenicol	56-75-7	0,08 – 0,12
Carbamazepine	298-46-4	0,011 – 0,017
2-(4-isobutylphenyl)propionic Acid	51146-56-6	0,245 – 0,36
Fluoxetine hidrocloruro	54910-89-3	<0,000195
Estrone	53-16-7	0,000029 – 0,00015
Diclofenac	15307-86-5	0,05 – 0,08

Description of the generic treatment of priority and emerging pollutants

The goal is reduce the concentration of micro-pollutants of different species and opposite chemical nature, polar and non-polar.

The process combines a sequence of treatments:

- Filtration – adsorption columns (gravel-silex and activated carbon) in order to reduce solids, organic matters and micro-pollutants in treated wastewater.

- Filtration by membrane to reduce SDI and EPs

- Advanced Oxidation for removal EPs which escaped of previous steps.

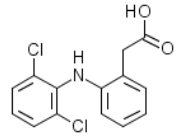
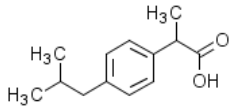
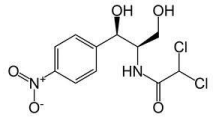
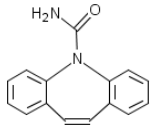
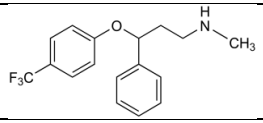
- Finally, electrochemical advanced oxidation process to treat the concentrate water from membrane filtration operation.

4.3.2. Emerging pollutants selected as indicators

The emerging contaminants selected in this project as indicators of the removal efficiency of persistant organic compounds by the pilot treatment plant are pharmaceutical products. We also selected prioritary substances, not covered in this chapter.

The following Table 4-27 shows the compounds and their main physical and chemical properties.

Table 4-27 *Physic-chemical properties of the selected pharmaceuticals. Modified from Verlicchi, et al., 2012*

	Pharmaceutical	MW	Chemical formula	pK_a	Log K_{ow}	S_w 25°C (mg L^{-1})	Log K_d	k_{biol} (L gSS^{-1} d^{-1})	Charge at pH 7	Molecular structure
Analgesics/Anti-inflammatories	Diclofenac CAS # 15307-86-5	296	$C_{14}H_{11}Cl_2NO_2$	4.15	4.51/0.7	4.52	1.2	<0.04-1.2 ≤0.1 ≤0.1 <0.002-<0.1	Negative	
	Ibuprofen CAS # 15687-27-1	206	$C_{13}H_{18}O_2$	4.51	3.97/0.45	41.05	0.9	1.5-20 21-35 9-22 1.33->3	Negative	
Antibiotics	Chloramphenicol CAS # 56-75-7	323	$C_{11}H_{12}Cl_2N_2O_5$	5.5	1.14	388.5			Neut./Neg.	
Psychiatric drugs	Carbamazepine CAS # 298-46-4	236	$C_{15}H_{12}N_2O$	13.9	2.45	17.66	0.1	≤0.1 <0.03-<0.06 <0.005-<0.008	Neutral	
	Fluoxetine CAS # 54910-89-3	309	$C_{17}H_{18}F_3NO$	9.5	4.05	38.35	0.7	5-9	positive	
Hormones	Estradiol CAS # 50-28-2	272	$C_{18}H_{24}O_2$	10.27	3.94	81.97	2.4-2.8	175-460 280-950	Neutral	
	Estrone CAS # 53-16-7	270	$C_{18}H_{22}O_2$	10.25	3.43	146.8	2.4-2.9	10-162 28-430 >20	Neutral	
	Ethinylestradiol CAS # 57-63-6	296	$C_{20}H_{24}O_2$	10.24	4.12	116.4	2.5-2.8	0.4-20 1.2-8 1.5-6 >0.5->0.7	Neutral	

The analysis of the physical and chemical properties can lead to different suppositions about the behavior in the ambient, which must verified locally. The presence of active compounds, the composition of the suspended matter or specific biomass, among other conditions, can alter the expected behavior.

As the selected pharmaceutical substances have low coefficient of adsorption, the sorption to the biomass or to suspended solids is weak. From the kinetic biodegradation coefficient (k_{biol}) it can be concluded that diclofenac and carbamazepine are persistent compounds, as opposed to estradiol and estrone which are highly biodegradable. The remaining compounds have k_{biol} between 0.1 and 10 L/(gSS d), which implies quite good biodegradability.

If we observe the water-octanol partition coefficient (K_{ow}) the compounds ethinylestradiol, fluoxetine, and partially diclofenac are highly lipophilic, which makes them potentially assimilated by the biomass. On the other hand carbamazepine, chloramphenicol, and under certain circumstances ibuprofen and diclofenac have hydrophilic behavior, not showing affinity for lipids.

Fluoxetine shows positive charge at pH7, so it can be potentially adsorbed by microorganisms, with their negatively charged surfaces. Compounds with neutral charges tend to generate van der Waals links with lipidic fractions of sediments or organic matter.

Emerging contaminants can be detected in affluent and effluents of conventional treatment plants. The following table shows the average concentrations in the affluent and effluents of conventional treatment plants, and the removal percentage of the compounds selected as indicators.

Table 4-28 *Removal efficiencies of Pharmaceutical compounds in Conventional WWTP. Modified from Verlicchi, et al., 2012*

Class by use	Name of substance	Average concentration raw influent (µg/L)	Average concentration effluent (µg/L)	Average Percentage removal efficiencies in WWTP with CAS (%)
Analgesic/anti-inflamatories	Diclofenac	1	0,8	29
	Ibuprofen	37	3,6	87
Antibiotics	Chloramphenicol	1	0,05	95
Psychiatric drugs	Carbamazepine	1,2	1,04	18
	Fluoxetine	0,54	0,24	56
Hormones	Estradiol	0,25	0,01	80
	Estrone	0,08	0,03	76
	Ethinylestradiol	0,02	0,003	78

The ibuprofen is one of the compounds in the Analgesic/anti-inflamatories group with highest concentrations in the affluent, and together with diclofenac are the most studied compounds in treatment plants. They are widely used prescription-free substances.

Fluoxetine and Carbamazepine are among the most studied psychiatric drugs, but they are not notable because of their concentrations in the WWTP afluent. Fluoxetine shows concentrations in the solid phase above the 20% of the total.

Among the hormones the most studied compounds are estrone, estadiol and ethinylestradiol. The compounds with the highest concentration in the influent are estradiol and estrone.

The removal of ibuprofen in the pretreatment is negligible. A possible explanation is that at pH7 it has negative charge which impedes the adsorption, and its low partition coefficient indicates that this compounds is found mainly in the liquid phase. The estrone shows an increase in concentration at the output of the pretreatment compared to the influx, which is explained by oxidation from estradiol into estrone, which in turn means that part of the registered removal of estradiol in pretreatment is trough generation of estrone as sub-product.

The main removal mechanisms in the biological reactor are biodegradation and sorption. Both processes have different incidence y the percentage of removal, biodegradation being the main process. Diclofenac exhibits wide dispersion in the removal percentage, varying between 0% and 90%. Ibuprofen exhibited some cases of higher concentration at the output of the biological reactor compared to the input, due to the fact that the compound can be regenerated from it derivatives trough hydrolysis. Carbamezapine is the most persistent compound, and in some cases an increase in concentration has been registered in the effluent compared to the affluent, due to compound liberation. On the other hand the hormones present high removal rates, between 76% and 80%, although cases of negative removal due to estradiol oxidation into estrone and partial deconjugation of other estrogens found in the water were also registered.

The next table shows the main removal mechanisms operating in the biological reactor on the selected pharmaceutical compounds. It can be seen that adsorption has very low incidence on the removal, which favours the use of these compounds as indicators of the removal efficiency of diverse technologies.

Table 4-29 *Fractions with respect to the influent mass load of selected PhCs removed during secondary biological treatment, sorbed to sludge and discharged with secondary effluent. Modified from Verlicchi, et al. 2012.*

Compound	Sludge age (days)	Biolotransform (%)	Sorption onto sludge (%)	Effluent (%)
Diclofenac	4–60	5–45	<5	55–95
	6	25	<5	70–75
	16	10	5	85
	<20	5	0	95
	>50	10–30	0	70–90
Ibuprofen	4–60	90–100	<5	0–10
	2	<5	<5	95–100
	<20	35–40	0	60–65
	>50	95	0	5

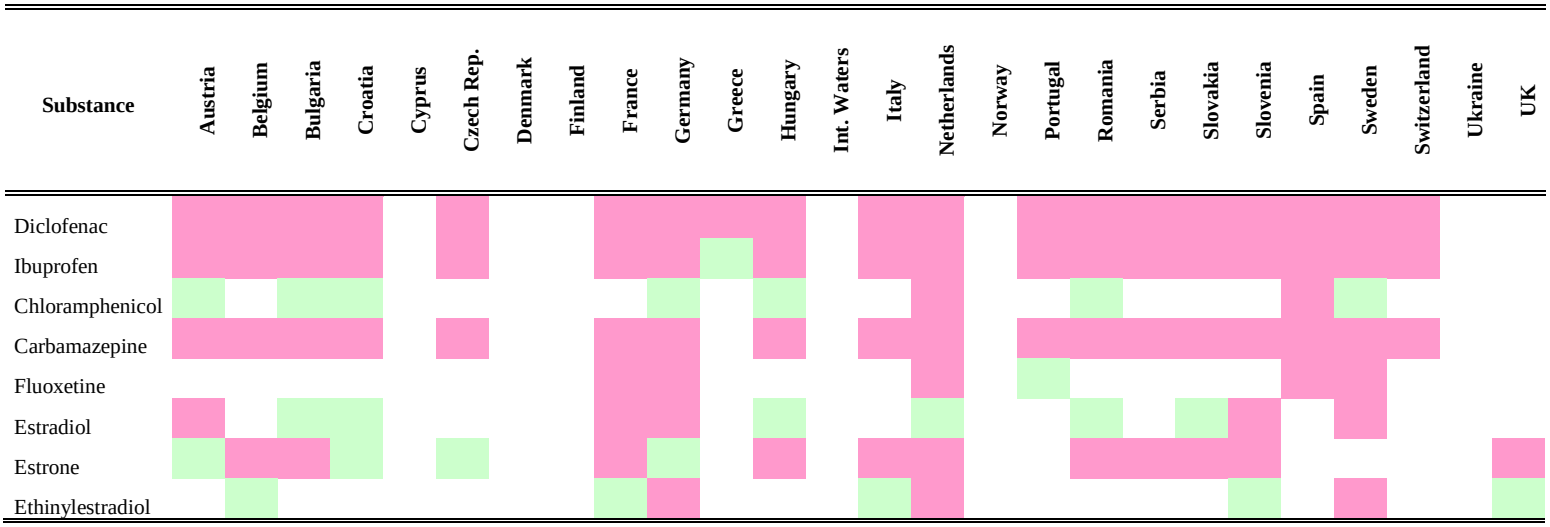
Compound	Sludge age (days)	Biolotransform (%)	Sorption onto sludge (%)	Effluent (%)
Chloramphenicol	6	0	0	100
Fluoxetine	<20	80	0	20
	>50	90	0	10
Estradiol	10–30	85–99	<5	<15
Estrone	10–30	35–97	≤5	5–60
Ethinylestradiol	10–30	45–95	≤5	5–50
	<20	25	5	70
	>50	80–90	0	10–20

An analysis of the ambiental risks at the undiluted effluent of a conventional treatment plant shows that the compounds fluoxetine, ibuprofen and the three hormones estradiol, Estone and Ethinylestradiol high risk (RQ>1). The remaining compounds display a low risk with RQ less than 0.1. The toxicity tests used to determine the PNEC, used to estimate the ambiental risk of all the compounds except hormones, were acute toxicological tests, to which a factor of 1000 was applied to compensate for effect on more sensitive species. For the hormones long term exposure were made, with no correction coefficient; there might be controversy if the the species are representative of the local biota. The estimation of adverse effects usually causes the highest levels of incertitude in the studies of ambiental risks from contaminatio by emerging contaminants.

In studies of ambiental risks made in four european basins Elbe, Scheldt, Danube and Llobregat, over 500 emerging contaminants, it was concluded that diclofenac, ibuprofen, carbamazepin were detected in the environment but the PNEC must be studied in more depth; and that Ethinylestradiol, estradiol, estrone were registered rarely and the PNEC are estimations, so the exposure levels generated in the bodies of water and the effect on the biota needing more studies.

From the mapping made in Chapter 4.1.5 and summarize in the following Table 4-30 can be observed that diclofenac, ibuprofen and carbamazepine are the most searched compounds (9 in 18 countries) and that chloramphenicol, ethinylestradiol and fluoxetine are the less searched (9, 8 and 6 countries, respectivelly). These last three compounds were also the less frequently detected.

Table 4-30 *Eropean mapping of emerging contaminants. Red: Emerging contaminants evaluated and detected at environmentally relevant concentrations[2] Green: Emerging contaminants evaluated and non-detected at environmentally relevant concentrations White: no available data Source: Network Norman.*



[2] The European mapping was conducted analyzing a data base with more than 9,700,000 samples. Each sample was analytically analyzed at a different laboratory and following different analytical techniques. Therefore, it is not possible to report a single limit of quantification (LOQ). However, all the reported samples were evaluated at environmentally relevant concentrations; that is in the range of micro to nanograms per liter concentrations. The main objective of the mapping is to show the presence and occurrence of emerging contaminants all over Europe considering that in some countries these compounds were evaluated and found, in other countries these compounds were evaluated and not found (that is the compounds are either not present in the water sample, or are at a concentrations below the LOQ of the analytical technoque), and in the remaining countries these compounds were not even evaluated.

CHAPTER 5 **Emerging Pollutants in Basin Santa Lucia Chico**

5.1. Problem statement

The presence of micro-pollutants in the water cycle is a problem that is becoming increasingly important. The increased exploitation of freshwater bodies by all human activities both as source of water as effluent receiving body are shortening the distances between one use and another. This makes that the freshwater found in a natural water body is probably indirect or direct reused by some activity.

Emerging micro-pollutants are generally non-biodegradable and persistent chemicals. These characteristics make that once introduced into the water can travel all the water cycle, being present in all activities. Protection barriers to environmental and health are the treatment plants. These barriers do not cover contamination from diffuse sources. On the other hand, as already mentioned, the conventional treatment plants are not designed to removal micro-pollutants and it is necessary for each particular case introduce specific removal processes.

The general situation is translating into changes in environmental monitoring, constantly updating regulations on the production, use and discharge of chemicals, concomitantly with epidemiological and biological researches, pollutant removal systems, analytical techniques, etc.
The problem of contamination with micro-pollutants has ecosystemic, cultural, social, political, economic compounds, depends of management and availability of the quantity and quality of water resources. That means that approach of the problem of pollution should be particular and specific to each basin.

In Uruguay the Ministry of Livestock Agriculture and Fisheries (MGAP) is responsible for authorizing and controlling the use of pesticides, fertilizers and veterinary drugs. There is control of 14 organic compounds in effluent discharges and water bodies depending on their use regulated in the national standard 253/79. In addition, each company discharges generating must request authorization to do so to the National Directorate of Environment (DINAMA) which can add requirements to discharges.

This control is far from the number of substances that are monitoring in Europe, US, etc.
Several studies conducted in Uruguay demonstrate the presence in the environment of micro-pollutants both regulated and unregulated what should translate into a systematic approach to this problem by agencies and authorities.

5.2. Objective

The present work seeks carry out a risk analysis in surface water by emerging pollutants in a basin of interest in Uruguay. In the field of emerging pollutants we work with incomplete knowledge, either due to lack of development of adequate methods of detection, unfinished studies of toxic effects, ignorance of the behaviour of the compound in the environment among others.

In the case of Uruguay, there are few documented antecedents of studies with emerging pollutants in surface waters, which implies not having jobs with which to contrast the possible local results obtained.

For the study of environmental risk will be followed the methodology described in chapter 4.1.7. This methodology gives a conceptual framework and clear definitions of the terms used and the scope and objective of the study.

It is worth noting that risk analysis allows, among the thousands of emerging substances, to rank them and order them according to the potential of emerging substances to become emerging pollutants.

The hierarchy allows to identify those compounds on which it is necessary to prioritize to deepen the studies to cover the bumps of knowledge in order to discard them as a substance of environmental risk or on the other side to define the necessary palliative measures.

The analysis risk in surface water will be done first by identifying the potential sources of emerging pollutants, then estimating the PEC for a limited number of substances by reason of available time to develop the present work, then from the literature review obtain the PNECs for these substances, estimate the environmental risk through the relation of the PEC and PNEC and finally to analyze the results and mark future actions.

5.3. Description of the study area

5.3.1. Basin Santa Lucia

The "Santa Lucía" basin of Uruguay is to the south of the country and is the fourth basin in magnitude with an area of approximately 13,480 km^2. The main channel of the basin is the Santa Lucia River that rises in the Cerro Pelado de la Sierra Carapé and flows into the Rio de la Plata through the Tigre Delta. The main tributaries are Santa Lucía Chico River and San José River. The location of the basin can be seen in Figure **5-1**.

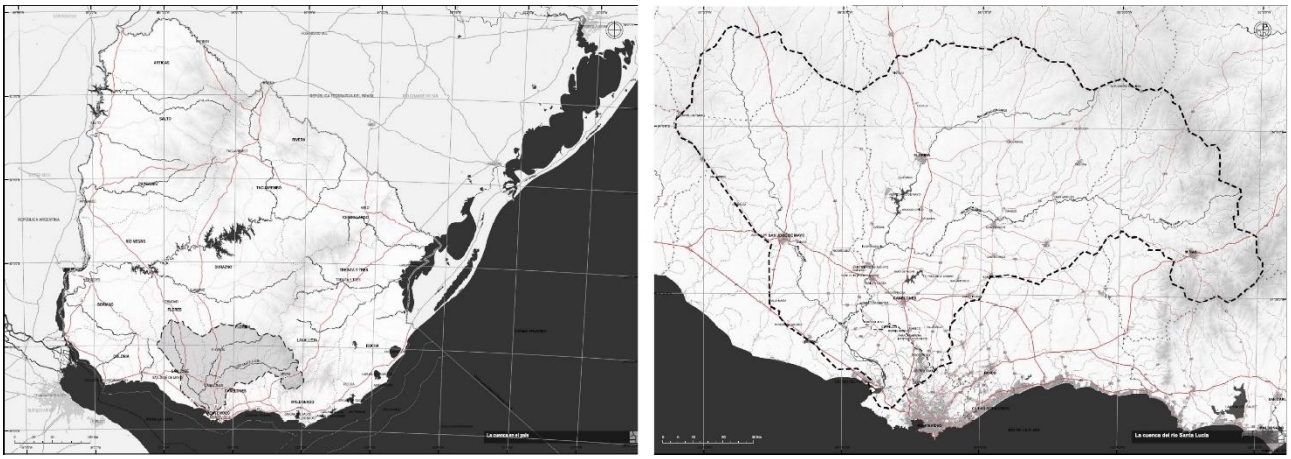


Figure 5-1 *Location Santa Lucía basin. Source: DINOT (ed), 2016.*

Climate is characterized by a temperate climate, the average temperatures of summer and winter are 23°C and 12°C respectively. The average maximum and minimum annual temperatures are 40°C and - 3° C. The annual precipitation is between 1200 and 1300 mm. The rainfall regime is characterized by its great variability and irregularity, which is why the availability of water is difficult to predict.

The Santa Lucia basin is composed of 9 sub-basins, which are detailed in the Table **5-1** and can be seen in the Figure **5-2**.

Table 5-1 *Sub basin of Santa Lucía basin*

Code	Sub Basin	Area (km^2)	Population
60	River "Santa Lucía" between the rising and River "Santa Lucía Chico"	5,171	72,021
61	River "Santa Lucía Chico"	2,570	41,017
62	River "Santa Lucía" between River "Santa Lucía Chico" and Stream "Canelón Grande"	667	23,773
63	Stream "Canelón Grande"	724	49,367
64	River "Santa Lucía" between Stream "Canelón Grande" and River "San José"	145	4,018
65	River "San José"	3,567	56,064
66	River "Santa Lucía" between River "San José" and Stream "Colorado"	369	9,862
67	Stream "Colorado"	165	116,041
68	River "Santa Lucía" between Stream "Colorado" and River "de la Plata"	100	24,264

Total	Basin “Santa Lucía”	13,477	396,427

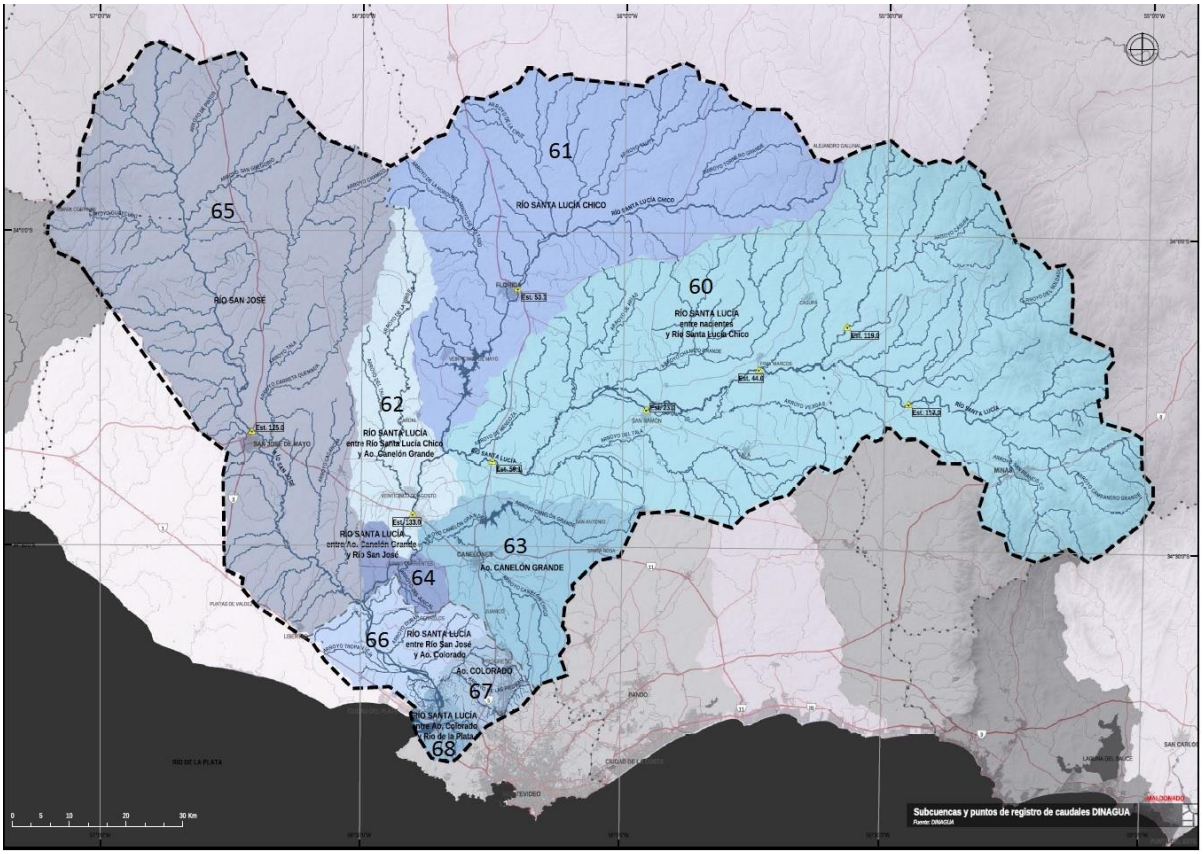


Figure 5-2 *Sub basin of Santa Lucia basin Source: DINOT (ed), 2016.*

The basin has relevant areas to the conservation of biodiversity. The most significant is the wetland of the Santa Lucia River at the mouth that forms part of the National System of Protected Areas.

In the basin there are approximately 400,000 inhabitants, mostly in urban centers (DINOT (ed), 2016).

The surface waters of the Santa Lucia River are used for irrigation, industry, recreational use and as source for the production of drinking water. Of all the uses, the main in quantity and importance is the use as source of drinking water of the metropolitan system that supplies 1,760,000 inhabitants which represents more than half of the population of the country. The supply is made through the water treatment plant located in the town Aguas Corrientes where the water intake is also. Four sub-basins supply the plant, 60, 61, 62 and 63.

The 61 sub-basin contains the main water reserve in the country, the Paso Severino reservoir with a surface area of 20 km^2 and a capacity of 70 million m^3. Basin 63 has a second reservoir of 8 km^2 of surface area and 22.5 million m^3 of reserve capacity.

About 44% of the territory is dedicated to livestock farming and approximately 43% is dedicated to dairy production. Other activities are forestation, agriculture, fruit, horticulture and winery. There are also industrial activities such as slaughterhouses, dairy processing plants, paper mills, chemical products etc.

The monitoring of the water quality of the Santa Lucía Basin shows that the parameter with less compliance with the standard 253/79 is the concentration of total phosphorus associated with the contribution of nutrients from diffuse sources and of specific contributions of sub-basins that are developed in the Metropolitan area.

Monitoring of five organic compounds shows compliance with 100% of the standard by atrazine, endusulfan and glyphosate and 24% of the concentrations of absorbable organic halides (AOX) sampled exceeded the guideline value of 25 µg/l.

The trophic state of the basin is in a process of deterioration starting with a mesotrophic state in the nascent to supereutrophic states in the mouths (DINAMA/MVOTMA, 2015).

These conditions have led to algal blooms and cyanobacteria. In the year 2013 an episode of bad taste and smell in the drinking water occurred due to the presence of geosmins, a fact that alerted on the degradation of the waters of the basin.

In response, a basin recovery plan has been drawn up with 11 measures (MVOTMA, 2013). These measures focus on regulating the activities, enforcing regulations and reducing nutrient contribution. It does not include measures to develop the issue of contamination with micro-pollutants beyond what is already regulated. On the other hand the company in charge of water purification is implementing additional treatment processes for the removal of microcontaminants associated with algal blooms and cyanobacteria.

Given that sub-basin 61 is highly sensitive because it contains the main drinking water reservoir and because of the diversity of activities carried out in them, this basin is selected as a case study to carry out the environmental risk analysis of contamination by emerging pollutants.

5.4. Environmental risk analysis for Sub basin 61 - Santa Lucía Chico

The basin 61 has an area of 2,570 km^2 and its main course is the Santa Lucia Chico River on which the reservoir of Paso Severino is developed which is the main drinking water reserve in the metropolitan area. In the basin live approximately 41,000 inhabitants, of these 33,640 live in the city of Florida. In this city 80% of the houses have connections of sanitation the rest has static sanitation.

To carry out the risk analysis for emerging pollutants, the activities that were developed in the basin and generated spills were first collected. Among these activities it is identified those that can generate discharges with emerging pollutants.

Then the methodology proposed in the guide (EC, 2003) is developed and detailed in the Chapter 4.1.7 for the selected compounds Ivermectin and Ethion and for the domestic effluent treatment plant. First the local risks will be identified, then the corresponding PECs and PNECs will be estimated, and finally the risk will be calculated and the areas in which the studies should be further analysed.

In addition to this risk estimate, a prospective sample campaign was conducted at four points in the basin for a limited number of compounds in the aqueous phase.

5.4.1. Activities located in the basin 61

In the basin are located two milk processing plants, a tannery, a chemical industry, a wool laundry, an egg-producing plant and the domestic wastewater treatment plant in the city of Florida.

On the other hand, several agricultural activities are carried out such as pasture, livestock, feedlots, forestation and small and medium-scale dairy farming. The Table **5-2** summarizes the main activities in the basin.

The Appendix D includes a listing of each industry and agricultural establishment with controlled spills by the environmental authority. The tabs detail the location, production, chemical substances and water used in the production process in addition to reporting the production of effluents, the treatment they receive and the body receiving them.

In the Figure **5-3** we can see the spatial distribution of the controlled spills and the distribution of the dairy farming.

Table 5-2 *Summary of activities in the basin 61*

Activity		Amount	Unit
Agricultural activities			
Cattle		297,460	head
	In feedlots	2,358	head
Dairy cattle		114,377	head
Sheep		95,693	head
Fowl		15,077	head
Hive		9,220	head
Pig		688	head
Meadow cultivation		61,143	Ha
Forage cultivation		44,556	Ha
	Sorghum	16,896	Ha
	Oats	13,896	Ha
	Raigas	9,517	Ha
	Wheat	1,994	Ha
			Ha
Forestation		3,766	Ha

	Eucalyptus	3,640	Ha
Coverage cultivation		18,656	Ha
	Lotus Rincon	12,108	Ha
Cereal cultivation		12,594	Ha
	Soy	6,716	Ha
	Wheat	2,968	Ha
	Sorghum	2,228	Ha
Fruit plantations		334	Ha
	Olives	253	
	Industries		
Milk processing plant		19,257	m^3 processed milk/month
Milk processing plant		33	Ton cheese/month
Tannery		854	Processed leather/month
Chemical industry			
6 dairy farms with more than 500 cows		3,052	Milk cow
Egg Producer		5,000	fowls
FeedLot		2,358	Head
	Domestic Efluents		
WWTP - Florida		4,979	m^3/day

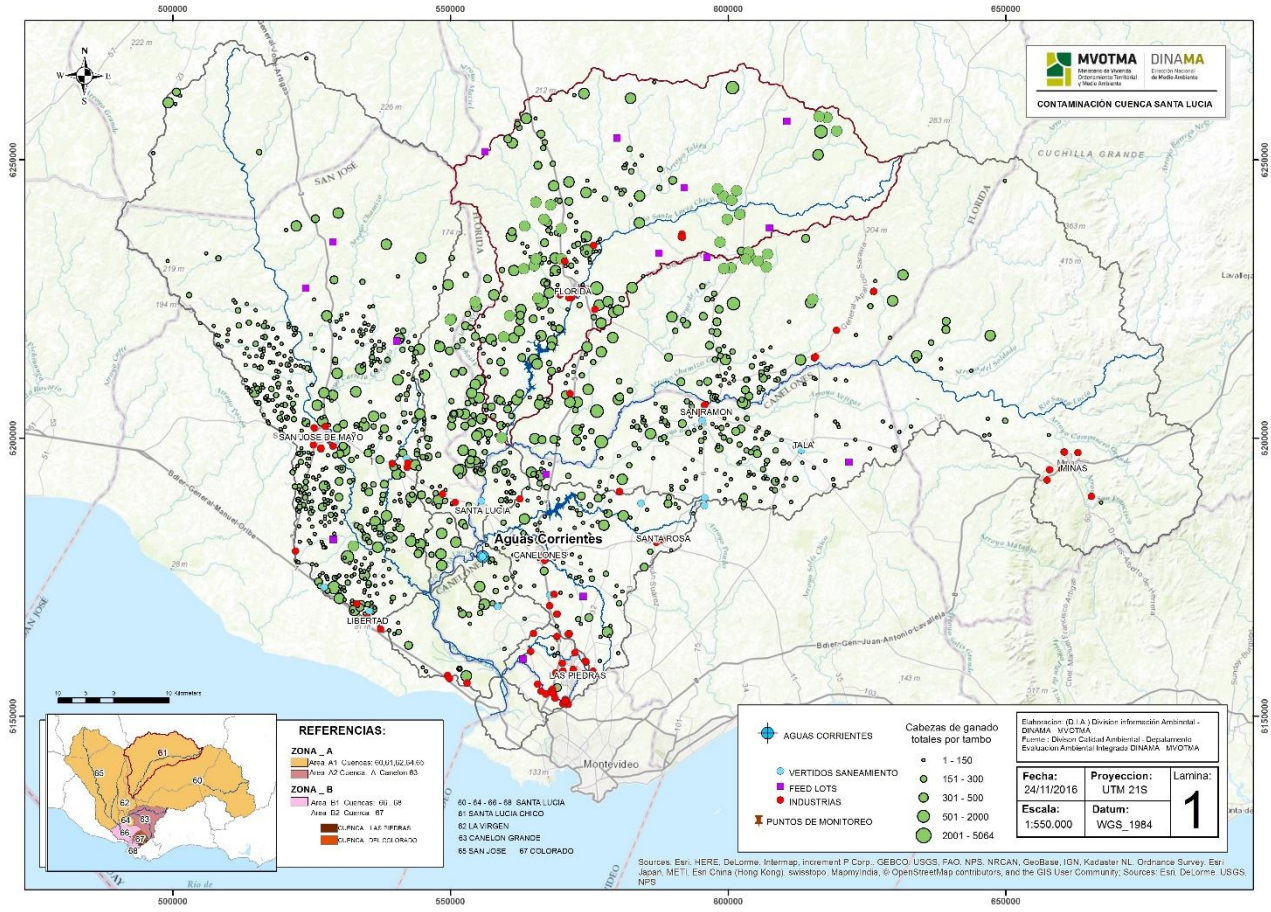


Figure 5-3 *Location of activities in the basin 61. Source: DINAMA*

Industrial activities do not discharge into municipal sewerage and have their own treatment plants. Dairy establishments and feedlots with more than 500 head of livestock must also have effluent treatment. Of the 297,460 head of cattle 2,358 are in feedlots, so that only 0.8% of the discharges of this activity go through a treatment and in the case of dairy cattle are 3,052 the heads that are in establishments that treat the effluents over a total of 114,377 heads representing 2.7% of the total of this activity.

Through the review of the treatment systems that have the industries can be excluded from the risk analysis the chemical industry as it treats its effluents and recirculates eliminating the surplus in summer evaporation lagoon so that the potential emissions are gaseous.

In the milk processing plant the compounds that were identified for analysis are those used in the cleaning of reverse osmosis membranes. This plant has effluent treatment through a DAF reactor and the final disposal is irrigation.

In the tannery 267 kg/month of naphthalene sulfonic acid is used, which is an emerging pollutant in the retanning and dyeing processes. In this same process the use of substances whose composition could not be acceded and should be analysed as in the milk processing plant are declared. The effluent treatment train is a neutralization tank, settler, aerobic reactor, anoxic reactor and secondary settler. The treated effluent is discharged into the Santa Lucia Chico River downstream the city of Florida.

The effluents of dairy farms that have effluent treatment consists of a manure heap, anaerobic lagoon, then a facultative lagoon and the final disposition is the irrigation of land that after rest are used for grazing. These effluents may have loads of veterinary drugs to be tested.

The wool laundry installed in this basin uses ethoxylated fatty alcohol which replaces those that use nonylphenols as active ingredient. The laundry treats its effluents with the train: primary settler, anaerobic treatment, refine lagoon and storage for the later irrigation of the forest and discharge in the river. As long as the laundry maintains this type of detergent it will not be a potential source of emerging contamination.

The wastewater treatment plant of Florida has grids, grit chambers, extended aeration, chemical removal of phosphorus, secondary sedimentation and UV. This plant does not receive industrial effluents. The plant is a potential source of emerging pollutants such as human drugs, insecticides, surfactants, etc.

Summarizing the agricultural activities, the treatment plants of domestic effluents added to the milk processing plant and the tannery are the activities that potentially can be sources of emerging pollutants.

5.4.2. Flows of the main channel

To estimate the PECs it is necessary to know the flow rates of the receiving bodies of each discharge. The Santa Lucia Chico River has a control section in the city of Florida. Through

the data measured in that section, provided by DINAGUA, the following values of river flows are obtained:

- Average specific Flow = 19.18 L/s/km^2
- Specific Flow 10 percentile = 0.20 L/s/km^2

The basin that contributes to this section has an area of 1,748 km^2 and the total area of basin 61 is 2,570 km^2.
Therefore the resulting flows in the Santa Lucia Chico River are:

	Average Flow m^3/s	10th percentile flow m^3/s
Station 15_3 Florida	33.52	0.35
Closing point	49.29	0.51

For the analysis of environmental risk in the aquatic environment, the percentile flow rate 10 will be considered.
Depending on the location of the discharge, the flow will be taken in the city of Florida or at the point of closure. In a more exhaustive study it may be necessary measure the flow in the main stream tributaries.

5.4.3. Analysis of emerging pollutants in Feedlots

Information regarding the number of livestock that the Feedlot has currently could not be determined. According to the 2011 Census there were approximately 2,350 cattle.

Generally these establishments renew the cattle every 3 and a half months and are dosed once only upon admission a deworm. Effluents are collected by ditches and discharged into anaerobic lagoons. Then from there the water is irrigated or discharged to the nearest course.
In the case of feedlot located in this sub-basin it has not been possible to determine what type of treatment the effluents receive or what type of veterinary medication is applied in the particular case. Following maneuvers of neighboring feedlots it can be presumed that it is used antiparasitic Ivermectin and Closantel subcutaneous injectable whose composition is 12.5g of Closantel, 1g of and Ivermectin in 100 g of excipient. A single dose of 1 ml every 50 kg is given.

Ivermectin is a highly lipophilic substance that dissolves in most organic solvents but is virtually insoluble in water (see Table 5-4). Ivermectin is very little affected by metabolism and most of the dose is excreted unchanged. Ivermectin is mainly eliminated in feces, faecal excretion represents 90% of the dose administered with <2% of the dose excreted in the urine (González Canga, et al., 2009). 90% of Closantael is eliminated with excreta and 0.5% via urine without metabolizing (Michiels, et al, 1987).

The Table 5-3 details the amount of Ivermectin and Closantel that is applied and how much is deposited in the soil with the excreta. A feddot with 2350 cattle provides 750 g / year of ivermectin and 9372 g / year of Closantel.

Table 5-3 *PEC soil of Emerging pollutants from Feed Lots*

Live cow		4,075	Ton/year
Dosed excipient		81,5	l/year
Dosed Ivermectin		815	g/year
Dosed Closanatel		10187	g/year
PEC soil			
Ivermectin		750	g/year
	Feces	733	g/year
	Urine	16	g/year
Closantel		9372	g/year
	Feces	9168	g/year
	Urine	204	g/year

Table 5-4 *Physicochemical properties of Ivermectin*

Molecular mass	874.7	g/mol
pKa	Neutral at all pH	
Melting point	349.8	°C
Vapor pressure	$< 1.5x10^{-9}$	Pa
Henry constant	$4.8x10^{-26}$	
Water solubility	4.0, 4.1, 2.0	mg/l
Log Kow	3.2	
Log Koc	3.6-4.4	l/kg
UV-visible absortion spectrum	Max 237, 245 and 253 nm (subject to direct photolysis)	

Indirect entry of drugs into water can generally occur by leaching contaminated soil into groundwater or by runoff from soils after the application of manure from treated animals. The sediment compartment may be contaminated by transfer of surface water to sediments or sedimentation of eroded material.

The Ivermectin dissipates rapidly from the aqueous phase to the sediment. Due to its high affinity for soil and particulate matter, neither leaching nor runoff is assumed to be a major source of contamination of freshwater ecosystems with Ivermectin. However, the transport of Ivermectin sorbed with eroded soil may be important.

In different studies the partition coefficient for Ivermectin was estimated, which presented values between 57 and 396 l/kg (see Table **5-4**). The soil of the sub-basin under study is mostly basaltic soil, which makes presumed low partition coefficients for this compound.

The PEC in surface water was estimated by applying the range of partition coefficients compiled from the literature. The PEC obtained does not take into account the effective transport of contaminated soil to the water or processes of degradation, photolysis, etc. The obtained PEC is for Ivermectin between 1.17 - 0.17 ng/L and for Closantel 835 ng/L. These values have the limitations that have already been exposed and should be taken as a first estimate to be checked against samples that allow to evaluate if further studies are necessary.

Table 5-5 *Load of Emerging pollutants to river from Feed Lots*

	Ivermectin	Closantel
Total discharged (g/year)	749,7	9218,8
kd (l/kg)	57 - 396	---
Dissolved mass (g/year)	2 - 13	---
River flow (m3/s)	0,35	0,35
River concentration (ng/L) (*)	1,17 - 0,17	835

(*)Without taking into account the base concentrations

From work on environmental risk by Ivermectin made by Liebig, et al., 2010, toxicological data were obtained that allow the construction of a PNEC. From the acute toxicological tests for fish, Daphnia and algae the most sensitive species turned out to be Daphnia with EC (50) mean of 5.7 ng/L. Following the guide the PNEC corresponds to this value reduce 1000 times. For Closantel it was not possible to obtain toxicity data from the three aquatic species of the trophic chain required to establish a first PNEC.

5.4.4. Analysis of emerging pollutants in livestock activities

In the basin the presence of cattle and sheep stands out. Cattle have two destinations: meat production or milk production. In total there are approximately 412,000 cattle and 96,000 sheep. The Table **5-6** shows the ages and nominal weight associated with the Cattle Census 2011.

Table 5-6 *Cattle and associated weight in basin 61*

	Number of heads	Nominal weight (kg)	Total nominal weigth (kg)
Cattle			
VA02 Cantidad de toros	3,477	395	1,373,415
VA03 Cantidad de vacas de cría y vaquillonas entoradas	117,160	395	46,278,200
VA04 Cantidad Vacas de refugo o invernada	9,320	350	3,262,000
VA05 Cantidad de novillos de más de 3 años	15,084	395	5,958,180
VA06 Cantidad de novillos de 2 a 3 años	18537	325	6,024,525
VA07 Cantidad de novillos de 1	17,042	225	3,834,450
VA08 Cantidad de vaquillonas de más de 2 años sin entorar	16,434	280	4,601,520
VA09 Cantidad de vaquillonas de 1	28189	225	6,342,525
VA10 Cantidad de terneros y terneras menores de un año	72,185	125	9,023,125
VA11 Cantidad de bueyes	2	395	790
VA12 Total cattle	297,430		86,698,730
Dairy cattle			
LE04 Vacas de ordeñe	50,610	395	19,990,950
LE05 Vacas secas	20,637	395	8,151,615
LE06 Terneros machos menores a 1	7,371	125	921,375

LE03 Total dairy cattle	114,377		29,063,940
Sheep			
OV02 Cantidad de carneros	2,722	40	108,880
OV03 Cantidad de ovejas de cría	54,136	40	2,165,440
OV04 Cantidad de ovejas de descarte	3,733	40	149,320
OV05 Cantidad de capones	4,487	40	179,480
OV06 Cantidad de borregas de 2 a 4 dientes sin encarnear	4,422	35	154,770
OV07 Cantidad de corderas diente de leche	12,014	30	360,420
OV08 Cantidad de corderos diente de leche	9,484	30	284,520
OV09 Cantidad de corderos y corderas mamones	4,695	20	93,900
OV10 Total sheeps	95,693		3,496,730

Unlike what happens in the feedlots where the cattle are in the pre-slaughter stage and no vaccine or drug is administered to less than one deworming on entry, in this case it is found in all stages of growth.

The cattle are given vaccines and drugs that can be grouped into 4 classes, (i) anthelmintic, (ii) defasciolizids, (iii) antibiotics, (iv) anti-inflammatories. The administration of the drugs is by several routes being the intramuscular the main.

It is noteworthy that in Uruguay it is prohibited to provide rations with antibiotics to cattle. Vaccines of a mandatory nature are for Foot-and-mouth disease (FMD) (one dose in February and for bovine animals under two years old another dose in May), vaccine for brucellosis (one dose of Rb51 and revaccination to females older than 4 months) and finally against Anthrax for dairy cattle. Clostridial vaccines are also provided but not mandatory.

The anthelmintic drugs generally used are benzimidazole, macrocyclic lactones and organophosphates, and there is a great variety of other drugs that also apply but to a lesser extent. The dosages are strategic against outbreaks, pregnant cattle, recreation, etc.

The drugs used to combat hepatic fasciola are based on actives such as Triclabendazole, Rafoxanide, Nitroxinil, etc. and applies to adult cattle and sheep.

In the field of antibiotics there is a great variety of drugs that can be supplied orally, injected or applied locally.

Mastitis and paws disease are usually treated locally. The paws baths are usually with copper sulfate, zink or formaldehyde. The major groups of antibiotics are penicillin tetracycline cephalosporins and enrofloxacin. Antibiotics are prescribed by registered veterinarians.
Anti-inflammatories may be nonsteroidal or steroidal.

The drugs applied are registered in the local control offices in a non-computerized manner and it has not been possible to collect this information within the time frames available to carry out this work. That is why it will do an estimate of some drugs of systematic use based on interviews and studies of prevalence of diseases of INIA. Repiso, M. et al. (2005).

According to this latest study, the producers stated that the following diseases are usually treated:
- Gastro-Intestinal are treated by 90% ± 3 of the producers.
- Horn fly are treated by 91% ± 2 of the producers.
- Faciolasis is treated by 60% ± 7 of the producers.
- Garrapata is treated by 49% ± 7 of the producers.

The control of the tick is carried out with the application of a combination of organophosphates with synthetic pyrethroids (Cypermethrin with Ethion) with one or two treatments by generation of tick having 3 generations per year.

In the following Table 5-7 we can see the estimation of the compounds applied as first approximation on the 49% of cattle that are treated.

Table 5-7 *Estimate Cypermethrin, Ethion apllied*

Tick		
Cypermethrin 6% + Ethion 24%		
Dosage: 10 ml per animal. Dermal Use		
Composition: 100ml contains 6 gr Cypermethrin and 24 gr Ethion		
Total sheep and cattle	507,500	head
Total applied	5,075,000	ml
Total Cipemethrin	304,500	gr/treatment
Total Ethion	1,218,000	gr/treatment
Number treatements	6	per year
Cattle treated	49	%
Total Cypermethrin apllied	895	kg/year
Total Ethion apllied	3,581	kg/year

Ethion is a compound that is strongly absorbed into the soil so it can accumulate in sediments. The mechanism of transport to the river would be primarily due to soil erosion. In the water the Ethion is persistent. Potential biodegradation is limited by its hydrophobicity and the tendency to be adsorbed by organic material and soil. However, there are studies that show that Ethion can be a source of carbon for microbial growth, identifying species capable of rapidly degrading it (Foster, et al., 2004).

From the study by Hela, et al., 2005, the properties of the compound are obtained that are shown in Table **5-8**.

Table 5-8 *Physicochemical properties of Ethion. (Hela, et al., 2005)*

Solubility	1.1	mg/l
$t_{1/2}$ soil	150	d
$t_{1/2}$ water	26	d
Kd	428.4	l/kg
Koc	10,000	

From the estimated annual loads of Ethion the concentration in the water is estimated considering only the possible adsorption to the soil. This compound is also used in pest control in plantations so that to this value must be added the base concentration from these activities.

Table 5-9 *Load of Ethion to river from Tick Control*

	Ethion
Total applied (kg/year)	3580.9
kd (l/kg)	428.4
Dissolved mass (g/year)	8339
River Flow (m3/s)	0,51
River concentration (µg/L) (*)	0.52

(*)Without taking into account base concentration

From the toxicity data collected in Hela, et al., 2005, included in the Table **5-10** can be inferred a PNEC of 5 ng/L to which the safety factor of 1000 was applied.

Table 5-10 *Toxicity data (µg/L) for Ethion in different organisms. (Hela, et al., 2005)*

		Zooplankton (Daphnia)		Fish (Cyprinidae)		Invertebrates	
	Algae (96-h EC50[a])	*Daphnia magna* (48-h LC50)[b]	*Daphnia pulex* (48-h LC50)	*Cyprinus carpio* (48-h LC50)	*Carrassius carrassius* (48-h LC50)	*Tubificidae* (48-h LC50)	*Chironomidae* (48-h LC50)
Ethion	1000	6	5	1160	---	1500	---

a- 96-h EC50 5 effect concentration of pesticides for 50% of the population of the tested aquatic species within 96 h of exposure.

b- 48-h LC50 5 lethal concentration of pesticides for 50% of the population of the tested aquatic species within 48 h of exposure.

If it assumes that 80% of stomach-intestinal diseases are treated with Ivermectin and Closantel once a year, 90% of the cattle obtained, following the same procedure for the Feedlots, the concentrations at the point of closure of the basin that are detailed in Table **5-11**.

Table 5-11 *Load of Ivermectin to river from livestock*

	Ivermectin
Total discharged (g/year)	21.944
kd (l/kg)	57 – 396
Dissolved mass (g/year)	55 – 378
River Flow (m3/s)	0,51
River Concentration (ng/L)	23,52 - 3,44

5.4.5. Ivermectin environmental risk analysis

The presence of Ivermectin in surface water comes from livestock activities. In this basin, several forms of livestock exploitation were identified, each of which has a characteristic management of this drug.

To calculate the risk, the total PEC of the basin must be found, which is obtained by adding the contributions to the surface water of all activities. The Table **5-12** summarizes the contribution of the activities and estimate the PEC which gives between 3.6 and 24.3 ng/L in the aqueous phase.

This value was obtained with desktop estimates. Through a sampling campaign, measured values can be contrasted with estimates. This comparison can define the need for complementary actions such as determination of the local k_d, analyze if there are missing or overestimate sources, analyze if the compound undergoes other relevant processes among others.

On the other hand to have a finished PEC it is necessary to introduce the PEC in the sediments so that besides adding this parameter in the sampling campaign it is necessary to determine the erosion of the soil and the contribution to the courses in this way.

Table 5-12 *PEC /PNEC and RQ surface water of Ivermectin*

	Ivermectin
Dissolved mass from feedlots (g/year)	2 - 13
Dissolved mass from livestock (g/year)	55 – 378
Total Dissolved mass Ivermectin (g/year)	57 – 391
River Flow (m3/s)	0,51
PEC Ivermectin (ng/L)	3,6 – 24,3
PNEC Ivermectin (ng/L)	5,7
RQ	0,63 – 4,26

The PNEC estimate of 5.7 ng/L was based on standard acute toxicity tests on three species of different trophic levels which, for use as indicators of toxicity at long exposures, a safety factor of 1000 is applied. It generally makes the PNEC on the security side. The obtaining of a PNEC that represents more accurately the local characteristics must be done through long term toxicity studies on species representative of the aquatic ecosystem of the Rio Santa Lucía Chico in the aqueous compartment as well as in sediment compartment. Obtaining the PNEC and PEC in sediments would allow a complete environmental risk assessment to be carried out of river.

The categorization of risk in the aqueous phase made from the PEC / PNEC ratio gives it a range between 0.63 and 4.26 which means that we are facing a risk between medium and high. The risk has range of variation due to taking different K_d of soil.

The potential environmental risk of medium to high determined in the water phase of the river by Ivermectin indicates that it is necessary to deepen the studies that allow to determine with greater levels of certainty both the presence of this compound in the environment and the effects that it has.

The description of how the PEC and PNEC were determined for this result provide guidance on which studies should be prioritized because of their importance in understanding the situation and the levels of uncertainty that translate the results obtained.

These actions are a campaign to sample this compound in the environment, determine what is adsorbed, its level of persistence, determine if erosion is a source of income to the river and determine the PNEC for the particular ecosystem.

It is important to emphasize that the methodology used and the results obtained as environmental risk does not allow to conclude whether the compartment analyzed is contaminated or not. The conclusion is whether or not it merits further study of the compound under study. We recall that this methodology is used to prioritize among a large number of potential pollutants which should be prioritized in the analysis and monitoring.

5.4.6. Ethion Environmental Risk Analysis

The Ethion is a compound of extended use for the combat of the ticks and the horned fly that having also phytosanitary applications. The PEC obtained was based only on the rate of national application to livestock, which means that it may not be contemplating local particularities. On the other hand, a partition coefficient K_d of bibliography was used, which introduces another uncertainty to the estimation of the portion adsorbed by the soil. Then are worth the observations they made for the calculation of PEC of Ivemectin in the risk analysis.

The studies on toxic effects of Ethion are more developed in the area of food sanitation for humans, there are regulations and controls regarding their presence in the meat. In order to avoid that the animals have contact with soils with high concentrations of Ethion there are plans of rotation and controls in the application of the product. However for aquatic resources there is not so profuse research.

Kuzmanović, et al. 2015, performed a risk analysis to prioritize 200 organic emergent contaminants in 4 rivers in the Iberian Peninsula. In 3 of the 4 rivers analyzed the Ethion presented environmental risk greater than 1 for Dahnia not registering risk for fish and algae in the water phase. The highest environmental risk was recorded in the Jucar River with an RQ of 23. In this study the detection frequency of the compound was 8% in 2010 and 22% in 2011, with a detection limit of 0.5ng / l. Among the 200 compounds analyzed, Ivermectin was not included.

The potential environmental risk estimated with all the limitations described above for Ethion in basin 61 of a QR ratio equal to 104. This value is necessary to contrast it with an Ethion sampling campaign in the water phase and sediments.

In addition to these actions the environmental risk indicator indicates that it is necessary to prioritize this compound for studies that allow analyzing the presence, behavior and effects of the compound on the particular ecosystem.

5.4.7. Environmental risk analysis of emerging domestic pollutants

The prediction of the presence of emerging pollutants in domestic wastewater was based on national studies and supplemented with extrapolated data collected in the literature review. The data of national origin come from predictive studies since there are no sampling campaigns despite finding substances that qualify to be monitored according to these risk studies.

According to the city's sanitation coverage it can be inferred that 83% of the loads arrive at the treatment plant by the network and 14% arrive through barometric discharges assuming all the pits are cleaned. The treatment plant consists of grids, grit chamber, extended aeration reactors, chemical removal of phosphorus, disinfection with UV and discharge is in the Santa Lucia Chico River. While the effluent is 4979 m^3/day, the river has a 10 percentile flow rate of 0.35 m^3/s so the dilution factor is 7.

Based on the estimates of discharges of hormonal active principles by the consumption of contraceptive to the effluents carried out by Pitzer, 2014, for Uruguay can be estimated for the city of Florida the loads discharged to the sanitation and the concentrations in the river which are shown in the Table **5-13**.

Table 5-13 *Estimation of the hormonal actives discharged to domestic sewage of the city of Florida*

PAH	Discharge in afluent[1] (g/year)	Estimated removals[2] (%)	Discharge in effluent (g/year)	Effluent concentration[3] (ng/L)	Surface wáter concentration[4] (ng/L)	PNEC[5] (ng/L)	RQ River
Drospirenone	33,7 - 76,8	na	16.9–38.4	9.27– 21.13	1,53 – 3,48	6.6	0,23 - 0,53
Levonorgestrel	5,2 - 8,2	nd (75)	1,3– 2.1	0,72 – 1.13	0.12 – 0.19	0.08	1,47 - 2,32
Gestodene	0,2 - 0,4	nd (75)	0,1-0,1	0.03 – 0.06	0.00 – 0.01	0.01	0,45 - 0,81
Cyproterone Acetate	1,3 - 3,0	na (50)	0.7–1.5	0.36 – 0.83	0.06 – 0.14	na	na
Dienogest	1,0 - 2,0	na (50)	0.5-1,0	0.28 – 0.55	0.05 – 0.09	na	na
Norgestimate	0,1 - 0,2	na (50)	0,1-0,1	0.03 – 0.06	0.00 - 0.01	na	na
Desogestrel	0,01	na (50)	0,005	0.003	0.000	na	na
Ethinylestradiol	4,4 - 6,3	78	1.0–1.4	0.53 – 0.76	0.09 – 0.13	1	0,09 - 0,13
Linestrenol	0,8 - 1,7	na (50)	0,4–0.9	0.22 - 0.47	0.04 – 0.08	na	na

N.a. : Not available

1- Estimate made from Pitzer, A. (2014)

2- For compounds where there is no data of removal is considered removal between ( ) taking into account removals of other hormones with solubility and similar k_{OW}.

3- Average WWTP flow 4979 m^3/day
4- Percentile 10 River Santa Lucia Chico Flow 0.35 m^3/s. The resulting concentration is without considering the adsorption of the compound by suspended matter.
5- Chimchirian, RF. et al. (2007)

If the environmental risk analysis is done to the plant effluent without diluting the PEC / PNEC ratio gives more than one for the compounds Drospirenone, Levonorgestrel and Gestodene. But because of the dilution capacity of receptor body, only Levonogestrel is a risk to the aquatic compartment.

From the literature review emerges as potential pollutants present in the wastewater the compounds shown in the **Table 5-14**. Only those that present an environmental risk in the effluent without dilution are summarized and then the dilution factor is applied and the environmental risk is re-calculated. From the analysis it emerges that the pharmaceutical compounds Erythromycin, Ofloxacin, Sulfamethoxazole, pesticide diuron and PCP Phantolide (AHMI), Traseolide (ATII), Cashmeran and 4-benzophenone can pose an environmental risk with the levels of dilution it has in the river.

Table 5-14 *Estimation of emerging pollutans discharged to domestic sewage of the city of Florida and the environmental risk*

Class	Compound	Average concentration raw influent[2] µg/L	Average concentration effluent[2] µg/L	PNEC µg/L	Risk effluent	Risk River[1]
Pharmaceutical	Ibuprofen	37	3,6	1,65	2,2	0,36
	Mefenamic acid	1,1	0,63	0,43	1,5	0,24
	Amoxicillin	0,24	0,01	0,0037	2,7	0,44
	Azithromycin	0,4	0,16	0,15	1,1	0,18
	Clarithromycin	1,3	0,29	0,07	4,1	0,68
	Erythromycin	1,8	0,7	0,02	35	5,76
	Ofloxacin	5,1	0,45	0,016	28,1	4,63
	Sulfamethoxazole	0,92	0,28	0,027	10,4	1,71
	Tetracycline	0,33	0,14	0,09	1,6	0,26
	Fenofibrate	no available	0,11	0,1	1,1	0,18
	Fenofibric acid	0,21	11	7,6	1,4	0,24
	Gemfibrozil	2,4	0,93	0,9	1	0,17
	Diazepam	22	9,1	2	4,6	0,75
	Fluoxetine	0,54	0,24	0,05	4,8	0,79
Pesticides		ng/l	ng/l	ng/l		
	atrazine	1.24	124	59	2,1	0,35
	simazine	7.27	169	40	4,2	0,70
	terbuthylazine	20.6	20	12	1,7	0,27
	chlortoluron	3.94	98,2	24	4,1	0,67
	diuron	93	127	2,7	47	7,74

	isoproturon	---	13,2	13	1.0	0,17
	diazinon	133	281	3100	281	0,01
Personal care product (PCP)		µg/l	µg/l	µg/l		
	Phantolide (AHMI)	0,042	< 0,018	0,00122	7	1,21
	Traseolide (ATII)	0,168	0,045	0,00095	47,4	7,8
	Cashmeran	0,21 – 0,69	0,08	0,01166	6,9	1,13
	4-benzophenone	4152	3370	48,97	68,8	11,33
	Propylparaben	3090	26	8	3,3	0,54

1- Average WWTP Florida flow 4979 m^3/day; Percentile 10 River Santa Lucia Chico Flow 0,35 m^3/s. The concentration in the river is without considering the adsorption of the compound by suspended solids.
2- Data obtained from literature review. They are not local data.

5.5. Results and Discussion

The environmental risk assessment due to the use of Ivermectin and Ethion from the livestock activity and the environmental risk due to the domestic effluent was carried out on the main channel of the Santa Lucia Chico basin.

The environmental risk assessment was based on the relationship between the predicted environmental concentration concentration (PEC) and the predicted non-effect concentration (PNEC) of the different compounds following the methodology proposed by Technical Guidance Document on Risk Assessment (EC, 2003).

The PEC of the emerging contaminants Ivermectin and Ethion was based on an estimation of the use in function of the livestock population in the area and the physiochemical processes of transformation through the pathway of the compounds, from the emission to the surface water, was based on literature data. In the case of domestic effluents, on the one hand the PEC of hormones for the use of contraceptive pills was estimated based on an estimation study carried out at the national level and for the rest of the possible pollutants present in the wastewater was extrapolated results of studies made in Europe to local area.

All PNECs used were data from the literature review.

The study showed that the following compounds present a potential environmental risk:

Source	Class	Compound
Agriculture	Veterinary pharmaceutical	Ivermectin
		Ethion
Domestic Effluent	Pharmaceutical	Levonorgestrel
		Erythromycin
		Ofloxacin
		Sulfamethoxazole
	Pesticides	Diuron
	Personal care product	Phantolide (AHMI)
		Traseolide (ATII)

Source	Class	Compound
		Cashmeran
		4-benzophenone

This result due to the high degree of uncertainty that has associated does not allow to conclude if these compounds are polluting or not. What it can conclude is that the study of micro-contaminants in this basin must include these compounds.

Other information that provide this study is that reviewing the process of obtaining the PEC and PNEC, it can identify which are the parameters that introduce greater uncertainty in the analysis and therefore prioritize the studies to be performed.

The necessary studies are, in the case of veterinary drugs, carry out a sampling campaign in the watercourses of the basin including the sediments over a year to contemplate the productive cycles. If concentrations measured in the environment continue to give a risk quotient greater than one, studies must be carried out to better describe the path of the pollutant in the environment and the effects it has on biota. This is, determine the coefficient of partitioning water-soil and water-sediment, the degree of erosion of soil and extend the sampling of water in sensitive uses such as drinking water. To study the processes of transformation of the compounds in the environment like rate of biodegradability and the by-products that generates. Carry out long term toxicological studies and multiple effects on representative species of the studied basin.

In the case of domestic effluents discharged by the Florida WWTP, it is necessary to sample the substances prioritized in the discharge of the plant at the point of complete mixing. This sampling should also be over a year to contemplate possible seasonal variations. For compounds that have concentrations that continue to give an environmental risk, the sampling must be incorporated the affluent of WWTP, determine the sources of the pollutants, analyze the treatment plant removal efficiencies and perform toxicological studies to obtain a PNEC with local worth.

Moreover it is necessary to complete the environmental risk assesses of the other activities summarized in this paper and identified as possible sources of emission of emerging pollutants.

In order to obtain conclusions that may be inputs for management measures and national legislation, studies should be local with acceptable levels of uncertainty to take sustained measures. The proposed methodology allows to elaborate a work plan that allows to conclude whether or not to take mitigation measures with respect to certain compounds. Therefore it is recommended to follow the studies under this methodology.

CHAPTER 6 **References**

6.1. Reference Chapter 4

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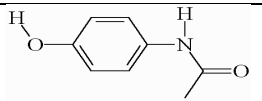
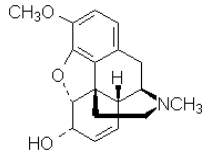
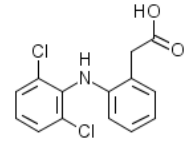
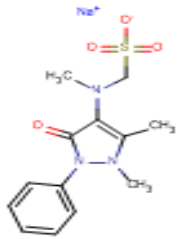
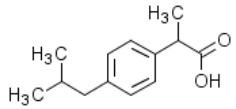
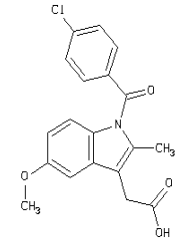
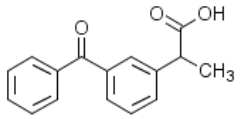
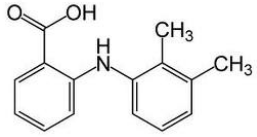
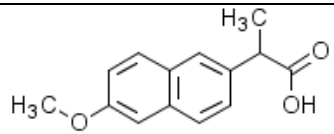
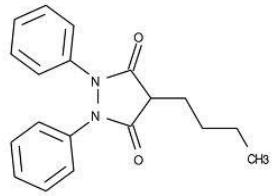
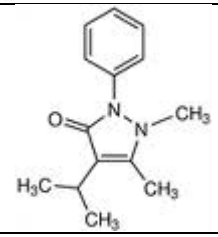
CHAPTER 7 **Appendices**

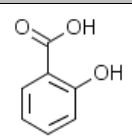
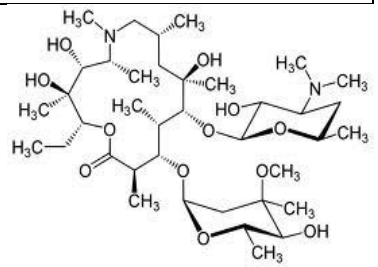
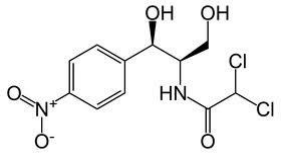
Appendix A **Physic-chemical properties of the pharmaceutical compounds**

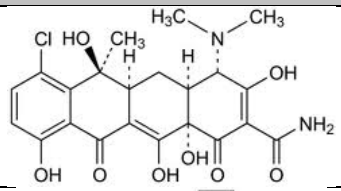
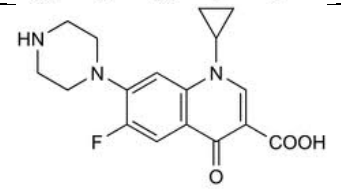
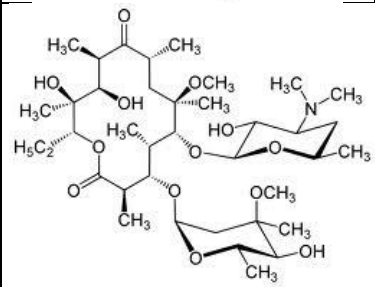
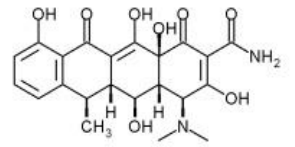
Table Physic-chemical properties of the selected pharmaceuticals. Modified from Verlicchi, P., et al. (2012)

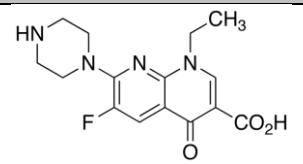
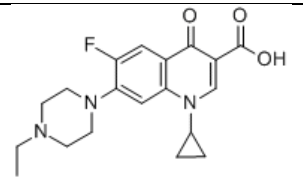
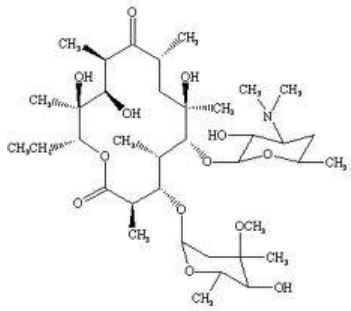
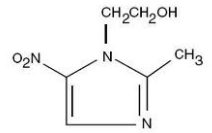
	Pharmaceutical	**MW**	**Chemical formula**	**pK_a**	**Log K_{ow}**	**S_w 25°C (mg l^{-1})**	**Log K_d**	**k_{biol} (L gSS^{-1} d^{-1})**	**Charge at pH 7**	**Molecular structure**
Analgesics/Anti-inflammatories	5-aminosalicylic acid CAS # 89-57-6	153	$C_7H_7NO_3$						Negative	
	Acetaminophen CAS # 103-90-2	151	$C_8H_9NO_2$	9.38	0.46	3.035 10^4	3.06[t]	58-80 106*-240*	Neutral	
	Acetylsalicylic acid CAS # 50-78-2	180	$C_9H_8O_4$	3.5[h]	1.13	5295			Negative	
	Aminopyrine CAS # 58-15-1	231	$C_{13}H_{17}N_3O$		0.6	4191			Neutral	
	Codeine CAS # 76-57-3	299	$C_{18}H_{21}NO_3$	8.21	1.19	1.21 10^4	1.15[j]	4.7-4.8 [j]	Positive	
	Dextropropoxyphene CAS # 469-62-5	339	$C_{22}H_{29}NO_2$						Positive	
	Diclofenac CAS # 15307-86-5	296	$C_{14}H_{11}Cl_2NO_2$	4.15[a]	4.51/0.7	4.52	1.2[l]	<0.04-1.2 [o] ≤0.1 ≤0.1* <0.002*-<0.1*	Negative	

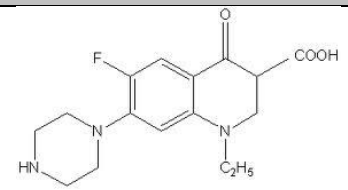
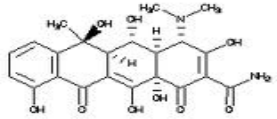
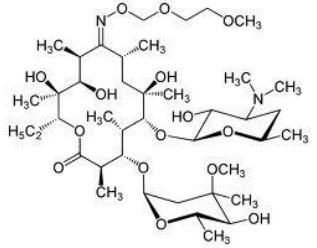
	Pharmaceutical	MW	Chemical formula	pK_a	Log K_{ow}	S_w 25°C (mg l^{-1})	Log K_d	k_{biol} (L gSS^{-1} d^{-1})	Charge at pH 7	Molecular structure
Analgesics/Anti-inflammatories	Dipyrone CAS # 68-89-3	333	$C_{13}H_{16}N_3NaO_4S$		-4.76	1 10^6				
	Fenoprofen CAS # 31879-05-7	242	$C_{15}H_{14}O_3$	7.3	3.9	30.13		10-14 3.3*-5.9*	Negative	
	Flurbiprofen CAS # 5104-49-4	244	$C_{15}H_{13}FO_2$		3.81	17.7.13			Negative	
	Hydrocodone CAS # 125-29-1	299	$C_{18}H_{21}NO_3$	8.48	2.16	1788	1.23[j]		Positive	
	Ibuprofen CAS # 15687-27-1	206	$C_{13}H_{18}O_2$	4.51[e]	3.97/0.45	41.05	0.9[l]	1.5-20 [o] 21-35 9*-22* 1.33*->3* [s]	Negative	
	Indomethacin CAS # 53-86-1	358	$C_{19}H_{16}ClNO_4$	4.5	4.27	3.114		≤0.3 ≤0.21*	Negative	
Analgesics/Anti-inflammatories	Ketoprofen CAS # 22071-15-4	254	$C_{16}H_{14}O_3$	4.45[f]	3.12/-0.44	120.4	1.2[t]		Negative	
	Ketorolac CAS # 74103-06-3	255	$C_{15}H_{13}NO_3$		2.32	572.3			Negative	

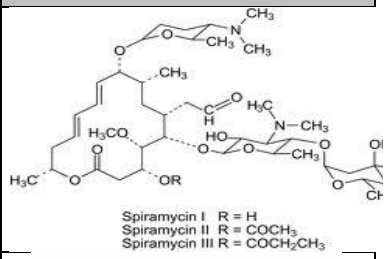
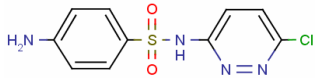
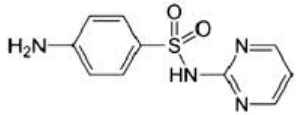
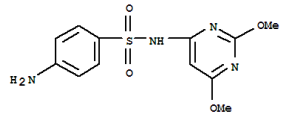
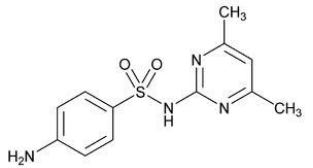
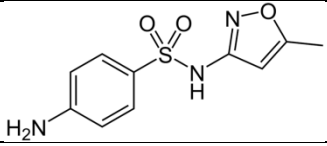
	Pharmaceutical	MW	Chemical formula	pK_a	Log K_{ow}	S_w 25ºC (mg l^{-1})	Log K_d	k_{biol} (L gSS^{-1} d^{-1})	Charge at pH 7	Molecular structure
	Meclofenamic acid CAS # 644-62-2	296	$C_{14}H_{11}Cl_2NO_2$		6.02	0.0934			Negative	
	Mefenamic acid CAS # 61-68-7	241	$C_{15}H_{15}NO_2$	4.2	5.12	1.121	2.6[t]		Negative	
	Naproxen CAS # 22204-53-1	230	$C_{14}H_{14}O_3$	4.2[b]	3.18/-0.34	144.9	1.1[o]	<0.2-9 [o] 1.0-1.9 0.4*-0.8* 0.08*-0.4* [s]	Negative	
	Phenazone CAS # 60-80-0	188	$C_{11}H_{12}N_2O$	1.4	0.38	2.376 10^4			Neutral	
	Phenylbutazone CAS # 50-33-9	230	$C_{14}H_{18}N_2O$	4.5	3.16	21.95			Negative	
Analgesics/Anti-inflammatories	Propyphenazone CAS # 479-92-5			---	1.96	668.2			Neutral	

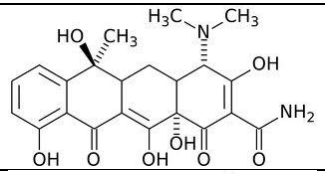
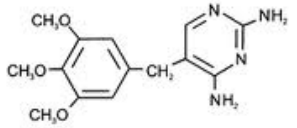
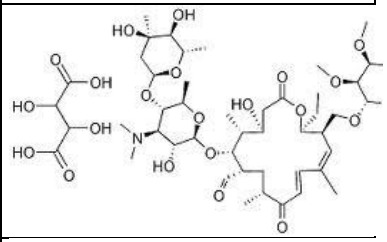
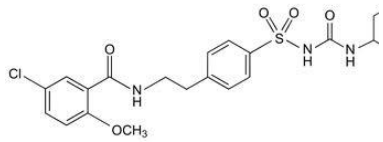
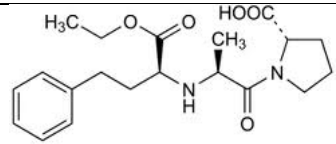
	Pharmaceutical	MW	Chemical formula	pK_a	Log K_{ow}	S_w 25°C (mg l^{-1})	Log K_d	k_{biol} (L gSS^{-1} d^{-1})	Charge at pH 7	Molecular structure
	Salicylic acid CAS # 69-72-7	138	$C_7H_6O_3$	3.5 [b]	2.26/-2.42	3808			Negative	
	Tolfenamic acid CAS # 13710-19-5	262	$C_{14}H_{12}ClO_2$		5.38	0.782			Negative	
	Tramadol CAS # 27203-92-5	263	$C_{16}H_{25}NO_2$		3.01	1151	1.11[j]	≤0.11-≤0.13 [j]	Positive	
Antibiotics	Amoxicillin CAS # 26787-78-0	365	$C_{16}H_{19}N_3O_5S$	2.4[d]	0.87 [b]	3433			Neut./Neg.	
	Azithromycin CAS # 83905-01-5	749	$C_{38}H_{72}N_2O_{12}$	pK_1 =8.7 pK_2= 9.5	4.02	0.06204	2.5-2.7[k]	≤0.1 ≤1.2* 0.17* [s]	positive	
	Cefaclor CAS # 53994-73-3	368	$C_{15}H_{14}ClN_3O_4S$		0.35	119				
	Cefalexin CAS # 15686-71-2	347	$C_{16}H_{17}N_3O_4S$						Neut./Neg.	
Antibiotics	Cefotaxime CAS # 63527-52-6	456	$C_{16}H_{17}N_5O_7S_2$		0.64	394.5			Negative	
	Chloramphenicol CAS # 56-75-7	323	$C_{11}H_{12}Cl_2N_2O_5$	5.5	1.14	388.5			Neut./Neg.	

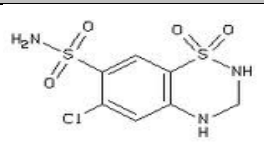
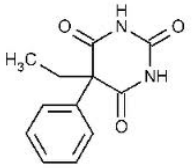
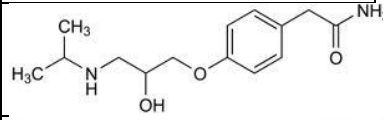
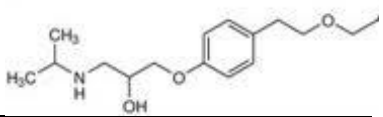
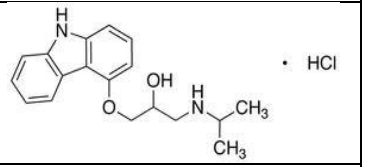
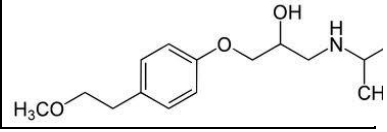
	Pharmaceutical	MW	Chemical formula	pK_a	Log K_{ow}	S_w 25ºC (mg l^{-1})	Log K_d	k_{biol} (L gSS^{-1} d^{-1})	Charge at pH 7	Molecular structure
	Chlortetracycline CAS # 57-62-5	479	$C_{22}H_{23}ClN_2O_8$	pK_1= 3.3 pK_2= 7.4 pK_3= 9.3	-0.62	615.7			Negative	
	Ciprofloxacin CAS # 85721-33-1	331	$C_{17}H_{18}FN_3O_3$	6.38[g]	0.4[j]	1.148 10^4	4.3[k]		Pos./Neut.	
	Clarithromycin CAS # 81103-11-9	748	$C_{38}H_{69}NO_{13}$	8.99	3.16	0.342	2.5-2.6[k]	≤0.4 ≤1.7* 0.034*-0.2* [s]	Positive	
	Clindamycin CAS # 18323-44-9	425	$C_{18}H_{33}ClN_2O_5S$		2.01	30.61			Pos./Neut.	
	Cloxacillin CAS # 61-72-3	436	$C_{19}H_{18}ClN_3O_5S$		3.22	13.94			Negative	
Antibiotics	Doxycycline CAS # 564-25-0	463	$C_{22}H_{24}N_2O_8$	pK_1= 3.5 pK_2= 7.7 pK_3= 9.5	-0.02	312.9				

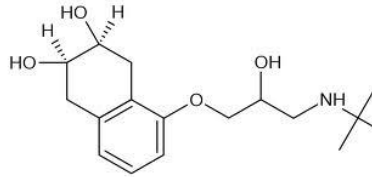
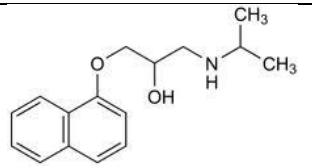
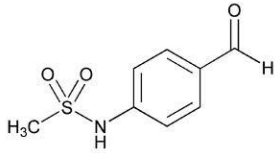
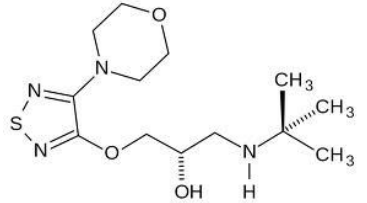
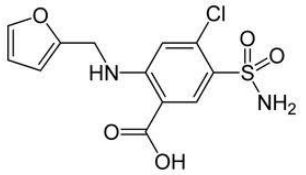
	Pharmaceutical	MW	Chemical formula	pK_a	Log K_{ow}	S_w 25ºC (mg l^{-1})	Log K_d	k_{biol} (L gSS^{-1} d^{-1})	Charge at pH 7	Molecular structure
	Enoxacin CAS # 74011-58-8	320	$C_{15}H_{17}FN_4O_3$	pK_1= 6.3 pK_2= 8.7	-0.2	3.43 10^4			Neutral	
	Enrofloxacin CAS # 93106-60-6	359	$C_{19}H_{22}FN_3O_3$	6.27[g]	1.1[h]	3397	4.5[u]		Neut./Neg.	
	Erythromycin CAS # 114-07-8	734	$C_{37}H_{67}NO_{13}$	8.8-8.9 [b]	3.06	0.5168	2.2[l]	0.15-6 [o]	Positive	
	Lincomycin CAS # 154-21-2	407	$C_{18}H_{34}N_2O_6S$		0.29	92.19			Pos./Neut.	
	Lomefloxacin CAS # 98079-51-7	351	$C_{17}H_{19}F_2N_3O_3$		0.31	2.72 10^4	4.16[u]		Neutral	
Antibiotics	Metronidazole CAS # 443-48-1	171	$C_6H_9N_3O_3$	2.5	-0.1; -0.02	2.573 10^4			Neutral	

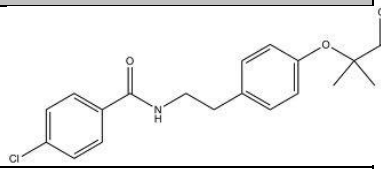
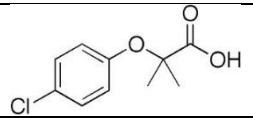
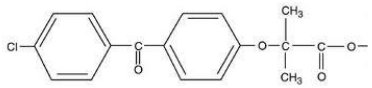
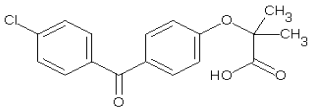
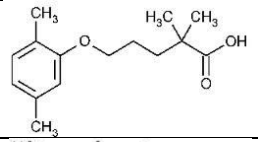
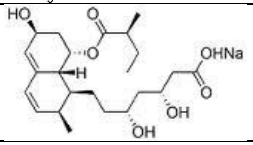
	Pharmaceutical	MW	Chemical formula	pK_a	Log K_{ow}	S_w 25ºC (mg l^{-1})	Log K_d	k_{biol} (L gSS^{-1} d^{-1})	Charge at pH 7	Molecular structure
	Norfloxacin CAS # 70458-96-7	319	$C_{16}H_{18}FN_3O$	pK_1= 6.3, pK_2= 8.4	-1.03	$1.779\ 10^5$	4.2[k]		Positive	
	Ofloxacin CAS # 82419-36-1	361	$C_{18}H_{20}FN_3O_4$	5.97	0.35	$2.826\ 10^4$	4.2[u]		Neut./Neg.	
	Oxytetracycline CAS # 79-57-2	460	$C_{22}H_{24}N_2O_9$	pK_1= 3.27 pK_2= 7.3 pK_3= 9.1	-0.90; -1.6 (pH 7.5) 1.22	1399			Negative	
	Penicillin G CAS # 61-33-6	334	$C_{16}H_{18}N_2O_4S$	2.74					Negative	
	Penicillin V CAS # 87-08-1	350	$C_{16}H_{18}N_2O_5S$	2.79	1.87	101.1			Negative	
Antibiotics	Roxithromycin CAS # 80214-83-1	837	$C_{41}H_{76}N_2O_{15}$	8.8[c]	2.75	0.01887	2.2-2.7[k] 2.3-2.6[l]	0.2-9 [o] ≤0.2 ≤0.3* 0.022*-0.023* [s]	Positive	

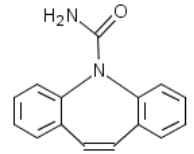
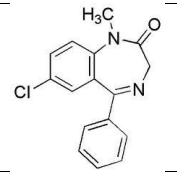
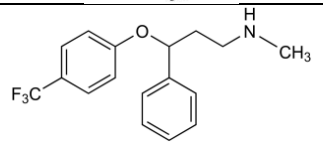
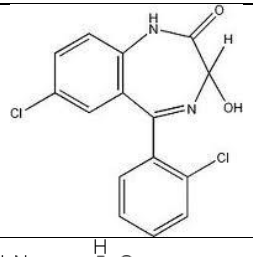
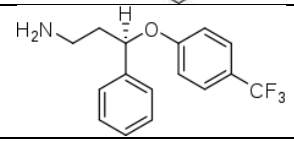
	Pharmaceutical	MW	Chemical formula	pK_a	Log K_{ow}	S_w 25°C (mg l^{-1})	Log K_d	k_{biol} (L gSS^{-1} d^{-1})	Charge at pH 7	Molecular structure
	Spiramycin CAS # 8025-81-8	843	$C_{43}H_{74}N_2O_{14}$	8.0					Positive	
	Sulfachloropyridazine CAS # 80-32-0	285	$C_{10}H_9ClN_4O_2S$		0.31	8235			Neut./Neg.	
	Sulfadiazine CAS # 68-35-9	250	$C_{10}H_{10}N_4O_2S$	pK_1= 6.36 pK_2= 2.1	-0.09	2.814 10^4			Neut./Neg.	
	Sulfadimethoxine CAS # 122-11-2	310	$C_{12}H_{14}N_4O_4S$		1.17	433.1			Neut./Neg.	
	Sulfamethazine CAS # 57-68-1	278	$C_{12}H_{14}N_4O_2S$	2.65[q]	0.89[h]	1.124 10^4			Neut./Neg.	
Antibiotics	Sulfamethoxazole CAS # 723-46-6	253	$C_{10}H_{11}N_3O_3$	5.7[c]	0.89[i]	3942	2.1-2.7[k] 2.3-2.6[l]	0.3 [o]	Neut./Neg.	
	Sulfapyridine CAS # 144-83-2	249	$C_{11}H_{11}N_3O_2S$	Pk1=8043 Pk2=2.3	0.35	1.199 10^4	2.3-2.6[k]		Neut./Neg.	
	Sulfasalazine CAS # 599-79-1	398	$C_{18}H_{14}N_4O_5S$		3.81	2.44			Negative	

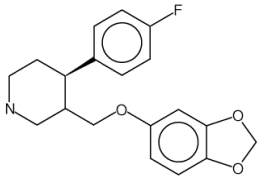
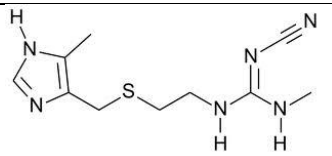
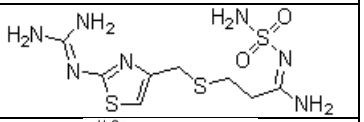
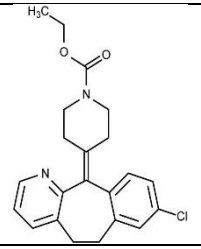
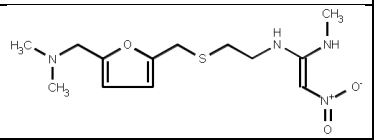
	Pharmaceutical	MW	Chemical formula	pK_a	Log K_{ow}	S_w 25°C (mg l^{-1})	Log K_d	k_{biol} (L gSS^{-1} d^{-1})	Charge at pH 7	Molecular structure
	Sulfathiazole CAS # 72-14-0	255	$C_9H_9N_3O_2S_2$		0.72	$2.003\ 10^4$			Negative	
	Tetracycline CAS # 60-54-8	444	$C_{22}H_{24}N_2O_8$	pK_1=3.3 pK_2=7.7 pK_3=9.7	-1.30	3877	3.9[k]		Negative	
	Trimethoprim CAS # 738-70-5	290	$C_{14}H_{18}N_4O_3$	7.2	0.91	2334	2.2-2.6[k] 2.3[l]	0.15 [o]	Pos./Neut.	
	Tylosin CAS # 1401-69-0	916	$C_{46}H_{77}NO_{17}$	7.1[p]	1.63	0.5065			Pos./Neut.	
Antidiabetics	Glibenclamide CAS # 10238-21-8	494	$C_{23}H_{28}ClN_3O_5S$	5.3	4.8	0.0635	2.4[t]		Negative	
Antifungals	Clotrimazole CAS # 23593-75-1	345	$C_{22}H_{17}ClN_2$		6.26	0.0299			Pos./Neut.	
Antihypertensives	Diltiazem CAS # 42399-41-7	415	$C_{22}H_{26}N_2O_4S$		2.79	12.3			Positive	
	Enalapril CAS # 75847-73-3	377	$C_{20}H_{28}N_2O_5$	---	2.45	34.88			Negative	

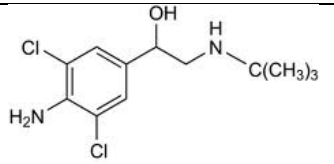
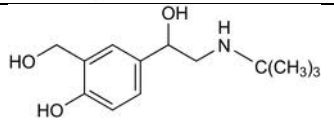
	Pharmaceutical	MW	Chemical formula	pK_a	Log K_{ow}	S_w 25ºC (mg l^{-1})	Log K_d	k_{biol} (L gSS^{-1} d^{-1})	Charge at pH 7	Molecular structure
	Hydrochlorothiazide CAS # 58-93-5	298	$C_7H_8ClN_3O_4S_2$	7.9	-0.07	1292	1.8[t]		Negative	
Barbiturates	Phenobarbital CAS # 50-06-6	232	$C_{12}H_{12}N_2O_3$	7.3	1.47	1644			Negative	
Beta-blokers	Acebutolol CAS # 37517-30-9	336	$C_{18}H_{28}N_2O_4$		1.71[i]	259				
	Atenolol CAS # 29133-68-7	266	$C_{14}H_{22}N_2O_3$	9.6	0.16	685.2	-0.68[i]	1.1-1.9 [j]	positive	
	Betaxolol CAS # 63659-18-7	307	$C_{18}H_{29}NO_3$	---	2.81	450.7		6.0 [j]	Positive	
	Bisoprolol CAS # 66722-44-9	325	$C_{18}H_{31}NO_4$		1.84	2240		0.64-0.77 [j]	Positive	
Beta-blokers	Carazolol CAS #57775-29-8	298	$C_{18}H_{22}N_2O_2$	---	3.59	8.254			Positive	
	Celiprolol CAS # 56980-93-9	379	$C_{20}H_{33}N_3O_4$		1.93	93.92		0.18-0.24 [j]	Positive	
	Metoprolol CAS # 37350-58-6	267	$C_{15}H_{25}NO_3$	9.6	1.88	4777		0.35-0.40 [j]	Positive	

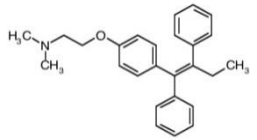
	Pharmaceutical	MW	Chemical formula	pK_a	Log K_{ow}	S_w 25ºC (mg l^{-1})	Log K_d	k_{biol} (L gSS^{-1} d^{-1})	Charge at pH 7	Molecular structure
	Nadolol CAS # 42200-33-9	309	$C_{17}H_{27}NO_4$	9.67	0.81	$2.24\ 10^4$			Positive	
	Oxprenolol CAS # 6452-71-7	265	$C_{15}H_{23}NO_3$		1.83	3182			Positive	
	Propranolol CAS # 525-66-6	259	$C_{16}H_{21}NO_2$	9.42	3.48	228	2.6[t]	0.36-0.46 [j]	Positive	
	Sotalol CAS # 3930-20-9	272	$C_{12}H_{20}N_2O_3S$	pK_1=8.2 pK_2=9.8	0.24	5513		0.40-0.43 [j]	positive	
Beta-blokers	Timolol CAS # 26839-75-8	316	$C_{13}H_{24}N_4O_3S$	9.21	1.83	2741			Positive	
Diuretics	Bendroflumethiazide CAS # 73-48-3	421	$C_{15}H_{14}F_3N_3O_4S_2$		1.82	4.87			Neut./Neg.	
	Furosemide CAS # 54-31-9	331	$C_{12}H_{11}ClN_2O_5S$	3.9	2.03	149.3			Negative	

	Pharmaceutical	MW	Chemical formula	pK_a	Log K_{ow}	S_w 25ºC (mg l^{-1})	Log K_d	k_{biol} (L gSS^{-1} d^{-1})	Charge at pH 7	Molecular structure
Lipid regulators	Bezafibrate CAS # 41859-67-0	362	$C_{19}H_{20}ClNO_4$	3.6[c]	4.25	1.224		2.1-3.0 3.4*-4.5* 0.77*->2.9* [s]	Negative	
	Clofibrate CAS # 637-07-0	243	C12H15ClO3		3.62	20.97			Neutral	
	Clofibric acid CAS # 882-09-7	215	$C_{10}H_{11}O_3Cl$	-3.18[m]	2.57	582.5		0.3-0.8 0.1*-0.23* 0.09*-0.1* [s]	Negative	
	Etofibrate CAS # 31637-97-5	364	$C_{18}H_{18}ClNO_5$		3.43	6.033			Neutral	
	Fenofibrate CAS # 49562-28-9	361	$C_{20}H_{21}ClO_4$	---	5.19	0.1957			Neutral	
Lipid regulators	Fenofibric acid CAS # 42017-89-0	319	$C_{17}H_{15}ClO_4$		2.9			7.2-10.8 0.4*-1.7*;	Negative	
	Gemfibrozil CAS # 25812-30-0	250	$C_{15}H_{22}O_3$	4.8	4.77	4.964	1.28[t]	6.4-9.6 0.5*-1.8*	Negative	
	Pravastatin CAS # 81093-37-0	425	$C_{23}H_{36}O_7$	---	-0.23	2464			Negative	
	Simvastatin CAS # 79902-63-9	419	$C_{25}H_{38}O_5$		5.19	0.765			Neutral	
Psychiatric drugs	Amitriptyline CAS # 50-48-6	277	$C_{20}H_{23}N$		4.95	0.823			Positive	

	Pharmaceutical	MW	Chemical formula	pK_a	Log K_{ow}	S_w 25ºC (mg l^{-1})	Log K_d	k_{biol} (L gSS^{-1} d^{-1})	Charge at pH 7	Molecular structure
	Carbamazepine CAS # 298-46-4	236	$C_{15}H_{12}N_2O$	13.9 [b]	2.45	17.66	0.1[l]	≤0.1 [j] <0.03-<0.06 [o] <0.005*-<0.008* [s]	Neutral	
	Diazepam CAS # 439-14-5	285	$C_{16}H_{13}ClN_2O$	3.4	2.82	58.78	1.3[l]	≤0.16 [j] <0.25-<0.4 [o]	Neutral	
Psychiatric drugs	Fluoxetine CAS # 54910-89-3	309	$C_{17}H_{18}F_3NO$	9.5	4.05	38.35	0.7[n]	5-9 [o]	positive	
	Gabapentin CAS # 60142-96-3	171	$C_9H_{17}NO_2$			4491			Neutral	
	Lorazepam CAS # 846-49-1	321	$C_{15}H_{10}Cl_2O_2N_2$	pK_1=1.3 pK_2=11.5	2.39	83.87			Neutral	
	Norfluoxetine CAS # 126924-38-7	295	$C_{16}H_{16}F_3NO$	9.05[d]	4.07[d]					
	Oxcarbazepine CAS # 28721-07-5	252	$C_{15}H_{12}N_2O_2$		1.11	202.8			Neutral	

	Pharmaceutical	MW	Chemical formula	pK_a	Log K_{ow}	S_w 25ºC (mg l^{-1})	Log K_d	k_{biol} (L gSS^{-1} d^{-1})	Charge at pH 7	Molecular structure
	Paroxetine CAS # 61869-08-7	329	$C_{19}H_{20}FNO_3$	9.0	3.95	35.27			Positive	
	Valproic acid CAS # 99-66-1	144	$C_8H_{16}O_2$		2.96	894.6			Negative	
Receptor antagonists	Cimetidine CAS # 51481-61-9	252	$C_{10}H_{16}N_6S$	6.8	0.40	$1.046\ 10^4$			Pos./Neut.	
	Famotidine CAS # 76824-35-6	337	$C_8H_{15}N_7O_2S_3$	---	-0.64	1271			Positive	
	Loratadine CAS # 79794-75-5	383	$C_{22}H_{23}ClN_2O_2$	---	5.20	0.01099	3.5[t]		Neutral	
	Omeprazole CAS # 73590-58-6		$C_{17}H_{19}N_3O_3S$		3.4	82.28			Neutral	
	Ranitidine CAS # 66357-35-5	314	$C_{13}H_{22}N_4O_3S$	2.4	0.27	$2.466\ 10^4$			Positive	
	Valsartan CAS # 137862-53-4	436	$C_{24}H_{29}N_5O_3$						Negative	

	Pharmaceutical	MW	Chemical formula	pK_a	Log K_{ow}	S_w 25ºC (mg l^{-1})	Log K_d	k_{biol} (L gSS^{-1} d^{-1})	Charge at pH 7	Molecular structure
Hormones	Estradiol CAS # 50-28-2	272	$C_{18}H_{24}O_2$	10.27[m]	3.94	81.97	2.4-2.8[l]	175-460 [r] 280*-950* [r]	Neutral	
	Estriol CAS # 50-27-1	288	$C_{18}H_{24}O_3$		2.81	440.8			Neutral	
	Estrone CAS # 53-16-7	270	$C_{18}H_{22}O_2$	10.25[m]	3.43	146.8	2.4-2.9[l]	10-162 [r] 28*-430* [r] >20 [s]	Neutral	
Hormones	Ethinylestradiol CAS # 57-63-6	296	$C_{20}H_{24}O_2$	10.24[m]	4.12	116.4	2.5-2.8[l]	0.4-20 [o] 1.2-8 [r] 1.5*-6* [r] >0.5->0.7 [s]	Neutral	
Beta-agonists	Clenbuterol CAS # 037148-27-9	277	$C_{12}H_{18}Cl_2N_2O$	---	2.00	3320			Positive	
	Salbutamol CAS # 35763-26-9	303	$C_{17}H_{21}NO_4$	pK_1=9.3, pK_2=10.3	0.6, 0.01	--			Positive	
	Fenoterol CAS # 13392-18-2	239	$C_{13}H_{21}NO_3$		1.22	4.13 10^4			Positive	
	Terbutaline CAS # 23031-25-6	226	$C_{12}H_{19}NO_3$		0.67	2.128 10^5			Positive	
Antineoplastic	Cyclophosphamide CAS # 50-18-0	261	$C_7H_{15}Cl_2N_2O_2P$		0.97	5943			Neutral	
	Ifosfamide CAS # 3778-73-2	261	$C_7H_{15}Cl_2N_2O_2P$		0.97	3781			Neutral	

	Pharmaceutical	MW	Chemical formula	pK_a	Log K_{ow}	S_w 25°C (mg l^{-1})	Log K_d	k_{biol} (L gSS^{-1} d^{-1})	Charge at pH 7	Molecular structure
	Tamoxifen CAS # 10540-29-1	372	$C_{26}H_{29}NO$		6.30	0.1936			Positive	
Topical Products	Crotamiton CAS # 483-63-6	203	$C_{13}H_{17}NO$		2.73	195.3			Neutral	
Antiseptics	Triclosan CAS # 3380-34-5	290	$C_{12}H_7Cl_3O_2$	8.1[n]	5.34	4.621			Neut./Neg.	
Contrast media	Iopromide CAS # 73334-07-3	791	$C_{18}H_{24}I_3N_3O_8$		-2.49	23.75	1[l]	1.6-2.5 1.0*-2.0* 0.12*-0.026* [s]	Pos./Neut.	

Data were from Ternes and Joss, 2006; Petrovic and Barcelò 2007 (pKa), EPISuite v4.00 (S_w, logK_{ow}, logK_{oc}); Chemamox (charge at pH=7). For LogK_d, references are specified.

References

[a]Avdeef et al. 2002; [b] Jones et al. 2002; [c] Huber et al. 2003; [d] Khan and Ongerth 2002; [e] Wan et al. 2002; [f] Tixier et al. 2003; [g] Nowara et al. 1997; [h] Meylan 1993; [i] Vieno et al.,2007; [j] Wick et al.,2009; [k] Le-Minh et al., 2010; [l] Suarez et al., 2008; [m] Zorita et al.2009; [n] Munoz et al.2009; [o] Suarez et al.,2010; [p] Wollenberger 2000; [q] Papastephanou and Frantz 1997; [r] Joss et al., 2004 [s] Abegglen et al., 2009; [t] Radjenovic et al., 2009; u Jia et al., 2012

Appendix B **European mapping of emerging contaminants**

Table - Eropean mapping of emerging contaminants. Red: Emerging contaminants evaluated and detected at environmentally relevant concentrations[3]
Green: Emerging contaminants evaluated and non-detected at environmentally relevant concentrations White: no available data Source: Network Norman.

Substance	CAS No.	Austria	Belgium	Bulgaria	Croatia	Cyprus	Czech Rep.	Denmark	Finland	France	Germany	Greece	Hungary	Int. Waters	Italy	Netherlands	Norway	Portugal	Romania	Serbia	Slovakia	Slovenia	Spain	Sweden	Switzerland	Ukraine	UK
Algal toxins																											
Microcystin-LR	101043-37-2																										
Microcystin-RR	111755-37-4																										
Microcystin-YR	101064-48-6																										
Biocide tranformation products																											
Methyl triclosan	4640-01-1																										
Biocides																											
Bromochloro-5,5-dimethylimidazolidine-2,4-dione	32718-18-6																										
Chloramine-T / Tosylchloramide sodium	127-65-1																										
Chlorfenapyr	122453-73-0																										
Chlorocresol	59-50-7																										
Chlorodimethylphenol (Chloroxylenol)	88-04-0																										
Diclosan / 5-chloro-2-(4-chlorphenoxy)phenol	3380-30-1																										
Difethialone	104653-34-1																										
Fenoxycarb / Ethyl N-[2-(4-phenoxyphenoxy)ethyl]carbamate	72490-01-8																										
Flocoumafen	90035-08-8																										
Flufenoxuron	101463-69-8																										
Methyl-iso-propylcyclohexenone, Carvone	6485-40-1																										
N,N-Diethyltoluamide	134-62-3																										

[3] The European mapping was conducted analyzing a data base with more than 9,700,000 samples. Each sample was analytically analyzed at a different laboratory and following different analytical techniques. Therefore, it is not possible to report a single limit of quantification (LOQ). However, all the reported samples were evaluated at environmentally relevant concentrations; that is in the range of micro to nanograms per liter concentrations. The main objective of the mapping is to show the presence and occurrence of emerging contaminants all over Europe considering that in some countries these compounds were evaluated and found, in other countries these compounds were evaluated and not found (that is the compounds are either not present in the water sample, or are at a concentrations below the LOQ of the analytical technoque), and in the remaining countries these compounds were not even evaluated.

Substance	CAS No.	Austria	Belgium	Bulgaria	Croatia	Cyprus	Czech Rep.	Denmark	Finland	France	Germany	Greece	Hungary	Int. Waters	Italy	Netherlands	Norway	Portugal	Romania	Serbia	Slovakia	Slovenia	Spain	Sweden	Switzerland	Ukraine	UK
o-Benzyl-p-chlorophenol (Chlorophene)	120-32-1																										
Omethoate	1113-02-6																										
Paclobutrazol	76738-62-0																										
Parathion	56-38-2																										
Piperonyl butoxide / 2-(2-butoxyethoxy)ethyl 6-propylpiperonyl ether	51-03-6																										
Propan-2-o	67-63-0																										
Triclocarban	101-20-2																										
Bio-terrorism / Sabotage agents																											
Trichloronitromethane (Chloropicrin)	76-06-2																										
Disinfection by-products (drinking water)																											
1,2,3-Benzotriazole	95-14-7																										
2,4,4'-tribromodiphenylether	41318-75-6																										
2,4,5-Trichlorophenol	95-95-4																										
2,4,6-Tribromophenol	118-79-6																										
4-Chlorophenol	106-48-9																										
Bromochloroacetic acid	5589-96-8																										
Bromochloromethane	74-97-5																										
Bromodichloroacetc acid	71133-14-7																										
Bromonitromethane	563-70-2																										
Dibromomethane	74-95-3																										
Hexabromocyclododecane	25637-99-4																										
Disinfection by-products (drinking water) / Flame retardants																											
Decabromodiphenyl ethane	84852-53-9																										
Drug of abuse																											
Amphetamine	300-62-9																										
Methamphetamine	537-46-2																										
Cocaine	50-36-2																										
Dihydrocodeine	125-28-0																										
Heroin	561-27-3																										

Substance	CAS No.	Austria	Belgium	Bulgaria	Croatia	Cyprus	Czech Rep.	Denmark	Finland	France	Germany	Greece	Hungary	Int. Waters	Italy	Netherlands	Norway	Portugal	Romania	Serbia	Slovakia	Slovenia	Spain	Sweden	Switzerland	Ukraine	UK
Morphine	57-27-2																										
Oxycodone	76-42-6																										
Drug of abuse (metabolite)																											
Benzoylecgonine (Cocaine)	519-09-5																										
Flame retardants																											
1,1,1-Trichloro-2,2-dihydroxyethane (Chloral hydrate)	302-17-0																										
1,2-benzisothiazol-3(2H)-one	2634-33-5																										
1,2,5,6,9,10-Hexabromocyclododecane	3194-55-6																										
1,3-Dichloropropene	542-75-6																										
1,4-Dichlorobenzene	106-46-7																										
2,4-Dihydroxybenzophenone	131-56-6																										
2,4-Dinitrophenol	51-28-5																										
3,4:5,6-Dibenzo-2H-1,2-oxaphosphorin-2-oxide	35948-25-5																										
4-(1,2-Dibromoethyl)-1,2-dibromocyclohexane	3322-93-8																										
Hexabromobenzene	87-82-1																										
Hexachlorocyclopentadiene	77-47-4																										
Octabromodiphenyl ethers	32536-52-0																										
Pentabromoethylbenzene	85-22-3																										
Pentabromotoluene	87-83-2																										
Perchloropentacyclodecane	2385-85-5																										
Resorcinol bis(diphenyl phosphate)	57583-54-7																										
Tetrabromobisphenol A	79-94-7																										
Tetrabromobisphenol bis(2,3-dibromopropyl) ether	21850-44-2																										
Tributyl phosphate	126-73-8																										
Triethyl phosphate	78-40-0																										
Triphenyl phosphate	115-86-6																										
Tris(1,3-dichloroisopropyl) phosphate	13674-87-8																										
Tris(2-chloroethyl) phosphate	115-96-8																										
Tris(2-methylpropyl) phosphate	126-71-6																										

Substance	CAS No.	Austria	Belgium	Bulgaria	Croatia	Cyprus	Czech Rep.	Denmark	Finland	France	Germany	Greece	Hungary	Int. Waters	Italy	Netherlands	Norway	Portugal	Romania	Serbia	Slovakia	Slovenia	Spain	Sweden	Switzerland	Ukraine	UK
Tris(methylphenyl) phosphate	1330-78-5																										
Food additives																											
Sucralose	56038-13-2																										
Triacetin	102-76-1																										
Industrial chemicals																											
1,1,2-Trichloroethane	79-00-5																										
4-Chloroaniline	106-47-8																										
Acetaldehyde	75-07-0																										
Aniline	62-53-3																										
Benzenesulfonamide	98-10-2																										
Benzo(a)anthracene	56-55-3																										
Benzothiazol-2-sulfonic acid	941-57-1																										
Benzothiazole	95-16-9																										
Biphenyl	92-52-4																										
Carbazole	86-74-8																										
Dibutyl tin ion	1002-53-5																										
Dicyclohexylamin	101-83-7																										
Diphenylamine	122-39-4																										
Diphenyltin ion	1135-99-5																										
Ethylenediaminetetraacetic acid	60-00-4																										
Hexa(methoxymethyl)melamine	68002-20-0																										
Irganox 1076	2082-79-3																										
Methyl-1H-benzotriazole / Tolyltriazole	29385-43-1																										
Monobutyl tin ion	78763-54-9																										
N-methyl-Aniline	100-61-8																										
Nitrilotriacetic acid	139-13-9																										
p-Cresol	106-44-5																										
Phenanthrene	85-01-8																										
Styrene	100-42-5																										
Tetraacetylethylenediamine	10543-57-4																										

Substance	CAS No.	Austria	Belgium	Bulgaria	Croatia	Cyprus	Czech Rep.	Denmark	Finland	France	Germany	Greece	Hungary	Int. Waters	Italy	Netherlands	Norway	Portugal	Romania	Serbia	Slovakia	Slovenia	Spain	Sweden	Switzerland	Ukraine	UK
Tetrabutyl tin ion	1461-25-2																										
Tetrachloromethane	56-23-5																										
Toluene	108-88-3																										
Triphenylphosphine oxide	791-28-6																										
Xylene (mixed isomers)	1330-20-7																										
Zinc	7440-66-6																										
Industrial chemicals / Biocides																											
Anthraquinone	84-65-1																										
Cybutryne (Irgarol)	28159-98-0																										
Formaldehyde	50-00-0																										
Triphenyltin cation	668-34-8																										
Industrial chemicals / Flame retardants																											
Tris(1-chloro-2-propanyl) phosphate	13674-84-5																										
Tris(2-butoxyethyl) phosphate	78-51-3																										
Moth repellent / Antimicrobial agent																											
Camphor	76-22-2																										
Isoborneol	124-76-5																										
Other																											
1-Hydroxy Ibuprofen	53949-53-4																										
2-(Methylthio)benzothiazol	615-22-5																										
2-[(2-Chlorophenyl)amino]benzaldehyde	71758-44-6																										
2-[2-[4-(1,1,3,3-tetramethylbutyl)phenoxy]ethoxy]ethanol / 4-Octylphenol di-ethoxylate	2315-61-9																										
2-[4-(1,1,3,3-tetramethylbutyl)phenoxy]ethanol / 4-Octylphenol mono-ethoxylate	2315-67-5																										
2-Aminobenzimidazole	934-32-7																										
2-Chlorophenol	95-57-8																										
2-Mercapto-benzothiazole	149-30-4																										
2-Methyl-1-phenylpropan-2-ol	100-86-7																										

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2-methyl-4-chlorophenoxyacetic acid	94-74-6																										
2-Nitrophenol	88-75-5																										
2-Phenoxyethanol	122-99-6																										
2,6-Di-tert-butylquinone	719-22-2																										
4-Bromophenol	106-41-2																										
Aminodiphenylsulfone	4273-98-7																										
Chinoline	91-22-5																										
Chlorate	14866-68-3																										
Cotinine	486-56-6																										
Cyanide-Free	57-12-5																										
Decahydronaphtalene (Dekalin)	91-17-8																										
Ioxitalamic acid	28179-44-4																										
Isoquinoline	119-65-3																										
Metaldehyde	108-62-3																										
N-Ethylaniline	103-69-5																										
N-methylperfluorooctanesulfonamide	31506-32-8																										
N-Nitrosodibutylamine	924-16-3																										
N-nitrosodiethylamine	55-18-5																										
n-Nitrosodimethylamine	62-75-9																										
N-nitrosodiphenylamine	86-30-6																										
N-nitrosomethylethylamine	10595-95-6																										
N-nitrosopiperidine	100-75-4																										
N-Nitrosopyrrolidine	930-55-2																										
Nadolol	42200-33-9																										
Naphthalene sulphonic acid	120-18-3																										
Naproxen	22204-53-1																										
Nitrobenzene	98-95-3																										
Perfluorodecane sulfonate (anion)+	126105-34-8																										
Perfluorodecanoic acid	335-76-2																										
Perfluoroalkylated substances and their transformation products																											

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2,2',3,3',4,4',5,5',6,6'-Decabromodiphenyl ether	1163-19-5																										
2,2',3,4,4',5',6-Heptabromodiphenyl ether	207122-16-5																										
2,2',4,4'-Tetrabromodiphenyl ether	5436-43-1																										
2,2',4,4',5-Pentabromodiphenyl ether (BDE-99)	60348-60-9																										
2,2',4,4',5,5'-Hexabromodiphenyl ether	68631-49-2																										
2,2',4,4',5,6'-Hexabromodiphenyl ether	207122-15-4																										
2,2',4,4',6-Pentabromodiphenyl ether (BDE-100)	189084-64-8																										
2,2',4,5'-Tetrabromodiphenylether	60044-24-8																										
2,3,4-Trichloroaniline	634-67-3																										
2,3,4,6-Tetrachlorophenol	58-90-2																										
2,4-Dibromophenol	615-58-7																										
2,4-Dichlorophenol	120-83-2																										
3-Chloroaniline	108-42-9																										
3-iodo-2-propynyl butylcarbamate	55406-53-6																										
4-Methyl-1H-benzotriazole	29878-31-7																										
4-Methylbenzylidene camphor	36861-47-9																										
4-nitrosomorpholine	59-89-2																										
4-Nonylphenol di-ethoxylate / 2-(2-(4-Nonylphenoxy)ethoxy)ethanol	20427-84-3																										
4-Nonylphenol mono-ethoxylate	104-35-8																										
4-tetr-Butylcyclohexanone (2isomers)	98-53-3																										
4-tert-Butylphenol	98-54-4																										
5-chloro-2-methyl-3(2H)-isothiazolone	26172-55-4																										
5-Methyl-1H-benzotriazole (5-Tolyltriazole)	136-85-6																										
5,6-Dimethyl-1H-benzotriazole	4184-79-6																										
6-Deisopropylatrazine / 6-chloro-N-ethyl-1,3,5-Triazine-2,4-diamine	1007-28-9																										
N-ethylperfluorooctanesulfonamide	4151-50-2																										
Perfluoro-n-undecanoic acid	2058-94-8																										
Perfluorobutanesulfonate (anion)	45187-15-3																										
Perfluorobutanoic acid	375-22-4																										

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Perfluorododecanoic acid	307-55-1																										
Perfluoroheptanoic acid	375-85-9																										
Perfluorohexane sulfonate (anion)	108427-53-8																										
Perfluorohexanoic acid	307-24-4																										
Perfluorononanoic acid	375-95-1																										
Perfluorooctane sulfonamide	754-91-6																										
Perfluorooctane sulfonate (anion)	45298-90-6																										
Perfluorooctane sulfonate (PFOS)	1763-23-1																										
Perfluorooctanoic acid	335-67-1																										
Perfluoropentanoic acid	2706-90-3																										
Perfluorotetradecanoic acid	376-06-7																										
Personal care products																											
4-Oxoisophorone	1125-21-9																										
Acetylcedrene	32388-55-9																										
ADBI (Celestolide)	13171-00-1																										
AHDI (Phantolide)	15323-35-0																										
ATII (Traseolide)	68140-48-7																										
Benzophenone	119-61-9																										
Betamethasone	378-44-9																										
Boisvelone / Iso-E super	54464-57-2																										
Drometrizole	2440-22-4																										
Ethyl paraben	120-47-8																										
Ethylhexyl methoxycinnamate	5466-77-3																										
Galaxolide	1222-05-5																										
Homosalate	118-56-9																										
Isobutyl paraben	4247-02-3																										
Methyl paraben	99-76-3																										
Methyl-tert-butyl ether	1634-04-4																										
Methyldihydrojasmonate (Methyl 3-oxo-2-pentylcyclopentaneacetate)	24851-98-7																										

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Methylsalicylate	119-36-8																										
Musk ambrette	83-66-9																										
Musk ketone	81-14-1																										
Musk xylene	81-15-2																										
Oxybenzone	131-57-7																										
Propyl paraben	94-13-3																										
Tonalide	1506-02-1																										
Personal care products / Biocides																											
Triclosan	3380-34-5																										
Personal care products / Food additives																											
2,6-Di-tert-butylphenol	128-39-2																										
Butylated hydroxytoluene	128-37-0																										
Triethylcitrate	77-93-0																										
Pharmaceuticals																											
17-alpha-Estradiol	57-91-0																										
17-alpha-Ethinylestradiol	57-63-6																										
17-beta-Estradiol	50-28-2																										
Acetaminophen (Paracetamol)	103-90-2																										
Acetazolamide	59-66-5																										
Acetylsalicylic acid (Aspirin)	50-78-2																										
Alprazolam	28981-97-7																										
Aluminium metal (nanoparticles)	7429-90-5																										
Amitryptiline	50-48-6																										
Amoxicillin	26787-78-0																										
Ampicillin	69-53-4																										
Arsenic	7440-38-2																										
Atenolol	29122-68-7																										
Azithromycin	83905-01-5																										
Beta-sitosterol	83-46-5																										
Betaxolol	63659-18-7																										

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Bezafibrate	41859-67-0																										
Bisoprolol	66722-44-9																										
Bromazepam	1812-30-2																										
Butalbital	77-26-9																										
Caffeine	58-08-2																										
Carazolol	57775-29-8																										
Carbamazepine	298-46-4																										
Cefazoline	25953-19-9																										
Chloramphenicol	56-75-7																										
Chlortetracycline	57-62-5																										
Chromium	7440-47-3																										
Ciprofloxacin	85721-33-1																										
Clarithromycin	81103-11-9																										
Clenbuterol	37148-27-9																										
Clofibrate																											
Clofibric acid (metabolite of CLOFIBRATE)	882-09-7																										
Clotrimazole	23593-75-1																										
Cloxacillin	7081-44-9																										
Codeine	76-57-3																										
Copper	7440-50-8																										
Copper (nanoparticles)	7440-50-8																										
Crotamiton	483-63-6																										
Cyclophosphamide	50-18-0																										
Dapsone	80-08-0																										
Dexamethasone	50-02-2																										
Diatrizoate	117-96-4																										
Diazepam	439-14-5																										
Diazinon	333-41-5																										
Dichlofluanid	1085-98-9																										
Dichloroaniline-2,3	608-27-5																										

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Dichlorodiphenyldichloroethane (Mitotane)	53-19-0																										
Dichlorvos	62-73-7																										
Diclofenac	15307-86-5																										
Dicloxacillin	3116-76-5																										
Diethylstilbestrol	56-53-1																										
Diphenhydramine	58-73-1																										
Doxepine	1668-19-5																										
Doxycycline (anhydrous)	94088-85-4																										
Doxycycline (monohydrate)	564-25-0																										
Enoxacin	74011-58-8																										
Enrofloxacin	93106-60-6																										
Erythromycin	114-07-8																										
Estriol	50-27-1																										
Estrone	53-16-7																										
Famotidine	76824-35-6																										
Fenofibrate	49562-28-9																										
Fenofibric acid (metabolite of FENOFIBRATE)	42017-89-0																										
Fenoprofen	31879-05-7																										
Fenoterol	13392-18-2																										
Flumequine	42835-25-6																										
Fluoxetine	54910-89-3																										
Fluvoxamine	54739-18-3																										
Furosemide	54-31-9																										
Fused silica (nanoparticles)	60676-86-0																										
Gabapentin	60142-96-3																										
Gemfibrozil	25812-30-0																										
Gentamicin	1403-66-3																										
Glibenclamide (Glyburide)	10238-21-8																										
Hydrochlorothiazide	58-93-5																										
Hydrocodone	125-29-1																										

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Ibuprofen	15687-27-1																										
Ifosfamide	3778-73-2																										
Imapramine	50-49-7																										
Iminostilbene	256-96-2																										
Indomethacin	53-86-1																										
Iohexol	66108-95-0																										
Iomeprol	78649-41-9																										
Iopamidol	60166-93-0																										
Iopromide	73334-07-3																										
Irbesartan	138402-11-6																										
Ivermectin	70288-86-7																										
Josamycin	16846-24-5																										
Ketoprofen	22071-15-4																										
Lamotrigine	84057-84-1																										
Lansoprazole	103577-45-3																										
Lidocaine	137-58-6																										
Lincomycin	859-18-7																										
Loratadine	79794-75-5																										
Lorazepam	846-49-1																										
Losartan	114798-26-4																										
Marbofloxacin	115550-35-1																										
Medazepam	2898-12-6																										
Mefenamic acid	61-68-7																										
Meprobamate	57-53-4																										
Mestranol	72-33-3																										
Metformin	657-24-9																										
Metoprolol	37350-58-6																										
Mevastatin	73573-88-3																										
Nordiazepam	1088-11-5																										
Norfloxacin	70458-96-7																										

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Ofloxacin	82419-36-1																										
Omeprazole	73590-58-6																										
Oxacillin	66-79-5																										
Oxazepam	604-75-1																										
Oxolinic acid	14698-29-4																										
Oxytetracycline	79-57-2																										
Paroxetine	61869-08-7																										
Penicillin G	61-33-6																										
Penicillin V	87-08-1																										
Pentobarbital	76-74-4																										
Pentoxifylline	6493-05-6																										
Phenazone	60-80-0																										
Phenobarbital	50-06-6																										
Phenylbutazone	50-33-9																										
Pindolol	13523-86-9																										
Pipamperon	1893-33-0																										
Pravastatin	81093-37-0																										
Prednisolone	50-24-8																										
Primidone	125-33-7																										
Propranolol	525-66-6																										
Propyphenazone	479-92-5																										
Ranitidine	66357-35-5																										
Roxithromycin	80214-83-1																										
Salbutamol	35763-26-9																										
Secobarbital	76-73-3																										
Sertraline	79617-96-2																										
Simvastatin	79902-63-9																										
Sotalol	3930-20-9																										
Spiramycin	8025-81-8																										
Streptomycin	57-92-1																										

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Sulfadiazine	68-35-9																										
Sulfadimethoxin	122-11-2																										
Sulfadoxin	2447-57-6																										
Sulfamerazine	127-79-7																										
Sulfamethazine	57-68-1																										
Sulfamethoxazole	723-46-6																										
Sulfapyridine	144-83-2																										
Taloxa	25451-15-4																										
Temazepam	846-50-4																										
Terbutaline	23031-25-6																										
Tetracycline	60-54-8																										
Tiamulin	55297-95-5																										
Tilmicosin	108050-54-0																										
Timolol	26839-75-8																										
Tolfenamic acid	1370-19-5																										
Tramadol	27203-92-5																										
Trimethoprim	738-70-5																										
Tylosin	1401-69-0																										
Valsartan	137862-53-4																										
Venlafaxine	93413-69-5																										
Verapamil	52-53-9																										
Zolpidem	82626-48-0																										
Plant protection products																											
2,4-Dichlorophenoxyacetic acid	94-75-7																										
2,4,6-Trichlorophenol	88-06-2																										
4-(4-chloro-o-tolyloxy) butyric acid	94-81-5																										
4,4'-Dichlorobenzophenone	90-98-2																										
4,5-Dichloro-2-n-octyl-4-isothiazolin-3-one	64359-81-5																										
Abamectin	71751-41-2																										
Aclonifen	74070-46-5																										

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Aldicarb	116-06-3																										
Aldicarb sulfone	1646-88-4																										
Ametryn	834-12-8																										
Amino methyl phosphoric acid	1066-51-9																										
Aminotriazole	61-82-5																										
Azinphos-ethyl	2642-71-9																										
Azoxystrobin	131860-33-8																										
Bentazone	25057-89-0																										
Bifenox	42576-02-3																										
Bromacil	314-40-9																										
Bromofos-ethyl	4824-78-6																										
Bromoxynil octanoate	1689-99-2																										
Carbaryl	63-25-2																										
Carboxin	5234-68-4																										
Chloridazon	1698-60-8																										
Chloroxuron	1982-47-4																										
Chlorpropham	101-21-3																										
Chlorpyrifos	2921-88-2																										
Chlorthal-dimethyl	1861-32-1																										
Clopyralid	1702-17-6																										
Cyanazine	21725-46-2																										
Cycloxydim	101205-02-1																										
Cyprodinil	121552-61-2																										
Desethylatrazine	6190-65-4																										
Desethylterbutylazin	30125-63-4																										
Desmedipham	13684-56-5																										
Desmetryn	1014-69-3																										
Dicamba	1918-00-9																										
Dichlobenil	1194-65-6																										
Dicofol	115-32-2																										

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Diflufenican	83164-33-4																										
Dimethenamid	87674-68-8																										
Dimethomorph	110488-70-5																										
Dinoterb	1420-07-1																										
Echio (Ethion)	563-12-2																										
Eptenofos	23560-59-0																										
Ethofumesate	26225-79-6																										
Ethoprophos	13194-48-4																										
Fenarimol	60168-88-9																										
Fenthion	55-38-9																										
Flufenacet	142459-58-3																										
Fluroxypyr	69377-81-7																										
Flusilazole	85509-19-9																										
Flutriafol	76674-21-0																										
Foramsulfuron	173159-57-4																										
Furathiocarb	65907-30-4																										
g-Methylionone	127-51-5																										
Glyphosate	1071-83-6																										
Heptachlor	76-44-8																										
Heptachlor epoxide	1024-57-3																										
Hexazinone	51235-04-2																										
Icaridin	119515-38-7																										
Iodofenphos	18181-70-9																										
Linuron	330-55-2																										
Mecoprop	7085-19-0																										
Mecoprop-p	16484-77-8																										
Metalaxyl	57837-19-1																										
Metamitron	41394-05-2																										
Metazachlor	67129-08-2																										
Methiocarb	2032-65-7																										

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Methiocarb sulfoxide	2635-10-1																										
Methoxychlor	72-43-5																										
Metolachlor	51218-45-2																										
Metosulam	139528-85-1																										
Metoxuron	19937-59-8																										
Metrifonate (Trichlorfon)	52-68-6																										
Mevinphos	7786-34-7																										
Molinate	2212-67-1																										
Nicosulfuron	111991-09-4																										
Orbencarb	34622-58-7																										
Oxadiazon	19666-30-9																										
Oxadixyl	77732-09-3																										
Parathion methyl	298-00-0																										
Pendimethalin	40487-42-1																										
Pethoxamid	106700-29-2																										
Phenmedipham	13684-63-4																										
Prochloraz	67747-09-5																										
Prometon	1610-18-0																										
Propachlor	1918-16-7																										
Propamocarb	24579-73-5																										
Propan-1-o	71-23-8																										
Propanil	709-98-8																										
Propazine	139-40-2																										
Propyzamide	23950-58-5																										
Prosulfocarb	52888-80-9																										
Quinmerac	90717-03-6																										
Quinoxyfen	124495-18-7																										
Secbumeton	26259-45-0																										
Thiodicarb	59669-26-0																										
Tolclofos methyl	57018-04-9																										

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Triadimefon	43121-43-3																										
Triallate	2303-17-5																										
Plant protection products / Biocides																											
Abamectin / Avermectin B1A	65195-55-3																										
alpha-Cypermethrin / [1.alpha.(S*),3.alpha.]-(.alpha.)-cyano-(3-phenoxyphenyl)methyl 3-(2,2-dichloroethenyl)-2.2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate	67375-30-8																										
Azamethiphos / S-[(6-chloro-2-oxooxazolo[4,5-b]pyridin-3(2H)-yl)methyl] O,O-dimethyl thiophosphate	35575-96-3																										
Bendiocarb	22781-23-3																										
Bifenthrin	82657-04-3																										
Brodifacoum	56073-10-0																										
bromadiolone	28772-56-7																										
Bronopol / Bronosol	52-51-7																										
Carbendazim	10605-21-7																										
Chlorophacinone	3691-35-8																										
Chlorothalonil	1897-45-6																										
Chlorotoluron	15545-48-9																										
Chlorpyriphos methyl	5598-13-0																										
Clothianidin	210880-92-5																										
Coumatetralyl	5836-29-3																										
Cyfluthrin	68359-37-5																										
Cypermethrin	52315-07-8																										
Cyproconazole	94361-06-5																										
Cyromazine / N-cyclopropyl-1,3,5-triazine-2,4,6-triamine	66215-27-8																										
Danofloxacin	112398-08-0																										
Dazomet	533-74-4																										
Deltamethrin	52918-63-5																										

Substance	CAS No.	Austria	Belgium	Bulgaria	Croatia	Cyprus	Czech Rep.	Denmark	Finland	France	Germany	Greece	Hungary	Int. Waters	Italy	Netherlands	Norway	Portugal	Romania	Serbia	Slovakia	Slovenia	Spain	Sweden	Switzerland	Ukraine	UK
Diethyl phthalate	84-66-2																										
Diethylenetriaminepentaacetic acid	67-43-6																										
Difenacoum	56073-07-5																										
Dimethoate	60-51-5																										
Diuron	330-54-1																										
Endosulfan-sulfate	1031-07-8																										
Esfenvalerate / (S)-.alpha.-Cyano-3-phenoxybenzyl (S)-2-(4-chlorophenyl)-3-methylbutyrate	66230-04-4																										
Etofenprox / 3-phenoxybenzyl-2-(4-ethoxyphenyl)-2-methylpropylther	80844-07-1																										
Fenpropimorph	67564-91-4																										
Fipronil	120068-37-3																										
Folpet / N-(trichloromethylthio)phthalimide	133-07-3																										
Imazalil / 1-[2-(allyloxy)-2-(2,4-dichlorophenyl)ethyl]-1H-imidazole	35554-44-0																										
Imidaclopride	138261-41-3																										
Indoxacarb	173584-44-6																										
Isoproturon / 3-(4-isopropylphenyl)-1,1-dimethylurea	34123-59-6																										
lambda-Cyhalothrin	91465-08-6																										
Malathion	121-75-5																										
Methomyl	16752-77-5																										
Octhilinone / 2-octyl-2H-isothiazol-3-one	26530-20-1																										
Permethrin	52645-53-1																										
Phoxime	14816-18-3																										
Pirimiphos-methyl	29232-93-7																										
Prometryn	7287-19-6																										
Propiconazole	60207-90-1																										
Pyriproxyfen / 2-(1-methyl-2-(4-phenoxy-phenoxy)-ethoxy)-pyridine	95737-68-1																										
Spinosad	168316-95-8																										

Substance	CAS No.	Austria	Belgium	Bulgaria	Croatia	Cyprus	Czech Rep.	Denmark	Finland	France	Germany	Greece	Hungary	Int. Waters	Italy	Netherlands	Norway	Portugal	Romania	Serbia	Slovakia	Slovenia	Spain	Sweden	Switzerland	Ukraine	UK
Tebuconazole	107534-96-3																										
Terbuthylazine	5915-41-3																										
Terbutryn	886-50-0																										
Thiabendazole	148-79-8																										
Thiacloprid	111988-49-9																										
Thiamethoxam	153719-23-4																										
Thiram / Tetramethylthiuram disulfide	137-26-8																										
Tolylfluanid	731-27-1																										
Warfarin / Coumadin	81-81-2																										
Plasticisers																											
Benzylbutylphthalate	85-68-7																										
Bisphenol A	80-05-7																										
Di-n-butylphthalate	84-74-2																										
Di-n-octylphthalate	117-84-0																										
Diisodecyl phthalate	26761-40-0																										
Diisononyl phthalate	28553-12-0																										
Dimetylphthalate	131-11-3																										
N-butyl-benzenesulfonamide	3622-84-2																										
Tributylacetylcitrate	77-90-7																										
Surfactants																											
4-Nonylphenoxy acetic acid	3115-49-9																										
C10-C14-LAS	69669-44-9																										
Surfinol-104	126-86-3																										
Trace metals and their compounds																											
Tetraethyl lead	78-00-2																										

Appendix C **Environmental risk of emerging organic micro-contaminants**

Table S1: Compounds of Category 2 with their Chemical Abstract Number (CAS), the use category (Use), the priority substance number (PS), chronic-based Predicted No-Effect Concentration (PNECchronic), acute-based PNEC (PNECacute), provisional PNEC (P-PNEC), LC50-basis of the P-PNEC (Ref), trophic level used for P-PNEC (TL), number of sites monitored before 2005 (# of sites ≤ 2005), frequency of exceedance before 2005 (Frequency ≤ 2005), number of sites monitored since 2005 (# of sites > 2004), frequency of exceedance since 2005 (Frequency > 2004), priority ranking value (PR) and the river basins monitored (RB). The lowest PNEC value is indicated in bold. Source: von der Ohe, P. C., et al. (2011)

CAS	Compound [a]	Use [b]	PS	$PNEC_{chronic}$ [µg / L]	$PNEC_{acute}$ [µg / L]	P-PNEC [µg / L]	Ref [c]	TL[d]	# of sites < 2005	Frequency < 2005	# of sites > 2004	Frequency > 2004	PR	RB [e]
1031-07-8	endosulfan sulfate	P		**0.0050**		0.78	E	D	191	31%	32	41%	0.41	L, S
1918-16-7	propachlor	P		0.10		**0.015**	E	A	140	9%	32	19%	0.19	S
1014-69-3	desmetryn	P			0.025	**0.0069**	P	A	115	11%			0.11	S
950-37-8	methidathion	P		**0.0022**		0.20	P	D	144	8%			0.08	S
534-52-1	DNOC	P		**1.0**		2.4	E	F	140	2%	32	6%	0.06	S
63-25-2	carbaryl	P			0.015	**0.010**	E	D	66	6%			0.06	S
124-40-3	dimethylamine	P		40		**7.5**	E	A	71	4%			0.04	S
84-74-2	di-n-butylphthalate	I		10		**0.74**	E	A	71	4%			0.04	S
121-75-5	malathion	P		**0.0060**		0.015	E	D	191	9%	464	4%	0.04	E, L, S
108-95-2	phenol	I		**7.7**		21	E	D	187	18%	32	3%	0.03	L, S
109-89-7	diethylamine	I			20	**20**	E	A	71	3%			0.03	S
85-68-7	butylbenzylphthalate	I		7.5		**0.27**	E	A	71	3%			0.03	S
87674-68-8	dimethenamid	P		0.20		**0.018**	E	A			481	2%	0.02	E
563-12-2	ethion	P			0.00056	**0.000058**	E	D	191	2%			0.02	L, S
79-11-8	monochloroacetic acid	I		**0.58**		77	E	D	71	1%			0.01	S
1113-02-6	omethoate	P		**0.00084**		0.021	E	D	85	1%			0.01	S
52-68-6	trichlorfon	P		**0.00050**		0.00096	E	D	110	1%			0.01	E, S
298-00-0	methyl parathion	P		0.017		**0.012**	E	D	220	1%	946	0.7%	0.01	E, L, S
12002-48-	trichlorobenzene	I		4.0		**0.90**	E	A	190	1%			0.01	D, S

1														
1746-81-2	monolinuron	P		1.0		**0.30**	P	A	140	4%	614	0.5%	0.005	E, S
115-32-2	dicofol	P		**0.010**		0.15	E	D			481	0.4%	0.004	E
3060-89-7	metobromuron	P			0.26	**0.22**	P	A	104	13%	786	0.4%	0.004	E, S
1806-26-4	4-n-octylphenol	I	25	**0.10**		0.29	P	F	47	0%	513	0.2%	0.002	E, S
62-53-3	aniline	P			0.44	**0.44**	E	D			897	0.1%	0.001	E
87-61-6	1,2,3-trichloro-benzene	I	31	**0.40**		0.90	E	A	320	0.3%	909	0.1%	0.001	D, E, L, S
709-98-8	propanil	P		0.20		**0.029**	E	A	140	4%	32	0%		S
106-44-5	4-methylphenol	B			18	**18**	E	D	140	4%	32	0%		S
59-50-7	4-chloro-3-methylphenol	B			9.2	**1.2**	E	D	140	4%	32	0%		S
122-14-5	phenitrothion	P		**0.0087**		0.035	E	D	191	3%	62	0%		E, L, S
108-39-4	3-methylphenol	P			18	**18**	E	D	140	3%	32	0%		S
95-76-1	3,4-dichloroaniline	I		**0.20**		0.91	E	D	71	3%	30	0%		E, S
1689-83-4	ioxynil	P		**0.26**		4.0	E	D	140	1%	513	0%		E, S
106-47-8	4-chloroaniline	I		1.0		**0.25**	E	D	71	1%	744	0%		E, S
108-42-9	3-chloroaniline	I		1.3		**0.25**	E	D	71	1%	545	0%		E, S
58-90-2	2,3,4,6-tetrachlorophenol	I			0.36	**0.36**	E	F	111	0.9%	692	0%		E, S
933-78-8	2,3,5-trichlorophenol	I			**0.60**	1.6	E	A	126	0.8%	62	0%		E, S
100-42-5	styrene	I			40	**1.2**	E	A	144	0.7%	32	0%		S
106-48-9	4-chlorophenol	I			**2.4**	5.5	E	D	162	0.6%	62	0%		E, S
98-82-8	isopropylbenzene	I		22		**2.6**	E	A	189	0.5%	929	0%		E, L, S
608-93-5	pentachloro-benzene	P	26	**0.0070**		0.31	E	F	212	0.5%	959	0%		E, L, S
108-70-3	1,3,5-trichloro-benzene	I	31	**0.40**		1.4	E	A	216	0.5%	62	0%		E, L, S
100-00-5	1-chloro-4-nitrobenzene	I		**2.0**		4.3	P	A	100	0%	927	0%		E, S
100-02-7	4-nitrophenol	I			4.2	**4.2**	E	A			714	0%		E
100-44-7	a-chlorotoluene	I			**1.3**	3.3	E	D	71	0%				S
10265-92-6	methamidophos	P		2.6		**0.27**	E	D	85	0%				S
106-43-4	4-chlorotoluene	I		32		**8.7**	E	D	171	0%	62	0%		E, L, S
106-89-8	epichlorohydrin	I		**1.3**		12	E	F	71	0%	402	0%		E, S
107-07-3	2-chloroethanol	I		**19**		54	E	F	71	0%				S
108-43-0	3-chlorophenol	I			**4.7**	5.5	E	D	162	0%	62	0%		E, S
108-77-0	2,4,6-trichloro-1,3,5-	I		640		**620**	E	A	71	0%				S

	triazine													
110-86-1	pyridine	I			0.075	**0.075**	E	A	26	0%				L
121-14-2	2,4-dinitrotoluol	I		**2.0**		2.0	E	A	29	0%	897	0%		E
121552-61-2	cyprodinil	P		**1.2**		2.3	E	F			481	0%		E
121-73-3	1-chloro-3-nitrobenzene	I		**3.2**		19	E	F	100	0%	30	0%		E, S
131-11-3	dimethylphthalate	I			32	**32**	E	D	71	0%				S
156-60-5	trans-1,2-dichloroethylene	I			61	**20**	B	A	220	0%	62	0%		E, L, S
15950-66-0	2,3,4-trichlorophenol	I			**0.60**	1.7	E	D	126	0%	62	0%		E, S
16606-02-3	PCB-31	I			0.062	**0.062**	E	A	140	0%	32	0%		S
1689-84-5	bromoxynil	P		**2.5**		7.8	E	A	140	0%	850	0%		E, S
2212-67-1	molinate	P		3.8		**0.22**	E	A	47	0%				L
301-12-2	demeton-S+oxydemeton-methyl	P		0.56		**0.19**	E	D	53	0%				S
302-17-0	trichloroacetaldehyde-hydrate	Ph			**13**	146	B	A	71	0%				S
3424-82-6	2,4'-DDE	P			**0.030**	0.032	P	D	220	0%	959	0%		E, L, S
465-73-6	isodrin	P	9a	**0.010**		0.045	P	D	250	0%	724	0%		D, E, L, S
4901-51-3	2,3,4,5-tetrachlorophenol	I			0.36	**0.36**	E	F	126	0%	62	0%		E, S
541-73-1	1,3-dichlorobenzene	I		**6.0**		6.3	E	D	320	0%	959	0%		D, E, L, S
554-00-7	2,4-dichloroaniline	I			0.91	**0.91**	E	D	71	0%	30	0%		E, S
56-72-4	coumafos	P		0.0034		**0.0010**	E	D	115	0%				S
576-24-9	2,3-dichlorophenol	I			3.1	**3.1**	E	D	126	0%	62	0%		E, S
583-78-8	2,5-dichlorophenol	I			3.1	**3.1**	E	D	104	0%	32	0%		S
591-35-5	3,5-dichlorophenol	I			2.0	**2.0**	E	A	126	0%	62	0%		E, S
606-20-2	2,6-dinitrotoluol	I			7.4	**7.4**	E	F	29	0%	897	0%		E
608-27-5	2,3-dichloroaniline	I			0.91	**0.91**	E	D	71	0%				S
608-31-1	2,6-dichloroaniline	I			0.91	**0.91**	E	D	71	0%				S
608-73-1	hexachloro-cyclohexane	P	18	**0.020**		0.022	E	F	120	0%	14	0%		S

609-19-8	3,4,5-trichlorophenol	I			1.7	**1.7**	E	D	126	0%	62	0%		E, S
626-43-7	3,5-dichloroaniline	I			0.91	**0.91**	E	D	71	0%				S
67-64-1	acetone	I			6997	**6997**	E	A	27	0%				L
67-72-1	hexachloroethane	I			**0.98**	1.4	E	F	140	0%	916	0%		E, S
68631-49-2	PBDE-153	I		0.0030			WS	-			604	0%		D, E
71-55-6	1,1,1-trichloroethane	I		130		**47**	E	F	220	0%	959	0%		E, L, S
75-01-4	vinylchloride	I			62	**22**	B	A	79	0%	784	0%		E, S
75-05-8	acetonitrile	I			794	**794**	E	A	27	0%				L
75-34-3	1,1-dichloroethane	I			92	**6.5**	P	A	291	0%	816	0%		D, E, L, S
75-35-4	1,1-dichloroethene	I			**12**	52	E	D	97	0%	927	0%		E, L, S
78-83-1	isobutyl alcohol	I			225	**225**	E	A	27	0%				L
78-87-5	1,2-dichloropropane	I		409		**53**	E	D	191	0%	563	0%		E, L, S
78-88-6	2,3-dichloropropene	I			**1.0**	12	B	A	140	0%	19	0%		S
79-00-5	1,1,2-trichloroethane	I		300		**82**	E	F	191	0%	695	0%		E, L, S
79-34-5	1,1,2,2-tetrachloroethane	I		140		**20**	E	F	220	0%	62	0%		E, L, S
82-68-8	pentachloronitrobenzene	P			**0.012**	0.81	E	D	84	0%				S
84-66-2	diethylphthalate	I			73	**32**	E	F	71	0%				S
87-65-0	2,6-dichlorophenol	I			3.1	**3.1**	E	D	104	0%	32	0%		S
87-68-3	hexachloro-butadiene	I	17	0.10		**0.090**	E	F	220	0%	880	0%		E, L, S
88-06-2	2,4,6-trichlorophenol	P			**1.6**	1.7	E	D	162	0%	959	0%		E, S
88-72-2	2-nitrotoluol	I		**10**		12	E	D	29	0%	927	0%		E
88-73-3	1-chloro-2-nitrobenzene	I		26		**19**	E	F	100	0%	744	0%		E, S
88-75-5	2-nitrophenol	I			4.2	**4.2**	E	A			714	0%		E
89-59-8	4-chloro-2-nitrotoluene	I		**6.0**		6.4	E	D	71	0%	30	0%		E, S
89-63-4	4-chloro-2-nitroaniline	I		13		**2.4**	E	D	71	0%	30	0%		E, S
92-87-5	benzidine	I			**0.60**	0.61	E	D	71	0%	30	0%		E, S
933-75-5	2,3,6-trichlorophenol	I			2.2	**1.7**	E	D	126	0%	62	0%		E, S
935-95-5	2,3,5,6-tetrachlorophenol	I			0.36	**0.36**	E	F	162	0%	62	0%		E, S
93-76-5	2,4,5-T	P		**1.0**		5	E	D	140	0%	916	0%		E, S
94-81-5	MCPB	P		0.50		**0.42**	E	A	140	0%	547	0%		E, S

94-82-6	24-DB	P			**0.93**	5.0	P	A	140	0%	798	0%		E, S
95-48-7	2-methylphenol	B			18	**18**	E	D	140	0%	32	0%		S
95-49-8	2-chlorotoluene	I		14		**8.7**	E	D	171	0%	62	0%		E, L, S
95-51-2	2-chloroaniline	I		0.64		**0.25**	E	D	71	0%	927	0%		E, S
95-57-8	2-chlorophenol	I			5.5	**5.5**	E	D	162	0%	776	0%		E, S
95-77-2	3,4-dichlorophenol	I			3.1	**3.1**	E	D	162	0%	62	0%		E, S
95-82-9	2,5-dichloroaniline	I		1.6		**0.91**	E	D	71	0%				S
95-85-2	2-amino-4-chlorophenol	I			**0.90**	1.3	P	D	71	0%				S
95-94-3	1,2,4,5-tetrachlorobenzene	I		**0.32**		0.53	E	F	140	0%	32	0%		S
95-95-4	2,4,5-trichlorophenol	I			**0.60**	1.7	E	D	162	0%	62	0%		E, S
96-18-4	1,2,3-trichloropropane	I		**4.1**		29	E	D	144	0%	19	0%		S
96-23-1	1,3-dichloro-2-propanol	I		208		**152**	B	A	71	0%				S
97-00-7	1-chloro-2,4-dinitrobenzene	I		1.6		**0.82**	E	D	71	0%				S
98-87-3	a,a-dichlorotoluene	I			**1.0**	2.6	P	F	71	0%				S

[a] DNOC = 4,6-dinitro-o-cresol, PCB = polychlorinated biphenyls, PBDE = polybrominated diphenyl ether, MCPB = (2-methyl-4-chlorophenoxy)butyric acid

[b] P = pesticide, I = industrial product, B = biocide, C = combustion product, N = natural product, Ph = pharmaceutical

[c] E = experimental value, P = predicted LC50, B = baseline prediction, WS = water solubility exceeded

[d] D = *Daphnia*, F = fish, A = algae

[e] D = Danube, E = Elbe, L =Llobregat, S = Scheldt

Table S2: Compounds of Category 3 with their Chemical Abstract Number (CAS), the use category (Use), the priority substance number (PS), chronic-based Predicted No-Effect Concentration (PNECchronic), acute-based PNEC (PNECacute), provisional PNEC (P-PNEC), LC50-basis of the P-PNEC (Ref), trophic level used for P-PNEC (TL), number of sites monitored since 2005 (# of sites > 2004), exceedance of the lowest PNEC since 2005 (Exceedance > 2004), frequency of exceedance since 2005 (Frequency > 2004), priority ranking value (PR) and the river basins monitored (RB). The lowest PNEC value is indicated in bold. Source: von der Ohe, P. C., et al. (2011)

CAS	**Compound** [a]	**Use** [b]	**PS**	**$PNEC_{chronic}$ [µg / L]**	**$PNEC_{acute}$ [µg / L]**	**P-PNEC [µg / L]**	**Ref** [c]	**TL**[d]	**# of sites > 2004**	**Exceedance > 2004**	**Frequency > 2004**	**PR**	**RB** [e]
2163-68-0	2-hydroxy-atrazine	P				**0.022**	P	A	32	20	88%	1.08	S
375-95-1	perfluorononanoate	I				**0.00040**	P	M	123	3	50%	0.60	D
1222-05-5	HHCB (Galaxolide®)	I				**0.038**	E	M	897	7	49%	0.59	E, S
870-08-6	dioctyltin	B				**0.000096**	P	F	897	66	15%	0.35	E
335-67-1	perfluorooctanoate	I				**0.0029**	P	M	604	11	12%	0.32	D, E
142459-58-3	flufenacet	P				**0.0035**	E	A	766	27	10%	0.30	E
39475-55-3	chlorphyriphos-ethyl	P				**0.0013**	E	M	897	5	16%	0.26	E, S
3115-49-9	nonylphenol-1-carboxylate	I				**0.18**	P	F	123	2	11%	0.21	D
1506-02-1	AHTN (Tonalide®)	I				**0.030**	P	M	897	3	11%	0.21	E
50563-36-5	dimetachlor	P				**0.030**	P	A	481	5	7%	0.17	E
6339-19-1	desphenyl-chloridazon	P				**0.063**	P	A	481	2	2%	0.12	E
5466-77-3	octyl-methoxycinnamate	I				**0.066**	P	M	481	6	2%	0.12	E
36861-47-9	4-methylbenzilidene camphor	I				**0.036**	P	M	481	4	1%	0.11	E
10605-21-7	carbendazim	P				**0.30**	E	M	850	3	1%	0.11	E, S
126-71-6	triisobutylphosphate	I				**0.70**	P	F	897		3%	0.03	E, S
80-05-7	bisphenol A	I		**1.5**		2.9	E	A	1020		2%	0.02	D, E, S
1763-23-1	perfluorooctansulfonate	I				**0.027**	P	F	604		1%	0.01	D, E
76-13-1	1,1,2-trichlorotrifluoroethane	I				**7.9**	B	A	916		0%		E, S
83-46-5	beta-sitosterol	N					WS	-	818		0%		E, S
41859-67-0	bezafibrat	Ph				**2.8**	B	A	153		0%		D, E
1163-19-5	PBDE-209	I					WS	-	123		0%		D
75-27-4	bromodichloromethane	I				**58**	B	A	929		0%		E, L, S
75-25-2	bromoform	N				**47**	E	M	929		0%		E, L, S
58-08-2	caffeine	N				**151**	E	F	941		0%		D, E, S

298-46-4	carbamazepin	Ph				**32**	P	M	1050		0%		D, E, S
156-59-2	cis-1,2-dichloroethylene	I				**20**	B	A	959		0%		E, L, S
882-09-7	clofibric acid	Ph				**13**	B	A	927		0%		D, E
81777-89-1	clomazone	P				**3.5**	E	A	766		0%		E
14488-53-0	dibutyltin	B				**371**	B	A	1064		0%		D, E, S
15307-86-5	diclofenac	Ph				**4.5**	P	F	1050		0%		D, E
83164-33-4	diflufenican	P				**0.33**	P	A	897		0%		E
106325-08-0	epoxiconazole	P				**9.0**	E	A	818		0%		E
78-51-3	ethanol, 2-butoxy-, phosphate	I				**5.7**	P	A	818		0%		E, S
101-42-8	fenuron	P				**1.0**	E	M	897		0%		E
96525-23-4	flurtamone	P				**19**	B	A	766		0%		E
25812-30-0	gemfibrozil	Ph				**0.80**	P	F	123		0%		D
15687-27-1	ibuprofen	Ph				**2.5**	P	F	1050		0%		D, E
479-92-5	isopropylphenazone	Ph				**11**	P	M	897		0%		D, E
7085-19-0	mecoprop	P				**35**	P	F	1082		0%		D, E, S
78763-54-9	monobutyltin	B				**50**	E	M	941		0%		E, S
3091-25-6	monooctyltin	B				**0.22**	E	A	897		0%		E, S
541-91-3	moschus-ketone	I				**0.049**	P	A	481		0%		E
81-15-2	musk-xylene	I				**0.16**	E	M	481		0%		E
134-62-3	N,N-diethyl-m-toluamide	B				**4.0**	P	A	897		0%		E, S
22204-53-1	naproxen	Ph				**9.5**	B	A	123		0%		D
375-85-9	perfluoroheptanoate	I				**0.020**	P	M	123		0%		D
125-33-7	primidon	Ph				**276**	B	A	897		0%		E, S
114-26-1	propoxur	P				**1.4**	E	M	818		0%		E
723-46-6	sulfamethoxazole	Ph				**0.52**	E	A	123		0%		D
13674-84-5	TCPP	I				**59**	E	A	897		0%		E
3380-34-5	triclosan	B				**0.30**	E	F	818		0%		E, S
115-96-8	tris (2-chloroethyl) phosphate	I				**98**	B	A	818		0%		E, S

[a] PBDE = polybrominated diphenyl ether, TCPP = tris(monochlorpropyl)phosphat

[b] P = pesticide, I = industrial product, B = biocide, C = combustion product, N = natural product, Ph = pharmaceutical

[c] E = experimental value, P = predicted LC50, B = baseline prediction, WS = water solubility exceeded

[d] D = *Daphnia*, F = fish, A = algae

[e] D = Danube, E = Elbe, L =Llobregat, S = Scheldt

Table S3: Compounds of Category 4 with their Chemical Abstract Number (CAS), the use category (Use), the priority substance number (PS), chronic-based Predicted No-Effect Concentration (PNECchronic), acute-based PNEC (PNECacute), provisional PNEC (P-PNEC), LC50 basis of the P-PNEC (Ref), trophic level used for P-PNEC (TL), number of sites monitored since 2005 (# of sites > 2004), frequency of exceedance since 2005 (Frequency > 2004), priority ranking value (PR) and the river basins monitored (RB). The lowest PNEC value is indicated in bold. Source: von der Ohe, P. C., et al. (2011)

CAS	Compound [a]	Use [b]	PS	$PNEC_{chronic}$ [µg / L]	$PNEC_{acute}$ [µg / L]	P-PNEC [µg / L]	Ref [c]	TL[d]	# of sites > 2004	Frequency > 2004	PR	RB [e]
57018-04-9	tolclofos-methyl	P				**0.0025**	P	M	32	47%	0.47	S
62-73-7	dichlorvos	P		**0.000016**		0.00018	L	M	62	27%	0.27	E, S
2921-88-2	chlorpyrifos	P	9	0.030		**0.0013**	L	M	32	19%	0.19	D, E, L
23560-59-0	heptenophos	P				**0.0022**	L	M	19	5%	0.05	S
29232-93-7	pirimiphos-methyl	P			0.0021	**0.00023**	L	M	32	3%	0.03	S
32774-16-6	PCB-169	I				**0.00060**	L	F	32	3%	0.03	S
35065-30-6	PCB-170	I				**0.00047**	P	M	32	3%	0.03	S
13457-18-6	pyrazofos	P				**0.00037**	L	M	32	3%	0.03	S
2701-86-2	trans-chlorfenvinphos	P				**0.00031**	L	M	32	3%	0.03	S
31508-00-6	PCB-118	I		**0.000034**		0.0046	L	A	828	2%	0.02	E, L, S
298-04-4	disulfoton	P		**0.0037**		0.040	L	M	681	2%	0.02	E, S
1461-25-2	tetrabutyltin	B				**0.000046**	P	M	941	1%	0.01	E, S
21087-64-9	metribuzin	P			**0.0079**	0.048	L	M	897	1%	0.01	E
7786-34-7	mevinfos	P			0.0013	**0.00095**	L	M	694	1%	0.01	E, S
72-43-5	methoxychlor	P		**0.00050**		0.053	L	M	850	1%	0.01	D, E, S
314-40-9	bromacil	P			**0.0068**	0.0068	L	A	766	1%	0.01	E
834-12-8	ametryne	P		0.11		**0.0042**	L	A	927	1%	0.01	D, E, L
470-90-6	chlorfenvinphos	P	8	0.10		**0.00030**	L	M	850	1%	0.01	E, L, S
56-38-2	parathion-ethyl	P		**0.00020**		0.0020	L	M	880	1%	0.01	E, L, S
1982-47-4	chloroxuron	P			**0.0024**	0.016	L	A	754	1%	0.01	E
86-50-0	azinphos-methyl	P		0.025		**0.0013**	L	M	62	0%	0.00	E, S
5598-13-0	chlorpyrifos-methyl	P		**0.0010**		0.017	L	M	32	0%	0.00	S
68359-37-5	cyfluthrin	P				**0.00017**	L	M	32	0%	0.00	S
919-86-8	demeton-S-methyl	P			**0.010**	0.011	P	M	500	0%	0.00	E, S
2642-71-9	ethyl azinfos	P			**0.0011**	0.0018	L	M	19	0%	0.00	L, S
55-38-9	fenthion	P		**0.0013**		0.026	L	M	49	0%	0.00	E, S
14816-18-3	foxim	P		**0.00050**		0.00084	L	M	531	0%	0.00	E, S
2385-85-5	mirex	B				**0.0022**	P	F	662	0%	0.00	E

24017-47-8	triazofos	P		0.032		**0.0031**	L	M	19	0%	0.00	S

[a] PCB = polychlorinated biphenyls

[b] P = pesticide, I = industrial product, B = biocide, C = combustion product, N = natural product, Ph = pharmaceutical

[c] E = experimental value, P = predicted LC50, B = baseline prediction

[d] D = *Daphnia*, F = fish, A = algae

[e] D = Danube, E = Elbe, L =Llobregat, S = Scheldt

Table S4: Compounds of Category 5 with their Chemical Abstract Number (CAS), the use category (Use), the priority substance number (PS), chronic-based Predicted No-Effect Concentration ($PNEC_{chronic}$), acute-based PNEC ($PNEC_{acute}$), provisional PNEC (P-PNEC), LC50 basis of the P-PNEC (Ref), trophic level used for P-PNEC (TL), number of sites monitored before 2005 (# of sites ≤ 2005), frequency of exceedance before 2005 (Frequency ≤ 2005), number of sites monitored since 2005 (# of sites > 2004), frequency of exceedance since 2005 (Frequency > 2004), priority ranking value (PR) and the river basins monitored (RB). The lowest PNEC value is indicated in bold. Source: von der Ohe, P. C., et al. (2011)

CAS	Compound [a]	Use [b]	PS	$PNEC_{chronic}$ [µg / L]	$PNEC_{acute}$ [µg / L]	P-PNEC [µg / L]	Ref [c]	TL[d]	# of sites < 2005	Frequency < 2005	# of sites > 2004	Frequency > 2004	PR	RB[e]
104-35-8	nonylphenol-1-ethoxylate	I				**0.33**	P	F	27	56%			0.56	L
20427-84-3	nonylphenol-2-ethoxylate	I				**0.42**	P	F	27	48%			0.48	L
42576-02-3	bifenox	P				**0.69**	L	M	104	19%	32	19%	0.19	E
141-78-6	ethylacetate	I				**230.15**	L	F	144	5%	32	6%	0.06	L
10061-01-5	cis-1,3-dichloropropene	I				**0.24**	L	F	104	13%	32	6%	0.06	E, L, S
1420-07-1	dinoterb	P				**0.49**	L	M	140	0%	19	5%	0.05	S
605-45-8	di-isopropylphthalate	I				**3.56**	P	M	71	4%			0.04	S
335-76-2	perfluorodecanoate	I				**0.00**	P	M			123	4%	0.04	D
99-54-7	1,2-dichloro-4-nitrobenzene	I				**1.00**	L	A	100	0%	30	3%	0.03	E, L
88-04-0	chloroxylenol	B				**0.80**	P	M	104	2%	32	3%	0.03	S
84-76-4	dinonylphthalate	I				**0.00**	P	F	71	3%			0.03	S
88-85-7	dinoseb	P				**0.25**	L	M	71	3%			0.03	S
84-75-3	di-n-hexylphthalate	I				**0.19**	L	M	71	1%			0.01	S
117-84-0	di-n-octylphthalate	I				**0.00**	P	F	71	1%			0.01	S
28044-83-9	heptachloro-exo-epoxide (trans, isomer B)	P				**0.25**	L	M	104	1%			0.01	L
2058-94-8	perfluoroundecanoate	I				**0.00**	P	M			123	1%	0.01	D
2104-96-3	bromophos-methyl	P				**0.00**	L	M	144	1%			0.01	S
13171-21-6	phosfamidon	P				**0.11**	L	M	144	1%			0.01	S
74-83-9	bromomethane	B				**2.22**	L	M			766	0.1%	0.001	S
668-34-8	triphenyltin	B				**0.01**	L	M			862	0.1%	0.001	E, L

108-86-1	bromobenzene	I				**5.60**	L	F			970	0%		L, S
74-95-3	dibromomethane	I				**19.39**	P	F	191	0%	929	0%		E, L, S
142-28-9	1,3-dichloropropane	I				**110.93**	L	F	29	0%	927	0%		S
14938-35-3	4-n-pentylphenol	I				**1.38**	L	M	29	0%	927	0%		S
7774-68-7	bis-2,3-dichlor-1-propyl-ether	I				**8.91**	P	F	29	0%	927	0%		E
	PBDE-17	I					WS	-	29	0%	927	0%		D
1677-68-7	pentoxifylline	Ph				**213.30**	P	M			897	0%		E
96-22-0	3-pentanone	I				**26.83**	P	A	29	0%	848	0%		L
39638-32-9	bis-(2-chloroisopropyl)-ether	I				**1.40**	P	M			818	0%		S
06/05/3813	benazolin	P				**6.33**	P	M			766	0%		S
879-39-0	2,3,4,5-tetrachloronitrobenzene	I				**0.60**	L	M			714	0%		S
5103-71-9	cis-chlordane	P				**0.32**	L	M	191	0%	547	0%		S
13121-70-5	tricyclohexyltin	B				**0.01**	L	M			531	0%		E
105-67-9	2,4-dimethylphenol	I				**6.10**	L	M	100	0%	511	0%		S
98-28-2	2-chloro-4-tertbutylphenol	I				**1.54**	P	M	71	0%	511	0%		S
110-19-0	isobutylacetate	I				**34.68**	P	F	21	0%	511	0%		L
68515-44-6	diheptylphthalate	I				**0.00**	P	F	22	0%	481	0%		S
50-78-2	aspirin	Ph				**72.64**	P	F			481	0%		E
637-92-3	propane, 2-ethoxy-2methyl	I				**27.17**	P	A			481	0%		E
53112-28-0	pyrimethanil	P				**2.99**	L	M			481	0%		E
56038-13-2	sucralose	I				**6117.57**	B	A			481	0%		E
7286-69-3	sebuthylazine	P				**0.03**	P	A	144	4%	225	0%		E, L
123-07-9	4-ethylphenol	I				**5.84**	L	M	104	0%	225	0%		S
57-63-6	ethinylestradiol	N				**2.81**	B	A			137	0%		S
72-33-3	mestranol	N				**1.31**	B	A	100	0%	123	0%		S
192-97-2	benzo[e]pyrene	C				**0.01**	L	A			123	0%		S
207122-	PBDE-183	I					WS	-			123	0%		D

16-5														
	PBDE-196	I					WS	-			123	0%		D
	PBDE-197	I					WS	-			123	0%		D
337513-72-1	PBDE-203	I					WS	-			123	0%		D
63387-28-0	PBDE-206	I					WS	-			123	0%		D
437701-79-6	PBDE-207	I					WS	-			123	0%		D
	PBDE-208	I					WS	-			123	0%		D
41318-75-6	PBDE-28	I				**0.09**	P	F			123	0%		D
243982-82-3	PBDE-49	I				**0.02**	P	F			123	0%		D
189084-61-5	PBDE-66	I				**0.02**	P	F			123	0%		D
182346-21-0	PBDE-85	I				**0.02**	L	M			123	0%		D, E
34883-43-7	PCB-8	I				**0.10**	L	M			123	0%		D
75-71-8	dichlorodifluoromethane	I				**31.71**	B	A	191	0%	62	0%		S
630-20-6	1,1,1,2-tetrachloroethane	I				**24.64**	L	M	118	0%	62	0%		E, L
10061-02-6	trans-1,3-dichloropropene	I				**0.24**	L	F	191	1%	32	0%		L, S
95-63-6	1,2,4-trimethylbenzene	I				**7.72**	L	F	189	2%	32	0%		L, S
59440-90-3	1,3-dichlor-2-propyl-2,3-dichlor-1-propyl-ether	I				**5.82**	P	A	189	1%	32	0%		E
103-65-1	n-propylbenzene	I				**1.80**	L	A	189	2%	32	0%		L, S
74-97-5	bromochloromethane	I				**49.55**	P	F	171	0%	32	0%		S
22071-15-4	ketoprofen	Ph				**12.13**	B	A	171	1%	32	0%		D
104-51-8	n-butylbenzene	I				**0.43**	L	M	171	2%	32	0%		L, S
135-98-8	sec-butylbenzene	I				**2.14**	B	M	171	0%	32	0%		L, S
98-06-6	t-butylbenzene	I				**2.09**	P	M	171	1%	32	0%		L, S
594-20-7	2,2-dichloropropane	I				**6.05**	B	A	144	0%	32	0%		S
697-82-5	2,3,5-trimethylphenol	I				**3.39**	L	M	144	0%	32	0%		S
1715-40-8	bromocyclen	B				**0.04**	P	F	144	0%	32	0%		E
23593-75-	clotrimazol	Ph				**2482.75**	B	M	144	0%	32	0%		D

1														
41464-40-8	PCB-49	I				**0.01**	L	F	144	0%	32	0%		S
297-78-9	telodrin	P				**0.42**	P	F	144	0%	32	0%		S
5103-74-2	trans-chlordane	P				**0.03**	P	F	144	0%	32	0%		S
634-66-2	1,2,3,4-tetrachlorobenzene	I				**0.53**	L	F	140	0%	32	0%		S
634-90-2	1,2,3,5-tetrachlorobenzene	I				**0.53**	L	F	140	0%	32	0%		S
615-58-7	2,4-dibromophenol	I				**1.51**	P	F	140	0%	32	0%		S
51-28-5	2,4-dinitrophenol	I				**4.48**	L	M	140	1%	32	0%		S
89-61-2	2,5-dichloronitrobenzene	I				**5.00**	L	A	140	0%	32	0%		E, L
576-26-1	2,6-dimethylphenol	I				**6.10**	L	M	140	0%	32	0%		S
28994-41-4	2-benzylphenol	I				**1.20**	P	M	140	0%	32	0%		S
591-78-6	2-hexanone	I				**428.25**	L	F	140	0%	32	0%		L
609-85-8	3,5-dibromo-anthranilic acid	I				**3.20**	P	M	140	0%	32	0%		D
87-60-5	3-chloro-2-methylaniline	I				**0.82**	L	M	140	0%	32	0%		S
99-08-1	3-nitrotoluol	I				**12.06**	L	M	140	1%	32	0%		E
108-10-1	4-methyl-2-pentanone	I				**400.03**	L	A	140	1%	32	0%		L
198-55-0	perylene	I				**0.01**	L	A	104	5%	32	0%		S
60-80-0	phenanzone	Ph				**24.81**	P	M	121	0%	30	0%		D, E
95-87-4	2,5-dimethylphenol	I				**6.10**	L	M	100	0%	30	0%		S
1610-17-9	atraton	P				**0.03**	P	A	21	0%	30	0%		L
53494-70-5	endrin ketone	P				**2.78**	B	A	191	0%	19	0%		S
117-18-0	2,3,5,6-tetrachloronitrobenzene	I				**0.60**	L	M	144	0%	19	0%		S
3209-22-1	2,3-dichloronitrobenzene	I				**2.15**	L	A	140	0%	19	0%		S
107-87-9	2-pentanone	I				**209.21**	P	A	140	0%	19	0%		L
108-41-8	3-chlorotoluene	I				**8.70**	L	M	140	0%	19	0%		S
620-17-7	3-ethylphenol	I				**5.84**	L	M	140	0%	19	0%		S
124-48-1	dibromochloromethane	I				**31.35**	P	F	140	0%	19	0%		E, L, S
131-18-0	dipentylphthalate	I				**0.15**	P	F	140	1%	19	0%		S
126-75-0	demeton-S	P				**1.70**	P	M	129	0%	19	0%		S

611-06-3	2,4-dichloronitrobenzene	I				**2.00**	P	A	104	0%	19	0%		E, L
3017-95-6	2-bromo-1-chloropropane	I				**19.49**	B	A	104	0%	19	0%		L
83-42-1	2-chloro-6-nitrotoluene	I				**6.43**	L	M	104	3%	19	0%		S
91-94-1	3,3'-dichlorobenzidine	I				**1.08**	L	M	104	5%	19	0%		S
95-69-2	4-chloro-2-methylaniline	I				**0.82**	L	M	104	9%	19	0%		S
615-74-7	2-chloro-5-methylphenol	I				**1.16**	L	M	95	4%	19	0%		S
57-91-0	estradiol	N				**4.21**	P	A			19	0%		S
131-16-8	dipropylphthalate	I				**5.52**	P	F			14	0%		S
50-27-1	estriol	N				**4.18**	P	A			14	0%		S
53-16-7	estrone	N				**1.86**	P	A			14	0%		D, S
13194-48-4	ethopropos	P				**0.05**	L	M			14	0%		S
79-20-9	methyl acetate	I				**356.61**	L	F			14	0%		L
2406-68-0	monophenyltin	B				**3.54**	B	A			14	0%		S
205-82-3	benzo(j)fluoranthene	I				**0.00**	P	F	102	0%				D
540-59-0	1,2-dichloroethene	I			61	**224.10**	L	M	100	0%				D
108-67-8	1,3,5-trimethylbenzene	I				**7.72**	L	F	100	0%				L, S
606-00-8	3,5-dibromoanthranilic acid methyl ester	I				**0.48**	P	M	100	0%				D
618-62-2	3,5-dichloronitrobenzene	I				**2.15**	L	A	100	0%				S
110-82-7	cyclohexane	I				**4.53**	L	F	100	0%				L
944-22-9	fonofos	P				**0.01**	L	M	100	0%				S
60166-93-0	iopamidol	I					WS	-	100	0%				E
83-15-8	N-acetyl-4-aminoantipyrine	I				**1074.45**	B	A	100	0%				D
1672-58-8	N-formyl-4-aminoantipyrine	I				**159.59**	P	F	100	0%				D
103-90-2	paracetamol	Ph				**24.96**	P	A	100	0%				D
75-69-4	trichlorofluoromethane	I				**23.02**	B	A	97	0%				L, S
33284-50-3	PCB-7	I				**0.10**	L	M	90	0%				S
563-58-6	1,1-dichloropropene	I				**10.44**	B	A	84	0%				S
189084-66-0	2,3,4,4',6-pentabromdiphenylether	I				**0.02**	L	M	84	0%				E
123-86-4	butyl acetate	I				**7.93**	L	M	84	0%				L
124-18-5	decane	I				**0.07**	P	M	84	0%				L

3689-24-5	sulfotep	P				**0.00**	L	M	84	0%				S
145213-12-3	trans-heptachloroepoxide	P				**0.25**	L	M	84	0%				S
526-75-0	2,3-dimethylphenol	I				**6.10**	L	M	71	0%				S
121-86-8	2-chloro-4-nitrotoluene	I				**6.43**	L	M	71	0%				E, L
91-58-7	2-chloronaphthalene	I				**1.66**	L	M	71	0%				S
90-00-6	2-ethylphenol	I				**5.84**	L	M	71	0%				S
95-65-8	3,4-dimethylphenol	I				**6.10**	L	M	71	0%				S
108-68-9	3,5-dimethylphenol	I				**6.10**	L	M	71	0%				S
107-05-1	3-chloropropene	I				**5.05**	P	A	71	0%				S
1570-64-5	4-chloro-2-methylphenol	P				**1.16**	L	M	71	0%				E, L
63283-80-7	bis-1,3-dichlor-2-propyl-ether	I				**14.64**	B	A	71	0%				E
108-83-8	diisobutyl ketone	I				**87.00**	L	A	71	0%				L
1011-95-6	diphenyltin	B				**0.66**	L	M	71	0%				S
112-40-3	dodecane	I				**0.01**	P	M	71	0%				L
13071-79-9	terbufos	P				**0.00**	L	M	66	0%				S
615-65-6	2-chloro-4-methylaniline	I				**0.82**	L	M	53	0%				S
4824-78-6	bromophos-ethyl	P				**0.00**	P	M	50	0%				S
74-87-3	chloromethane	I				**28.65**	P	F	50	0%				S
101-21-3	chloropropham	P				**1.47**	L	M	50	0%				S
60-29-7	diethyl ether	I				**59.09**	B	A	50	0%				L
7421-93-4	endrin aldehyde	P				**0.59**	P	F	50	0%				L, S
80-46-6	4-tert-pentylphenol	I				**2.59**	L	M	47	0%				S
117-96-4	amidotrizoate	I					WS	-	47	0%				E
142-82-5	heptane	I				**1.20**	P	M	47	0%				L
78-93-3	2-butanone	I				**2812.01**	L	M	42	0%				L
1610-18-0	prometon	P				**0.10**	L	A	42	0%				L
71626-11-4	benalaxyl	P				**0.61**	L	M	39	0%				E
26259-45-0	sec-bumeton	P				**0.02**	P	A	39	0%				L
1014-70-6	simetryn	P				**0.01**	L	A	39	0%				L
126-99-8	2-chloro-1,3-butadiene	I				**0.70**	P	M	27	0%				S
88-69-7	2-isopropylphenol	I				**11.42**	P	F	27	0%				S
90-43-7	2-phenylphenol	P				**2.58**	L	M	27	0%				S

120-32-1	4-chloro-2-benzylphenol	I				**0.09**	P	M	27	0%				S
99-99-0	4-nitrotoluol	I				**12.06**	L	M	27	0%				E
75-00-3	chloroethane	I				**21.74**	P	A	27	0%				S
96-12-8	DBCP	P				**5.58**	P	F	27	0%				S
298-03-3	demeton-O	P				**0.03**	P	M	27	0%				E, L
67-43-6	diethylenetriaminepentaacetic acid	I				**44.82**	P	A	27	0%				E
84-69-5	di-isobutylphthalate	I				**0.90**	L	F	27	0%				S
1537-22-2	e-HCH	P				**0.08**	L	F	27	0%				S
31879-05-7	fenoprofen	Ph				**0.05**	P	M	27	0%				D
110-54-3	hexane	I				**2.50**	L	F	27	0%				L
53-86-1	indometacin	Ph				**2.89**	P	A	27	0%				D
99-87-6	isopropyltoluol	N				**1.64**	L	M	27	0%				L, S
443-48-1	metronidazole	Ph				**39.75**	L	A	27	0%				D
111-84-2	nonane	I				**0.18**	P	M	27	0%				L
111-65-9	octane	I				**0.39**	L	M	27	0%				L
109-66-0	pentane	I				**6.39**	L	M	27	0%				L
109-60-4	propyl acetate	I				**60.00**	L	F	27	0%				L
109-99-9	tetrahydrofurane	I				**22.26**	P	A	27	0%				L
1120-21-4	undecane	I				**0.03**	P	M	27	0%				L
108-05-4	vinyl acetate	I				**22.46**	P	A	27	0%				L

[a] PBDE = polybrominated diphenyl ether, PCB = polychlorinated biphenyls, DBCP = 1,2-dibromo-3-chloropropane, HCH = hexachlorocyclohexane

[b] P = pesticide, I = industrial product, B = biocide, C = combustion product, N = natural product, Ph = pharmaceutical

[c] E = experimental value, P = predicted LC50, B = baseline prediction, WS = water solubility exceeded

[d] D = *Daphnia*, F = fish, A = algae

[e] D = Danube, E = Elbe, L =Llobregat, S = Scheldt

Table S5: Compounds of Category 6 with their Chemical Abstract Number (CAS), the use category (Use), the priority substance number (PS), chronic-based Predicted No-Effect Concentration ($PNEC_{chronic}$), acute-based PNEC ($PNEC_{acute}$), provisional PNEC (P-PNEC), LC50-basis of the P-PNEC (Ref), trophic level used for the P-PNEC (TL), number of sites monitored since 2005 (# of sites > 2004), exceedance of the lowest PNEC since 2005 (Exceedance > 2004), frequency of exceedance since 2005 (Frequency > 2004), priority ranking value (PR) and the river basins monitored (RB). The lowest PNEC value is indicated in bold. Source: von der Ohe, P. C., et al. (2011)

CAS	Compound [a]	Use [b]	PS	$PNEC_{chronic}$ [µg / L]	$PNEC_{acute}$ [µg / L]	P-PNEC [µg / L]	Ref [c]	TL[d]	# of sites > 2004	Exceedance > 2004	Frequency > 2004	PR	RB[e]
1071-83-6	glyphosate	P		**24**		40	B	A	1082	0.32	3.1%	0.031	S
218-01-9	chrysene	I			**0.070**	0.075	P	D	994	0.73	1.0%	0.010	D, E, L, S
85-01-8	phenanthrene	I		1.3		**0.41**	E	A	959	0.32	0.8%	0.008	D, E, L, S
120-12-7	anthracene	I	2	**0.10**		0.43	E	D	1082	0.47	0.6%	0.006	D, E, L, S
25057-89-0	bentazone	P		80		**4.5**	E	A	1082	0.36	0.4%	0.004	D, E, S
60207-90-1	propiconazole	P		1.8		**1.4**	E	A	850	0.23	0.4%	0.004	E
60-00-4	EDTA	I		2200		**41**	P	A	897	0.85	0.2%	0.002	E
108-88-3	toluene	I		74		**11**	E	A	1102	0.06	0.2%	0.002	D, E, L, S
75-09-2	dichloromethane	I	11	**20**		220	E	D	1082	0.13	0.2%	0.002	D, E, L, S
127-18-4	tetrachloroethylene	I	29a	**10**		15	E	D	818	0.18	0.2%	0.002	D, E, L, S
189084-64-8	PBDE-100	I		**0.00050**		0.015	E	D	818	0.52	0.2%	0.002	D, E
23950-58-5	propyzamide	P		8.2		**0.76**	E	A	818	0.29	0.1%	0.001	E
90-13-1	1-chloronaphthalene	I			**0.070**	1.7	E	D	959	0.35	0.1%	0.001	E, S
126-73-8	tributylphosphat	I		82		**3.4**	E	D	959	0.19	0.1%	0.001	E, S
91-20-3	naphthalene	I	22	**2.4**		6.1	E	F	897	0.04	0.1%	0.001	D, E, L, S
79-01-6	trichloroethylene	I	29b	**10**		44	E	F	959	0.13	0.1%	0.001	D, E, L, S
120-83-2	2,4-dichlorophenol	P			**0.80**	3.1	E	D	1082	0.13	0.0%		E, S
56-23-5	carbon tetrachloride	B	6a	**12**		56	E	D	1082	0.06	0.0%		D, E, L, S
95-47-6	o-xylene	I			**1.0**	4.4	E	A	1082	0.41	0.0%		D, E, L, S
106-46-7	1,4-dichlorobenzene	I		20		**6.3**	E	D	1052	0.06	0.0%		D, E, L, S
107534-96-3	tebuconazole	P			**1.4**	2.8	E	A	994	0.28	0.0%		E
95-50-1	1,2-dichlorobenzene	I		6.3		**6.3**	E	D	959	0.08	0.0%		D, E, L, S
107-06-2	1,2-dichloroethane	I	10	**10**		135	E	F	959	0.08	0.0%		D, E, L, S
94-75-7	2,4-D	P		**27**		41	E	A	959	0.02	0.0%		D, E, S
1066-51-9	aminomethylphosphonic acid	P			80	**40**	E	D	959	0.26	0.0%		S
120-36-5	dichlorprop	P		**1.3**		103	E	D	959	0.87	0.0%		E, S

100-41-4	ethylbenzene	I		100		**5.3**	E	A	959	0.04	0.0%		D, E, L, S
1330-20-7	m(p)-xylene	I			**1.0**	4.4	E	A	959	0.29	0.0%		D, E, L, S
108-90-7	monochlorobenzene	I		32		**17**	E	F	959	0.06	0.0%		D, E, L, S
83-32-9	acenaphthene	I		3.8		**0.52**	E	A	929	0.06	0.0%		D, E, L, S
92-52-4	diphenyl	I		**1.7**		2.3	E	F	927	0.01	0.0%		E, S
2164-08-1	lenacil	P			**0.77**	0.92	P	A	927	0.21	0.0%		E, S
98-95-3	nitrobenzene	I			38	**28**	E	A	927	0.01	0.0%		E, L
1634-04-4	MTBE	I		2600		**138**	E	D	911	0.02	0.0%		E, L, S
26225-79-6	ethofumesate	P		25		**18**	E	D	818	0.02	0.0%		E
41394-05-2	metamitron	P		**3.8**		134	E	D	818	0.11	0.0%		E
57837-19-1	metalaxyl	P		120		28	E	D	766	0.19	0.0%		E
15299-99-7	napropamide	P		5.1		**3.8**	E	A	766	0.11	0.0%		E
115-86-6	phosphoric acid, triphenyl ester	I			0.87	**0.87**	E	F	766	0.12	0.0%		E, S
71-43-2	benzene	N	4	**10**		18	E	F	604	0.04	0.0%		D, E, L, S
207122-15-4	PBDE-154	I		0.0030		**0.00090**	P	F	604	0.00	0.0%		D, E
208-96-8	acenaphthylene	I		**1.3**		2.2	P	A	32	0.01	0.0%		E, L, S
86-73-7	fluorene	I		2.5		**0.45**	E	D	32	0.06	0.0%		D, E, L, S

[a] EDTA = ethylenediaminetetraacetic acid, PBDE = polybrominated diphenyl ether, MTBE = methyl-tert-butylether

[b] P = pesticide, I = industrial product, B = biocide, C = combustion product, N = natural product, PH = pharmaceutical

[c] E = experimental value, P = predicted LC50, B = baseline prediction

[d] D = *Daphnia*, F = fish, A = algae

[e] D = Danube, E = Elbe, L =Llobregat, S = Scheldt

Appendix D **Potential sources of emerging pollutants in Santa Lucía Chico Basin**

Dairy industry

Name: Conaprole Florida Planta N°7, **Location**: (-56,23519 ; -34,05218)				
Production:				
Milk powderDemineralized whey	2357,5	ton/mes 2016		
Demineralized whey	333,2	ton/mes 2016		
Caramel	318,5	ton/mes 2016		
Butter	816,0	ton/mes 2016		
Butter Oil	201,1	ton/mes 2016		
Buttermilk Powder	115,3	ton/mes 2016		
Chemicals and raw materials used:				
Nombre comercial del insumo	Nombre químico del insumo	Punto de consumo en el proceso o en la PTE	Consumo mensual	
Suero de queso	No aplica	Producción	1832	m3
Soda cáustica	NaOH	Limpieza de equipos	30,9	ton
Crema de Leche	No aplica	Producción de manteca	1503	m3
Leche	No aplica	Producción	19257	m3
Nitrógeno Líquido	N2	Producción	15446	m3
Aditivo limpiador BD SF 617 y BD EZ 600	SD	Ósmosis inversa	21,3	kg
Aditivo Gengard GN8020	SD	Ósmosis inversa	26,8	kg
Limpiador Kleen MCT 103 y 511	SD	Ósmosis inversa	33,3	kg
Bioremediador B 250	SD	Efluentes	20	kg
Ácido peracético al 15%	CH3CO3H	Desinfección	0,98	m3
Hipoclorito de sodio	NaClO	Agua de abastecimiento y desinfección	3,8	m3
Detergente	SD	Limpieza general	105	l
Ácido nítrico	HNO3	Limpieza de equipos	34,3	ton
Anhídrico carbónico	CO2	Producción	9987	m3
Consumo de agua:				
Subterranea	483	m3/dia		
Superficial	738	m3/dia		
Re-Utilización	463	m3/dia		
Tratamiento:	biológico (secundario) y lagunas (terceario)			
Lugar de vertido 1:				
Lugar de vertido	Descripcion	Cuenca/Subcuenca		
Curso de agua	Humedal B	Rio Santa Lucia		

Caudal de descarga de efluentes 1:				
	Caudal medio diario (m3/d)	Caudal maximo diario (m3/d)	Horario de vertido	Días de vertido totales en el bimestre
Bimestre 1	955	955	0 a 24	60
Bimestre 2	915	955	0 a 24	61
Bimestre 3	997	1039	0 a 24	61
Lugar de vertido 2:				
Lugar de vertido		Descripcion	Cuenca/Subcuenca	
Curso de agua		Humedal A	Rio Santa Lucia	
Caudal de descarga de efluentes 2:				
	Caudal medio diario (m3/d)	Caudal maximo diario (m3/d)	Horario de vertido	Días de vertido totales en el bimestre
Bimestre 1	997	1039	0 a 24	60
Bimestre 2	1130	1221	0 a 24	61
Bimestre 3	1039	1039	0 a 24	61
La Feliciana, Location : (-56,34585 ; -34,19039)				
Producción:				
Queso muzzarella	15,0		ton/mes (capacidad max)	
Queso Colonia	15,0		ton/mes (capacidad max)	
Ricota	2,6		ton/mes (capacidad max)	
Dulce de leche	20,0		ton/mes (capacidad max)	
Tratamiento:	Tanque homogenización agitado y reactor de flotación por aire disuelto (DAF)			
Lugar de vertido 1:				
Lugar de vertido	Descripcion		Cuenca/Subcuenca	
Infiltración	Riego		Rio Santa Lucia	
Caudal de descarga de efluentes 1:				
	Caudal medio diario (m3/d)			
Efluente 1	12			

Tannery

Name: Cooperativa El Aguila, **Location:** (-56,222912 ; -34,112242)				
Production:				
Cueros	854	cueros/mes 2016		
Sustancias químicas y materias primas usadas:				
Nombre comercial del insumo	Nombre químico del insumo	Punto de consumo en el proceso o en la PTE	Consumo mensual	
Formiato de Sodio	Formiato de Sodio	Recurtido y teñido	180	kg/mes
Acido fórmico	Acido fórmico	Recurtido y teñido	483	kg/mes
?ancotan SN/Daxitan DCM	Naphthalene sulfonic acid	Recurtido y teñido	267	kg/mes
?upon LE/Nutrapol CDX	Recurtiente sintético	Recurtido y teñido	1517	kg/mes
OP 7201	Aceite pull up	Terminación	130	kg/mes

Sulfato de cromo	Sulfato de cromo Chromium sulfate	Recurtido y teñido	227	kg/mes
Sellatan	Synthetic tannin	Recurtido y teñido	180	kg/mes
PLC909/915 PD6010/6011	Pigmentos	Terminación	195	kg/mes
Magnopal / Trupotan UM/Marbrasyn B47	Recurtiente plimérico acrílicos	Recurtido y teñido	240	kg/mes
Alcohol isopropílico	Alcohol isopropílico	Terminación	400	kg/mes
Auxiliar de penetración	Auxiliar de penetración	Recurtido y teñido	83	kg/mes
WP7503/WP7550/FW2315	Mezcla de ceras	Terminación	710	kg/mes
Uretanos/poliuretanos	Uretanos	Terminación	430	kg/mes
Anilina	Colorantes	Recurtido y teñido	357	kg/mes
Nutrapol LE	Lecitina	Recurtido y teñido	452	kg/mes
Bicarbonato de Sodio	Bicarbonato de Sodio	Recurtido y teñido	270	kg/mes
Trupotan EH	Cromo / recurtientes sintéticos	Recurtido y teñido	133	kg/mes
Tara	Recurtiente vegetal	Recurtido y teñido	213	kg/mes
Daxioil SG	Pescdo sulfitado	Recurtido y teñido	483	kg/mes
Amoníaco	Amoníaco	Recurtido y teñido	62	kg/mes
Consumo de agua:				
Subterranea	0,4	m3/dia		
Superficial	16	m3/dia		
OSE	3,8	m3/dia		
Tratamiento: Neutralizacion, Sdiementador, Reactor aeróbio, Reactor anóxico, sedimentador secundario,				

Lugar de vertido 1:

Lugar de vertido	Descripcion	*Cuenca/Subcuenca*		
Curso de agua		*Rio Santa Lucia*		

Caudal de descarga de efluentes 1:

	Caudal medio diario (m3/d)	*Caudal maximo diario (m3/d)*	Horario de vertido	Días de vertido totales en el bimestre
Bimestre 1	0	*0*	0	60
Bimestre 2	18,3	*31,5*	6-16	9
Bimestre 3	16	*64*	6-16	44

Chemical industry

Name: Fenasol, **Location:** (-56,17449 ; -34,12873)		
Production:		
Azoxistrobin 200g/l + Tebuconazol 125g/l	17235	l/año
Imidacioprid 600g/l	22159	l/año
Glifosato sal Monoisopopilamina 480 g/l	11840	l/año
Glifosato sal Dimetilamina 610g/l	41440	l/año
Imidacloprid 350 g/l	250	l/año
Antraquinona 92% p/p	2000	kg/año
Azoxistrobin 50% p/p	1039	kg/año

Clorantraniliprole 80% p/p	940	kg/año
Benzoato de Emamctina 30% p/p	4517	kg/año

Sustancias químicas y materias primas usadas:

Nombre comercial del insumo	Nombre químico del insumo	Punto de consumo en el proceso o en la PTE	Consumo mensual	
Acido Clorhidrico 32%	Cloruro de Hidrógeno	Tratamiento de efluetnes	0,5	kg
Aerosil 200	Dióxido de Silicio coloidal	Produccion	0,6	kg
Alimidon de maiz	Molécula fromada por amillosa y amilopectina	Produccion	19	kg
Antiespumante siliconado	No se cuenta con la fórmula	Produccion	29	kg
Antiespumante siliconado en polvo	No se cuenta con la fórmula	Produccion	5	kg
Antraquinona TC	9,10 - Antracenediona	Produccion	156	kg
Aquapol	Mezcla de alfa-3-(3-(2H-benzotriazol-2-il)-5-terc-butil-4-hidroxifenil)propionil-omega-hidroxipol(oxietileno) y alfa-3-(3-(2H-benzotriazol-2-il)-5-terc-butil-4-hidroxifenil)propionil-omega-3-(3-((2H-benzotraizol-2-il)-5-terc-butil-4-hidroxifenil)propioniloxipoli(oxietileno)	Tratamiento de efluetnes	94	kg
Azoxistrobin TC	Methyl (2E)-2-(2{[6-(2-cyanophenoxy)pyrimidin-4-yl]oxy}phenyl)-3-methoxyacrylate	Produccion	349	kg
Benzoato de Emamctina TC	Benzoato de 4"-epi-metilmanino-4"-deoxiavermectina B1 (mexcla con un mínimode 90% y unmáximo de 10% de benzoato de 4 "-epi-metilamino-4" -deoxiavermectina B1a y B1b)	Produccion	140	kg
Borresperse	Lignosulfonato de sodio	Produccion	54	kg
Caollin malla 325	Silicato de aluminio hidratado	Produccion	29	kg
Clorantraniliprole TC	1H-Pirazol-5-carboxamida	Produccion	65	kg
Colorante Rojo R4	Colorante Rojo R4	Produccion	0,4	kg
Empicol	Laurisulfato de sodio	Produccion	25	kg
Formol 40	Metanal	Produccion	44	kg
Fosfon 225/50	Acido amino trimetilen fosfórico	Produccion	13	kg
Glicerina	1,2,3 propanotriol	Produccion	321	kg
Glifosato TC	N-(fosfonometil)glicina-isopropilamina (1:1)	Produccion	2100	kg
Goma Xantano	Goma xantano - polisacárido	Produccion	5	kg
G-OXO	Mezcla de ácido peracético y peróxido de hidrógeno	Tratamiento de efluetnes	7,5	kg
Hidróxido de potasio 90%	Hidfróxido de potasio	Tratamiento de efluetnes	7	kg
Imidacloprid TC	N-[1-[(6-Chloro-3-pyridyl)methy]-4,5-dihydroimidazol-2-yl]nitramida	Produccion	1200	kg

Isopropanol	propan-2-ol	Produccion	104	kg
Lactosa	4-O-(b-Dgalactopiranosil)-D-glucopiranosa	Produccion	125	kg
Monoisopropilamina 99%	2-Aminopropano	Produccion	161	kg
Oleosol FL 100	Mezcla: sal de alquilariláido y plímero alquilaril oxirano	Produccion	74	kg
Oleosol FL 650	No se cuenta con la fórmula	Produccion	29	kg
Orotan TM SN Dispersant	mezcla - no se cuenta con la fórmula	Produccion	9,1	kg
Pigmento Rojo	No se cuenta con la fórmula	Produccion	7	kg
Propilenglicol	propano-1,2-diol	Produccion	10	kg
QS-302-P50 (SG Powder)	polialquilenoxido modificado heptametiltrisiloxano	Produccion	1,7	kg
Rishfloc 8180	policrilamida aniónica	Tratamiento de efluetnes	1,2	kg
Solutab	Carboximetilcelulosa de sodio	Produccion	80	kg
Synergen 9962	No se cuenta con la fórmula	Produccion	225	kg
Synergen 9903	No se cuenta con la fórmula	Produccion	58	kg
Tebuconazol TC	(RS)-1-p-clorofenil-4,4-dimetil-3-(1H-1,2,4-triazol-1-ilmetil)pentan-3-ol	Produccion	191	kg
Utramina 200	Amina etoxilada grasa	Produccion	25	kg
Ultranex NP 100	Nonilfenol etoxilado	Produccion	17	kg
Veegum	Silicato mineral hidratado de aluminio y magnesio	Produccion	14	kg

Consumo de agua:		
Subterranea	45	m3/año

Tratamiento: Hidrolisis--floculacion--decantacion--filtro de arena--pileta de retencion--pileta de fotodegradacion y evaporacion

Lugar de vertido 1:

Lugar de vertido	Descripcion	Cuenca/Subcuenca
Atmosfera	Evaporacion estival	Rio Santa Lucia

Caudal de descarga de efluentes 1: 120 -160 m3/año

Dairy farm

The information was collected on dairy farms with more than 500 cows that are those that are required to treat effluents. Minor dairy farms are sources of diffuse discharges.

Name: Doña Celia 2 **Location:** -55,927453 ; -33,943783

Production:

Milk	11178	l/dia
Cows	559	

Sustancias químicas y materias primas usadas:

Nombre comercial del insumo	Nombre químico del insumo	Punto de consumo en el proceso o en la PTE	Consumo mensual

Name: Doña Celia 3 **Location:** -55,910614 ; -33,950578			
Producción:			
Leche	10137	l/dia	
Cows	507		
Sustancias químicas y materias primas usadas:			
Nombre comercial del insumo	Nombre químico del insumo	Punto de consumo en el proceso o en la PTE	Consumo mensual
Name: La Gándara 1 **Location** -55,90017 ; -33,956503			
Producción:			
Leche	10553		
Cows	528		
Sustancias químicas y materias primas usadas:			
Nombre comercial del insumo	Nombre químico del insumo	Punto de consumo en el proceso o en la PTE	Consumo mensual
Name: La Gándara 2 **Location** -55,911892 ; -33,97725			
Producción:			
Leche	11639	l/dia	
Cows	582		
Sustancias químicas y materias primas usadas:			
Nombre comercial del insumo	Nombre químico del insumo	Punto de consumo en el proceso o en la PTE	Consumo mensual
Name: Leticia 3 **Location** -56,286075 ; -33,992681			
Producción:			
Leche	11045	l/dia	
Cows	841		
Sustancias químicas y materias primas usadas:			
Nombre comercial del insumo	Nombre químico del insumo	Punto de consumo en el proceso o en la PTE	Consumo mensual
Name. Leticia 4 Location -56,260953 ; -33,964586			
Producción:			
Leche	10849	l/dia	
Cows	542		
Sustancias químicas y materias primas usadas:			
Nombre comercial del insumo	Nombre químico del insumo	Punto de consumo en el proceso o en la PTE	Consumo mensual

Name: Doña Celia 2 **Location:** -55,927453 ; -33,943783		
Tratamiento:	Estercolero – Laguna Anaeróbica – Laguna Facultativa – Riego	
Lugar de vertido	Descripcion	Cuenca/Subcuenca
Infiltración	Riego 31 ha pastoreo	Rio Santa Lucia
Caudal de descarga de efluentes 1: 30 m3/dia		
Name: Doña Celia 3 **Location**: -55,910614 ; -33,950578		
Tratamiento:	Estercolero – Laguna Anaeróbica – Laguna Facultativa – Riego	
Lugar de vertido	Descripcion	Cuenca/Subcuenca

Infiltración	Riego 49 ha pastoreo	Rio Santa Lucia
Caudal de descarga de efluentes 1: 30 m3/dia		
Name: La Gándara 1 **Location:** -55,90017 ; -33,956503		
Tratamiento:	Estercolero – Laguna Anaeróbica – Laguna Facultativa – Riego	
Lugar de vertido	Descripcion	Cuenca/Subcuenca
Infiltración	Riego 31 ha pastoreo	Rio Santa Lucia
Caudal de descarga de efluentes 1: 30 m3/dia		
Name: La Gándara 2 **Location:** -55,911892 ; -33,97725		
Tratamiento:	Estercolero – Laguna Anaeróbica – Laguna Facultativa – Riego	
Lugar de vertido	Descripcion	Cuenca/Subcuenca
Infiltración	Riego 34 ha pastoreo	Rio Santa Lucia
Caudal de descarga de efluentes 1: 30 m3/dia		
Name: Leticia 3 **Location:** -56,286075 ; -33,992681		
Tratamiento:	Estercolero – Laguna Anaeróbica – Laguna Facultativa – Riego	
Lugar de vertido	Descripcion	Cuenca/Subcuenca
Infiltración	Riego 66 ha pastoreo	Rio Santa Lucia
Caudal de descarga de efluentes 1: 30 m3/dia		
Name: Leticia 4 **Location:** -56,260953 ; -33,964586		
Tratamiento:	Estercolero – Laguna Anaeróbica – Laguna Facultativa – Riego	
Lugar de vertido	Descripcion	Cuenca/Subcuenca
Infiltración	Riego 49 ha pastoreo	Rio Santa Lucia
Caudal de descarga de efluentes 1: 30 m3/dia		

Production of eggs

Name: Granja Guillen **Location**: (-56,212139 ; -34,076972)				
Producción:				
Eggs	17000	unidades/día		
Aves	5000	UP		
Sustancias químicas y materias primas usadas:				
Nombre comercial del insumo	Nombre químico del insumo	Punto de consumo en el proceso o en la PTE	Consumo mensual	
Ración		Producción	3	Ton/dia
Oleina		Racion	1	Ton/dia
Metionina -- Methionine		Racion	125	Kg/dia
Lisina		Racion	60	Kg/dia
Núcleo vitamínico M33		Racion	60	Kg/dia
Consumo de agua:				
Subterranea	500	m3/año		

Wool laundry

Name: Lanera Piedra Alta, **Location**: (-56,241202 ; -34,105759)					
Producción:					
Wool	2982,9	ton lana sucia / año 2015			
Sustancias químicas y materias primas usadas:					
Nombre comercial del insumo	Nombre químico del insumo	Punto de consumo en el proceso o en la PTE	Consumo mensual		
Alkosynt 65	Alcohol graso etoxilado	Lavado	2940	kg/mes	
Hidróxido Sodio 35%	Hidróxido sodio	Lavado y planchado	780	kg/mes	
SELBANA 4554	Aceite ensimaje	Peinaduría	1670	kg/mes	
Tratamiento: Sedimentador primario – tratamiento anaérobio – laguna afine y alamcenamiento - riego forestal y vertimiento cañada					
Lugar de vertido 1:					
Lugar de vertido	Descripcion	Cuenca/Subcuenca			
Curso de agua	Baños de enjuague	Rio Santa Lucia			
Caudal de descarga de efluentes 1:					
	Caudal medio diario (m3/d)	Caudal maximo diario (m3/d)	Horario de vertido	Días de vertido totales en el bimestre	
Bimestre 1	84	96	0 a 24	34	
Bimestre 2	84	96	0 a 24	47	
Bimestre 3	84	96	0 a 24	46	
Bimestre 4	84	96	0 a 24	45	
Bimestre 5	84	96	0 a 24	25	
Bimestre 6	84	96	0 a 24	46	
Lugar de vertido 2:					
Lugar de vertido	Descripción	Cuenca/Subcuenca			
Infiltración	Efluente de lavados	Rio Santa Lucia			
Caudal de descarga de efluentes 2:					
	Caudal medio diario (m3/d)	Caudal maximo diario (m3/d)	Horario de vertido	Días de vertido totales en el bimestre	
Bimestre 1	108	120	0 a 24	34	
Bimestre 2	108	120	0 a 24	47	
Bimestre 3	108	120	0 a 24	46	
Bimestre 4	108	120	0 a 24	45	
Bimestre 5	108	120	0 a 24	25	
Bimestre 6	108	120	0 a 24	46	

Wastewater treatment plant Florida

Name: OSE – WWTP Florida **Location:** (-56,216398 ; -34,108297)		
Production:		
Nro Conexiones	10099	
Población servida	33640	
Caudal de operación promedio	6070	m3/d

Sustancias químicas y materias primas usadas:

Nombre comercial del insumo	Nombre químico del insumo	Punto de consumo en el proceso o en la PTE	Consumo mensual	
Flopam FO 4690 SSH	Poliectrolíto	Deshidratación de lodos	60	Kg
Cloruro Férrico		Reducción Química de Fósforo	7197	ton

Consumo de agua:

OSE	78	m3/dia

Tratamiento: Rejas – Desarenador – Aeración extendida - Remoción química fósforo - Sedimentador secundario - UV

Lugar de vertido 1:

Lugar de vertido	Descripcion	Cuenca/Subcuenca
Curso de agua		Rio Santa Lucia

Caudal de descarga de efluentes 1:

	Caudal medio diario (m3/d)	Caudal maximo diario (m3/d)	Horario de vertido	Días de vertido totales en el bimestre
Bimestre 1	5843	10028	0 a 24	59
Bimestre 2	5671	7142	0 a 24	61
Bimestre 3	4614	6543	0 a 24	61
Bimestre 4	4403	5132	0 a 24	62
Bimestre 5	4351	4880	0 a 24	61
Bimestre 6	4993	6131	0 a 24	61