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

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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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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.
Thanks to the public education of my country for giving me opportunities.
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<th>Description</th>
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<tbody>
<tr>
<td>AE</td>
<td>Alcohol ethoxylate</td>
</tr>
<tr>
<td>AO</td>
<td>Amine oxide</td>
</tr>
<tr>
<td>APE</td>
<td>Ethoxylated alkylphenols</td>
</tr>
<tr>
<td>BCF</td>
<td>Bioconcentration factor</td>
</tr>
<tr>
<td>CAS</td>
<td>Conventional activated sludge</td>
</tr>
<tr>
<td>CMC</td>
<td>Critical micellar concentration</td>
</tr>
<tr>
<td>CWWTP</td>
<td>Conventional wastewater treatment plant</td>
</tr>
<tr>
<td>DBP</td>
<td>Dibutyl phthalate</td>
</tr>
<tr>
<td>EC50</td>
<td>Half maximal effective concentration</td>
</tr>
<tr>
<td>EP</td>
<td>Emerging pollutant</td>
</tr>
<tr>
<td>HRT</td>
<td>Hydraulic retention time</td>
</tr>
<tr>
<td>K_d</td>
<td>Coefficient partition water-solid</td>
</tr>
<tr>
<td>K_{oc}</td>
<td>Organic carbon-water partitioning coefficient</td>
</tr>
<tr>
<td>K_{ow}</td>
<td>Octanol-water coefficient</td>
</tr>
<tr>
<td>LC50</td>
<td>Half lethal concentration</td>
</tr>
<tr>
<td>LOEL</td>
<td>Lowest observable effect level</td>
</tr>
<tr>
<td>LOQ</td>
<td>Limit of quantification</td>
</tr>
<tr>
<td>MBR</td>
<td>Membrane biological reactor</td>
</tr>
<tr>
<td>NOAEL</td>
<td>No observed adverse effect level</td>
</tr>
<tr>
<td>NOEC</td>
<td>No observable effect concentration</td>
</tr>
<tr>
<td>NP</td>
<td>Nonylphenol</td>
</tr>
<tr>
<td>OP</td>
<td>Octylphenol</td>
</tr>
<tr>
<td>PAE</td>
<td>Phthalate ester</td>
</tr>
<tr>
<td>PCP</td>
<td>Personal care products</td>
</tr>
<tr>
<td>PEC</td>
<td>Predicted environmental concentration</td>
</tr>
<tr>
<td>PFC</td>
<td>Perfluorinated compound</td>
</tr>
<tr>
<td>PNEC</td>
<td>Predicted non-effect concentration</td>
</tr>
<tr>
<td>QAC</td>
<td>Quaternary ammonium compound</td>
</tr>
<tr>
<td>RQ</td>
<td>Risk quotient</td>
</tr>
<tr>
<td>SRT</td>
<td>Sludge retention time</td>
</tr>
<tr>
<td>SSD</td>
<td>Species sensitivity distribution</td>
</tr>
<tr>
<td>WWTP</td>
<td>Wastewater treatment plant</td>
</tr>
</tbody>
</table>
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.
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>
<thead>
<tr>
<th>Class of Emerging Pollutants</th>
<th>Example</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Antibiotics</td>
<td>Tetracycline, Erythromycin</td>
<td>Medications that fight bacterial infections, inhibiting or stopping bacterial growth.</td>
</tr>
<tr>
<td>Antimicrobials</td>
<td>Triclosan</td>
<td>Biochemicals that kill or inhibit the growth of microorganisms including bacteria and fungi.</td>
</tr>
<tr>
<td>Detergent metabolites</td>
<td>Nonylphenol</td>
<td>Chemical compounds formed when detergents are broken down by wastewater treatment or environmental degradation.</td>
</tr>
<tr>
<td>Disinfectants</td>
<td>Alcohols, Aldehydes and oxidizing agents</td>
<td>A chemical agent used on non-living surfaces to destroy, neutralize, or inhibit the growth of disease-causing microorganisms.</td>
</tr>
<tr>
<td>Disinfection by-products</td>
<td>Chloroform, Nitrosodimethylamine (NDMA)</td>
<td>Chemical substances resulting from the interaction of organic matter in water with disinfection agents such as chlorine.</td>
</tr>
<tr>
<td>Estrogenic compounds</td>
<td>Estrone, Estradiol, Nonylphenol, Bisphenol A</td>
<td>Natural or synthetic chemicals that can elicit an estrogenic response.</td>
</tr>
<tr>
<td>Fire or flame retardants</td>
<td>Polybrominated Diphenyl Ethers (PBDEs)</td>
<td>Any of several materials or coatings that inhibit or resist the spread of fire.</td>
</tr>
<tr>
<td>Fragrances</td>
<td>Galaxolide</td>
<td>Chemical substances that impart a sweet or pleasant odour.</td>
</tr>
</tbody>
</table>

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

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

### 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

- $k_{biol} < 0.1 \text{ L/(gSS d)}$: poor degradability
- $0.1 < k_{biol} < 10 \text{ L/(gSS d)}$: quite good biodegradability
- $k_{biol} > 10 \text{ L/(gSS d)}$: 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 ($K_{ow}$)

- $\log K_{ow} < 2.5$: high hydrophilic compound
- $2.5 < \log K_{ow} < 4$: moderate hydrophilic compound
- $\log K_{ow} > 4$: 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 ($K_d$)

- $\log K_d < 2.7$: low adsorption potential
- $\log K_d > 2.7$: 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 ($\log K_d < 2.7$) 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 absorption 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 (e.g., 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 observed 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 latter 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 ability of the plant to remove these; this is discussed in detail in section 4.2.1 Removal of emerging pollutants in conventional wastewater treatment plant.

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*
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<th>Therapeutic class</th>
<th>Pharmaceutical compound</th>
<th>Number of papers reported</th>
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<th>Average concentration effluent µg/L</th>
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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 fenofibric 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 spectrometry (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>
<thead>
<tr>
<th>Family</th>
<th>Pesticide</th>
<th>Detection Frequency %</th>
<th>Average concentration influent ng/L</th>
<th>Detection Frequency %</th>
<th>Average concentration effluent ng/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acids</td>
<td>2,4D</td>
<td>33</td>
<td>32.1</td>
<td>50</td>
<td>42.9</td>
</tr>
<tr>
<td></td>
<td>Bentazone</td>
<td>0</td>
<td>---</td>
<td>4</td>
<td>12.2</td>
</tr>
<tr>
<td></td>
<td>MCPA</td>
<td>25</td>
<td>7.64</td>
<td>8</td>
<td>15.1</td>
</tr>
<tr>
<td></td>
<td>Mecoprop</td>
<td>25</td>
<td>106</td>
<td>38</td>
<td>17.3</td>
</tr>
<tr>
<td>Anilides</td>
<td>Alachlor</td>
<td>4</td>
<td>2.59</td>
<td>0</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>Metolachlor</td>
<td>0</td>
<td>---</td>
<td>0</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>Propanil</td>
<td>33</td>
<td>8.98</td>
<td>46</td>
<td>9.42</td>
</tr>
<tr>
<td>organophosphates</td>
<td>Diazinon</td>
<td>96</td>
<td>133</td>
<td>88</td>
<td>281</td>
</tr>
<tr>
<td></td>
<td>Dimethoate</td>
<td>25</td>
<td>4</td>
<td>21</td>
<td>49.1</td>
</tr>
<tr>
<td></td>
<td>Fenitrothion</td>
<td>0</td>
<td>---</td>
<td>0</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>Malathion</td>
<td>0</td>
<td>---</td>
<td>4</td>
<td>0.48</td>
</tr>
<tr>
<td>Phenylureas</td>
<td>Chlortoluron</td>
<td>13</td>
<td>3.94</td>
<td>8</td>
<td>98.2</td>
</tr>
<tr>
<td></td>
<td>Diuron</td>
<td>88</td>
<td>93</td>
<td>88</td>
<td>127</td>
</tr>
<tr>
<td></td>
<td>Isoproturon</td>
<td>0</td>
<td>---</td>
<td>8</td>
<td>13.2</td>
</tr>
<tr>
<td></td>
<td>Linuron</td>
<td>0</td>
<td>---</td>
<td>0</td>
<td>---</td>
</tr>
<tr>
<td>Thiocarbamate</td>
<td>Molinate</td>
<td>0</td>
<td>---</td>
<td>0</td>
<td>---</td>
</tr>
<tr>
<td>Triazines</td>
<td>Atrazine</td>
<td>17</td>
<td>1.24</td>
<td>63</td>
<td>124</td>
</tr>
<tr>
<td></td>
<td>Cyanazine</td>
<td>0</td>
<td>---</td>
<td>0</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>Desethylatrazine</td>
<td>13</td>
<td>24.1</td>
<td>4</td>
<td>22.7</td>
</tr>
<tr>
<td></td>
<td>Desisopropylatrazine</td>
<td>38</td>
<td>13.7</td>
<td>21</td>
<td>38.8</td>
</tr>
<tr>
<td></td>
<td>Simazine</td>
<td>29</td>
<td>7.27</td>
<td>54</td>
<td>169</td>
</tr>
<tr>
<td></td>
<td>Terbuthylazine</td>
<td>46</td>
<td>20.6</td>
<td>5</td>
<td>---</td>
</tr>
</tbody>
</table>

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 at a 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
- Macro cyclic 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>
<thead>
<tr>
<th>Family</th>
<th>Personal care product (PCP)</th>
<th>Detection Frequency %</th>
<th>Average concentration influent µg/L</th>
<th>Detection Frequency %</th>
<th>Average concentration effluent µg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Insect repellent</td>
<td>N, N-diethyl-meta-toluamide (DEET)</td>
<td>0,066</td>
<td></td>
<td>0,040</td>
<td>(a)</td>
</tr>
<tr>
<td></td>
<td>Bayrepel</td>
<td>0,6 – 1,4</td>
<td></td>
<td>&lt; LOD</td>
<td>(b)</td>
</tr>
<tr>
<td>Polycyclic musk</td>
<td>Celestolide (ADBI)</td>
<td>72</td>
<td>0,0372</td>
<td>28</td>
<td>0,025</td>
</tr>
<tr>
<td></td>
<td>Phantolide (AHMI)</td>
<td>19</td>
<td>0,0420</td>
<td>0</td>
<td>&lt; 0,018</td>
</tr>
<tr>
<td></td>
<td>Traseolide (ATII)</td>
<td>81</td>
<td>0,168</td>
<td>67</td>
<td>0,045</td>
</tr>
<tr>
<td></td>
<td>Galaxolide (HHCB)</td>
<td>100</td>
<td>2,031</td>
<td>100</td>
<td>0,751</td>
</tr>
</tbody>
</table>
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)
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 alkyl 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

<table>
<thead>
<tr>
<th>Class</th>
<th>Abbreviation</th>
<th>Common name</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cationic</td>
<td>QAC</td>
<td>Quaternary ammonium compound</td>
</tr>
<tr>
<td></td>
<td>BAC</td>
<td>Benzalkonium chloride</td>
</tr>
<tr>
<td></td>
<td>CPB</td>
<td>Cetylpyridinium bromide</td>
</tr>
<tr>
<td></td>
<td>CPC</td>
<td>Cetylpyridinium chloride</td>
</tr>
<tr>
<td></td>
<td>HDTMA</td>
<td>Hexadecyltrimethylammonium bromide</td>
</tr>
<tr>
<td>Amphoteric</td>
<td>AO</td>
<td>Amine oxide</td>
</tr>
<tr>
<td>Non-ionic</td>
<td>APE</td>
<td>Alkylphenol ethoxylate</td>
</tr>
<tr>
<td></td>
<td>AE</td>
<td>Alcohol ethoxylate</td>
</tr>
<tr>
<td></td>
<td>FAE</td>
<td>Fatty acid ethoxylate</td>
</tr>
</tbody>
</table>
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 reinforcers 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.

![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>
<thead>
<tr>
<th>Group</th>
<th>Surfactant</th>
<th>Total Influent</th>
<th>Influent dissolved</th>
<th>Influent Sorbed</th>
<th>Total Effluent</th>
<th>Effluent dissolved</th>
<th>Effluent Sorbed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anionic</td>
<td>LAS (Linear alkylbenzene sulfates)</td>
<td>4,233 ng/L</td>
<td>2,166,667 ng/L</td>
<td>2,066,666 ng/L</td>
<td>13,277 ng/L</td>
<td>13,277 ng/L</td>
<td>-- (a)</td>
</tr>
<tr>
<td></td>
<td>AES (Alkyl ether sulfates)</td>
<td>3 ng/L</td>
<td>400 – 4,500 µg/L</td>
<td>&lt; 20 – 620 µg/L</td>
<td>&lt; 1 µg/L</td>
<td>&lt; 1 µg/L</td>
<td>(b)</td>
</tr>
<tr>
<td></td>
<td>AS (Alkyl sulfates)</td>
<td>&lt; 20 – 620 µg/L</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(b)</td>
</tr>
<tr>
<td>Cationic</td>
<td>BAC - C12 (alkyl benzyl ammonium chlorides)</td>
<td>55,111 ng/L</td>
<td>39,278 ng/L</td>
<td>6,901 ng/L</td>
<td>175 ng/L</td>
<td>177 ng/L</td>
<td>(a)</td>
</tr>
<tr>
<td></td>
<td>BAC - C14</td>
<td>4,233 ng/L</td>
<td>3,500 µg/L</td>
<td>74 ng/L</td>
<td>85 ng/L</td>
<td></td>
<td>(a)</td>
</tr>
<tr>
<td></td>
<td>BAC - C16</td>
<td>4,233 ng/L</td>
<td>3,500 µg/L</td>
<td>74 ng/L</td>
<td>85 ng/L</td>
<td></td>
<td>(a)</td>
</tr>
<tr>
<td></td>
<td>BAC - C18</td>
<td>563 ng/L</td>
<td>12 ng/L</td>
<td>---</td>
<td>---</td>
<td></td>
<td>(a)</td>
</tr>
<tr>
<td></td>
<td>DDAC - C10 (dialkyl ammonium chlorides)</td>
<td>68,444 ng/L</td>
<td>378 ng/L</td>
<td>--</td>
<td>--</td>
<td></td>
<td>(a)</td>
</tr>
<tr>
<td></td>
<td>DDAC – C12</td>
<td>240 ng/L</td>
<td>163 ng/L</td>
<td>--</td>
<td>--</td>
<td></td>
<td>(a)</td>
</tr>
<tr>
<td></td>
<td>DDAC – C16</td>
<td>18,100 ng/L</td>
<td>647 ng/L</td>
<td>--</td>
<td>--</td>
<td></td>
<td>(a)</td>
</tr>
<tr>
<td></td>
<td>ATAC – C12 (Trialkyl ammonium chlorides)</td>
<td>2,400 ng/L</td>
<td>17 ng/L</td>
<td>--</td>
<td>--</td>
<td></td>
<td>(a)</td>
</tr>
<tr>
<td></td>
<td>ATAC – C14</td>
<td>1,601 ng/L</td>
<td>10 ng/L</td>
<td>--</td>
<td>--</td>
<td></td>
<td>(a)</td>
</tr>
<tr>
<td></td>
<td>ATAC – C16</td>
<td>16,967 ng/L</td>
<td>216 ng/L</td>
<td>--</td>
<td>--</td>
<td></td>
<td>(a)</td>
</tr>
<tr>
<td></td>
<td>QAC (Quaternary ammonium compound)</td>
<td>&lt; 30 – 2,120 µg/L</td>
<td>&lt; LOD – 49 µg/L</td>
<td>1,608 – 219 µg/L</td>
<td>0.6 – 113 µg/L</td>
<td>742 – 724 ng/L</td>
<td>22 ng/L (a)</td>
</tr>
</tbody>
</table>

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

Review of Emerging Pollutants 17
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.
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)

<table>
<thead>
<tr>
<th>Phthalate</th>
<th>Detection Frequency %</th>
<th>Mean concentration Influent ng/L</th>
<th>Detection Frequency %</th>
<th>Mean concentration effluent ng/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethyl phthalate (DMP)</td>
<td>87</td>
<td>0.95</td>
<td>60</td>
<td>0.062</td>
</tr>
<tr>
<td>Diethyl phthalate (DEP)</td>
<td>100</td>
<td>4.1</td>
<td>80</td>
<td>0.20</td>
</tr>
<tr>
<td>Dibutyl phthalate (DBP)</td>
<td>53</td>
<td>2.2</td>
<td>53</td>
<td>0.54</td>
</tr>
<tr>
<td>Butylbenzyl phthalate (BBP)</td>
<td>100</td>
<td>0.95</td>
<td>100</td>
<td>0.36</td>
</tr>
<tr>
<td>Bis(2-ethylbenzyl) phthalate (DEHP)</td>
<td>100</td>
<td>18</td>
<td>100</td>
<td>1.6</td>
</tr>
<tr>
<td>Dioctyl phthalate (DOP)</td>
<td>80</td>
<td>0.49</td>
<td>7</td>
<td>0.017</td>
</tr>
</tbody>
</table>

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 phthalates 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.
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 perfluorooctanoic 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 weight.

Figure 4-4 Range of PFCs concentrations in influent wastewater (a) and sewage sludge (b), worldwide. Source: (Arvaniti, and Stasinakis 2015)
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 occurrence 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 Europe is presented in the form of a matrix where by country and contaminant 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>
<thead>
<tr>
<th>Use Category</th>
<th>Suspected health effects from environmental exposure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Antibiotics</td>
<td>Antibiotic resistance in disease causing bacteria complicating treatment of infections</td>
</tr>
<tr>
<td>Disinfectants</td>
<td>Genotoxicity, cytotoxicity, carcinogenicity</td>
</tr>
<tr>
<td>Fire retardants</td>
<td>Endocrine disruption, indications of increased risk for cancer</td>
</tr>
<tr>
<td>Industrial additives</td>
<td>Can be toxic to animals, ecosystems, and humans</td>
</tr>
<tr>
<td>Life-style products</td>
<td>Can cause cellular stress, negative effects on reproductive activity in animals</td>
</tr>
<tr>
<td>(Caffeine, Nicotine)</td>
<td></td>
</tr>
<tr>
<td>Nonprescription drugs</td>
<td>Unknown health effects</td>
</tr>
<tr>
<td>Other prescription drugs</td>
<td>Increased cancer rates, organ damage</td>
</tr>
<tr>
<td>Personal care products</td>
<td>Bacterial resistance, endocrine disruption</td>
</tr>
<tr>
<td>Pesticides</td>
<td>Endocrine disruption</td>
</tr>
<tr>
<td>Plasticizers</td>
<td>Endocrine disruption, increased risk of cancer</td>
</tr>
<tr>
<td>Reproductive hormones</td>
<td>Endocrine disruption</td>
</tr>
<tr>
<td>Solvents</td>
<td>Endocrine disruption, liver and kidney damage, respiratory impairment, cancer</td>
</tr>
<tr>
<td>Steroids</td>
<td>Endocrine disruption</td>
</tr>
</tbody>
</table>

**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 Technical 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 (Kd) 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 ($K_{oc}$) 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:

$$C_{local-water} = \frac{C_{local-eff}}{(1 + K_{p_{susp}} \cdot S_{water} \cdot 10^{-6}) \cdot Dilution}$$

Where:

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

The mean annual concentration in water is calculated by the following expression:
\[ C_{local-water,avg} = C_{local-water} \cdot \frac{T_{emission}}{365} \]

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

The PEC estimate for sediment in local scope can be calculated through the following expression:

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

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

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

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).

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 bioconcentration 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 \( K_{\text{ow}} \)). A high log \( K_{\text{ow}} \) value can be associated with a high tendency to bioaccumulate; however, there may be substances with a high log \( K_{\text{ow}} \) 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 \( K_{\text{ow}} \) 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*

<table>
<thead>
<tr>
<th>Therapeutic class</th>
<th>Pharmaceutical compound</th>
<th>Species assayed</th>
<th>Test (endpoint)</th>
<th>Toxicity µg/L</th>
<th>PNEC µg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Analgesics / anti-inflammatories</td>
<td>Acetaminophen</td>
<td>Daphnia</td>
<td>EC50 (24h)</td>
<td>136</td>
<td>1 (1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Daphnia</td>
<td>EC50 (48h)</td>
<td>9.2</td>
<td>(1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>S.proboscide u</td>
<td>LC50 (24h)</td>
<td>29.6</td>
<td>(1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fish</td>
<td>EC50 ECOSAR</td>
<td>1</td>
<td>(2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Daphnia</td>
<td>EC50 ECOSAR</td>
<td>42</td>
<td>(2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Algae</td>
<td>EC50 ECOSAR</td>
<td>2549</td>
<td>(2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Invertebrates</td>
<td>EC50</td>
<td>300</td>
<td>(3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Algae</td>
<td>EC50</td>
<td>105</td>
<td>(3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fish</td>
<td>EC50</td>
<td>900</td>
<td>(3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Daphnia</td>
<td>EC50 (48h-immobility)</td>
<td>9.2</td>
<td>(4)</td>
</tr>
<tr>
<td></td>
<td>Acetylsalicylic acid</td>
<td>Fish</td>
<td>EC50 ECOSAR</td>
<td>796</td>
<td>61 (2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Daphnia</td>
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<td>2</td>
<td>(2)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Algae</td>
<td>EC50 ECOSAR</td>
<td>5.5</td>
<td>(2)</td>
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</tr>
<tr>
<td></td>
<td>Fish</td>
<td>EC50</td>
<td>11</td>
<td>(3)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Invertebrates</td>
<td>EC50</td>
<td>90</td>
<td>(3)</td>
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</tr>
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<td>Algae</td>
<td>EC50</td>
<td>12</td>
<td>(3)</td>
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</tr>
<tr>
<td></td>
<td>Fish</td>
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<td>1.7</td>
<td>0.05 (2)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Daphnia</td>
<td>EC50 ECOSAR</td>
<td>0.17</td>
<td>(2)</td>
<td></td>
</tr>
<tr>
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<td>Algae</td>
<td>EC50 ECOSAR</td>
<td>0.8</td>
<td>(2)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fish</td>
<td>EC50</td>
<td>2</td>
<td>(3)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Invertebrates</td>
<td>EC50</td>
<td>0.9</td>
<td>(3)</td>
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</tr>
<tr>
<td></td>
<td>Algae</td>
<td>EC50</td>
<td>0.05</td>
<td>(3)</td>
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</tr>
<tr>
<td>Receptor antagonists</td>
<td>Cimetidine</td>
<td>Fish</td>
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<td>571</td>
<td>35 (2)</td>
</tr>
<tr>
<td></td>
<td>Daphnia</td>
<td>EC50 ECOSAR</td>
<td>35</td>
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</tr>
<tr>
<td></td>
<td>Algae</td>
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<td>40</td>
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<tr>
<td></td>
<td>Daphnia</td>
<td>EC50 (96h-immobility)</td>
<td>271.3</td>
<td>(21)</td>
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<tr>
<td></td>
<td>Ranitidine</td>
<td>Fish</td>
<td>EC50 ECOSAR</td>
<td>1076</td>
<td>63 (2)</td>
</tr>
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<td>Daphnia</td>
<td>EC50 ECOSAR</td>
<td>63</td>
<td>(2)</td>
<td></td>
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<tr>
<td></td>
<td>Algae</td>
<td>EC50 ECOSAR</td>
<td>66</td>
<td>(2)</td>
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</tr>
<tr>
<td></td>
<td>Beta-agonists</td>
<td>Clenbuterol</td>
<td>Fish</td>
<td>EC50 ECOSAR</td>
<td>30 (2)</td>
</tr>
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<td></td>
<td>Daphnia</td>
<td>EC50 ECOSAR</td>
<td>2</td>
<td>(2)</td>
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<tr>
<td></td>
<td></td>
<td>Algae</td>
<td>EC50 ECOSAR</td>
<td>10</td>
<td>(2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fish</td>
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<td>20</td>
<td>17.5 (2)</td>
</tr>
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<td>17.5</td>
<td>(2)</td>
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<td>Algae</td>
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<td>(2)</td>
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<tr>
<td></td>
<td></td>
<td>Terbutaline</td>
<td>Fish</td>
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<td>1.05 (2)</td>
</tr>
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<td>27</td>
<td>(2)</td>
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<td>Algae</td>
<td>EC50 ECOSAR</td>
<td>32</td>
<td>(2)</td>
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<tr>
<td></td>
<td>Antineopastics</td>
<td>Cyclophosphamide</td>
<td>Fish</td>
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<td>70 (2)</td>
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<tr>
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<td></td>
<td>Daphnia</td>
<td>EC50 ECOSAR</td>
<td>1795</td>
<td>(2)</td>
</tr>
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<td></td>
<td>Algae</td>
<td>EC50 ECOSAR</td>
<td>11</td>
<td>(2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ifosfamide</td>
<td>Fish</td>
<td>EC50 ECOSAR</td>
<td>140 (2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Daphnia</td>
<td>EC50 ECOSAR</td>
<td>1795</td>
<td>(2)</td>
</tr>
<tr>
<td>Therapeutic class</td>
<td>Pharmaceutical compound</td>
<td>Species assayed</td>
<td>Test (endpoint)</td>
<td>Toxicity µg/L</td>
<td>PNEC µg/L</td>
</tr>
<tr>
<td>-------------------</td>
<td>--------------------------</td>
<td>----------------</td>
<td>----------------</td>
<td>---------------</td>
<td>-----------</td>
</tr>
<tr>
<td>Contrast media</td>
<td>Iopromide</td>
<td>Algae</td>
<td>EC50 ECOSAR</td>
<td>11</td>
<td>(2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fish</td>
<td>EC50 ECOSAR</td>
<td>865,000</td>
<td>370,000(2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Daphnia</td>
<td>EC50 ECOSAR</td>
<td>766,000</td>
<td>(2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Algae</td>
<td>EC50 ECOSAR</td>
<td>370,000</td>
<td>(2)</td>
</tr>
</tbody>
</table>

(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-Sørensen 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) Kümmener and Henninger (2003); (18) Halling-Sørensen (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

Fourteen compounds present high risk (RQ ratios higher than one) of which seven are antibiotics (erythromycin, ofloxacin, sulfaemethoxazole, clarithromycin, amoxicillin, tetracycline, and azithromycin), tow psychiatric drugs (fluoxetine, and diazepam), two analgesics-anti/inflammatories (ibuprofen, and mfenamic 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, enrofloxacin, tetracycline, and azithromycin), and four are gastric drugs (omeprazole, ranitidine, famotidine, and cimetidine).
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 shawyscha) 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>
<thead>
<tr>
<th>Compound</th>
<th>Lowest observable effects level (LOEL)</th>
<th>Reported effect(s)</th>
<th>Mean effluent level</th>
</tr>
</thead>
<tbody>
<tr>
<td>17α-Ethynylestradiol (EE2)</td>
<td>1 ng/L^a</td>
<td>↑Vitellogenin</td>
<td>&lt; 1 ng/L^a</td>
</tr>
<tr>
<td>17β-Estradiol (E2)</td>
<td>1–10 ng/L^c</td>
<td>↑Vitellogenin</td>
<td>5.5 ng/L</td>
</tr>
<tr>
<td>Estrone (E1)</td>
<td>25–50 ng/L^c</td>
<td>↑Vitellogenin</td>
<td>41 ng/L</td>
</tr>
</tbody>
</table>

^aExcluding extreme value of 131 ng/L for this substance found in the week 8 effluent. ^Jobling et al. (2003); ^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 Kow of each pesticide. From Köck-Schulmeyer, et al. 2012

<table>
<thead>
<tr>
<th></th>
<th>Algae EC50a (mg/L)</th>
<th>Daphni EC50b (mg/L)</th>
<th>Fish LC50c (mg/L)</th>
<th>LogKcow(d)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Triazines</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>atrazine</td>
<td>0.059(1)</td>
<td>6.9(7)</td>
<td>4.5(1)</td>
<td>2.7(8)</td>
</tr>
<tr>
<td>cyanazine</td>
<td>0.2(3)</td>
<td>49(5)</td>
<td>10(6)</td>
<td>2.1(8)</td>
</tr>
<tr>
<td>desethylatrazine</td>
<td>0.1(3)</td>
<td>6.9(e)</td>
<td>4.5(e)</td>
<td>1.51(8)</td>
</tr>
<tr>
<td>deisopropylatrazine</td>
<td>0.050d</td>
<td>3.795d</td>
<td>47.25d</td>
<td>1.15(8)</td>
</tr>
<tr>
<td>simazine</td>
<td>0.04(1)</td>
<td>1.1(1)</td>
<td>90(1)</td>
<td>2.3(8)</td>
</tr>
<tr>
<td>terbuthylazine</td>
<td>0.012(2)</td>
<td>21.2(5)</td>
<td>2.2(2)</td>
<td>3.4(8)</td>
</tr>
<tr>
<td><strong>Phenylureas</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>chlortoluron</td>
<td>0.024(2)</td>
<td>67(2)</td>
<td>20(2)</td>
<td>2.5(8)</td>
</tr>
<tr>
<td>diuron</td>
<td>0.0027(3)</td>
<td>12(7)</td>
<td>4.3(5)</td>
<td>2.87(8)</td>
</tr>
<tr>
<td>isoproturon</td>
<td>0.013(2)</td>
<td>507(7)</td>
<td>37(7)</td>
<td>2.5(8)</td>
</tr>
<tr>
<td>linuron</td>
<td>0.016(2)</td>
<td>0.12(7)</td>
<td>3.15(7)</td>
<td>3(8)</td>
</tr>
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<td><strong>Organophosphates</strong></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>diazinon</td>
<td>6.4(2)</td>
<td>0.001(2)</td>
<td>3.1(2)</td>
<td>3.69(8)</td>
</tr>
<tr>
<td>dimethoate</td>
<td>90.4(2)</td>
<td>2(2)</td>
<td>30.2(2)</td>
<td>0.704(8)</td>
</tr>
<tr>
<td>fenitrothion</td>
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<td>0.0086(2)</td>
<td>1.3(2)</td>
<td>3.32(8)</td>
</tr>
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<td>malathion</td>
<td>13(1)</td>
<td>0.0007(2)</td>
<td>0.1(7)</td>
<td>2.75(8)</td>
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<td><strong>Anilides and Chloroacetanilides</strong></td>
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<td></td>
<td></td>
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</tr>
<tr>
<td>alachlor</td>
<td>0.966(3)</td>
<td>10(3)</td>
<td>1.8(1)</td>
<td>3.09(8)</td>
</tr>
<tr>
<td>metolachlor</td>
<td>57.1(3)</td>
<td>23.5(4)</td>
<td>3.9(4)</td>
<td>3.4(8)</td>
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<tr>
<td>propanil</td>
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<td>4.8(7)</td>
<td>2.3(5)</td>
<td>2.29(8)</td>
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<tr>
<td><strong>Thiocarbamate</strong></td>
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<tr>
<td>molinate</td>
<td>0.5(2)</td>
<td>14.9(2)</td>
<td>16(2)</td>
<td>2.86(8)</td>
</tr>
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<td></td>
</tr>
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<td>2,4D</td>
<td>24.2(2)</td>
<td>100(2)</td>
<td>100(7)</td>
<td>-0.83(8)</td>
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</table>
### Table 4-14 Risk of pesticides in conventional WWTP effluent.

<table>
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<tr>
<th></th>
<th>PEC Algae ng/L</th>
<th>PNEC Algae ng/L</th>
<th>PNEC Daphnia ng/L</th>
<th>PNEC Fish ng/L</th>
<th>RQ Algae</th>
<th>RQ Daphnia</th>
<th>RQ Fish</th>
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<td><strong>Triazines</strong></td>
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<tr>
<td>atrazine</td>
<td>124</td>
<td>59</td>
<td>6900</td>
<td>4500</td>
<td>2.1</td>
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<td>0.03</td>
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<td>---</td>
<td>200</td>
<td>49000</td>
<td>10000</td>
<td>---</td>
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<td>---</td>
</tr>
<tr>
<td>desethylatrazine</td>
<td>22.7</td>
<td>100</td>
<td>6900</td>
<td>4500</td>
<td>0.2</td>
<td>0.00</td>
<td>0.01</td>
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<td>50</td>
<td>3765</td>
<td>47250</td>
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<td>0.01</td>
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<td>40</td>
<td>1100</td>
<td>90000</td>
<td>4.2</td>
<td>0.15</td>
<td>0.00</td>
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<td>terbuthylazine</td>
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<td>12</td>
<td>121200</td>
<td>2200</td>
<td>1.7</td>
<td>0.00</td>
<td>0.01</td>
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</tr>
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<td>67000</td>
<td>20000</td>
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<td>0.00</td>
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<td>47.0</td>
<td>0.01</td>
<td>0.0</td>
</tr>
<tr>
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<td>507000</td>
<td>37000</td>
<td>1.0</td>
<td>0.00</td>
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</tr>
<tr>
<td>linuron</td>
<td>---</td>
<td>16</td>
<td>120</td>
<td>3150</td>
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<tr>
<td><strong>Organophosphates</strong></td>
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<td></td>
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<td></td>
<td></td>
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<tr>
<td>diazinon</td>
<td>281</td>
<td>6400</td>
<td>1</td>
<td>3100</td>
<td>0.0</td>
<td><strong>281.00</strong></td>
<td>0.1</td>
</tr>
<tr>
<td>dimethoate</td>
<td>49.1</td>
<td>90400</td>
<td>2000</td>
<td>30200</td>
<td>0.0</td>
<td>0.02</td>
<td>0.0</td>
</tr>
<tr>
<td>fenitrothion</td>
<td>---</td>
<td>1300</td>
<td>8.6</td>
<td>1300</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>malathion</td>
<td>0.48</td>
<td>13000</td>
<td>0.7</td>
<td>100</td>
<td>0.0</td>
<td>0.69</td>
<td>0.0</td>
</tr>
<tr>
<td><strong>Anilides and Chloroacetanilides</strong></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>alachlor</td>
<td>---</td>
<td>966</td>
<td>10000</td>
<td>1800</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

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

Table 4-15 Acute toxicity data for personal care products. Source: Brausch, and Rand 2011.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Category</th>
<th>Species</th>
<th>Trophic group</th>
<th>Endpoint /duration</th>
<th>LC50 (mg/L)</th>
<th>Additional tox. Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triclocarban</td>
<td>Antimicrobial</td>
<td><em>Xenopus laevis</em></td>
<td>Amphibian</td>
<td>96 h</td>
<td>0.399 (embryos)</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td><em>Acris blanchardii</em></td>
<td>Amphibian</td>
<td>96 h</td>
<td>0.259</td>
<td>(8)</td>
</tr>
<tr>
<td></td>
<td></td>
<td><em>Bufo woodhousii</em></td>
<td>Amphibian</td>
<td>96 h</td>
<td>0.367</td>
<td>(8)</td>
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<tr>
<td></td>
<td></td>
<td><em>Rana sphenoccephala</em></td>
<td>Amphibian</td>
<td>96 h</td>
<td>0.152</td>
<td>(8)</td>
</tr>
<tr>
<td></td>
<td></td>
<td><em>Pseudokirchneriella subcapitata</em></td>
<td>Algae</td>
<td>72 h Growth</td>
<td>0.53 (µg/L)</td>
<td>(9)</td>
</tr>
<tr>
<td></td>
<td></td>
<td><em>D. magna</em></td>
<td>Invert.</td>
<td>48 h</td>
<td>0.01</td>
<td>(10)</td>
</tr>
<tr>
<td></td>
<td></td>
<td><em>C. dubia</em></td>
<td>Invert.</td>
<td>48 h</td>
<td>0.0031</td>
<td>(10)</td>
</tr>
<tr>
<td></td>
<td></td>
<td><em>Mysisopsis bahia</em></td>
<td>Invert.</td>
<td>48, 96 h</td>
<td>0.015, .01</td>
<td>(10)</td>
</tr>
<tr>
<td></td>
<td></td>
<td><em>Salmo gairdneri</em></td>
<td>Fish</td>
<td>96 h</td>
<td>0.120</td>
<td>(10)</td>
</tr>
<tr>
<td></td>
<td></td>
<td><em>L. macrochirus</em></td>
<td>Fish</td>
<td>96 h</td>
<td>0.097</td>
<td>(10)</td>
</tr>
<tr>
<td></td>
<td></td>
<td><em>Scenedesmus subspicatus</em></td>
<td>Algae</td>
<td>72 h Growth</td>
<td>0.02</td>
<td>(10)</td>
</tr>
<tr>
<td></td>
<td></td>
<td><em>P. subcapitata</em></td>
<td>Algae</td>
<td>72 h Growth</td>
<td>0.017 (µg/L)</td>
<td>89</td>
</tr>
<tr>
<td>Benzophenone</td>
<td>Fixative</td>
<td><em>Caenorhabditis elegans</em></td>
<td>Nematode</td>
<td>24 h</td>
<td>56.8</td>
<td>(11)</td>
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<tr>
<td></td>
<td></td>
<td><em>P. promelas</em></td>
<td>Fish</td>
<td>96 h</td>
<td>10.89</td>
<td>(12)</td>
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<tr>
<td>1,4-dichlorobenzene</td>
<td>Insect repellant</td>
<td><em>D. magna</em></td>
<td>Invert.</td>
<td>24, 48 h Immobilization</td>
<td>1.6, 0.7</td>
<td>(13), (14)</td>
</tr>
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<td></td>
<td><em>Artemia salina</em></td>
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<td>24 h</td>
<td>14</td>
<td>(15)</td>
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<tr>
<td></td>
<td></td>
<td><em>Palaemonetes pugio</em></td>
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<td>96 h</td>
<td>60</td>
<td>(16)</td>
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<tr>
<td></td>
<td></td>
<td><em>M. bahia</em></td>
<td>Invert.</td>
<td>96 h</td>
<td>1.99</td>
<td>(17)</td>
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<tr>
<td></td>
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<td><em>Danio rerio</em></td>
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<td>24, 96 h</td>
<td>4.25, 2.1</td>
<td>(18), (19)</td>
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<td></td>
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<td>2.05</td>
<td>(20)</td>
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<td><em>P. promelas</em></td>
<td>Fish</td>
<td>96 h</td>
<td>4.2</td>
<td>(21)</td>
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<tr>
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<td></td>
<td><em>O. mykiss</em></td>
<td>Fish</td>
<td>24 h</td>
<td>1.18</td>
<td>(19)</td>
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<td></td>
<td></td>
<td><em>L. macrochirus</em></td>
<td>Fish</td>
<td>96 h</td>
<td>4.3</td>
<td>(22)</td>
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<td></td>
<td></td>
<td><em>Cyprinodon variegatus</em></td>
<td>Fish</td>
<td>96 h</td>
<td>7.4</td>
<td>(23)</td>
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<td><em>Selenastrum capricornutum</em></td>
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<td>96 h Growth</td>
<td>0.57</td>
<td>(14)</td>
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<td></td>
<td><em>Scenedesmus pannonicus</em></td>
<td>Algae</td>
<td>72 h Growth</td>
<td>31</td>
<td>(13)</td>
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<td></td>
<td><em>S. subspicatus</em></td>
<td>Algae</td>
<td>48 h Growth, Biomass</td>
<td>38, 28</td>
<td>(22)</td>
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<tr>
<td>Compound</td>
<td>Category</td>
<td>Species</td>
<td>Trophic group</td>
<td>Endpoint/duration</td>
<td>LC50 (mg/L)</td>
<td>Additional tox. Values</td>
</tr>
<tr>
<td>--------------------------------</td>
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<td>N,N-diethyl-m-toluamide (DEET)b</td>
<td>Insect repellant</td>
<td>Skeletonema costatum</td>
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<td>96 h Growth</td>
<td>59.1</td>
<td>(17)</td>
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<tr>
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<td></td>
<td>D. magna</td>
<td>Invert.</td>
<td>48 h, 96 h</td>
<td>160, 108</td>
<td>(25)</td>
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<td>Gammarus fasciatus</td>
<td>Invert.</td>
<td>96 h</td>
<td>100</td>
<td>(26)</td>
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<tr>
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<td></td>
<td>P. promelas</td>
<td>Fish</td>
<td>96 h</td>
<td>110</td>
<td>(27)</td>
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<td></td>
<td>Gambusia affinis</td>
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<td>24–48 h</td>
<td>235</td>
<td>(28)</td>
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<td>Oncorhynchus mykiss</td>
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<td>96 h</td>
<td>71.3</td>
<td>(29)</td>
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<td></td>
<td></td>
<td>Chlorella protothecoides</td>
<td>Algae</td>
<td>4 h Photosynthesis</td>
<td>388</td>
<td>(30)</td>
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<td></td>
<td></td>
<td>Vibrio fischeri</td>
<td>Bacteria</td>
<td>Microtox</td>
<td>&gt;Sol.</td>
<td>(31)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pseudokirchneriella subcapitata</td>
<td>Algae</td>
<td>72 h</td>
<td>&gt;Sol.</td>
<td>(31)</td>
</tr>
<tr>
<td>Musk ambrette (MA)</td>
<td>Nitro musk</td>
<td>V. fischeri</td>
<td>Bacteria</td>
<td>Microtox</td>
<td>&gt;Sol.</td>
<td>(31)</td>
</tr>
<tr>
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<td></td>
<td>Nitocra spinipes</td>
<td>Invert.</td>
<td>96 h</td>
<td>&gt;1.0</td>
<td>(32)</td>
</tr>
<tr>
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<td></td>
<td>Acartia tonsa</td>
<td>Invert.</td>
<td>48 h</td>
<td>1.32</td>
<td>(33)</td>
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<tr>
<td></td>
<td></td>
<td>D. magna</td>
<td>Invert.</td>
<td>24, 48 h</td>
<td>&gt;Sol., 5.6</td>
<td>(33)</td>
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<td>D. magna</td>
<td>Invert.</td>
<td>48 h</td>
<td>&gt;0.46</td>
<td>(31)</td>
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<td></td>
<td>D. rerio</td>
<td>Fish</td>
<td>96 h Survival, Hatching</td>
<td>&gt;0.4</td>
<td>(28)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>P. subcapitata</td>
<td>Algae</td>
<td>72 h</td>
<td>&gt;Sol.</td>
<td>(31)</td>
</tr>
<tr>
<td>Musk ketone (MK)</td>
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<td>V. fischeri</td>
<td>Bacteria</td>
<td>Microtox</td>
<td>&gt;Sol.</td>
<td>(31)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>D. magna</td>
<td>Invert.</td>
<td>96 h</td>
<td>&gt;Sol.</td>
<td>(31)</td>
</tr>
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<td></td>
<td></td>
<td>Danio rerio</td>
<td>Fish</td>
<td>96 h Survival, Hatching</td>
<td>&gt;0.4</td>
<td>(34)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>P. subcapitata</td>
<td>Algae</td>
<td>72 h</td>
<td>&gt;Sol.</td>
<td>(31)</td>
</tr>
<tr>
<td>Musk moskene (MM)</td>
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<td>V. fischeri</td>
<td>Bacteria</td>
<td>Microtox</td>
<td>&gt;Sol.</td>
<td>(31)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>D. magna</td>
<td>Invert.</td>
<td>24 h</td>
<td>&gt;Sol.</td>
<td>(31)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Danio rerio</td>
<td>Fish</td>
<td>96 h Survival, Hatching</td>
<td>&gt;0.4</td>
<td>(34)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>P. subcapitata</td>
<td>Algae</td>
<td>72 h</td>
<td>&gt;Sol.</td>
<td>(31)</td>
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<tr>
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<td>Nitro musk</td>
<td>V. fischeri</td>
<td>Bacteria</td>
<td>Microtox</td>
<td>&gt;Sol.</td>
<td>(31)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>P. subcapitata</td>
<td>Algae</td>
<td>72 h</td>
<td>&gt;Sol.</td>
<td>(31)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>V. fischeri</td>
<td>Bacteria</td>
<td>Microtox</td>
<td>&gt;Sol.</td>
<td>(31)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>D. magna</td>
<td>Invert.</td>
<td>24, 48 h Mobility</td>
<td>EC50 ≤ Sol.</td>
<td>(35)</td>
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<tr>
<td></td>
<td></td>
<td>Oncorhynchus mykiss</td>
<td>Fish</td>
<td>96 h</td>
<td>&gt;1000</td>
<td>(36)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>L. macrochirus</td>
<td>Fish</td>
<td>96 h</td>
<td>1.2</td>
<td>(37)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>D. rerio</td>
<td>Fish</td>
<td>96 h Survival, Hatching</td>
<td>&gt;0.4</td>
<td>(34)</td>
</tr>
<tr>
<td>Compound</td>
<td>Category</td>
<td>Species</td>
<td>Trophic group</td>
<td>Endpoint /duration</td>
<td>LC50 (mg/L)</td>
<td>Additional tox. Values</td>
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<td>Celestolide (ADBI)</td>
<td>Polycyclic musk</td>
<td><em>P. subcapitata</em></td>
<td>Algae</td>
<td>72 h</td>
<td>&gt;Sol.</td>
<td>(31)</td>
</tr>
<tr>
<td></td>
<td></td>
<td><em>N. spinipes</em></td>
<td>Invert.</td>
<td>96 h</td>
<td>&gt;2.0</td>
<td>(38)</td>
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<tr>
<td></td>
<td></td>
<td><em>A. tonsa</em></td>
<td>Invert.</td>
<td>48 h</td>
<td>&gt;2.0</td>
<td>(38)</td>
</tr>
<tr>
<td></td>
<td></td>
<td><em>D. rerio</em></td>
<td>Fish</td>
<td>96 h Survival, Hatching</td>
<td>&gt;1.0</td>
<td>(38)</td>
</tr>
<tr>
<td></td>
<td></td>
<td><em>D. rerio</em></td>
<td>Fish</td>
<td>96 h Malformation</td>
<td>LOEC~0.65</td>
<td>(39)</td>
</tr>
<tr>
<td></td>
<td></td>
<td><em>O. latipes</em></td>
<td>Fish</td>
<td>96 h Survival</td>
<td>1.97</td>
<td>(40)</td>
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<tr>
<td>Galaxolide (HHCB)</td>
<td>Polycyclic musk</td>
<td><em>N. spinipes</em></td>
<td>Invert.</td>
<td>96 h</td>
<td>1.90</td>
<td>(28)</td>
</tr>
<tr>
<td></td>
<td></td>
<td><em>A. tonsa</em></td>
<td>Invert.</td>
<td>48 h</td>
<td>0.47</td>
<td>(38)</td>
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<td></td>
<td><em>Lampsilis cardium</em></td>
<td>Benthic invert.</td>
<td>24, 48 h</td>
<td>1.0, 0.99</td>
<td>(41)</td>
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<td></td>
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<td>Fish</td>
<td>96 h Survival, Hatching</td>
<td>&gt;0.67</td>
<td>(39)</td>
</tr>
<tr>
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<td><em>D. rerio</em></td>
<td>Fish</td>
<td>96 h Malformations</td>
<td>LOEC~0.45</td>
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<tr>
<td></td>
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<td><em>O. latipes</em></td>
<td>Fish</td>
<td>96 h Survival</td>
<td>0.95</td>
<td>(40)</td>
</tr>
<tr>
<td>Tonalide (AHTN)</td>
<td>Polycyclic musk</td>
<td><em>N. spinipes</em></td>
<td>Invert.</td>
<td>96 h</td>
<td>0.61</td>
<td>(31)</td>
</tr>
<tr>
<td></td>
<td></td>
<td><em>A. tonsa</em></td>
<td>Invert.</td>
<td>48 h</td>
<td>0.71</td>
<td>(32)</td>
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<td><em>L. cardium</em></td>
<td>Benthic invert.</td>
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<td></td>
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<td>96 h Malformation</td>
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<td>96 h Survival</td>
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<td>Traseolide (ATII)</td>
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<td>0.95</td>
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<td>Phantolide (AHMI)</td>
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<td>Cachmeran (DPMI)</td>
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<td>11.6</td>
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<td>Benzylparaben</td>
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<td>24 h, 28 h</td>
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<td>15 min, 30 min</td>
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<td>24 h, 48 h Mobility</td>
<td>5.2, 6.0</td>
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<td>48 h</td>
<td>3.3</td>
<td>(43)</td>
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<th>Endpoint /duration</th>
<th>LC50 (mg/L)</th>
<th>Additional tox. Values</th>
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<td>(43)</td>
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<td>25, 30</td>
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<td>(43)</td>
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<td>Fish</td>
<td>48 h</td>
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<td>(43)</td>
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<td>(43)</td>
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<td>Fish</td>
<td>48 h</td>
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<td>(43)</td>
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<td>25, 30</td>
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<td>15 min, 30 min</td>
<td>9.6, 10</td>
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<td>Bacteria</td>
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<td>24.6</td>
<td>(42)</td>
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<td>24 h, 48 h Mobility</td>
<td>32, 21</td>
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<td>48 h</td>
<td>&gt;Sol.</td>
<td>(43)</td>
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<td>(43)</td>
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<td>24 h, 48 h Mobility</td>
<td>13, 7</td>
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<td>9.7</td>
<td>(43)</td>
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<td>Benzophenone-3</td>
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<td>1.9</td>
<td>(44)</td>
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<td>Benzophenone-4</td>
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<td>48 h</td>
<td>50</td>
<td>(44)</td>
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<td>4-Methylbenzylidene camphor</td>
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<td>Invert.</td>
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<td>0.29</td>
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Review of Emerging Pollutants
<table>
<thead>
<tr>
<th>Compound</th>
<th>Category</th>
<th>Species</th>
<th>Trophic level</th>
<th>Endpoint/duration</th>
<th>LOEC (µg L(^{-1}))</th>
<th>NOEC (µg L(^{-1}))</th>
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<tbody>
<tr>
<td>Triclosan</td>
<td>Antimicrobial</td>
<td>D. magna</td>
<td>Invert.</td>
<td>21 d Survival, Reproduction</td>
<td>Repro.=200 (LOEC)</td>
<td>Surv.=200 (NOEC)</td>
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<td>C. dubia</td>
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<td>7 d Survival, Reproduction</td>
<td>50,6</td>
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<td>C. dubia</td>
<td>Invert.</td>
<td>7 d Survival, Reproduction</td>
<td>IC25=170</td>
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<td>Chironomus riparius</td>
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<td>28 d Survival</td>
<td>Emergence</td>
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<td>Chironomus tentans</td>
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<td>10 d Survival</td>
<td>Growth</td>
<td>LC25=100</td>
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<td>Hyalella azteca</td>
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<td>Growth</td>
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<tr>
<td>O. mykiss</td>
<td>Fish</td>
<td>96 d ELS(^{a}) Hatching, Survival</td>
<td>No Effect, 71.3</td>
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<td>O. latipes</td>
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<td>14 d Hatching</td>
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<td>200, No Effect, 200</td>
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<td>14 d Hatching</td>
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<td>200, No Effect, 200</td>
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<td>Gambusia affinis</td>
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<td>35 d Sperm Count, VTG</td>
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<td>Danio rerio</td>
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<td>IC25=160</td>
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<td>Xenopus laevis</td>
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<tr>
<td>Rana catesbeiana</td>
<td>Amphibian</td>
<td>18 d Development</td>
<td>300</td>
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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>
<thead>
<tr>
<th>Compound</th>
<th>Category</th>
<th>Species</th>
<th>Trophic level</th>
<th>Endpoint/duration</th>
<th>LOEC (µg L(^{-1}))</th>
<th>NOEC (µg L(^{-1}))</th>
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<td></td>
<td>24 d Survival, Growth</td>
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<td>Bufo americanus</td>
<td>Amphibian</td>
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<td>S. capricornutum</td>
<td>Algae</td>
<td>96 h Growth</td>
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<td>EC50 = 4.46</td>
<td>EC25 = 2.44</td>
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<td>S. subspicatus</td>
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<td>96 h Biomass, Growth Rate</td>
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<td>EC50 = 1.2, 1.4</td>
<td>EC50 = 0.5, 0.69</td>
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<td>Nitro musk</td>
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Musk (MM) moskene Nitro musk

Musk (MX) xylene Nitro musk

Celestolide Polycyclic

**Review of Emerging Pollutants** 52
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<th>Compound</th>
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<th>Trophic level</th>
<th>Endpoint/duration</th>
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<th>EC10</th>
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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

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<th>PNEC µg/L</th>
<th>PNEC µg/L</th>
<th>PNEC µg/L</th>
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### Review of Emerging Pollutants

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<td>0,29</td>
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<td></td>
<td></td>
<td>n/d</td>
<td></td>
</tr>
</tbody>
</table>

**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** Toxicity of different types of surfactants against various organisms. Modified form Ivankovic and Hrenovic, 2010.

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

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

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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 priority 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 of 95% 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 shows 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-pollutant**

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 BODs, 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**


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 assessment 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 processes 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 and 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 compound 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.](image)

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 (Kd) usually is considered for describing the behavior of several substances (Petrovic et al., 2016).

The sorption process is commonly described using several coefficients: (i) The soil adsorption coefficient (Kd) = concentration of chemical in soil/concentration of chemical substance in water; (ii) The organic matter adsorption coefficient (Koc) = concentration of chemical in organic matter/concentration of chemical in water (also referred as the organic carbon-water partition coefficient); and (iii) The octanol-water partition coefficient (Kow).

The Kd of many neutral hydrophobic organic compounds depends on the carbon content of the sorbent; therefore, a standard Koc sorption coefficient is defined for this type of compound. In addition, a relationship has been established between Koc and Kow (octanol-water coefficient). Because of the ease of measurement offered by the Kow versus the other coefficients, the use of Kow as a measure of sorption is widely used. The Koc coefficient does not take into account the non-hydrophobic interactions or other sorption mechanisms (also not considered by the Kow), which can lead to considerable under or over estimations (Tolls, 2001). The Kd 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 matrix (Petrovic et al., 2016).

**Volutilization**

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 reactor 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 promote catabolic 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 $k_{\text{biol}}$) 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 $k_{\text{biol}}$ 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). Conventional WWTPs generally operate in a controlled and 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 usually 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 pharmaceutical compounds**

The pharmaceutical 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 and their 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 WWTPs. 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*
<table>
<thead>
<tr>
<th>Therapeutic class</th>
<th>Pharmaceutical Compound</th>
<th>Average removal efficiencies CAS (%)</th>
<th>Average removal efficiencies MBR (%)</th>
<th>Negative removal efficiencies CAS (%)</th>
<th>Negative removal efficiencies MBR (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Analgesics / anti-inflammatories</td>
<td>5-Aminosalicylic acid</td>
<td>94</td>
<td>no available</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Acetaminophen</td>
<td>93</td>
<td>99</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Acetylsalicylic acid</td>
<td>90</td>
<td>no available</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Aminopyrine</td>
<td>38</td>
<td>no available</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Codeine</td>
<td>68</td>
<td>no available</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Dextropropoxyphene</td>
<td>no available</td>
<td>no available</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>Diclofenac</td>
<td>29</td>
<td>60</td>
<td>-12, -11, -111</td>
<td>-8, -7</td>
</tr>
<tr>
<td></td>
<td>Dipyrene</td>
<td>65</td>
<td>no available</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fenoprofen</td>
<td>82</td>
<td>no available</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Flurbiprofen</td>
<td>no available</td>
<td>no available</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hydrocrodone</td>
<td>no available</td>
<td>96</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ibuprofen</td>
<td>87</td>
<td>98</td>
<td>-4.4, -4.3, -13</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Indomethacin</td>
<td>37</td>
<td>43</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ketoprofen</td>
<td>56</td>
<td>70</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ketorolac</td>
<td>44</td>
<td>no available</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Meclomenamic acid</td>
<td>no available</td>
<td>no available</td>
<td></td>
<td></td>
</tr>
<tr>
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Review of Emerging Pollutants
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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 the biodegradability 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 necessarily 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. However, the removal processes are generally complex making extremely difficult to predict the potential removal mechanism by 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 shows compounds exhibiting a negative removal efficiencies in conventional WWTPs. This phenomenon can be explained by: (i) the presence of large concentration of particulate compounds in the raw wastewater not determined since only dissolved compounds are measured; (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 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 efficiencies 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 are released at the WWTP. Similar trends were observed for ciprofloxacin, 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).

<table>
<thead>
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<th>Compound</th>
<th>SRT (days)</th>
<th>Biotransform (%)</th>
<th>Sorption onto sludge (%)</th>
<th>Effluent (%)</th>
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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**
The effect of the temperature on drug removal on a laboratory-scale MBR reported that 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. The second evaluated WWTP was just provided with biological 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](image)

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.
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 pesticides families at the different WWTPs did not follow a similar pattern except the triazines whose concentration where higher at the effluent stream 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*
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 provided 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 either 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 evaluation, galaxolide, 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 solubility and has lowest $K_{oc}$. That is, higher concentrations of this compound are found in the effluent than in the sludge. In addition to the adsorption, cashmeram is also biotransformed in the reactor (Clara, et al. 2011). HHCB and AHTN presented removal efficiencies of 99 and 98%, respectively in lagoon systems (Lishman, et al. 2006). Lagoons performed better than CAS systems on the removal of these two compounds. A removal efficiency 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 report 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>
<thead>
<tr>
<th>Group</th>
<th>Surfactant</th>
<th>Influent dissolved µg/L</th>
<th>Effluent dissolved µg/L</th>
<th>Removal CAS %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anionic</td>
<td>LAS (Linear alkylbenzene sulfates)</td>
<td>2166</td>
<td>13.277</td>
<td>&gt; 99 (a)</td>
</tr>
<tr>
<td></td>
<td>AES (Alkyl ether sulfates)</td>
<td>400 - 4500</td>
<td>&lt; 1</td>
<td>99.9 (b)</td>
</tr>
<tr>
<td></td>
<td>AS (Alkyl sulfates)</td>
<td>&lt; 20 – 620</td>
<td>&lt; 1</td>
<td>99.9 (b)</td>
</tr>
<tr>
<td>Cationic</td>
<td>BAC - C12 (alkyl benzyl ammonium chlorides)</td>
<td></td>
<td></td>
<td>96.9 - &gt; 99 (a)</td>
</tr>
<tr>
<td></td>
<td>BAC - C14</td>
<td></td>
<td></td>
<td>94.8 - &gt; 99 (a)</td>
</tr>
</tbody>
</table>

Review of Emerging Pollutants
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 ethoxy 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 (positively 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 degraded (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.

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

*Figure 4-10 Mass balance for the investigated phthalate in two WWTPs ((a) WWTP 1 and (b) WWTP 2. Source: Clara, et al. 2010.*
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 efficiency 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 PFCs. 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 micropollutant) 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>
<thead>
<tr>
<th>Initial concentration</th>
<th>Source water</th>
<th>Ozonation conditions</th>
<th>Removal efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Hormone</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Estriol</td>
<td>100 mg/L</td>
<td>Ultrapure water</td>
<td>30 mL/min for 0-90 min, pH 3-4</td>
</tr>
<tr>
<td>Estrone</td>
<td>100 mg/L</td>
<td>Ultrapure water</td>
<td>30 mL/min for 0-90 min, pH 3-4</td>
</tr>
<tr>
<td></td>
<td>5-20 mg/L</td>
<td>Water</td>
<td>0.38 mg/min for 12 min, pH 6.5</td>
</tr>
<tr>
<td></td>
<td>5 mg/L</td>
<td>Ultrapure water</td>
<td>1.31 mg/min for 60 min, pH 6.5</td>
</tr>
<tr>
<td>17-b Estradiol</td>
<td>5-20 mg/L</td>
<td>Water</td>
<td>0.38 mg/min for 8 min, pH 6.5</td>
</tr>
<tr>
<td><strong>Antibiotics</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulfamethoxazole</td>
<td>0.15 mM</td>
<td>Ultrapure water</td>
<td>0.2 mM for 10 min, pH 2 and 8</td>
</tr>
<tr>
<td></td>
<td>0.05-5 mg/L</td>
<td>Water</td>
<td>2 mg/L for 60 min, pH 7</td>
</tr>
<tr>
<td></td>
<td>60 mg/L</td>
<td>Ultrapure water/wastewater</td>
<td>83 mg/L, pH 7.1, 17 °C</td>
</tr>
<tr>
<td></td>
<td>100 µg/L</td>
<td>Wastewater</td>
<td>14 mg/L, pH 7.1, 17 °C</td>
</tr>
<tr>
<td></td>
<td>1 mg/L</td>
<td>Deionized water</td>
<td>1.3-3.6 mg/L for 180 min, pH 2, 22 °C</td>
</tr>
<tr>
<td>Trimethoprim</td>
<td>50 µM</td>
<td>Ultrapure water</td>
<td>3.5 mg/L, pH 7</td>
</tr>
<tr>
<td>Erythromycin</td>
<td>0.68 µM</td>
<td>Ultrapure water</td>
<td>3.4 µM, 6.8 µM for 2 min, 20 °C</td>
</tr>
<tr>
<td>Ofloxacin</td>
<td>15 mg/L</td>
<td>Water</td>
<td>290 ml/min, pH 2,7,12, 25 °C</td>
</tr>
<tr>
<td></td>
<td>22 mg/L</td>
<td>Ultrapure water/wastewater</td>
<td>390 mL/min, pH 7.4, 25 °C</td>
</tr>
<tr>
<td>Ciprofloxacin</td>
<td>200 µg/L</td>
<td>Wastewater</td>
<td>7.5 mg/min for 30 min, pH 9</td>
</tr>
<tr>
<td></td>
<td>45.27 µM</td>
<td>Deionized water</td>
<td>2.5 g/L for 90 min, pH 7,27.5 °C, H2O2 concentration of 10 µmol/L</td>
</tr>
<tr>
<td></td>
<td>15 mg/L</td>
<td>Deionized water</td>
<td>2.5 g/L for 75 min, pH 7, 27.5 °C, H2O2 concentration of 10 µmol/L</td>
</tr>
<tr>
<td>Sulfadiazine</td>
<td>1 mg/L</td>
<td>Deionized water</td>
<td>1.1-3.1 mg/L for 180 min, pH 2, 22 °C</td>
</tr>
<tr>
<td>Sulfamethazine</td>
<td>10-40 mg/L</td>
<td>Deionized water</td>
<td>10-20 mg/L for 120 min, pH 3-11, catalyst 0.1-0.4 g/L</td>
</tr>
<tr>
<td>Tetracycline</td>
<td>2.08 mmol/L</td>
<td>Deionized water</td>
<td>0.53-1.13 mmol/L for 90 min, pH 7.8,</td>
</tr>
</tbody>
</table>

**Table 4-23 Removal by Ozone oxidation of PPCPs, Wang, and Wang, 2016.**
<table>
<thead>
<tr>
<th>Initial concentration</th>
<th>Source water</th>
<th>Ozonation conditions</th>
<th>Removal efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 mM</td>
<td>Deionized water</td>
<td>10 mg/min for 30 min, pH 7.0, 20 °C</td>
<td>100 (17)</td>
</tr>
<tr>
<td>426 µg/L</td>
<td>Drinking water</td>
<td>2 mg/L for 10 min, pH 7.3</td>
<td>&gt;89 (18)</td>
</tr>
<tr>
<td>1 mg/L</td>
<td>Ultrapure water</td>
<td>160 mg/L for 20 min, pH 9, 25°C</td>
<td>99 (19)</td>
</tr>
<tr>
<td>Lipid regulator</td>
<td>Bezafibrate</td>
<td>426 µg/L</td>
<td>Drinking water</td>
</tr>
<tr>
<td>Clorfibric acid</td>
<td>1 mg/L</td>
<td>Ultrapure water</td>
<td>100 (17)</td>
</tr>
<tr>
<td>Nonsteroidal anti-inflammatory drugs</td>
<td>Ibuprofen</td>
<td>1-10 mg/L</td>
<td>Ultrapure water</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8 mg/L</td>
<td>Ultrapure water</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30 mg/L</td>
<td>Ultrapure water</td>
</tr>
<tr>
<td></td>
<td>Paracetamol</td>
<td>1 µM</td>
<td>Ultrapure water</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5 mM</td>
<td>Ultrapure water</td>
</tr>
<tr>
<td></td>
<td>Naproxen</td>
<td>15 mg/L</td>
<td>Water</td>
</tr>
<tr>
<td></td>
<td>Phenazone</td>
<td>0.16 mM</td>
<td>Ultrapure water</td>
</tr>
<tr>
<td></td>
<td>Ketoprofen</td>
<td>0.1 mM</td>
<td>Ultrapure water</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50 µM</td>
<td>Natural water/ultrapure water</td>
</tr>
<tr>
<td>Beta-blocker</td>
<td>Atenolol</td>
<td>100 mg/L</td>
<td>Ultrapure water</td>
</tr>
<tr>
<td></td>
<td>Metoprolol</td>
<td>100 mg/L</td>
<td>Ultrapure water</td>
</tr>
<tr>
<td></td>
<td>Acebutolol</td>
<td>100 mg/L</td>
<td>Ultrapure water</td>
</tr>
<tr>
<td></td>
<td>Propanolol</td>
<td>10 µM</td>
<td>Water</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.38 mM</td>
<td>Ultrapure water</td>
</tr>
<tr>
<td>Antidepressant</td>
<td>Fluxetine</td>
<td>50 mg/L</td>
<td>Ultrapure water</td>
</tr>
<tr>
<td>Anticonvulsants</td>
<td>Carbamazepine</td>
<td>278 µg/L</td>
<td>Drinking water</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15 mg/L</td>
<td>Water</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10 mg/L</td>
<td>Ultrapure water</td>
</tr>
<tr>
<td></td>
<td></td>
<td>11 mg/L</td>
<td>Ultrapure water</td>
</tr>
<tr>
<td></td>
<td>Primidone</td>
<td>50 µM</td>
<td>Natural water/ultrapure water</td>
</tr>
</tbody>
</table>

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<table>
<thead>
<tr>
<th></th>
<th>Initial concentration</th>
<th>Source water</th>
<th>Ozonation conditions</th>
<th>Removal efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ifosfamide</td>
<td>20 mg/L</td>
<td>Deionized water</td>
<td>3 g/h for 15 min, pH 9, 11, 20 °C</td>
<td>100 (36)</td>
</tr>
<tr>
<td>Methotrexate</td>
<td>100 ng/L</td>
<td>Deionized water</td>
<td>10 mg/L for 2 h, pH 8.1, 20 °C</td>
<td>96 (37)</td>
</tr>
<tr>
<td>Cyclophosphamide</td>
<td>20 mg/L</td>
<td>Deionized water</td>
<td>3 g/h for 15 min, pH 9, 11, 20 °C</td>
<td>100 (36)</td>
</tr>
<tr>
<td></td>
<td>200 ng/L</td>
<td>Drinking Water</td>
<td>10 mg/L for 2 h, pH 8.1, 20 °C</td>
<td>&gt;90 (37)</td>
</tr>
</tbody>
</table>

**Diagnostic Contrast Media**

<table>
<thead>
<tr>
<th></th>
<th>Initial concentration</th>
<th>Source water</th>
<th>Ozonation conditions</th>
<th>Removal efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iopromide</td>
<td>114 µg/L</td>
<td>River water</td>
<td>0.5-2.0 mg/L for 15 min, pH 7.4, 25 °C</td>
<td>47-92 (38)</td>
</tr>
<tr>
<td></td>
<td>1 µg/L</td>
<td>WTPs effluents/synthetic water</td>
<td>1-3 mg/L for 10 min, pH 8</td>
<td>20-70 (39)</td>
</tr>
<tr>
<td></td>
<td>10 mg/L</td>
<td>Ultrapure water</td>
<td>16 mg/L for 30 min, pH 7.5, 21 °C</td>
<td>~60 (40)</td>
</tr>
<tr>
<td>Iomeprol</td>
<td>10 mg/L</td>
<td>Ultrapure water</td>
<td>16 mg/L for 30 min, pH 7.5, 21 °C</td>
<td>55 (40)</td>
</tr>
<tr>
<td>Diatrizoate</td>
<td>50 µM</td>
<td>Natural water/ultrapure water</td>
<td>80 µM for 20 min, pH 3.9, 20 °C</td>
<td>100 (41)</td>
</tr>
<tr>
<td></td>
<td>10 mg/L</td>
<td>Ultrapure water</td>
<td>16 mg/L for 30 min, pH 7.5, 21 °C</td>
<td>26 (42)</td>
</tr>
</tbody>
</table>

**Fragrances**

<table>
<thead>
<tr>
<th></th>
<th>Initial concentration</th>
<th>Source water</th>
<th>Ozonation conditions</th>
<th>Removal efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Musk xylene</td>
<td>200-400 µg/L</td>
<td>Tap water</td>
<td>5 mg/L for 120 min, 28 °C</td>
<td>no removal (43)</td>
</tr>
<tr>
<td>Musk ketone</td>
<td>200-400 µg/L</td>
<td>Tap water</td>
<td>5 mg/L for 120 min, 28 °C</td>
<td>no removal (43)</td>
</tr>
</tbody>
</table>

**Preservatives**

<table>
<thead>
<tr>
<th></th>
<th>Initial concentration</th>
<th>Source water</th>
<th>Ozonation conditions</th>
<th>Removal efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methylyparaben</td>
<td>100 µM</td>
<td>Ultrapure water</td>
<td>0.67 g/h for 12 min, pH 6.9, 25 °C</td>
<td>99 (44)</td>
</tr>
</tbody>
</table>

**Disinfectants**

<table>
<thead>
<tr>
<th></th>
<th>Initial concentration</th>
<th>Source water</th>
<th>Ozonation conditions</th>
<th>Removal efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triclosan</td>
<td>1.4-4.5 mg/L</td>
<td>Water</td>
<td>1.1-1.7 mg/L, pH 7, room temperature</td>
<td>94-99.9 (45)</td>
</tr>
</tbody>
</table>

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., 2014; (19) Quero-Pastor et al., 2014; (20) Quero-Pastor et al., 2014; (21) Sein et al., 2009; (22) Beltrán et al., 2009; (23) El Najjar et al., 2014; (24) Neamtu 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., 2015; (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 regarding 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 filtration as 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 beneficial.

Several studies evaluated the removal of emerging contaminants by combining UV with hydrogen peroxide (advanced oxidation process). This process consists of the generation of hydroxyl 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>
<thead>
<tr>
<th>Compounds</th>
<th>Initial concentration</th>
<th>Source water</th>
<th>Conditions</th>
<th>Removal efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Hormone</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Estriol</td>
<td>N.A.</td>
<td>River water</td>
<td>1000 mJ/cm², 15 mg/L H₂O₂, pH 7.0</td>
<td>&gt;95 (1)</td>
</tr>
<tr>
<td>Estrone</td>
<td>50 µg/L</td>
<td>Deionized water</td>
<td>350 µW/cm², 25 °C, 50 min, H₂O₂ = 15 mg/L</td>
<td>&gt;60 (2)</td>
</tr>
<tr>
<td>17-b Estradiol</td>
<td>50 µg/L</td>
<td>Deionized water</td>
<td>350 µW/cm², 25 °C, 120 min, H₂O₂ = 15 mg/L</td>
<td>&gt;90 (2)</td>
</tr>
<tr>
<td><strong>Antibiotics</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulfamethoxazole</td>
<td>120 ng/L</td>
<td>Wastewater</td>
<td>2768 mJ/cm²; room temperature, pH 6.5 , H₂O₂ = 1.72 g/L, 15 min</td>
<td>100 (3)</td>
</tr>
<tr>
<td></td>
<td>578 ng/L</td>
<td>Wastewater</td>
<td>550 w/m², 17 °C, pH 2.5, H₂O₂ = 50 mg/L, 30 min</td>
<td>100 (4)</td>
</tr>
</tbody>
</table>

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<table>
<thead>
<tr>
<th>Compounds</th>
<th>Initial concentration</th>
<th>Source water</th>
<th>Conditions</th>
<th>Removal efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trimethoprim</td>
<td>~95 ng/L</td>
<td>Wastewater</td>
<td>2768 mJ/cm²; room temperature, pH 6.5, H₂O₂ = 1.72 g/L, 15 min</td>
<td>100 (3)</td>
</tr>
<tr>
<td></td>
<td>10 uM</td>
<td>Synthetic fresh and hydrolyzed human urines</td>
<td>2.57 x 10⁻⁶ E L⁻¹ s⁻¹, pH 9, H₂O₂ = 294 uM</td>
<td>&gt;99 (6)</td>
</tr>
<tr>
<td></td>
<td>131 ng/L</td>
<td>Wastewater</td>
<td>550 w/m², 17 °C, pH 2.5, H₂O₂ = 50 mg/L, 30 min</td>
<td>100 (4)</td>
</tr>
<tr>
<td></td>
<td>68.9 µM</td>
<td>Ultrapure water</td>
<td>2000 mJ/cm², room temperature, pH 7.4, H₂O₂ = 10 mg/L, 30 min</td>
<td>&gt;99 (7)</td>
</tr>
<tr>
<td>Amoxicillin</td>
<td>25 mg/L</td>
<td>Distilled water</td>
<td>2768 mJ/cm²; room temperature, pH 6.5, H₂O₂ = 1.72 g/l, 15 min</td>
<td>~90 (8)</td>
</tr>
<tr>
<td>Erythromycin</td>
<td>110 ng/L</td>
<td>Wastewater</td>
<td>2768 mJ/cm²; room temperature, pH 6.5, H₂O₂ = 1.72 g/l, 15 min</td>
<td>~98 (3)</td>
</tr>
<tr>
<td></td>
<td>2.48 µg/L</td>
<td>Ultrapure water</td>
<td>500 mJ/cm²; pH 6.5, H₂O₂ = 10 mg/L,</td>
<td>&gt;99 (5)</td>
</tr>
<tr>
<td>Ofloxacin</td>
<td>41 ng/L</td>
<td>Wastewater</td>
<td>550 w/m², 17 °C, pH 2.5, H₂O₂ = 50 mg/L, 30 min</td>
<td>100 (4)</td>
</tr>
<tr>
<td>Ciprofloxacin</td>
<td>129 ng/L</td>
<td>Wastewater</td>
<td>550 w/m², 17 °C, pH 2.5, H₂O₂ = 50 mg/L, 30 min</td>
<td>100 (4)</td>
</tr>
<tr>
<td></td>
<td>6.04 µM</td>
<td>Ultrapure water</td>
<td>2000 mJ/cm², room temperature, pH 7.4, H₂O₂ = 10 mg/L, 30 min</td>
<td>&gt;99 (7)</td>
</tr>
<tr>
<td>Penicillin</td>
<td>29.9 µM</td>
<td>Ultrapure Water</td>
<td>2000 mJ/cm², room temperature, pH 7.4, H₂O₂ = 10 mg/L, 30 min</td>
<td>&gt;99 (7)</td>
</tr>
<tr>
<td>Tylosin</td>
<td>65 µM</td>
<td>Nanopure water</td>
<td>7.2 x 10⁻⁵ E s⁻¹, 25 °C, pH 3.0, H₂O₂ = 3 mM, 3 min</td>
<td>100 (9)</td>
</tr>
<tr>
<td>Enoxacin</td>
<td>0.06 mM</td>
<td>Ultrapure water</td>
<td>2 x 10⁶ photon s⁻¹, H₂O₂ = 0.05 mM, 30 min</td>
<td>100 (10)</td>
</tr>
<tr>
<td>Tetracycline</td>
<td>~70 ng/L</td>
<td>Wastewater</td>
<td>2768 mJ/cm²; room temperature, pH 6.5, H₂O₂ = 1.72 g/L, 15 min</td>
<td>~99 (3)</td>
</tr>
<tr>
<td>Lipid regulator</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bezafibrate</td>
<td>120 ng/L</td>
<td>Wastewater</td>
<td>2768 mJ/cm²; room temperature, pH 6.5, H₂O₂ = 1.72 g/L, 15 min</td>
<td>100 (3)</td>
</tr>
<tr>
<td></td>
<td>426 ng/L</td>
<td>Wastewater</td>
<td>550 w/m², 17 °C, pH 2.5, H₂O₂ = 50 mg/L, 30 min</td>
<td>100 (4)</td>
</tr>
<tr>
<td></td>
<td>1 µg/L</td>
<td>Ultrapure water</td>
<td>500 mJ/cm²; pH 6.5, H₂O₂ = 10 mg/L,</td>
<td>&gt;90 (5)</td>
</tr>
<tr>
<td>Clorfluracid</td>
<td>1 mg/L</td>
<td>Distilled-deionized water</td>
<td>UV 254 nm, 25 °C, pH 5, 30 min, H₂O₂ = 11 mM</td>
<td>&gt;60 (11)</td>
</tr>
<tr>
<td></td>
<td>~10 ng/L</td>
<td>Wastewater</td>
<td>2768 mJ/cm²; room temperature, pH 6.5, H₂O₂ = 1.72 g/L, 15 min</td>
<td>&gt;90 (3)</td>
</tr>
<tr>
<td></td>
<td>1.0 µg/L</td>
<td>Ultrapure Water</td>
<td>500 mJ/cm²; pH 6.5, H₂O₂ = 10 mg/L,</td>
<td>&gt;99 (5)</td>
</tr>
<tr>
<td></td>
<td>10 mg/L</td>
<td>Ultrapure Water</td>
<td>2.09 x 10⁻⁵ Einstein cm⁻² s⁻¹, 30°C, pH 7.1, H₂O₂ = 100 mg/L, 15 min</td>
<td>99.6</td>
</tr>
<tr>
<td></td>
<td>46.7 mM</td>
<td>Deionized water</td>
<td>2.12 w/cm², H₂O₂ = 1 mM, 60 min</td>
<td>100 (12)</td>
</tr>
<tr>
<td>Compounds</td>
<td>Initial concentration</td>
<td>Source water</td>
<td>Conditions</td>
<td>Removal efficiency (%)</td>
</tr>
<tr>
<td>----------------------------</td>
<td>-----------------------</td>
<td>--------------------</td>
<td>-----------------------------------------------------------------------------</td>
<td>------------------------</td>
</tr>
<tr>
<td>Gemfibrozil</td>
<td>25 ng/L</td>
<td>Wastewater</td>
<td>550 w/m², 17 °C, pH 2.5, H₂O₂ = 50 mg/L, 30 min</td>
<td>&gt;100 (4)</td>
</tr>
<tr>
<td></td>
<td>1.0 µg/L</td>
<td>Ultrapure water</td>
<td>500 mJ/cm²; pH 6.5, H₂O₂ = 10 mg/L</td>
<td>&gt;99 (5)</td>
</tr>
<tr>
<td>Nonsteroidal anti-inflammatory drugs</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ibuprofen</td>
<td>112 ng/L</td>
<td>Wastewater</td>
<td>550 w/m², 17 °C, pH 2.5, H₂O₂ = 50 mg/L, 30 min</td>
<td>100 (4)</td>
</tr>
<tr>
<td></td>
<td>95.82 µM</td>
<td>Nanopure water</td>
<td>7.2x10^5 E s⁻¹, 25 °C, pH 7.0, H₂O₂ = 1 mM, 3 min</td>
<td>100 (9)</td>
</tr>
<tr>
<td>Diclofenac</td>
<td>1 mg/L</td>
<td>Distilled-deionized water</td>
<td>UV 254 nm, 25 °C, pH 5, 30 min, H₂O₂ = 11 mM</td>
<td>100 (11)</td>
</tr>
<tr>
<td></td>
<td>~90 ng/L</td>
<td>Wastewater</td>
<td>2768 mJ/cm²; room temperature, pH 6.5, H₂O₂ = 1.72 g/L, 15 min</td>
<td>100 (3)</td>
</tr>
<tr>
<td></td>
<td>518 ng/L</td>
<td>Wastewater</td>
<td>550 w/m², 17 °C, pH 2.5, H₂O₂ = 50 mg/L, 30 min</td>
<td>100 (4)</td>
</tr>
<tr>
<td></td>
<td>31.4 µM</td>
<td>Deionized water</td>
<td>2.12 w/cm², H₂O₂ = 1 mM, 60 min</td>
<td>100 (12)</td>
</tr>
<tr>
<td>Naproxen</td>
<td>~5 ng/L</td>
<td>Wastewater</td>
<td>2768 mJ/cm²; room temperature, pH 6.5, H₂O₂ = 1.72 g/L, 15 min</td>
<td>100 (3)</td>
</tr>
<tr>
<td></td>
<td>178 ng/L</td>
<td>Wastewater</td>
<td>550 w/m², 17 °C, pH 2.5, H₂O₂ = 50 mg/L, 30 min</td>
<td>100 (4)</td>
</tr>
<tr>
<td>Acetaminophen</td>
<td>~9 ng/L</td>
<td>Wastewater</td>
<td>2768 mJ/cm²; room temperature, pH 6.5, H₂O₂ = 1.72 g/L, 15 min</td>
<td>~90 (3)</td>
</tr>
<tr>
<td>Ketoprofen</td>
<td>100 ng/L</td>
<td>Wastewater</td>
<td>2768 mJ/cm²; room temperature, pH 6.5, H₂O₂ = 1.72 g/L, 15 min</td>
<td>100 (3)</td>
</tr>
<tr>
<td></td>
<td>123 ng/L</td>
<td>Wastewater</td>
<td>550 w/m², 17 °C, pH 2.5, H₂O₂ = 50 mg/L, 30 min</td>
<td>100 (4)</td>
</tr>
<tr>
<td>Beta blocker</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Atenolol</td>
<td>~90 ng/L</td>
<td>Wastewater</td>
<td>2768 mJ/cm²; room temperature, pH 6.5, H₂O₂ = 1.72 g/L, 15 min</td>
<td>100 (3)</td>
</tr>
<tr>
<td></td>
<td>669 ng/L</td>
<td>Wastewater</td>
<td>550 w/m², 17 °C, pH 2.5, H₂O₂ = 50 mg/L, 30 min</td>
<td>100 (4)</td>
</tr>
<tr>
<td></td>
<td>1.0 µg/L</td>
<td>Ultrapure water</td>
<td>500 mJ/cm²; pH 6.5, H₂O₂ = 10 mg/L</td>
<td>&gt;90 (5)</td>
</tr>
<tr>
<td>Metoprolol</td>
<td>~85 ng/L</td>
<td>Wastewater</td>
<td>2768 mJ/cm²; room temperature, pH 6.5, H₂O₂ = 1.72 g/L, 15 min</td>
<td>100 (3)</td>
</tr>
<tr>
<td></td>
<td>179 ng/L</td>
<td>Wastewater</td>
<td>550 w/m², 17 °C, pH 2.5, H₂O₂ = 50 mg/L, 30 min</td>
<td>100 (4)</td>
</tr>
<tr>
<td></td>
<td>1.0 µg/L</td>
<td>Ultrapure water</td>
<td>500 mJ/cm²; pH 6.5, H₂O₂ = 10 mg/L</td>
<td>&gt;99 (5)</td>
</tr>
<tr>
<td>Propanolol</td>
<td>~70 ng/L</td>
<td>Wastewater</td>
<td>2768 mJ/cm²; room temperature, pH 6.5, H₂O₂ = 1.72 g/L, 15 min</td>
<td>100 (3)</td>
</tr>
<tr>
<td>Sotalol</td>
<td>260 ng/L</td>
<td>Wastewater</td>
<td>550 w/m², 17 °C, pH 2.5, H₂O₂ = 50 mg/L, 30 min</td>
<td>100 (4)</td>
</tr>
<tr>
<td>Antidepressant</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diazepam</td>
<td>~90 ng/L</td>
<td>Wastewater</td>
<td>2768 mJ/cm²; room temperature, pH 6.5, H₂O₂ = 1.72 g/L, 15 min</td>
<td>100 (3)</td>
</tr>
<tr>
<td>Anticonvulsants</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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### Compounds

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

(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) BŁeđza 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 contrasted with 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](image)

**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 combines 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, propranolol, 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>
<thead>
<tr>
<th>Compound</th>
<th>MQL, ng/L</th>
<th>c (Primary effluent), µg/L</th>
<th>Elimination from the aqueous phase (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Range</td>
<td>Mean</td>
</tr>
<tr>
<td><strong>Analgesics and anti-inflammatory drugs</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ibuprofen</td>
<td>115.3</td>
<td>14.6–31.3</td>
<td>21.7</td>
</tr>
<tr>
<td>Naproxen</td>
<td>65.1</td>
<td>0.13–0.67</td>
<td>0.463</td>
</tr>
<tr>
<td>Ketoprofen</td>
<td>139.0</td>
<td>0.70–1.2</td>
<td>1.08</td>
</tr>
<tr>
<td>Diclofenac</td>
<td>96.2</td>
<td>1.0–1.6</td>
<td>1.32</td>
</tr>
<tr>
<td>Mefenamic acid</td>
<td>5.3</td>
<td>0.80–1.2</td>
<td>1.07</td>
</tr>
<tr>
<td>Propyphenazone</td>
<td>4.8</td>
<td>0.046–0.097</td>
<td>0.065</td>
</tr>
<tr>
<td>Acetaminophen</td>
<td>75.3</td>
<td>7.1–11.4</td>
<td>9.90</td>
</tr>
<tr>
<td>Indomethacin</td>
<td>134.7</td>
<td>0.66–1.0</td>
<td>0.875</td>
</tr>
<tr>
<td><strong>Anti-histamines</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ranitidine</td>
<td>8.2</td>
<td>0.072–0.54</td>
<td>0.347</td>
</tr>
<tr>
<td>Loratidine</td>
<td>12.7</td>
<td>0.015–0.043</td>
<td>0.028</td>
</tr>
<tr>
<td>Famotidine</td>
<td>1.2</td>
<td>0.027–0.14</td>
<td>0.080</td>
</tr>
<tr>
<td><strong>Anti-epileptic drug</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbamazepine</td>
<td>15.8</td>
<td>0.054–0.22</td>
<td>0.156</td>
</tr>
<tr>
<td><strong>Psychiatric drugs</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fluoxetine</td>
<td>32.5</td>
<td>0.12–2.3</td>
<td>0.573</td>
</tr>
<tr>
<td><strong>Antibiotics</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Erythromycin</td>
<td>12.8</td>
<td>0.32–2.7</td>
<td>0.82</td>
</tr>
<tr>
<td>Sulfamethoxazole</td>
<td>1.7</td>
<td>0.25–1.3</td>
<td>0.093</td>
</tr>
<tr>
<td>Ofloxacin</td>
<td>21.5</td>
<td>0.89–31.7</td>
<td>10.5</td>
</tr>
<tr>
<td>Trimethoprim</td>
<td>5.5</td>
<td>0.15–0.43</td>
<td>0.204</td>
</tr>
<tr>
<td><strong>β-blockers</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Atenolol</td>
<td>8.2</td>
<td>0.84–2.8</td>
<td>2.0</td>
</tr>
<tr>
<td>Sotalol</td>
<td>9.2</td>
<td>0.17–0.85</td>
<td>0.509</td>
</tr>
<tr>
<td>Metoprolol</td>
<td>2.3</td>
<td>0.026–0.063</td>
<td>0.039</td>
</tr>
<tr>
<td>Compound</td>
<td>MQL, ng/L</td>
<td>c (Primary effluent), µg/L</td>
<td>Elimination from the aqueous phase (%)</td>
</tr>
<tr>
<td>----------------------------------------</td>
<td>-----------</td>
<td>-----------------------------</td>
<td>----------------------------------------</td>
</tr>
<tr>
<td>Propranolol</td>
<td>8.6</td>
<td>0.108–1.13 0.292</td>
<td>58.8 ± 24.5 77.6 ± 12.2 65.5 ± 22.4</td>
</tr>
<tr>
<td>Glibenclamide</td>
<td>25.8</td>
<td>0.12–15.9 9.89</td>
<td>46.1 ± 40.8 95.6 ± 4.4 82.2 ± 28.6</td>
</tr>
<tr>
<td>Gemfibrozil</td>
<td>11.5</td>
<td>2.0–5.9 3.08</td>
<td>n.e. 42.2 ± 36.7 32.5 ± 49.3</td>
</tr>
<tr>
<td>Bezafibrate</td>
<td>15.6</td>
<td>1.9–29.8 14.9</td>
<td>80.8 ± 20.9 90.3 ± 10.1 88.2 ± 15.3</td>
</tr>
<tr>
<td>Pravastatin</td>
<td>47.3</td>
<td>0.46–1.5 0.886</td>
<td>59.4 ± 16.2 86.1 ± 9.1 83.1 ± 12.5</td>
</tr>
<tr>
<td>Hydrochlorothiazide</td>
<td>17.3</td>
<td>2.3–4.8 2.74</td>
<td>n.e. n.e. n.e.</td>
</tr>
</tbody>
</table>

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

Table 4-26 Removal of PPCPs by activated carbon (Wang, and Wang, 2016).
### Compounds

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Adsorbent</th>
<th>Initial concentration</th>
<th>Source water</th>
<th>qm (mg/g)</th>
<th>Removal efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Antidepressants</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diazepam</td>
<td>PAC (5 mg/L)</td>
<td>100 ng/L</td>
<td>Surface water</td>
<td>n.a.</td>
<td>~65 (1)</td>
</tr>
<tr>
<td><strong>Anticonvulsants</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbamazepine</td>
<td>PAC (5 mg/L)</td>
<td>100 ng/L</td>
<td>Surface water</td>
<td>n.a.</td>
<td>~70 (1)</td>
</tr>
<tr>
<td></td>
<td>GAC (10 mg/L)</td>
<td>500 ng/L</td>
<td>Synthetic water</td>
<td>3.2 mg/g</td>
<td>100 (6)</td>
</tr>
<tr>
<td>Primidone</td>
<td>PAC (50 mg/L)</td>
<td>900 ng/L</td>
<td>WWTPs effluents</td>
<td>n.a.</td>
<td>92 (2)</td>
</tr>
<tr>
<td></td>
<td>PAC (20 mg/L)</td>
<td>100 ng/L</td>
<td>Synthetic water</td>
<td>n.a.</td>
<td>~95 (3)</td>
</tr>
<tr>
<td></td>
<td>PAC (50 mg/L)</td>
<td>2.5 µg/L</td>
<td>WWTPs effluents</td>
<td>n.a.</td>
<td>90 (2)</td>
</tr>
<tr>
<td></td>
<td>PAC (5 mg/L)</td>
<td>100 ng/L</td>
<td>Surface water</td>
<td>n.a.</td>
<td>~30 (1)</td>
</tr>
<tr>
<td></td>
<td>PAC (50 mg/L)</td>
<td>15.4 µg/L</td>
<td>WWTPs effluents</td>
<td>n.a.</td>
<td>~40 (2)</td>
</tr>
<tr>
<td></td>
<td>PAC (5 mg/L)</td>
<td>100 ng/L</td>
<td>Surface water</td>
<td>n.a.</td>
<td>~60 (1)</td>
</tr>
<tr>
<td></td>
<td>PAC (50 mg/L)</td>
<td>100 ng/L</td>
<td>Surface water</td>
<td>n.a.</td>
<td>~65 (1)</td>
</tr>
<tr>
<td></td>
<td>PAC (5 mg/L)</td>
<td>100 ng/L</td>
<td>Surface water</td>
<td>n.a.</td>
<td>~90 (1)</td>
</tr>
</tbody>
</table>

(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 between 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 $K_{ow}$ 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:

<table>
<thead>
<tr>
<th>Name of priority substance</th>
<th>CAS</th>
<th>Identified as priority</th>
<th>Anual Average-EQS</th>
<th>Maximum Allowable</th>
</tr>
</thead>
</table>

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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:

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

(**) 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.

<table>
<thead>
<tr>
<th>Name of substance</th>
<th>CAS number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbamazepine</td>
<td>298-46-4</td>
</tr>
<tr>
<td>2-(4-isobutylphenyl)propionic Acid</td>
<td>51146-56-6</td>
</tr>
<tr>
<td>Fluoxetine</td>
<td>54910-89-3</td>
</tr>
<tr>
<td>Chloramphenicol</td>
<td>56-75-7</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Name of substance</th>
<th>CAS number</th>
<th>Maximum acceptable method detection limit (**)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Estrone</td>
<td>53-16-7</td>
<td>0,4 ng/l</td>
</tr>
</tbody>
</table>

(**) Directive 2015/495/UE
## Expected results

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

### 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 Physico-chemical properties of the selected pharmaceuticals. Modified from Verlicchi, et al., 2012

<table>
<thead>
<tr>
<th>Pharmaceutical</th>
<th>Chemical formula</th>
<th>MW</th>
<th>Chemical formula</th>
<th>Log ( K_{ow} )</th>
<th>Log ( K_{a} )</th>
<th>Log ( S_{w} )</th>
<th>( K_{biot} )</th>
<th>Charge at pH 7</th>
<th>Molecular structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Analgesics/Anti-inflammatories</td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Diclofenac CAS # 15307-86-5</td>
<td>C₁₄H₁₁Cl₂NO₂</td>
<td>296</td>
<td></td>
<td>4.15</td>
<td>4.51/0.7</td>
<td>4.52</td>
<td>1.2</td>
<td>&lt;0.04-1.2</td>
<td>Negative</td>
</tr>
<tr>
<td>Ibuprofen CAS # 15687-27-1</td>
<td>C₁₃H₁₈O₂</td>
<td>206</td>
<td></td>
<td>4.51</td>
<td>3.97/0.45</td>
<td>41.05</td>
<td>0.9</td>
<td>1.5-20</td>
<td>Negative</td>
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<tr>
<td>Antibiotics</td>
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<td></td>
</tr>
<tr>
<td>Chloramphenicol CAS # 56-75-7</td>
<td>C₁₁H₁₂Cl₂N₂O₅</td>
<td>323</td>
<td></td>
<td>5.5</td>
<td>1.14</td>
<td>388.5</td>
<td></td>
<td>Neut./Neg.</td>
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<td>Psychiatric drugs</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Carbamazepine CAS # 298-46-4</td>
<td>C₁₅H₁₂N₂O</td>
<td>236</td>
<td></td>
<td>13.9</td>
<td>2.45</td>
<td>17.66</td>
<td>0.1</td>
<td>≤0.1</td>
<td>Neutral</td>
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</tr>
<tr>
<td>Fluoxetine CAS # 54910-89-3</td>
<td>C₁₇H₁₃F₃NO</td>
<td>309</td>
<td></td>
<td>9.5</td>
<td>4.05</td>
<td>38.35</td>
<td>0.7</td>
<td>5-9</td>
<td>positive</td>
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<tr>
<td>Hormones</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Estradiol CAS # 50-28-2</td>
<td>C₁₈H₂₄O₂</td>
<td>272</td>
<td></td>
<td>10.27</td>
<td>3.94</td>
<td>81.97</td>
<td>2.4-2.8</td>
<td>175-460</td>
<td>Neutral</td>
</tr>
<tr>
<td>Estrone CAS # 53-16-7</td>
<td>C₁₈H₂₂O₂</td>
<td>270</td>
<td></td>
<td>10.25</td>
<td>3.43</td>
<td>146.8</td>
<td>2.4-2.9</td>
<td>10-162</td>
<td>Neutral</td>
</tr>
<tr>
<td>Ethinylestradiol CAS # 57-63-6</td>
<td>C₂₀H₂₄O₂</td>
<td>296</td>
<td></td>
<td>10.24</td>
<td>4.12</td>
<td>116.4</td>
<td>2.5-2.8</td>
<td>0.4-20</td>
<td>Neutral</td>
</tr>
</tbody>
</table>
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 (\(k_{\text{biol}}\)) 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 \(k_{\text{biol}}\) between 0.1 and 10 L/(gSS d), which implies quite good biodegradability.

If we observe the water-octanol partition coefficient (\(K_{\text{ow}}\)) 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**

<table>
<thead>
<tr>
<th>Class by use</th>
<th>Name of substance</th>
<th>Average concentration raw influent (µg/L)</th>
<th>Average concentration effluent (µg/L)</th>
<th>Average Percentage removal efficiencies in WWTP with CAS (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Analgesic/anti-inflammatory</td>
<td>Diclofenac</td>
<td>1</td>
<td>0.8</td>
<td>29</td>
</tr>
<tr>
<td></td>
<td>Ibuprofen</td>
<td>37</td>
<td>3.6</td>
<td>87</td>
</tr>
<tr>
<td>Antibiotics</td>
<td>Chloramphenicol</td>
<td>1</td>
<td>0.05</td>
<td>95</td>
</tr>
<tr>
<td>Psychiatric drugs</td>
<td>Carbamazepine</td>
<td>1.2</td>
<td>1.04</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>Fluoxetine</td>
<td>0.54</td>
<td>0.24</td>
<td>56</td>
</tr>
<tr>
<td>Hormones</td>
<td>Estradiol</td>
<td>0.25</td>
<td>0.01</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td>Estrone</td>
<td>0.08</td>
<td>0.03</td>
<td>76</td>
</tr>
<tr>
<td></td>
<td>Ethinylestradiol</td>
<td>0.02</td>
<td>0.003</td>
<td>78</td>
</tr>
</tbody>
</table>

The ibuprofen is one of the compounds in the Analgesic/anti-inflammatory 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 affluent. 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.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Sludge age (days)</th>
<th>Biolotransform (%)</th>
<th>Sorption onto sludge (%)</th>
<th>Effluent (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diclofenac</td>
<td>4–60</td>
<td>5–45</td>
<td>&lt;5</td>
<td>55–95</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>25</td>
<td>&lt;5</td>
<td>70–75</td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>10</td>
<td>5</td>
<td>85</td>
</tr>
<tr>
<td></td>
<td>&lt;20</td>
<td>5</td>
<td>0</td>
<td>95</td>
</tr>
<tr>
<td></td>
<td>&gt;50</td>
<td>10–30</td>
<td>0</td>
<td>70–90</td>
</tr>
<tr>
<td>Ibuprofen</td>
<td>4–60</td>
<td>90–100</td>
<td>&lt;5</td>
<td>0–10</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>95–100</td>
</tr>
<tr>
<td></td>
<td>&lt;20</td>
<td>35–40</td>
<td>0</td>
<td>60–65</td>
</tr>
<tr>
<td></td>
<td>&gt;50</td>
<td>95</td>
<td>0</td>
<td>5</td>
</tr>
</tbody>
</table>

Review of Emerging Pollutants 102
### Compound Sludge age (days) Biolotransform (%) Sorption onto sludge (%) Effluent (%)

<table>
<thead>
<tr>
<th>Compound</th>
<th>6</th>
<th>0</th>
<th>0</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloramphenicol</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fluoxetine</td>
<td>&lt;20</td>
<td>80</td>
<td>0</td>
<td>20</td>
</tr>
<tr>
<td>&gt;50</td>
<td></td>
<td>90</td>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td>Estradiol</td>
<td>10–30</td>
<td>85–99</td>
<td>&lt;5</td>
<td>&lt;15</td>
</tr>
<tr>
<td>Estrone</td>
<td>10–30</td>
<td>35–97</td>
<td>≤5</td>
<td>5–60</td>
</tr>
<tr>
<td>Ethinylestradiol</td>
<td>10–30</td>
<td>45–95</td>
<td>≤5</td>
<td>5–50</td>
</tr>
<tr>
<td>I&lt;20</td>
<td></td>
<td>25</td>
<td>5</td>
<td>70</td>
</tr>
<tr>
<td>&gt;50</td>
<td></td>
<td>80–90</td>
<td>0</td>
<td>10–20</td>
</tr>
</tbody>
</table>

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 European mapping of emerging contaminants. Red: Emerging contaminants evaluated and detected at environmentally relevant concentrations; Green: Emerging contaminants evaluated and non-detected at environmentally relevant concentrations; White: no available data. Source: Network Norman.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Austria</th>
<th>Belgium</th>
<th>Bulgaria</th>
<th>Croatia</th>
<th>Cyprus</th>
<th>Czech Rep.</th>
<th>Denmark</th>
<th>Finland</th>
<th>France</th>
<th>Germany</th>
<th>Greece</th>
<th>Hungary</th>
<th>Int. Waters</th>
<th>Italy</th>
<th>Netherlands</th>
<th>Norway</th>
<th>Portugal</th>
<th>Romania</th>
<th>Serbia</th>
<th>Slovakia</th>
<th>Slovenia</th>
<th>Spain</th>
<th>Sweden</th>
<th>Switzerland</th>
<th>Ukraine</th>
<th>UK</th>
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</thead>
<tbody>
<tr>
<td>Diclofenac</td>
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<td>Ibuprofen</td>
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<td>Carbamazepine</td>
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<td>Fluoxetine</td>
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<td>Estrone</td>
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<tr>
<td>Ethinylestradiol</td>
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</tbody>
</table>

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 technique), 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 to 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 behavior 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, we will follow 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 km². 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.
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**

<table>
<thead>
<tr>
<th>Code</th>
<th>Sub Basin</th>
<th>Area (km²)</th>
<th>Population</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>River “Santa Lucía” between the rising and River “Santa Lucía Chico”</td>
<td>5,171</td>
<td>72,021</td>
</tr>
<tr>
<td>61</td>
<td>River “Santa Lucía Chico”</td>
<td>2,570</td>
<td>41,017</td>
</tr>
<tr>
<td>62</td>
<td>River “Santa Lucía” between River “Santa Lucía Chico” and Stream “Canelón Grande”</td>
<td>667</td>
<td>23,773</td>
</tr>
<tr>
<td>63</td>
<td>Stream “Canelón Grande”</td>
<td>724</td>
<td>49,367</td>
</tr>
<tr>
<td>64</td>
<td>River “Santa Lucía” between Stream “Canelón Grande” and River “San José”</td>
<td>145</td>
<td>4,018</td>
</tr>
<tr>
<td>65</td>
<td>River “San José”</td>
<td>3,567</td>
<td>56,064</td>
</tr>
<tr>
<td>66</td>
<td>River “Santa Lucía” between River “San José” and Stream “Colorado”</td>
<td>369</td>
<td>9,862</td>
</tr>
<tr>
<td>67</td>
<td>Stream “Colorado”</td>
<td>165</td>
<td>116,041</td>
</tr>
<tr>
<td>68</td>
<td>River “Santa Lucía” between Stream “Colorado” and River “de la Plata”</td>
<td>100</td>
<td>24,264</td>
</tr>
</tbody>
</table>
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 km² and a capacity of 70 million m³. Basin 63 has a second reservoir of 8 km² of surface area and 22.5 million m³ 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 km² 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>
<thead>
<tr>
<th>Activity</th>
<th>Amount</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Agricultural activities</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cattle</td>
<td>297,460</td>
<td>head</td>
</tr>
<tr>
<td>In feedlots</td>
<td>2,358</td>
<td>head</td>
</tr>
<tr>
<td>Dairy cattle</td>
<td>114,377</td>
<td>head</td>
</tr>
<tr>
<td>Sheep</td>
<td>95,693</td>
<td>head</td>
</tr>
<tr>
<td>Fowl</td>
<td>15,077</td>
<td>head</td>
</tr>
<tr>
<td>Hive</td>
<td>9,220</td>
<td>head</td>
</tr>
<tr>
<td>Pig</td>
<td>688</td>
<td>head</td>
</tr>
<tr>
<td>Meadow cultivation</td>
<td>61,143</td>
<td>Ha</td>
</tr>
<tr>
<td>Forage cultivation</td>
<td>44,556</td>
<td>Ha</td>
</tr>
<tr>
<td>Sorghum</td>
<td>16,896</td>
<td>Ha</td>
</tr>
<tr>
<td>Oats</td>
<td>13,896</td>
<td>Ha</td>
</tr>
<tr>
<td>Raigas</td>
<td>9,517</td>
<td>Ha</td>
</tr>
<tr>
<td>Wheat</td>
<td>1,994</td>
<td>Ha</td>
</tr>
<tr>
<td>Forestation</td>
<td>3,766</td>
<td>Ha</td>
</tr>
</tbody>
</table>
Emerging Pollutants in Basin Santa Lucia Chico

<table>
<thead>
<tr>
<th>Coverage cultivation</th>
<th>Eucalyptus</th>
<th>3,640 Ha</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Lotus Rincon</td>
<td>12,108 Ha</td>
</tr>
<tr>
<td>Cereal cultivation</td>
<td>Soy</td>
<td>6,716 Ha</td>
</tr>
<tr>
<td></td>
<td>Wheat</td>
<td>2,968 Ha</td>
</tr>
<tr>
<td></td>
<td>Sorghum</td>
<td>2,228 Ha</td>
</tr>
<tr>
<td>Fruit plantations</td>
<td>Olives</td>
<td>253 Ha</td>
</tr>
</tbody>
</table>

Industries

<table>
<thead>
<tr>
<th>Milk processing plant</th>
<th>19,257 m³ processed milk/month</th>
</tr>
</thead>
<tbody>
<tr>
<td>Milk processing plant</td>
<td>33 Ton cheese/month</td>
</tr>
<tr>
<td>Tannery</td>
<td>854 Processed leather/month</td>
</tr>
<tr>
<td>Chemical industry</td>
<td>6 dairy farms with more than 500 cows</td>
</tr>
<tr>
<td></td>
<td>3,052 Milk cow</td>
</tr>
<tr>
<td>Egg Producer</td>
<td>5,000 fowls</td>
</tr>
<tr>
<td>FeedLot</td>
<td>2,358 Head</td>
</tr>
</tbody>
</table>

Domestic Efluents

| WWTP - Florida | 4,979 m³/day |

Emerging Pollutants in Basin Santa Lucia Chico

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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/km²
- Specific Flow 10 percentile = 0.20 L/s/km²

The basin that contributes to this section has an area of 1,748 km² and the total area of basin 61 is 2,570 km². Therefore the resulting flows in the Santa Lucia Chico River are:

<table>
<thead>
<tr>
<th>Station</th>
<th>Average Flow (m³/s)</th>
<th>10th percentile flow (m³/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15_3 Florida</td>
<td>33.52</td>
<td>0.35</td>
</tr>
<tr>
<td>Closing point</td>
<td>49.29</td>
<td>0.51</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>PEC (g/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Live cow</td>
<td>4,075</td>
</tr>
<tr>
<td>Dosed excipient</td>
<td>815</td>
</tr>
<tr>
<td>Dosed Ivermectin</td>
<td>815</td>
</tr>
<tr>
<td>Dosed Closantel</td>
<td>10187</td>
</tr>
<tr>
<td>PEC soil</td>
<td></td>
</tr>
<tr>
<td>Ivermectin</td>
<td>750</td>
</tr>
<tr>
<td>Feces</td>
<td>733</td>
</tr>
<tr>
<td>Urine</td>
<td>16</td>
</tr>
<tr>
<td>Closantel</td>
<td>9372</td>
</tr>
<tr>
<td>Feces</td>
<td>9168</td>
</tr>
<tr>
<td>Urine</td>
<td>204</td>
</tr>
</tbody>
</table>

### Table 5-4 Physicochemical properties of Ivermectin

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular mass</td>
<td>874.7 g/mol</td>
</tr>
<tr>
<td>pKa</td>
<td>Neutral at all pH</td>
</tr>
<tr>
<td>Melting point</td>
<td>349.8 °C</td>
</tr>
<tr>
<td>Vapor pressure</td>
<td>&lt; 1.5x10^-9 Pa</td>
</tr>
<tr>
<td>Henry constant</td>
<td>4.8x10^-26</td>
</tr>
<tr>
<td>Water solubility</td>
<td>4.0, 4.1, 2.0 mg/l</td>
</tr>
<tr>
<td>Log Kow</td>
<td>3.2</td>
</tr>
<tr>
<td>Log Koc</td>
<td>3.6-4.4</td>
</tr>
<tr>
<td>UV-visible absorption spectrum</td>
<td>Max 237, 245 and 253 nm (subject to direct photolysis)</td>
</tr>
</tbody>
</table>

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 weight (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                   |

Emerging Pollutants in Basin Santa Lucia Chico 115
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-inflammatory. 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-inflammatory 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>
<thead>
<tr>
<th>Table 5-7 Estimate Cypermethrin, Ethion applied</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tick</td>
</tr>
<tr>
<td>Cypermethrin 6% + Ethion 24%</td>
</tr>
<tr>
<td>Dosage: 10 ml per animal. Dermal Use</td>
</tr>
<tr>
<td>Composition: 100ml contains 6 gr Cypermethrin and 24 gr Ethion</td>
</tr>
<tr>
<td>Total sheep and cattle</td>
</tr>
<tr>
<td>Total applied</td>
</tr>
<tr>
<td>Total Cypermethrin</td>
</tr>
<tr>
<td>Total Ethion</td>
</tr>
<tr>
<td>Number treatments</td>
</tr>
<tr>
<td>Cattle treated</td>
</tr>
<tr>
<td>Total Cypermethrin applied</td>
</tr>
<tr>
<td>Total Ethion applied</td>
</tr>
</tbody>
</table>

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>
<thead>
<tr>
<th>Table 5-8 Physicochemical properties of Ethion. (Hela, et al., 2005)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solubility</td>
</tr>
<tr>
<td>t½ soil</td>
</tr>
<tr>
<td>t½ water</td>
</tr>
<tr>
<td>Kd</td>
</tr>
<tr>
<td>Koc</td>
</tr>
</tbody>
</table>
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**

<table>
<thead>
<tr>
<th>Ethion</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Total applied (kg/year)</td>
<td>3580.9</td>
</tr>
<tr>
<td>kd (l/kg)</td>
<td>428.4</td>
</tr>
<tr>
<td>Dissolved mass (g/year)</td>
<td>8339</td>
</tr>
<tr>
<td>River Flow (m³/s)</td>
<td>0.51</td>
</tr>
<tr>
<td>River concentration (µg/L) (*)</td>
<td>0.52</td>
</tr>
</tbody>
</table>

(*)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)**

<table>
<thead>
<tr>
<th></th>
<th>Zooplankton (Daphnia)</th>
<th>Fish (Cyprinidae)</th>
<th>Invertebrates</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ethion</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Algae (96-h EC50)</td>
<td>Daphnia magna (48-h LC50)</td>
<td>Daphnia pulex (48-h LC50)</td>
<td>Cyprinus carpio (48-h LC50)</td>
</tr>
<tr>
<td>1000</td>
<td>6</td>
<td>5</td>
<td>1160</td>
</tr>
</tbody>
</table>

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**

<table>
<thead>
<tr>
<th>Ivermectin</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Total discharged (g/year)</td>
<td>21,944</td>
</tr>
<tr>
<td>kd (l/kg)</td>
<td>57 – 396</td>
</tr>
<tr>
<td>Dissolved mass (g/year)</td>
<td>55 – 378</td>
</tr>
<tr>
<td>River Flow (m³/s)</td>
<td>0.51</td>
</tr>
<tr>
<td>River Concentration (ng/L)</td>
<td>23.52 - 3.44</td>
</tr>
</tbody>
</table>
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>
<thead>
<tr>
<th></th>
<th>Ivermectin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dissolved mass from feedlots (g/year)</td>
<td>2 - 13</td>
</tr>
<tr>
<td>Dissolved mass from livestock (g/year)</td>
<td>55 – 378</td>
</tr>
<tr>
<td>Total Dissolved mass Ivermectin (g/year)</td>
<td>57 – 391</td>
</tr>
<tr>
<td>River Flow (m3/s)</td>
<td>0,51</td>
</tr>
<tr>
<td>PEC Ivermectin (ng/L)</td>
<td>3,6 – 24,3</td>
</tr>
<tr>
<td>PNEC Ivermectin (ng/L)</td>
<td>5,7</td>
</tr>
<tr>
<td>RQ</td>
<td>0,63 – 4,26</td>
</tr>
</tbody>
</table>

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 Ivermectin 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>
<thead>
<tr>
<th>PAH</th>
<th>Discharge in effluent</th>
<th>Estimated removals</th>
<th>Discharge in effluent</th>
<th>Effluent concentration</th>
<th>Surface water concentration</th>
<th>PNEC</th>
<th>RQ River</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(g/year)</td>
<td>(%)</td>
<td>(g/year)</td>
<td>(ng/L)</td>
<td>(ng/L)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Drospirenone</td>
<td>33.7 - 76.8</td>
<td>na</td>
<td>16.9–38.4</td>
<td>9.27–21.13</td>
<td>1.53 – 3.48</td>
<td>6.6</td>
<td>0.23 - 0.53</td>
</tr>
<tr>
<td>Levonorgestrel</td>
<td>5.2 - 8.2</td>
<td>nd (75)</td>
<td>1.3–2.1</td>
<td>0.72–1.13</td>
<td>0.12 – 0.19</td>
<td>0.08</td>
<td>1.47 - 2.32</td>
</tr>
<tr>
<td>Gestodene</td>
<td>0.2 - 0.4</td>
<td>nd (75)</td>
<td>0.1–0.1</td>
<td>0.03 – 0.06</td>
<td>0.00 – 0.01</td>
<td>0.01</td>
<td>0.45 - 0.81</td>
</tr>
<tr>
<td>Cyproterone Acetate</td>
<td>1.3 - 3.0</td>
<td>na (50)</td>
<td>0.7–1.5</td>
<td>0.36 – 0.83</td>
<td>0.06 – 0.14</td>
<td>na</td>
<td>na</td>
</tr>
<tr>
<td>Dienogest</td>
<td>1.0 - 2.0</td>
<td>na (50)</td>
<td>0.5–1.0</td>
<td>0.28 – 0.55</td>
<td>0.05 – 0.09</td>
<td>na</td>
<td>na</td>
</tr>
<tr>
<td>Norgestimate</td>
<td>0.1 - 0.2</td>
<td>na (50)</td>
<td>0.1–0.1</td>
<td>0.03 – 0.06</td>
<td>0.00 – 0.01</td>
<td>na</td>
<td>na</td>
</tr>
<tr>
<td>Desogestrel</td>
<td>0.01</td>
<td>na (50)</td>
<td>0.005</td>
<td>0.003</td>
<td>0.000</td>
<td>na</td>
<td>na</td>
</tr>
<tr>
<td>Ethinylestradiol</td>
<td>4.4 - 6.3</td>
<td>78</td>
<td>1.0–1.4</td>
<td>0.53 – 0.76</td>
<td>0.09 – 0.13</td>
<td>1</td>
<td>0.09 - 0.13</td>
</tr>
<tr>
<td>Linestrenol</td>
<td>0.8 - 1.7</td>
<td>na (50)</td>
<td>0.4–0.9</td>
<td>0.22 - 0.47</td>
<td>0.04 – 0.08</td>
<td>na</td>
<td>na</td>
</tr>
</tbody>
</table>

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 pollutants discharged to domestic sewage of the city of Florida and the environmental risk

<table>
<thead>
<tr>
<th>Class</th>
<th>Compound</th>
<th>Average concentration raw influent$^1$</th>
<th>Average concentration effluent$^2$</th>
<th>PNEC</th>
<th>Risk effluent</th>
<th>Risk River$^1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pharmaceutical</td>
<td>Ibuprofen</td>
<td>37</td>
<td>3.6</td>
<td>1.65</td>
<td>2.2</td>
<td>0.36</td>
</tr>
<tr>
<td></td>
<td>Mefenamic acid</td>
<td>1.1</td>
<td>0.63</td>
<td>0.43</td>
<td>1.5</td>
<td>0.24</td>
</tr>
<tr>
<td></td>
<td>Amoxicillin</td>
<td>0.24</td>
<td>0.01</td>
<td>0.0037</td>
<td>2.7</td>
<td>0.44</td>
</tr>
<tr>
<td></td>
<td>Azithromycin</td>
<td>0.4</td>
<td>0.16</td>
<td>0.15</td>
<td>1.1</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>Clarithromycin</td>
<td>1.3</td>
<td>0.29</td>
<td>0.07</td>
<td>4.1</td>
<td>0.68</td>
</tr>
<tr>
<td></td>
<td>Erythromycin</td>
<td>1.8</td>
<td>0.7</td>
<td>0.02</td>
<td>35</td>
<td>5.76</td>
</tr>
<tr>
<td></td>
<td>Ofloxacin</td>
<td>5.1</td>
<td>0.45</td>
<td>0.016</td>
<td>28.1</td>
<td>4.63</td>
</tr>
<tr>
<td></td>
<td>Sulfamethoxazole</td>
<td>0.92</td>
<td>0.28</td>
<td>0.027</td>
<td>10.4</td>
<td>1.71</td>
</tr>
<tr>
<td></td>
<td>Tetracycline</td>
<td>0.33</td>
<td>0.14</td>
<td>0.09</td>
<td>1.6</td>
<td>0.26</td>
</tr>
<tr>
<td></td>
<td>Fenofibrate</td>
<td>no available</td>
<td>0.11</td>
<td>0.1</td>
<td>1.1</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>Fenofibrac acid</td>
<td>0.21</td>
<td>0.11</td>
<td>0.76</td>
<td>1.4</td>
<td>0.24</td>
</tr>
<tr>
<td></td>
<td>Gemfibrozil</td>
<td>2.4</td>
<td>0.93</td>
<td>0.9</td>
<td>1</td>
<td>0.17</td>
</tr>
<tr>
<td></td>
<td>Diazepam</td>
<td>22</td>
<td>9.1</td>
<td>2</td>
<td>4.6</td>
<td>0.75</td>
</tr>
<tr>
<td></td>
<td>Fluoxetine</td>
<td>0.54</td>
<td>0.24</td>
<td>0.05</td>
<td>4.8</td>
<td>0.79</td>
</tr>
<tr>
<td>Pesticides</td>
<td>atrazine</td>
<td>1.24</td>
<td>124</td>
<td>59</td>
<td>2.1</td>
<td>0.35</td>
</tr>
<tr>
<td></td>
<td>simazine</td>
<td>7.27</td>
<td>169</td>
<td>40</td>
<td>4.2</td>
<td>0.70</td>
</tr>
<tr>
<td></td>
<td>terbuthylazine</td>
<td>20.6</td>
<td>20</td>
<td>12</td>
<td>1.7</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td>chlortoluron</td>
<td>3.94</td>
<td>98.2</td>
<td>24</td>
<td>4.1</td>
<td>0.67</td>
</tr>
<tr>
<td></td>
<td>diuron</td>
<td>93</td>
<td>127</td>
<td>2.7</td>
<td>47</td>
<td>7.74</td>
</tr>
</tbody>
</table>
### 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:

<table>
<thead>
<tr>
<th>Source</th>
<th>Class</th>
<th>Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>Agriculture</td>
<td>Veterinary pharmaceutical</td>
<td>Ivermectin</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ethion</td>
</tr>
<tr>
<td>Domestic Effluent</td>
<td>Pharmaceutical</td>
<td>Levonorgestrel</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Erythromycin</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ofloxacin</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sulfamethoxazole</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Diuron</td>
</tr>
<tr>
<td>Pesticides</td>
<td></td>
<td>Diuron</td>
</tr>
<tr>
<td>Personal care product</td>
<td></td>
<td>Phantolide (AHMI)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Traseolide (ATII)</td>
</tr>
</tbody>
</table>

1- Average WWTP Florida flow 4979 m³/day; Percentile 10 River Santa Lucia Chico Flow 0.35 m³/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.
<table>
<thead>
<tr>
<th>Source</th>
<th>Class</th>
<th>Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Cashmeran</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4-benzophenone</td>
</tr>
</tbody>
</table>

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


6.2. Reference Chapter 5


DINAMA/MVOTMA, (2015), Evolución de la calidad en la cuenca del Santa Lucía 10 años de información. MVOTMA

DINOT/MVOTMA (ed), (2016), Atlas de la Cuenca del Río Santa Lucía. MVOTMA


MVOTMA, (2013), Plan de acción para la protección de la calidad ambiental y la disponibilidad de las fuentes de agua potable. MVOTMA


Repiso, M. et al. (2005). “Prevalencia de las principales enfermedades infecciosas que afectan el comportamiento reproductivo en la ganadería de carne y caracterización de los establecimientos de cría del Uruguay.” Serie FPTA N°13, INIA

**Interview:**
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)

<table>
<thead>
<tr>
<th>Pharmaceutical</th>
<th>MW</th>
<th>Chemical formula</th>
<th>pKₐ</th>
<th>Log Kₐw</th>
<th>S₀ 25°C (mg l⁻¹)</th>
<th>Log Kₐ</th>
<th>kₜot (L gSS⁻¹ d⁻¹)</th>
<th>Charge at pH 7</th>
<th>Molecular structure</th>
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*Note: The molecular structures are not included in the text.*
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<th>Log Kₛ</th>
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<td>Log K_a</td>
<td>k_{biol} (L gSS^{-1} d^{-1})</td>
<td>Charge at pH 7</td>
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<td>Log $K_d$</td>
<td>$k_{biof}$ (L gSS$^{-1}$ d$^{-1}$)</td>
<td>Charge at pH 7</td>
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Appendices
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<td>Log K&lt;sub&gt;d&lt;/sub&gt;</td>
<td>k&lt;sub&gt;biol&lt;/sub&gt; (L gSS&lt;sup&gt;-1&lt;/sup&gt; d&lt;sup&gt;-1&lt;/sup&gt;)</td>
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<td>( \text{Log } K_d )</td>
<td>( k_{bio} ) (L gSS d^{-1})</td>
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<td>Molecular structure</td>
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Appendices 9
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<th>Log (K_d)</th>
<th>(k_{bio}) (L gSS⁻¹ d⁻¹)</th>
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Appendices  12
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Data were from Ternes and Joss, 2006; Petrovic and Barcelò 2007 (pKa), EPISuite v4.00 ($S_w$, log$K_{ow}$, log$K_{oc}$); Chemamox (charge at pH=7). For log$K_{dc}$ references are specified.

References
³Avdeef et al. 2002; ³Jones et al. 2002; ³Huber et al. 2003; ³Khan and Ongerth 2002; ³Wan et al. 2002; ³Tixier et al. 2003; ³Nowara et al. 1997; ³Meylan 1993; ³Vieno et al.,2007; ³Wick et al.,2009; ³Le-Minh et al., 2010; ³Suarez et al., 2008; ³Zorita et al.2009; ³Munoz et al.2009; ³Suarez et al.,2010; ³Wollenberger 2000; ³Papastephanou and Frantz 1997; ³Joss et al., 2004 ³Abegglen et al., 2009; ³Radjenovic et al., 2009; u Jia et al., 2012
# Appendix B European mapping of emerging contaminants


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The European mapping was conducted analyzing a database 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 technique), and in the remaining countries these compounds were not even evaluated.

Appendices 17
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Perfluoroalkylated substances and their transformation products
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<th>Finland</th>
<th>France</th>
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**Plant protection products / Biocides**

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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 (PNEC\textsubscript{Chronic}), acute-based PNEC (PNEC\textsubscript{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)

<table>
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<tr>
<th>CAS</th>
<th>Compound a</th>
<th>Use b</th>
<th>PS</th>
<th>PNEC\textsubscript{Chronic} [µg / L]</th>
<th>PNEC\textsubscript{Acute} [µg / L]</th>
<th>P-PNEC</th>
<th>Ref c</th>
<th>TL,\textsuperscript{d}</th>
<th># of sites &lt; 2005</th>
<th>Frequency &lt; 2005</th>
<th># of sites &gt; 2004</th>
<th>Frequency &gt; 2004</th>
<th>PR</th>
<th>RB e</th>
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*DNOC = 4,6-dinitro-o-cresol, PCB = polychlorinated biphenyls, PBDE = polybrominated diphenyl ether, MCPB = (2-methyl-4-chlorophenoxy)butyric acid

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

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

D = *Daphnia*, F = fish, A = algae

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)

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<th>PNECacute [µg / L]</th>
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<th>TL d</th>
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Appendices
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* PBDE = polybrominated diphenyl ether, TCPP = tris(monochlorpropyl)phosphat
* P = pesticide, I = industrial product, B = biocide, C = combustion product, N = natural product, Ph = pharmaceutical
* E = experimental value, P = predicted LC50, B = baseline prediction, WS = water solubility exceeded
* D = Daphnia, F = fish, A = algae
* 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 (PNEChronic), 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)

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<th>CAS</th>
<th>Compound a</th>
<th>Use b</th>
<th>PS</th>
<th>PNEChronic [µg / L]</th>
<th>PNECacute [µg / L]</th>
<th>P-PNEC [µg / L]</th>
<th>Ref ¢</th>
<th>TL d</th>
<th># of sites &gt; 2004</th>
<th>Frequency &gt; 2004</th>
<th>PR</th>
<th>RB e</th>
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**Appendices**
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\(^a\) 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<sub>chronic</sub>), acute-based PNEC (PNEC<sub>acute</sub>), 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<sub>chronic</sub> [µg / L] | PNEC<sub>acute</sub> [µg / L] | P-PNEC | Ref c | TLd | # of sites < 2005 | Frequency < 2005 | # of sites > 2004 | Frequency > 2004 | PR | RB
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<td>undecane</td>
<td>I</td>
<td></td>
<td>0.03</td>
<td>P</td>
<td>M</td>
<td>27 0%</td>
<td>L</td>
<td></td>
<td></td>
</tr>
<tr>
<td>108-05-4</td>
<td>vinyl acetate</td>
<td>I</td>
<td></td>
<td>22.46</td>
<td>P</td>
<td>A</td>
<td>27 0%</td>
<td>L</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* PBDE = polybrominated diphenyl ether, PCB = polychlorinated biphenyls, DBCP = 1,2-dibromo-3-chloropropane, HCH = hexachlorocyclohexane
* P = pesticide, I = industrial product, B = biocide, C = combustion product, N = natural product, Ph = pharmaceutical
* E = experimental value, P = predicted LC50, B = baseline prediction, WS = water solubility exceeded
* D = *Daphnia*, F = fish, A = algae
* D = Danube, E = Elbe, L = Llobregat, S = Scheldt

Appendices 53
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\text{chronic}), acute-based PNEC (PNEC\text{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)

<table>
<thead>
<tr>
<th>CAS</th>
<th>Compound</th>
<th>Use</th>
<th>PS</th>
<th>PNEC\text{chronic} [µg / L]</th>
<th>PNEC\text{acute} [µg / L]</th>
<th>P-PNEC [µg / L]</th>
<th>Ref</th>
<th>TL</th>
<th># of sites &gt; 2004</th>
<th>Exceedance &gt; 2004</th>
<th>Frequency &gt; 2004</th>
<th>PR</th>
<th>RB</th>
</tr>
</thead>
<tbody>
<tr>
<td>1071-83-6</td>
<td>glyphosate</td>
<td>P</td>
<td>24</td>
<td>40</td>
<td>0.070</td>
<td>0.075</td>
<td>P</td>
<td>D</td>
<td>994</td>
<td>0.73</td>
<td>1.0%</td>
<td>0.010</td>
<td>D, E, L, S</td>
</tr>
<tr>
<td>218-01-9</td>
<td>chrysene</td>
<td>I</td>
<td>1.3</td>
<td>0.41</td>
<td>0.43</td>
<td>E</td>
<td>A</td>
<td>959</td>
<td>0.32</td>
<td>0.8%</td>
<td>0.008</td>
<td>0.008</td>
<td>D, E, L, S</td>
</tr>
<tr>
<td>85-01-8</td>
<td>phenantherene</td>
<td>I</td>
<td>2</td>
<td>0.10</td>
<td>0.43</td>
<td>E</td>
<td>D</td>
<td>1082</td>
<td>0.47</td>
<td>0.6%</td>
<td>0.006</td>
<td>0.004</td>
<td>D, E, L, S</td>
</tr>
<tr>
<td>120-12-7</td>
<td>anthracene</td>
<td>P</td>
<td>80</td>
<td>4.5</td>
<td>4.5</td>
<td>E</td>
<td>A</td>
<td>1082</td>
<td>0.36</td>
<td>0.4%</td>
<td>0.004</td>
<td>0.004</td>
<td>E</td>
</tr>
<tr>
<td>6207-90-1</td>
<td>propiconazole</td>
<td>P</td>
<td>1.8</td>
<td>1.4</td>
<td>1.4</td>
<td>E</td>
<td>A</td>
<td>850</td>
<td>0.23</td>
<td>0.4%</td>
<td>0.004</td>
<td>0.004</td>
<td>E</td>
</tr>
<tr>
<td>60-00-4</td>
<td>EDTA</td>
<td>I</td>
<td>2200</td>
<td>41</td>
<td>P</td>
<td>A</td>
<td>897</td>
<td>0.85</td>
<td>0.2%</td>
<td>0.002</td>
<td>0.002</td>
<td>0.002</td>
<td>E</td>
</tr>
<tr>
<td>108-88-3</td>
<td>toluene</td>
<td>I</td>
<td>74</td>
<td>11</td>
<td>E</td>
<td>A</td>
<td>1102</td>
<td>0.06</td>
<td>0.2%</td>
<td>0.002</td>
<td>0.002</td>
<td>0.002</td>
<td>D, E, L, S</td>
</tr>
<tr>
<td>75-09-2</td>
<td>dichloromethane</td>
<td>I</td>
<td>11</td>
<td>20</td>
<td>220</td>
<td>E</td>
<td>D</td>
<td>1082</td>
<td>0.13</td>
<td>0.2%</td>
<td>0.002</td>
<td>0.002</td>
<td>D, E, L, S</td>
</tr>
<tr>
<td>127-18-4</td>
<td>tetrachloroethylen</td>
<td>I</td>
<td>29a</td>
<td>15</td>
<td>0.015</td>
<td>E</td>
<td>D</td>
<td>818</td>
<td>0.18</td>
<td>0.2%</td>
<td>0.002</td>
<td>0.002</td>
<td>D, E, L, S</td>
</tr>
<tr>
<td>1898084-64-8</td>
<td>PBDE-100</td>
<td>I</td>
<td>0.00050</td>
<td>0.015</td>
<td>E</td>
<td>A</td>
<td>818</td>
<td>0.29</td>
<td>0.1%</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
<td>E</td>
</tr>
<tr>
<td>23950-58-5</td>
<td>propyzamide</td>
<td>P</td>
<td>8.2</td>
<td>8.2</td>
<td>0.070</td>
<td>1.7</td>
<td>E</td>
<td>D</td>
<td>959</td>
<td>0.35</td>
<td>0.1%</td>
<td>0.001</td>
<td>0.001</td>
</tr>
<tr>
<td>90-13-1</td>
<td>1-chloronaphthalene</td>
<td>I</td>
<td>82</td>
<td>3.4</td>
<td>E</td>
<td>D</td>
<td>959</td>
<td>0.19</td>
<td>0.1%</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
<td>E, S</td>
</tr>
<tr>
<td>126-73-8</td>
<td>tributylphosphat</td>
<td>I</td>
<td>22</td>
<td>2.4</td>
<td>6.1</td>
<td>E</td>
<td>F</td>
<td>897</td>
<td>0.04</td>
<td>0.1%</td>
<td>0.001</td>
<td>0.001</td>
<td>D, E, L, S</td>
</tr>
<tr>
<td>79-01-6</td>
<td>trichloroethylene</td>
<td>I</td>
<td>29b</td>
<td>10</td>
<td>4.4</td>
<td>E</td>
<td>F</td>
<td>959</td>
<td>0.13</td>
<td>0.1%</td>
<td>0.001</td>
<td>0.001</td>
<td>D, E, L, S</td>
</tr>
<tr>
<td>120-83-2</td>
<td>2,4-dichlorophenol</td>
<td>P</td>
<td>0.80</td>
<td>3.1</td>
<td>E</td>
<td>D</td>
<td>1082</td>
<td>0.13</td>
<td>0.0%</td>
<td>E</td>
<td>S</td>
<td></td>
<td></td>
</tr>
<tr>
<td>56-23-5</td>
<td>carbon tetrachloride</td>
<td>B</td>
<td>6a</td>
<td>12</td>
<td>56</td>
<td>E</td>
<td>D</td>
<td>1082</td>
<td>0.06</td>
<td>0.0%</td>
<td>E</td>
<td>S</td>
<td></td>
</tr>
<tr>
<td>95-47-6</td>
<td>o-xylene</td>
<td>I</td>
<td>20</td>
<td>4.4</td>
<td>6.3</td>
<td>E</td>
<td>D</td>
<td>1052</td>
<td>0.06</td>
<td>0.0%</td>
<td>E</td>
<td>S</td>
<td></td>
</tr>
<tr>
<td>106-46-7</td>
<td>1,4-dichlorobenzene</td>
<td>I</td>
<td>6.3</td>
<td>6.3</td>
<td>E</td>
<td>D</td>
<td>959</td>
<td>0.08</td>
<td>0.0%</td>
<td>E</td>
<td>S</td>
<td></td>
<td></td>
</tr>
<tr>
<td>107534-96-3</td>
<td>tebuconazole</td>
<td>P</td>
<td>1.4</td>
<td>2.8</td>
<td>E</td>
<td>A</td>
<td>994</td>
<td>0.28</td>
<td>0.0%</td>
<td>E</td>
<td>S</td>
<td></td>
<td></td>
</tr>
<tr>
<td>95-50-1</td>
<td>1,2-dichlorobenzene</td>
<td>I</td>
<td>10</td>
<td>10</td>
<td>135</td>
<td>E</td>
<td>F</td>
<td>959</td>
<td>0.08</td>
<td>0.0%</td>
<td>E</td>
<td>S</td>
<td></td>
</tr>
<tr>
<td>94-75-7</td>
<td>2,4-D</td>
<td>P</td>
<td>27</td>
<td>4.2</td>
<td>E</td>
<td>A</td>
<td>959</td>
<td>0.02</td>
<td>0.0%</td>
<td>E</td>
<td>S</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1066-51-9</td>
<td>aminomethylphosphonic acid</td>
<td>P</td>
<td>80</td>
<td>40</td>
<td>E</td>
<td>D</td>
<td>959</td>
<td>0.26</td>
<td>0.0%</td>
<td>S</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>120-36-5</td>
<td>dichlorprop</td>
<td>P</td>
<td>1.3</td>
<td>103</td>
<td>E</td>
<td>D</td>
<td>959</td>
<td>0.87</td>
<td>0.0%</td>
<td>E, S</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Appendices 54
| 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

Appendices 55
## 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:

<table>
<thead>
<tr>
<th>Product</th>
<th>Yearly Production</th>
<th>2016</th>
</tr>
</thead>
<tbody>
<tr>
<td>Milk powder</td>
<td></td>
<td>2357.5 ton/mes</td>
</tr>
<tr>
<td>Demineralized whey</td>
<td></td>
<td>333.2 ton/mes</td>
</tr>
<tr>
<td>Caramel</td>
<td></td>
<td>318.5 ton/mes</td>
</tr>
<tr>
<td>Butter</td>
<td></td>
<td>816.0 ton/mes</td>
</tr>
<tr>
<td>Butter Oil</td>
<td></td>
<td>201.1 ton/mes</td>
</tr>
<tr>
<td>Buttermilk Powder</td>
<td></td>
<td>115.3 ton/mes</td>
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</tbody>
</table>

### Chemicals and raw materials used:

<table>
<thead>
<tr>
<th>Nombre comercial del insumo</th>
<th>Nombre químico del insumo</th>
<th>Punto de consumo en el proceso o en la PTE</th>
<th>Consumo mensual</th>
</tr>
</thead>
<tbody>
<tr>
<td>Suero de queso</td>
<td>No aplica</td>
<td>Producción</td>
<td>1832 m3</td>
</tr>
<tr>
<td>Soda cáustica</td>
<td>NaOH</td>
<td>Limpieza de equipos</td>
<td>30.9 ton</td>
</tr>
<tr>
<td>Crema de Leche</td>
<td>No aplica</td>
<td>Producción de manteca</td>
<td>1503 m3</td>
</tr>
<tr>
<td>Leche</td>
<td>No aplica</td>
<td>Producción</td>
<td>19257 m3</td>
</tr>
<tr>
<td>Nitrógeno Líquido</td>
<td>N2</td>
<td>Producción</td>
<td>15446 m3</td>
</tr>
<tr>
<td>Aditivo limpiador BD SF 617 y BD EZ 600</td>
<td>SD</td>
<td>Ósmosis inversa</td>
<td>21.3 kg</td>
</tr>
<tr>
<td>Aditivo Gengard GN8020</td>
<td>SD</td>
<td>Ósmosis inversa</td>
<td>26.8 kg</td>
</tr>
<tr>
<td>Limpiador Kleen MCT 103 y 511</td>
<td>SD</td>
<td>Ósmosis inversa</td>
<td>33.3 kg</td>
</tr>
<tr>
<td>Bioremediador B 250</td>
<td>SD</td>
<td>Efluentes</td>
<td>20 kg</td>
</tr>
<tr>
<td>Ácido peracético al 15%</td>
<td>CH3CO3H</td>
<td>Desinfección</td>
<td>0.98 m3</td>
</tr>
<tr>
<td>Hipoclorito de sodio</td>
<td>NaClO</td>
<td>Agua de abastecimiento y desinfección</td>
<td>3.8 m3</td>
</tr>
<tr>
<td>Detergente</td>
<td>SD</td>
<td>Limpieza general</td>
<td>105 l</td>
</tr>
<tr>
<td>Ácido nítrico</td>
<td>HNO3</td>
<td>Limpieza de equipos</td>
<td>34.3 ton</td>
</tr>
<tr>
<td>Anhídrico carbónico</td>
<td>CO2</td>
<td>Producción</td>
<td>9987 m3</td>
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### Consumo de agua:

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<th>Tipo de agua</th>
<th>Consumo mensual</th>
</tr>
</thead>
<tbody>
<tr>
<td>Subterranea</td>
<td>483 m3/dia</td>
</tr>
<tr>
<td>Superficial</td>
<td>738 m3/dia</td>
</tr>
<tr>
<td>Re-Utilización</td>
<td>463 m3/dia</td>
</tr>
</tbody>
</table>

### Tratamiento:

Biológico (secundario) y lagunas (terceario)

### Lugar de vertido 1:

<table>
<thead>
<tr>
<th>Lugar de vertido</th>
<th>Descripción</th>
<th>Cuenca/Subcuenca</th>
</tr>
</thead>
<tbody>
<tr>
<td>Curso de agua</td>
<td>Humedal B</td>
<td>Rio Santa Lucia</td>
</tr>
</tbody>
</table>
Caudal de descarga de efluentes 1:

<table>
<thead>
<tr>
<th></th>
<th>Caudal medio diario (m3/d)</th>
<th>Caudal máximo diario (m3/d)</th>
<th>Horario vertido</th>
<th>Días de vertido totales en el bimestre</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bimestre 1</td>
<td>955</td>
<td>955</td>
<td>0 a 24</td>
<td>60</td>
</tr>
<tr>
<td>Bimestre 2</td>
<td>915</td>
<td>955</td>
<td>0 a 24</td>
<td>61</td>
</tr>
<tr>
<td>Bimestre 3</td>
<td>997</td>
<td>1039</td>
<td>0 a 24</td>
<td>61</td>
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</table>

Lugar de vertido 2:

<table>
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<th>Descripción</th>
<th>Cuenca/Subcuenca</th>
</tr>
</thead>
<tbody>
<tr>
<td>Humedal A</td>
<td>Rio Santa Lucia</td>
<td></td>
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</table>

Caudal de descarga de efluentes 2:

<table>
<thead>
<tr>
<th></th>
<th>Caudal medio diario (m3/d)</th>
<th>Caudal máximo diario (m3/d)</th>
<th>Horario vertido</th>
<th>Días de vertido totales en el bimestre</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bimestre 1</td>
<td>997</td>
<td>1039</td>
<td>0 a 24</td>
<td>60</td>
</tr>
<tr>
<td>Bimestre 2</td>
<td>1130</td>
<td>1221</td>
<td>0 a 24</td>
<td>61</td>
</tr>
<tr>
<td>Bimestre 3</td>
<td>1039</td>
<td>1039</td>
<td>0 a 24</td>
<td>61</td>
</tr>
</tbody>
</table>

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:

<table>
<thead>
<tr>
<th>Lugar de vertido</th>
<th>Descripción</th>
<th>Cuenca/Subcuenca</th>
</tr>
</thead>
<tbody>
<tr>
<td>Riego</td>
<td>Rio Santa Lucia</td>
<td></td>
</tr>
</tbody>
</table>

Caudal de descarga de efluentes 1:

<table>
<thead>
<tr>
<th></th>
<th>Caudal medio diario (m3/d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Efluente 1</td>
<td>12</td>
</tr>
</tbody>
</table>

Tannery

**Name:** Cooperativa El Aguila, **Location:** (-56,222912 ; -34,112242)

**Production:**

<table>
<thead>
<tr>
<th>Cueros</th>
<th>cueros/mes 2016</th>
</tr>
</thead>
<tbody>
<tr>
<td>854</td>
<td></td>
</tr>
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</table>

**Sustancias químicas y materias primas usadas:**

<table>
<thead>
<tr>
<th>Nombre comercial del insumo</th>
<th>Nombre químico del insumo</th>
<th>Punto de consumo en el proceso o en la PTE</th>
<th>Consumo mensual</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formiato de Sodio</td>
<td>Formiato de Sodio</td>
<td>Recurtido y teñido</td>
<td>180 kg/mes</td>
</tr>
<tr>
<td>Acido fórmico</td>
<td>Acido fórmico</td>
<td>Recurtido y teñido</td>
<td>483 kg/mes</td>
</tr>
<tr>
<td>?ancotan SN/Daxitan DCM</td>
<td>Naphthalene sulfonic acid</td>
<td>Recurtido y teñido</td>
<td>267 kg/mes</td>
</tr>
<tr>
<td>?upon LE/Nutrapol CDX</td>
<td>Recurtiente sintético</td>
<td>Recurtido y teñido</td>
<td>1517 kg/mes</td>
</tr>
<tr>
<td>OP 7201</td>
<td>Aceite pull up</td>
<td>Terminación</td>
<td>130 kg/mes</td>
</tr>
</tbody>
</table>

Appendices 57
<table>
<thead>
<tr>
<th>Material</th>
<th>Recurrido y teñido</th>
<th>227</th>
<th>kg/mes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfato de cromo</td>
<td>Recurrido y teñido</td>
<td>180</td>
<td>kg/mes</td>
</tr>
<tr>
<td>Sulfato de cromo</td>
<td>Terminación</td>
<td>195</td>
<td>kg/mes</td>
</tr>
<tr>
<td>Magnopal / Trupotan UM/Marbrasyn B47</td>
<td>Recurrido y teñido</td>
<td>240</td>
<td>kg/mes</td>
</tr>
<tr>
<td>Alcohol isopropílico</td>
<td>Terminación</td>
<td>400</td>
<td>kg/mes</td>
</tr>
<tr>
<td>Auxiliar de penetración</td>
<td>Recurrido y teñido</td>
<td>83</td>
<td>kg/mes</td>
</tr>
<tr>
<td>WP7503/WP7550/FW2315</td>
<td>Mezcla de ceras</td>
<td>710</td>
<td>kg/mes</td>
</tr>
<tr>
<td>Uretanos/poliuretanos</td>
<td>Uretanos</td>
<td>430</td>
<td>kg/mes</td>
</tr>
<tr>
<td>Anilina</td>
<td>Recurrido y teñido</td>
<td>357</td>
<td>kg/mes</td>
</tr>
<tr>
<td>Nutropol LE</td>
<td>Lecitina</td>
<td>452</td>
<td>kg/mes</td>
</tr>
<tr>
<td>Bicarbonato de Sodio</td>
<td>Recurrido y teñido</td>
<td>270</td>
<td>kg/mes</td>
</tr>
<tr>
<td>Trupotan EH</td>
<td>Recurrido y teñido</td>
<td>133</td>
<td>kg/mes</td>
</tr>
<tr>
<td>Tara</td>
<td>Recurrido vegetal</td>
<td>213</td>
<td>kg/mes</td>
</tr>
<tr>
<td>Daxioil SG</td>
<td>Recurrido y teñido</td>
<td>483</td>
<td>kg/mes</td>
</tr>
<tr>
<td>Amoníaco</td>
<td>Recurrido y teñido</td>
<td>62</td>
<td>kg/mes</td>
</tr>
</tbody>
</table>

**Consumo de agua:**

<table>
<thead>
<tr>
<th></th>
<th>m3/dia</th>
</tr>
</thead>
<tbody>
<tr>
<td>Subterránea</td>
<td>0,4</td>
</tr>
<tr>
<td>Superficial</td>
<td>16</td>
</tr>
<tr>
<td>OSE</td>
<td>3,8</td>
</tr>
</tbody>
</table>

**Tratamiento:** Neutralización, Sedimentador, Reactor aeróbico, Reactor anóxico, sedimentador secundario, Lugar de vertido 1:

<table>
<thead>
<tr>
<th>Lugar de vertido</th>
<th>Descripción</th>
<th>Cuenca/Subcuenca</th>
</tr>
</thead>
<tbody>
<tr>
<td>Curso de agua</td>
<td>Rio Santa Lucia</td>
<td></td>
</tr>
</tbody>
</table>

**Caudal de descarga de efluentes 1:**

<table>
<thead>
<tr>
<th>Bimestre</th>
<th>Caudal medio diario (m3/d)</th>
<th>Caudal máximo diario (m3/d)</th>
<th>Horario de vertido</th>
<th>Días de vertido totales en el bimestre</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bimestre 1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>60</td>
</tr>
<tr>
<td>Bimestre 2</td>
<td>18,3</td>
<td>31,5</td>
<td>6-16</td>
<td>9</td>
</tr>
<tr>
<td>Bimestre 3</td>
<td>16</td>
<td>64</td>
<td>6-16</td>
<td>44</td>
</tr>
</tbody>
</table>

**Chemical industry**

**Name:** Fenasol, **Location:** (-56,17449 ; -34,12873)

**Production:**

<table>
<thead>
<tr>
<th>Material</th>
<th>Producción</th>
</tr>
</thead>
<tbody>
<tr>
<td>Azoxistrobin 200g/l + Tebuconazol 125g/l</td>
<td>17235 l/año</td>
</tr>
<tr>
<td>Imidacloprid 600g/l</td>
<td>22159 l/año</td>
</tr>
<tr>
<td>Glifosato sal Monoisopropilamina 480 g/l</td>
<td>11840 l/año</td>
</tr>
<tr>
<td>Glifosato sal Dimetilamina 610g/l</td>
<td>41440 l/año</td>
</tr>
<tr>
<td>Imidacloprid 350 g/l</td>
<td>250 l/año</td>
</tr>
<tr>
<td>Antraquinona 92% p/p</td>
<td>2000 kg/año</td>
</tr>
<tr>
<td>Azoxistrobin 50% p/p</td>
<td>1039 kg/año</td>
</tr>
<tr>
<td>Sustancias químicas y materias primas usadas:</td>
<td></td>
</tr>
<tr>
<td>--------------------------------------------------</td>
<td>----</td>
</tr>
<tr>
<td><strong>Nombre comercial del insumo</strong></td>
<td><strong>Nombre químico del insumo</strong></td>
</tr>
<tr>
<td>Clorantraniliprole 80% p/p</td>
<td>940 kg/año</td>
</tr>
<tr>
<td>Benzoato de Emamctina 30% p/p</td>
<td>4517 kg/año</td>
</tr>
<tr>
<td><strong>Acido Clorhidrico 32%</strong></td>
<td>Cloruro de Hidrógeno</td>
</tr>
<tr>
<td><strong>Aerosil 200</strong></td>
<td>Dióxido de Silicio coloidal</td>
</tr>
<tr>
<td><strong>Alimidon de maiz</strong></td>
<td>Molécula formada por amilosa y amilopectina</td>
</tr>
<tr>
<td><strong>Antiespumante siliconado en polvo</strong></td>
<td>No se cuenta con la fórmula</td>
</tr>
<tr>
<td><strong>Antraquinona TC</strong></td>
<td>9,10 - Antracenediona</td>
</tr>
<tr>
<td><strong>Aquapol</strong></td>
<td>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-benzotriazol-2-il)-5-terc-butil-4-hidroxifenil)propioniloxipoli(oxietileno)</td>
</tr>
<tr>
<td><strong>Azoxistrobin TC</strong></td>
<td>Methyl (2E)-2-(2{6-(2-cyanophenoxy)pyrimidin-4-yl}oxy)phenyl)-3-methoxyacrylate</td>
</tr>
<tr>
<td><strong>Benzoato de Emamctina TC</strong></td>
<td>Benzoato de 4&quot;-epi-metilmanino-4&quot;-deoxiavermectina B1 (mexcla con un mínimo 90% y un máximo de 10% de benzoato de 4&quot;-epi-metilamino-4&quot;- deoxiavermectina B1a y B1b)</td>
</tr>
<tr>
<td><strong>Borresperse</strong></td>
<td>Lignosulfonato de sodio</td>
</tr>
<tr>
<td><strong>Caollin malla 325</strong></td>
<td>Silicato de aluminio hidratado</td>
</tr>
<tr>
<td><strong>Clorantraniliprole TC</strong></td>
<td>1H-Pirazol-5-carboxamida</td>
</tr>
<tr>
<td><strong>Colorante Rojo R4</strong></td>
<td>Colorante Rojo R4</td>
</tr>
<tr>
<td><strong>Empicol</strong></td>
<td>Laurisulfato de sodio</td>
</tr>
<tr>
<td><strong>Formol 40</strong></td>
<td>Metanal</td>
</tr>
<tr>
<td><strong>Fosfon 225/50</strong></td>
<td>Acido amino trimetilen fosfórico</td>
</tr>
<tr>
<td><strong>Glicerina</strong></td>
<td>1,2,3 propanotiol</td>
</tr>
<tr>
<td><strong>Glifosato TC</strong></td>
<td>N((fosfonometil)glicina-isopropilamina) (1:1)</td>
</tr>
<tr>
<td><strong>Goma Xantano</strong></td>
<td>Goma xantano - polisacárido</td>
</tr>
<tr>
<td><strong>G-OXO</strong></td>
<td>Mezcla de ácido peracético y peróxido de hidrógeno</td>
</tr>
<tr>
<td><strong>Hidróxido de potasio 90%</strong></td>
<td>Hidfróxido de potasio</td>
</tr>
<tr>
<td><strong>Imidacloriprid TC</strong></td>
<td>N([1-(6-Chloro-3-pyridyl)methyl]-4,5-dihydroimidazol-2-yl]nitramida)</td>
</tr>
<tr>
<td>Nombre comercial del insumo</td>
<td>Nombre químico del insumo</td>
</tr>
<tr>
<td>-----------------------------</td>
<td>---------------------------</td>
</tr>
<tr>
<td>Isopropanol</td>
<td>propan-2-ol</td>
</tr>
<tr>
<td>Lactosa</td>
<td>4-O-(b-Dgalactopiranosil)-D-glucopiranosa</td>
</tr>
<tr>
<td>Monoisopropilamina 99%</td>
<td>2-Aminopropano</td>
</tr>
<tr>
<td>Oleosol FL 100</td>
<td>Mezcla: sal de alquilarmuido y plímero alquilril oxirano</td>
</tr>
<tr>
<td>Oleosol FL 650</td>
<td>No se cuenta con la fórmula</td>
</tr>
<tr>
<td>Orotan TM SN Dispersant</td>
<td>mezcla - no se cuenta con la fórmula</td>
</tr>
<tr>
<td>Pigmento Rojo</td>
<td>No se cuenta con la fórmula</td>
</tr>
<tr>
<td>Propilenglicol</td>
<td>propano-1,2-diol</td>
</tr>
<tr>
<td>QS-302-P50 (SG Powder)</td>
<td>polialquilrenoxido modificado heptametiltrisiloxano</td>
</tr>
<tr>
<td>Rishfloc 8180</td>
<td>policrilamida aniónica</td>
</tr>
<tr>
<td>Solutab</td>
<td>Carboximetilcelulosa de sodio</td>
</tr>
<tr>
<td>Synergen 9962</td>
<td>No se cuenta con la fórmula</td>
</tr>
<tr>
<td>Synergen 9903</td>
<td>No se cuenta con la fórmula</td>
</tr>
<tr>
<td>Tebuconazol TC</td>
<td>(RS)-1-p-clorofenil-4,4-dimetil-3-(1H-1,2,4-triazol-1-ilmetil)pentan-3-ol</td>
</tr>
<tr>
<td>Utramina 200</td>
<td>Amina etoxilada grasa</td>
</tr>
<tr>
<td>Ultranex NP 100</td>
<td>Nonilfenol etoxilado</td>
</tr>
<tr>
<td>Veegum</td>
<td>Silicato mineral hidratado de aluminio y magnesio</td>
</tr>
</tbody>
</table>

**Consumo de agua:**

- Subterranea: 45 m3/año

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

**Lugar de vertido 1:**

<table>
<thead>
<tr>
<th>Lugar de vertido</th>
<th>Descripcion</th>
<th>Cuenca/Subcuenca</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atmosfera</td>
<td>Evaporacion estival</td>
<td>Rio Santa Lucia</td>
</tr>
</tbody>
</table>

**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:**

<table>
<thead>
<tr>
<th>Nombre comercial del insumo</th>
<th>Nombre químico del insumo</th>
<th>Punto de consumo en el proceso o en la PTE</th>
<th>Consumo mensual</th>
</tr>
</thead>
</table>

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**Appendices** 60
<table>
<thead>
<tr>
<th>Name: Doña Celia 3</th>
<th>Location: -55,910614 ; -33,950578</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Producción:</strong></td>
<td></td>
</tr>
<tr>
<td>Leche</td>
<td>10137</td>
</tr>
<tr>
<td>Cows</td>
<td>507</td>
</tr>
<tr>
<td><strong>Sustancias químicas y materias primas usadas:</strong></td>
<td></td>
</tr>
<tr>
<td>Nombre comercial del insumo</td>
<td>Nombre químico del insumo</td>
</tr>
<tr>
<td>Name: La Gándara 1</td>
<td>Location -55,90017 ; -33,956503</td>
</tr>
<tr>
<td><strong>Producción:</strong></td>
<td></td>
</tr>
<tr>
<td>Leche</td>
<td>10553</td>
</tr>
<tr>
<td>Cows</td>
<td>528</td>
</tr>
<tr>
<td><strong>Sustancias químicas y materias primas usadas:</strong></td>
<td></td>
</tr>
<tr>
<td>Nombre comercial del insumo</td>
<td>Nombre químico del insumo</td>
</tr>
<tr>
<td>Name: La Gándara 2</td>
<td>Location -55,911892 ; -33,97725</td>
</tr>
<tr>
<td><strong>Producción:</strong></td>
<td></td>
</tr>
<tr>
<td>Leche</td>
<td>11639</td>
</tr>
<tr>
<td>Cows</td>
<td>582</td>
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<tr>
<td><strong>Sustancias químicas y materias primas usadas:</strong></td>
<td></td>
</tr>
<tr>
<td>Nombre comercial del insumo</td>
<td>Nombre químico del insumo</td>
</tr>
<tr>
<td>Name: Leticia 3</td>
<td>Location -56,286075 ; -33,992681</td>
</tr>
<tr>
<td><strong>Producción:</strong></td>
<td></td>
</tr>
<tr>
<td>Leche</td>
<td>11045</td>
</tr>
<tr>
<td>Cows</td>
<td>841</td>
</tr>
<tr>
<td><strong>Sustancias químicas y materias primas usadas:</strong></td>
<td></td>
</tr>
<tr>
<td>Nombre comercial del insumo</td>
<td>Nombre químico del insumo</td>
</tr>
<tr>
<td>Name: Leticia 4</td>
<td>Location -56,260953 ; -33,964586</td>
</tr>
<tr>
<td><strong>Producción:</strong></td>
<td></td>
</tr>
<tr>
<td>Leche</td>
<td>10849</td>
</tr>
<tr>
<td>Cows</td>
<td>542</td>
</tr>
<tr>
<td><strong>Sustancias químicas y materias primas usadas:</strong></td>
<td></td>
</tr>
<tr>
<td>Nombre comercial del insumo</td>
<td>Nombre químico del insumo</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Name: Doña Celia 2</th>
<th>Location: -55,927453 ; -33,943783</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Tratamiento:</strong></td>
<td>Estercolero – Laguna Anaeróbica – Laguna Facultativa – Riego</td>
</tr>
<tr>
<td>Lugar de vertido</td>
<td>Descripcion</td>
</tr>
<tr>
<td>Infiltración</td>
<td>Riego 31 ha pastoreo</td>
</tr>
<tr>
<td><strong>Caudal de descarga de efluentes 1:</strong></td>
<td>30 m3/dia</td>
</tr>
<tr>
<td>Name: Doña Celia 3</td>
<td>Location: -55,910614 ; -33,950578</td>
</tr>
<tr>
<td><strong>Tratamiento:</strong></td>
<td>Estercolero – Laguna Anaeróbica – Laguna Facultativa – Riego</td>
</tr>
<tr>
<td>Lugar de vertido</td>
<td>Descripcion</td>
</tr>
</tbody>
</table>

Appendices 61
Infiltración | Riego | 30 m³/día | Rio Santa Luna

<table>
<thead>
<tr>
<th>Caudal de descarga de efluentes 1</th>
<th>30 m³/día</th>
</tr>
</thead>
</table>

**Name:** La Gándara 1  **Location:** -55,90017 ; -33,956503

**Tratamiento:** Estercolero – Laguna Anaeróbica – Laguna Facultativa – Riego

**Lugar de vertido:** Descricion
**Descripción:** Cuenca/Subcuenca

**Infiltración:** Riego 31 ha pastoreo | Rio Santa Luna

<table>
<thead>
<tr>
<th>Caudal de descarga de efluentes 1</th>
<th>30 m³/día</th>
</tr>
</thead>
</table>

**Name:** La Gándara 2  **Location:** -55,911892 ; -33,97725

**Tratamiento:** Estercolero – Laguna Anaeróbica – Laguna Facultativa – Riego

**Lugar de vertido:** Descricion
**Descripción:** Cuenca/Subcuenca

**Infiltración:** Riego 34 ha pastoreo | Rio Santa Luna

<table>
<thead>
<tr>
<th>Caudal de descarga de efluentes 1</th>
<th>30 m³/día</th>
</tr>
</thead>
</table>

**Name:** Leticia 3  **Location:** -56,286075 ; -33,992681

**Tratamiento:** Estercolero – Laguna Anaeróbica – Laguna Facultativa – Riego

**Lugar de vertido:** Descricion
**Descripción:** Cuenca/Subcuenca

**Infiltración:** Riego 66 ha pastoreo | Rio Santa Luna

<table>
<thead>
<tr>
<th>Caudal de descarga de efluentes 1</th>
<th>30 m³/día</th>
</tr>
</thead>
</table>

**Name:** Leticia 4  **Location:** -56,260953 ; -33,964586

**Tratamiento:** Estercolero – Laguna Anaeróbica – Laguna Facultativa – Riego

**Lugar de vertido:** Descricion
**Descripción:** Cuenca/Subcuenca

**Infiltración:** Riego 49 ha pastoreo | Rio Santa Luna

<table>
<thead>
<tr>
<th>Caudal de descarga de efluentes 1</th>
<th>30 m³/día</th>
</tr>
</thead>
</table>

**Production of eggs**

**Name:** Granja Guillen  **Location:** (-56,212139 ; -34,076972)

**Producción:**

<table>
<thead>
<tr>
<th>Eggs</th>
<th>17000</th>
<th>unidades/día</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aves</td>
<td>5000</td>
<td>UP</td>
</tr>
</tbody>
</table>

**Sustancias químicas y materias primas usadas:**

<table>
<thead>
<tr>
<th>Nombre comercial del insumo</th>
<th>Nombre químico del insumo</th>
<th>Punto de consumo en el proceso o en la PTE</th>
<th>Consumo mensual</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ración</td>
<td>Producción</td>
<td>3</td>
<td>Ton/día</td>
</tr>
<tr>
<td>Oleina</td>
<td>Racion</td>
<td>1</td>
<td>Ton/día</td>
</tr>
<tr>
<td>Metionina -- Methionine</td>
<td>Racion</td>
<td>125</td>
<td>Kg/dia</td>
</tr>
<tr>
<td>Lisina</td>
<td>Racion</td>
<td>60</td>
<td>Kg/dia</td>
</tr>
<tr>
<td>Núcleo vitamínico M33</td>
<td>Racion</td>
<td>60</td>
<td>Kg/dia</td>
</tr>
</tbody>
</table>

**Consumo de agua:**

| Subterranea | 500 | m³/año |

**Wool laundry**

Appendices 62
**Name:** Lanera Piedra Alta  
**Location:** (-56,241202 ; -34,105759)

**Producción:**

<table>
<thead>
<tr>
<th>Producto</th>
<th>Producción</th>
<th>Unidad</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wool</td>
<td>2982,9</td>
<td>ton lana sucia / año 2015</td>
</tr>
</tbody>
</table>

**Sustancias químicas y materias primas usadas:**

<table>
<thead>
<tr>
<th>Nombre comercial del insumo</th>
<th>Nombre químico del insumo</th>
<th>Punto de consumo en el proceso o en la PTE</th>
<th>Consumo mensual</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkosynt 65</td>
<td>Alcohol graso etoxilado</td>
<td>Lavado</td>
<td>2940 kg/mes</td>
</tr>
<tr>
<td>Hidróxido Sodio 35%</td>
<td>Hidróxido sodio</td>
<td>Lavado y planchado</td>
<td>780 kg/mes</td>
</tr>
<tr>
<td>SELBANA 4554</td>
<td>Aceite ensimaje</td>
<td>Peinaduría</td>
<td>1670 kg/mes</td>
</tr>
</tbody>
</table>

**Tratamiento:** Sedimentador primario – tratamiento anaeróbio – laguna afine y almacenamiento - riego forestal y vertimiento cañada

**Lugar de vertido 1:**

<table>
<thead>
<tr>
<th>Lugar de vertido</th>
<th>Descripción</th>
<th>Cuenca/Subcuenca</th>
</tr>
</thead>
<tbody>
<tr>
<td>Curso de agua</td>
<td>Baños de enjuague</td>
<td>Rio Santa Lucia</td>
</tr>
</tbody>
</table>

**Caudal de descarga de efluentes 1:**

<table>
<thead>
<tr>
<th>Bimestre</th>
<th>Caudal medio diario (m&lt;sup&gt;3&lt;/sup&gt;/d)</th>
<th>Caudal máximo diario (m&lt;sup&gt;3&lt;/sup&gt;/d)</th>
<th>Horario de vertido</th>
<th>Días de vertido totales en el bimestre</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>84</td>
<td>96</td>
<td>0 a 24</td>
<td>34</td>
</tr>
<tr>
<td>2</td>
<td>84</td>
<td>96</td>
<td>0 a 24</td>
<td>47</td>
</tr>
<tr>
<td>3</td>
<td>84</td>
<td>96</td>
<td>0 a 24</td>
<td>46</td>
</tr>
<tr>
<td>4</td>
<td>84</td>
<td>96</td>
<td>0 a 24</td>
<td>45</td>
</tr>
<tr>
<td>5</td>
<td>84</td>
<td>96</td>
<td>0 a 24</td>
<td>25</td>
</tr>
<tr>
<td>6</td>
<td>84</td>
<td>96</td>
<td>0 a 24</td>
<td>46</td>
</tr>
</tbody>
</table>

**Lugar de vertido 2:**

<table>
<thead>
<tr>
<th>Lugar de vertido</th>
<th>Descripción</th>
<th>Cuenca/Subcuenca</th>
</tr>
</thead>
<tbody>
<tr>
<td>Infiltración</td>
<td>Efluente de lavados</td>
<td>Rio Santa Lucia</td>
</tr>
</tbody>
</table>

**Caudal de descarga de efluentes 2:**

<table>
<thead>
<tr>
<th>Bimestre</th>
<th>Caudal medio diario (m&lt;sup&gt;3&lt;/sup&gt;/d)</th>
<th>Caudal máximo diario (m&lt;sup&gt;3&lt;/sup&gt;/d)</th>
<th>Horario de vertido</th>
<th>Días de vertido totales en el bimestre</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>108</td>
<td>120</td>
<td>0 a 24</td>
<td>34</td>
</tr>
<tr>
<td>2</td>
<td>108</td>
<td>120</td>
<td>0 a 24</td>
<td>47</td>
</tr>
<tr>
<td>3</td>
<td>108</td>
<td>120</td>
<td>0 a 24</td>
<td>46</td>
</tr>
<tr>
<td>4</td>
<td>108</td>
<td>120</td>
<td>0 a 24</td>
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<td>5</td>
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<td>120</td>
<td>0 a 24</td>
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</tr>
<tr>
<td>6</td>
<td>108</td>
<td>120</td>
<td>0 a 24</td>
<td>46</td>
</tr>
</tbody>
</table>

**Wastewater treatment plant Florida**

**Name:** OSE – WWTP Florida  
**Location:** (-56,216398 ; -34,108297)

**Producción:**

| Nro Conexiones | 10099 |
| Población servida | 33640 |
| Caudal de operación promedio | 6070 m<sup>3</sup>/d |
### Sustancias químicas y materias primas usadas:

<table>
<thead>
<tr>
<th>Nombre comercial del insumo</th>
<th>Nombre químico del insumo</th>
<th>Punto de consumo en el proceso o en la PTE</th>
<th>Consumo mensual</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flopam FO 4690 SSH</td>
<td>Poliectrolito</td>
<td>Deshidratación de lodos</td>
<td>60 Kg</td>
</tr>
<tr>
<td>Cloruro Férrico</td>
<td></td>
<td>Reducción Química de Fósforo</td>
<td>7197 ton</td>
</tr>
</tbody>
</table>

### Consumo de agua:

| OSE | 78 | m3/dia |

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

### Lugar de vertido 1:

<table>
<thead>
<tr>
<th>Lugar de vertido</th>
<th>Descripcion</th>
<th>Cuenca/Subcuenca</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Rio Santa Lucia</td>
</tr>
</tbody>
</table>

### Caudal de descarga de efluentes 1:

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