Wastewater Reuse in the Llobregat: The Experience at the Prat de Llobregat Treatment Plant

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Abstract Water scarcity is a consequence of both natural and anthropogenic factors including highly variable temporal and spatially heterogenic distribution of precipitations, growing populations, increasing water demand particularly for agriculture, and the widespread contamination of water resources by a plethora of organic and inorganic contaminants. In the countries bordering the Mediterranean Sea, water is a renewable resource relatively scarce during certain periods. Therefore, sustainable management of water resources is of utmost importance in these countries. In Catalonia a Mediterranean region located in the northeast of Spain, the reuse of tertiary treated wastewater is evaluated as alternative resource for water supply. On this basis, several campaigns on water reuse were conducted by the Catalan Water Agency in order to artificially enhance the flow along the river. In fall of 2009, the impact of tertiary treated effluent discharge on the ecology (pathogens and indicators, macroinvertebrate community assemblages, and biomarkers) and water quality of the river (priority and emerging pollutants: polar pesticides, illicit drugs, estrogens and pharmaceuticals as well as on the pathogens and microbial indicators of faecal contamination) and consequently to the drinking water supplies was evaluated in the lower stretch of the Llobregat River located in the vicinity of the town of Barcelona (NE Spain). The key findings of this study are reported in this book chapter. Chemical parameters were not significantly affected by the reclaimed water discharge with the exception of a slight increase in the ammonium concentration, conductivity, and TOC. Concerning priority substances, three pesticides increased in concentration but only diazinon exceed the quality threshold for human supply. Regarding the ecotoxicological assessment of illicit drugs and pharmaceuticals using algae for the toxicity value, differences between river upstream and downstream to the discharge of the treated tertiary wastewater were detected. For the other organisms the differences were imperceptibles. No perceptible effects were detected either in the ecological status of the river or in the load of pathogens and fecal indicators of the river water. In conclusion, the use of tertiary treated effluent for water reuse did not produce important alterations on river water quality downstream of the reclaimed water discharge.

Keywords Ecology, Emerging pollutants, Pathogens, Water quality, Water reuse

Contents

1 Introduction: Water Scarcity in the Mediterranean Region

Global hydrological change is a consequence of climate change including global warming and changes in rain events, increase of agricultural impacts, and also anthropogenic changes in the morphology of the rivers like water transfers and river engineering. One of the most critical consequences is caused by water scarcity in extended drought periods. This may result in changes in the hydrologic resources, in carbon and nutrients transfer as well as their storage affecting the biodiversity, water quality including pollution by chemicals, and river ecosystem functioning, sediment supply to ocean, and also economic sectors that use and depend on water such as agriculture, tourism, industry, energy, and transport. The lack of water is of growing concern, and it attracts attention worldwide particularly in the Mediterranean regions where water shortages are generally ascribable to a large extent to growing demand regardless of the limited renewable water resources of irregular and unequal quality. Mediterranean rivers are characterized by important fluctuations in flow rates, with typical low winter and summer discharges and periodical floods in spring and autumn. In addition, some rivers in the Mediterranean basin present heavy contamination pressures from extensive urban, industrial and agricultural activities which translate into generally higher contamination.

One of the regions included in the Mediterranean basin that suffers from periodic water scarcity and eventual droughts is Catalonia (NE Spain). The observed tendency in Catalonia indicates that water demands are close to available water resources. Moreover, available water resources are expected to decrease in the medium and longer run. Undoubtedly, demands during the last decade have been higher than they were during the historic droughts of the 1940s or 1970s. Nowadays, in Catalan basins, the total water demand, including domestic supply, industrial activities, and irrigation, amounts to 3,123 hm^3 per year. Under the pressure of water scarcity and the expected increasing occurrence of drought events in the Mediterranean area [1], measures like water reclaim and reuse, proposed to provide alternative resources, are gaining major relevance [2]. Such measures are doubtlessly necessary from the point of view of resource sustainability and are usually promoted by water authorities. The reutilization of treated wastewater aims to be introduced in the future Spanish National Plans for Water Management and must be a key component of the new environmental policy that promotes a new water culture, trying to enhance the exploitation of nonconventional resources while ensuring the physical, chemical, and bacteriological water quality. In Spain, the legal basis for the regulation of the quality standards for reclaimed water for different applications is established by the Real Decreto (Royal Decree) 1620/2007 [3]. It defines the concept of reuse, introduces the regenerated water designation, determines the qualifications necessary to carry out the activity of water reuse, procedures to obtain the demanded concession required by this law, and also defines permitted applications of reclaimed water and quality requirements in each case. It also defines compulsory minimum quality criteria for the use of the regenerated waters according to uses.

In 2010, the Catalan Water Agency released a Water Management Plan according to the Water Framework Directive (2000/60/EC) requirements. This new water plan introduces a provision for additional water sources for upcoming years, such as reclaimed water for several uses. However, this plan requires additional plans for water demand management based on the type of water usage, one of which is the Drought Management Plan (DMP). This plan must set up a policy of risk management through prevention and mitigation of drought effects. DMP is currently being developed and provides scenarios in which measures are applied to reduce demands progressively and activate alternative water sources. Moreover, the Catalan Water Reuse Programme (CWRP) has recently been enabled by the Catalan Water Agency in order to quantify water reuse possibilities and establish normative rules in the Catalan River Basin District scenario. Reuse of treated wastewater is promoted and incorporated into integrated resource planning, known as direct or planned reuse of reclaimed water, and is viewed as an alternative source for groundwater and surface water withdrawals. Water treated at wastewater treatment plants (WWTP) and then through further additional or complementary processes (tertiary treatments) in connection with reclamation has the sanitary and physicochemical quality required for certain uses. Two types of tertiary treatments of the effluents are usually applied in Catalan WWTPs depending on the end use of the water. The basic treatment encompasses coagulation, flocculation, filtration, post (additional) disinfection, and oxygen saturation. The advanced one includes additional treatment by ultrafiltration and reverse osmosis [4]. For instance, the water reclamation station "El Prat," located in the metropolitan area of the city of Barcelona, provides water for different purposes: After the basic treatment the water can be utilized for irrigation of agricultural land as well as for golf courses in the surroundings but also for industrial use. Furthermore, part of the treated wastewater is returned to the river and near wetlands to maintain minimum flow and suitable environmental water levels. At the same time, a part of the treated wastewater is directed to a reverse osmosis plant (advanced treatment) for further treatment and the water is pumped into the underground to avoid salt water from the sea to seep into the groundwater resources.

The CWRP is expected to treat 229 hm^3/year of water corresponding to the production (excluding waste) of 204 hm^3/year of reclaimed water. The Program of Urban Wastewater Treatment enabled by the Catalan Water Agency foresees that a total of 720 hm^3/year of wastewater will be treated in Catalonia on the horizon 2015. Therefore, 31% of the total wastewater treated flow will be processed on reclamation facilities or directly reused after applying proper measures. The volume of reused water is foreseen to be achieved as a sum of three components: reuse already in service (51 hm^3/year), an ever-increasing utilization of existing reuse facilities, and, finally, entry into service of new facilities under this program [5].

2 Reclaimed Wastewater Experiment in the Llobregat River

The Llobregat River (Catalonia, NE Spain) is a good example of a Mediterranean river, suffering from low flows during normal conditions (~5 m^3/s) and extraordinary peak events (maximum recorded of 2,500 m^3/s) that periodically reset the system. In addition, the river receives the effluent discharges of 63 WWTPs. The Llobregat and Ter rivers are the most important water supply system for Barcelona and nearby cities, which requires about 525 hm^3 from reservoirs to meet all demands. Of these demands, 400 hm^3 are consumed by urban uses. However, dams located in Llobragat and Ter have a maximum storage capacity of 612 hm^3 (including flood management provisions), and they are not able to store a sufficient volume of water so as to ensure the supply in dry years. Taking into account that 80% of the time during the past 40 years reservoirs were above 70% of their maximum capacity (ACA 2009), it is questionable if the most appropriate solution to the problem would be a permanent increase in total reservoir volume, or the use of external sources, especially given the high cost and elevated environmental impacts. Instead, rapidly implementable, temporary solutions such as reclaimed water and water exchange appear to be the better choice. During the years 2007 and 2008, the Llobregat River basin experienced a severe drought which affected the water supply of drinking water facilities. The Catalan Water Agency (ACA) implemented a reuse water plan using reclaimed water from the Barcelona WWTP, which usually discharges into the sea. The objective was to maintain the river flow rate in the lower Llobregat River. Before doing so, several pilot studies were carried out. A first attempt was set up in autumn 2008 (first campaign) and presented many problems in controlling the degree of actual dilution at all times since it rained frequently during the experiment. The second exploratory test (second campaign) was set up in autumn 2009; this is the experiment described in this chapter where the effects of the tertiary wastewater on the ecology and water quality of the river and consequently to the drinking water supplies were evaluated [5–7]. This study was carried out in the lower part of the Llobregat River between the cities of Molins de Rei (site R0) and Sant Joan Despí (site R2) [6]; the latter being particularly important because the intake of an important waterworks supplying drinking water to the city of Barcelona is located there. Water from the WWTP tertiary treatment of El Prat de Llobregat (site RW2) was pumped upstream ca. 16.6 km and discharged into the river at 0.2 km downstream of site R0 (Fig. 1). This test was carried out for 23 days, from October 29 to November 20 of 2009, and different dilutions between river flow and reclaimed water were tested 3:1 ($Q_{RW2}/Q_{R2} = 0.25$), 2:1 and 1:1 dilutions). At the R0 and R1 river sites, the main water-quality parameters affecting human consumption were analyzed according to the Directive 98/83/EC. In addition, other specific analyses were carried out in order to assess water supply and aquatic ecosystem damage. Three different parameters were evaluated in the river: (1) biological quality using macroinvertebrates evaluating biological indices and biomarkers responses of the caddisfly larvae *Hydropsyche exocellata* [7], (2) microbiological parameters (pathogens and

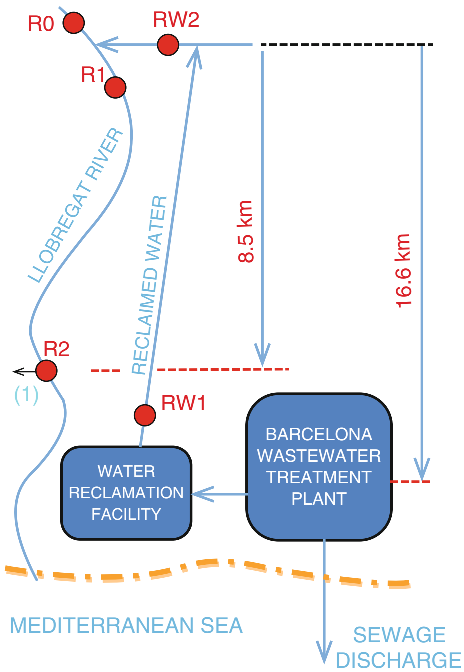

Fig. 1 Sampling points location in the lower stretch of the Llobregat River. *R0* Llobregat River at Molins de Rei; *R1* Llobregat River at Sant Joan Despí; *R2* WWTP El Prat de Llobregat, RW1 and RW2 are located in the pipe which transports reclaimed water

indicators [8]), and (3) occurrence of priority substances and emerging pollutants (pharmaceuticals, illicit drugs and estrogens, [9]). Several river points were sampled for the evaluation of the three parameters: upstream (R0) and downstream (R1 and R2) of the reclaimed water discharge site (Fig. 1) and also RW1 and RW2 sites for microbiological analysis, in order to detect the effect of reclaimed water transport on the concentration of microbiological indicators and pathogens. Microorganisms tested were: *Escherichia coli*, spores of sulfite-reducing clostridia, somatic coliphages, cytopathogenic enteroviruses, as well as total and infectious *Cryptosporidium* oocysts.

3 Chemical Analysis

In the last century, many contaminants have been detected in the aquatic environment and nowadays are considered classic pollutants like PCBs, PAH, some pesticides, etc. and included in the environmental regulatory lists. Recently, new contaminants have emerged as new contaminants, but most could have been in the environment for ages, and have remained undetected until recently. These are the emerging contaminants which are defined as compounds that are currently not covered by existing regulations of water quality (neither included in routine monitoring programs) and possible candidates for future regulation depending on research on their (eco)toxicity, potential health effects, public perception, and on monitoring data regarding their occurrence in the various environmental compartments [10, 11]. They include a diverse group of compounds including pharmaceuticals, illicit drugs, personal care products, steroids and hormones, surfactants, perfluorinated compounds, flame-retardants, industrial additives, and agents and gasoline additives as well as their transformation products [12]. Among these significant environmental trace pollutants, pharmaceuticals emerged as particularly relevant, due to several facts: (1) worldwide and continuous increase on their consumption and on their subsequent input into the environment; (2) design to be bioactive compounds which are able to cause potential effects on living organisms; (3) the possibility of antagonistic-synergistic interactions, for instance, growth inhibition of algae due to the simultaneous occurrence of a cocktail of pharmaceuticals [13].

Estrogens, both natural (e.g., estradiol, estrone, estriol, and their sulfate and glucuronide conjugates) and synthetic (e.g., ethynyl estradiol, used mainly as contraceptive), stand up for being aquatic contaminants present at very low concentrations (usually low ng/L or pg/L) but often sufficient to exert estrogenic effects, such as feminization and hermaphroditism, in aquatic organisms due to their very high estrogenic potency [14].

Illicit drugs (e.g., cocaine, heroin, cannabis, and their metabolites) represent a class of compounds recently discovered as emerging contaminants whose effects in the aquatic environment are still unknown [15]. All three compound classes were analyzed by online solid phase extraction–liquid chromatography–electrospray–tandem mass spectrometry (SPE–LC–ESI–MS/MS) following previously described methods [16–18].

3.1 Priority Contaminants and Chemical Parameters

The (physico-)chemical parameters ammonium concentration, conductivity, and TOC were monitored in the Llobregat River [6]. A slight increase in the river after the reclaimed water discharge was observed for all three parameters. Values for conductivity of 1,364 $\pm$ 262 μS/cm were measured in the site R0 while conductivity ranged from 2,231 to 2,765 μS/cm in R1 and R2 sites. In the same way, after the reclaimed water discharge, TOC concentrations also increased to some extent. TOC concentration varied from 4.23 mg/L in the site R0 to 8.5 mg/L in the R2 site. This is consistent with the organic load discharged by the water reclamation facility which doubled to the TOC concentration in the river [6]. Also, the concentrations of the organic target analytes increased to some degree. For instance, the concentrations of some pesticides such as terbutylazine (0.03 μg/L) and terbutryn (0.03 μg/L) were above the detection thresholds, but remained below the drinking water quality standards (Directive 98/83/EC) (<0.1 μg/L) [6]. However, the concentration of diazinon (maximum values of 0.24–0.39 μg/L) in surface waters exceeds the quality threshold for human water supply. It is worth mentioning that the water of the Llobregat River has to be treated in the drinking water facility prior becoming drinking water.

3.2 Occurrence and Evaluation of the Contamination Loads for Emerging Pollutants

Three classes of emerging contaminants were monitored in the Llobregat River water and in treated wastewater [9]. On the other hand, the conventional physical–chemical and microbiological contaminants, were covered by ACA. In the Llobregat River at some points, especially at drought periods, it is worth noting that WWTP effluents may represent almost 100% of the total flow of the river. Thus, relevant concentrations of organic pollutants are commonly found along the river, usually showing growing levels when moving downstream, due to the corresponding increase of WWTPs discharges and population density [19]. Moreover, the loads of sewage-borne contaminants could have been increased with the use of reclaimed waters for increasing drinking water supply. Although the reclaimed water originates from effluent wastewaters treated under efficient tertiary treatments, some compounds can be still present in the end product. Therefore, in this part of the work, we analyzed 103 emerging pollutants, including pharmaceuticals (74), illicit drugs (17), and estrogens (12), in the surface water and in the effluents pumped and discharged into the river from the WWTP el Prat de Llobregat after the tertiary treatment. Regarding pharmaceuticals in different samples, 58 compounds out of 74 target analytes were detected at least in one sample. In the treated effluent site RW2 (see map for location of the site in Fig. 1), levels of pharmaceuticals were higher than those detected in the surface waters, but still below 1,000 ng/L for the majority of the compounds with the exception of three antibiotics (azithromycin, erythromycin, and sulfamethazine) and the diuretic drug furosemide. Other compounds such as atenolol, bezafibrate, codeine, enrofloxacine, fenofibrate, metronidazole, and ofloxacine were detected occasionally at levels from 100 to 900 ng/L. At the site R0, located in the surface water upstream of the discharge of the tertiary effluent, three analgesics and anti-inflammatory drugs (acetaminophen, ibuprofen, and salicylic acid) were detected at levels higher than 100 ng/L, rarely exceeding 300 ng/L. Also other compounds were detected frequently, such as atenolol, carbamazepine, clarithromycin, erythromycin, metropolol, lorazepam, and sulfamethoxazole. Moreover, 39 compounds were detected at low ng/L levels. In general, at the site R2 the increase of concentrations was not significant for most of the compounds detected, with the exception of acetaminophen, diclofenac, erythromycin, and sulfamethazine, which were detected at levels higher than 100 ng/L or even higher for salicylic acid (500 ng/L) [9]. In order to have a better approaching on the relative influence of both the river upstream and the effluent discharge on the overall amount of pollutants detected downstream in the river, loads expressed as mass flows in mass/time units were calculated. In contrast to the direct comparison of the concentrations, the calculation of the mass loads provides a more convenient method to quantify and compare the relative contribution of each stream (river and effluent). The mass loads were calculated as the product of concentrations of emerging pollutants per flow in the three sampled sites for emerging pollutants analysis (R0, R2, and RW2). The loads for the site R1 were calculated by the sum of the load river upstream (site R0) and the load from the treated effluent (RW2) since R0 and RW2 were really close (ca. 0.2 km) so that in such short part of the river other contributions were deemed negligible. Regarding pharmaceutical pollution, the calculated loads of the effluent contribution (RW2) seem to predominate over that of the river upstream (R0) accounting for 40–65% of the total load (see Fig. 2). Comparing the results between the first and the second campaign (see section reclaimed wastewater experiment in the Llobregat River for further details), the contribution of the pharmaceuticals from the latter campaign was slightly higher than that reported in 2008 [20] possibly due to lower effluent dilution ratios. The highest effluent contributions were observed with the lowest effluent dilution (1:1) which corresponds to the last sampling date (Fig. 2).

In contrast, the relative contribution of the effluent to the total load of illicit drugs in the river downstream of the discharge point was lower than that of the river upstream (between around 30% and 50%), but, as for pharmaceuticals, this contribution was observed to increase to approximately 60–70% in the second campaign (see Fig. 3), which again could be explained by the comparatively lower river discharges. This important effluent contribution in the 2009 campaign led to increasing levels of illicit drugs downstream the river, i.e., to higher levels in R2 than in R0 (except in two sampling dates where overall illicit drug concentrations were practically the same). As compared to the previous campaign, both the number of illicit drugs detected and the levels measured in the 2009 campaign were lower. Of the five classes of illicit drugs measured, cocainics followed by amphetamine-like compounds and opiates were the most ubiquitous and abundant compounds in river water where cannabinoids and LSD and its metabolites were not detected at all. In treated wastewater the profile found was somewhat different, with a predominance of amphetamine-like compounds over opiates and cocainics (the latter are the drugs best removed in WWTPs). Of the 17 drugs of abuse analyzed, only 7 were detected namely amphetamine, ephedrine, ecstasy, methamphetamine, cocaine and its metabolite benzoylecgonine, and the opiate morphine. Individual drug concentrations did not surpass 40 ng/L in river water (the maximum concentration of benzoylecgonine was 39.6 ng/L in R0) and 80 ng/L in treated wastewater (maximum concentration for ephedrine was 79.5 ng/L).

In the case of estrogens (Fig. 3) only two free compounds, namely, estrone and diethylstilbestrol, were detected. Unlike pharmaceuticals and illicit drugs, estrogens were observed to decrease downstream the river, with levels in R0 (up to 15 ng/L) considerably higher than in R2 (below 2 ng/L and in two cases below method detection limits). In treated wastewater, only one out of the six samples analyzed was positive for estrogens (2.30 ng/L estrone in the last sampling date), thus, except in this case, contribution of the WWTP effluent to the total load of estrogens in the river downstream the discharge point was zero. Estradiol, estriol, ethynyl estradiol, and all conjugated estrogens (glucuronides and sulfates of estradiol, estriol, and estrone) were not detected in any sample. As in the case of illicit drugs, both the number of estrogens detected and the levels measured were lower in 2009 than in 2008.

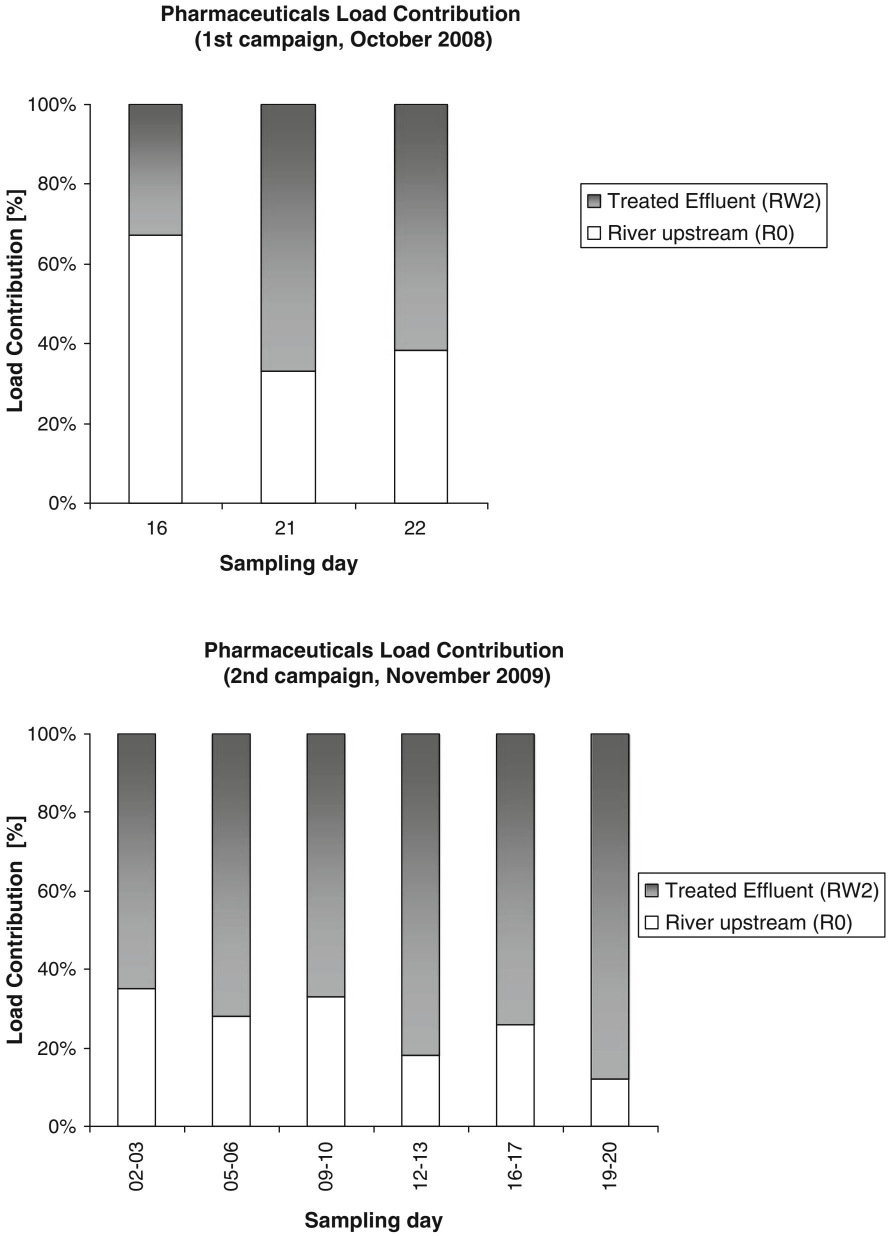

Fig. 2 Relative contribution (in percentage) of the river (R0) and the treated effluent (RW2) to the total mass load of pharmaceuticals in site R2 at different sampling dates of the two sampling campaigns (2008 and 2009)

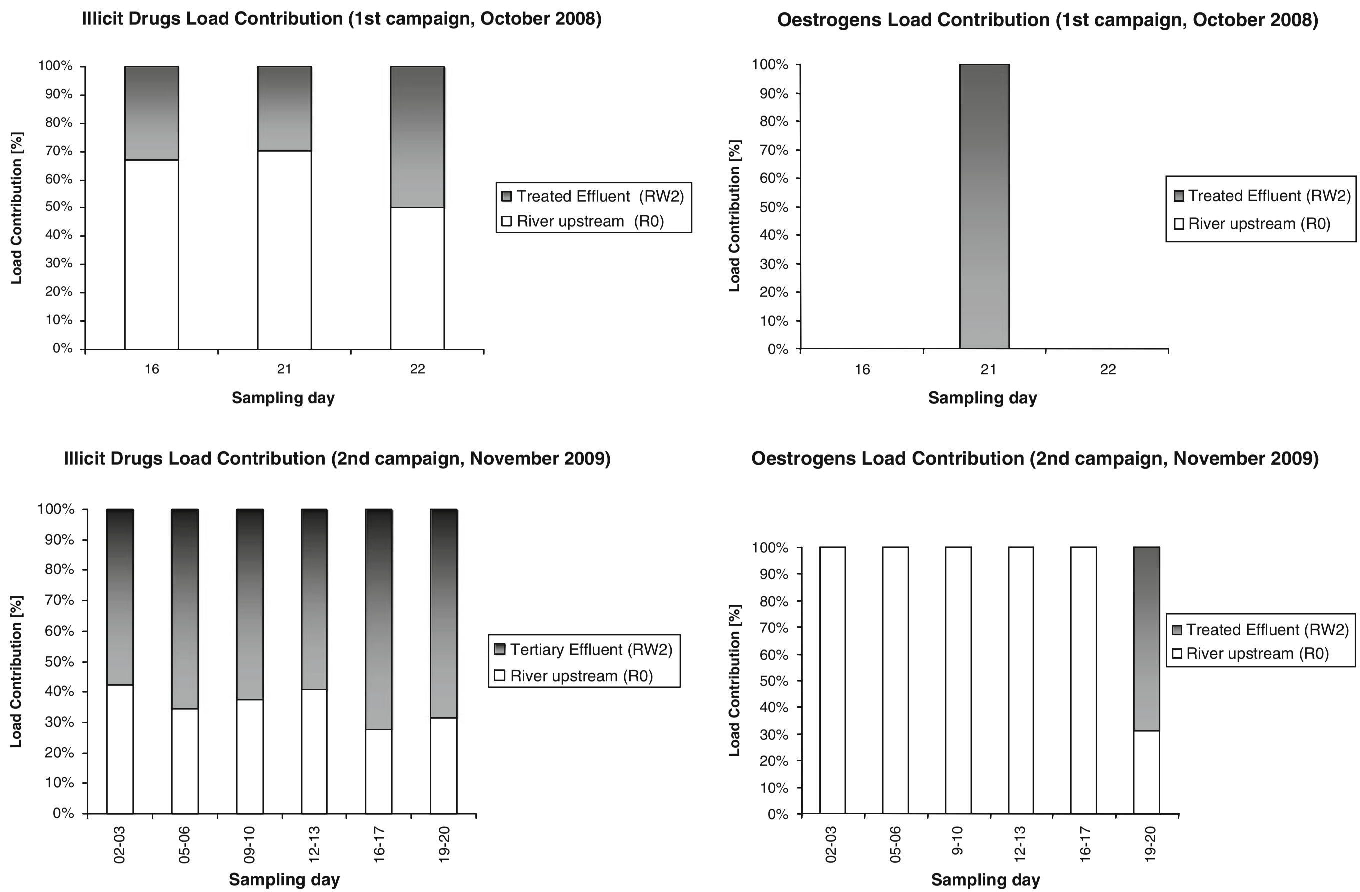

Fig. 3 Relative contribution (in percentage) of the river (R0) and the treated effluent (RW2) to the total mass load of illicit drugs and oestrogens in site R1 at different sampling dates of the two sampling campaigns (2008 and 2009)

4 Evaluation of Effects of the Reclaimed Water on the River Water

In this section, the effects of the reclaimed water discharge on the Llobregat River for the second experiment were assessed using both theoretical and experimental approaches. First, we assessed the risk of the emerging pollutants by computing hazard quotients for three freshwater organisms based on their presence and acute toxicity data. Second, the effects of the introduction of the reclaimed water on the microbial community and the biological status of the Llobregat River were evaluated.

4.1 Theoretical Approach: Environmental Risk Assessment of Emerging Pollutants

The main issue of the presence of drugs in the environment is that they are inherently bioactive and they can cause adverse toxicological effects to the environment and to humans through drinking water or food intake. While it is impracticable to evaluate the effects of exposure directly to humans and to a lesser extent to aquatic organisms, other nontarget organisms (bearing similar receptors or biomolecules to humans) are used for such purposes and generate ecotoxicological data for single compounds or mixtures to a nontarget organism. Using the ecotoxicological data the ecological risk of a target analyte can be estimated calculating the so-called hazard quotient. The hazard quotient (HQ) is basically the ratio of the exposure estimate (predicted environmental concentrations, PEC) to a “no adverse effects level” considered to reflect a “safe” environmental concentration or dose (predicted no-effect concentration, PNEC). Instead of PECs the measured environmental concentrations (MECs) are commonly used, and the acute toxicity values are used for PNECs. Therefore, HQ is MEC/PNEC. PNECs are typically calculated from EC_{50} values corrected by a safety factor of 1,000 as it is recommended by the Water Framework Directive (Directive 2000/60/EC). The Water Framework Directive [21] acknowledged the convenience of assessing the toxicity using three levels of the trophic chain. Algae, daphnids, and fish are usually employed as reference organisms. The calculation of the overall HQ for a mixture of compounds ($HQ = \sum HQ_i$) can be calculated under the assumption of concentration addition (CA) mode of action [22]. For a first approximation to estimate the toxicity of a mixture CA can be accepted as a common principle model. Thus, this entails that all the components contribute to the final effect and that neither synergic nor antagonic effects among compounds occur. Therefore, it is typically accepted that if HQ is equal or higher than 1, potential effects to the aquatic ecosystems are probable to take place. In order to take into account that chronic toxicity at lower concentrations of pharmaceuticals and illicit drugs can take place, a safety factor of 1,000 was applied in the calculation of the PNECs. EC_{50} values were extracted from the literature or they were estimated with USEPA's ECOSAR (Ecological Structure Activity Relationships, ECOSAR v1.00) model. For some compounds, more than one value was found; therefore, the lowest one was taken into account.

4.1.1 Environmental Risk Assessment of Emerging Pollutants

Table 1 shows the overall hazard quotients calculated for pharmaceuticals and illicit drugs in R0 and R2 river sites. It is worth to mention that only two compounds (ciprofloxacin and sulfamethoxazole) individually showed HQ above 1 (see Fig. 4). The overall HQs were in general low for both pharmaceuticals and illicit drugs, although in the case of algae the pharmaceuticals detected might represent a risk (overall HQ always above 1 in both R0 and R2). In general the HQ values were slightly higher for pharmaceuticals than for illicit drugs, in site R2 than in site R0, and in algae than in daphnids and in fish.

In the case of estrogens, the environmental concern focuses on their estrogenic activity, which can result in effects, such as feminization, in exposed organisms. For assessment of this risk estradiol equivalent concentrations (EEQ) were calculated for each river sample (R0 and R2) by multiplying the concentration measured of each detected compound by its corresponding estradiol equivalent factor (EEF, defined as the EC_{50} of the compound relative to the EC_{50} of 17β-estradiol) and applying the simple additive approach. In spite of the low levels of estrogens detected, EEQs above 1 were obtained for some samples from both R0 and R2, and reached 14 ng/L in the sample containing 12.2 ng/L of diethylstilbestrol (one of the most potent estrogens known with an EEF of 1.1), which alert about potential estrogenic effects in the aquatic ecosystems.

4.2 Experimental Approach

Introducing reclaimed water with chemical and biological contamination in the river can cause microbiological and ecological damage. Therefore, in this section the effects of the reclaimed water on the microbiological and ecological status are reviewed.

4.2.1 Effects of the Reclaimed Water on the Microbiological Quality of the River Water

Pathogens constitute recognized health hazards associated to municipal and animal related industries water reuse. However, present day reclamation technologies are able to control and reduce the risk posed by these hazards down to acceptable levels.

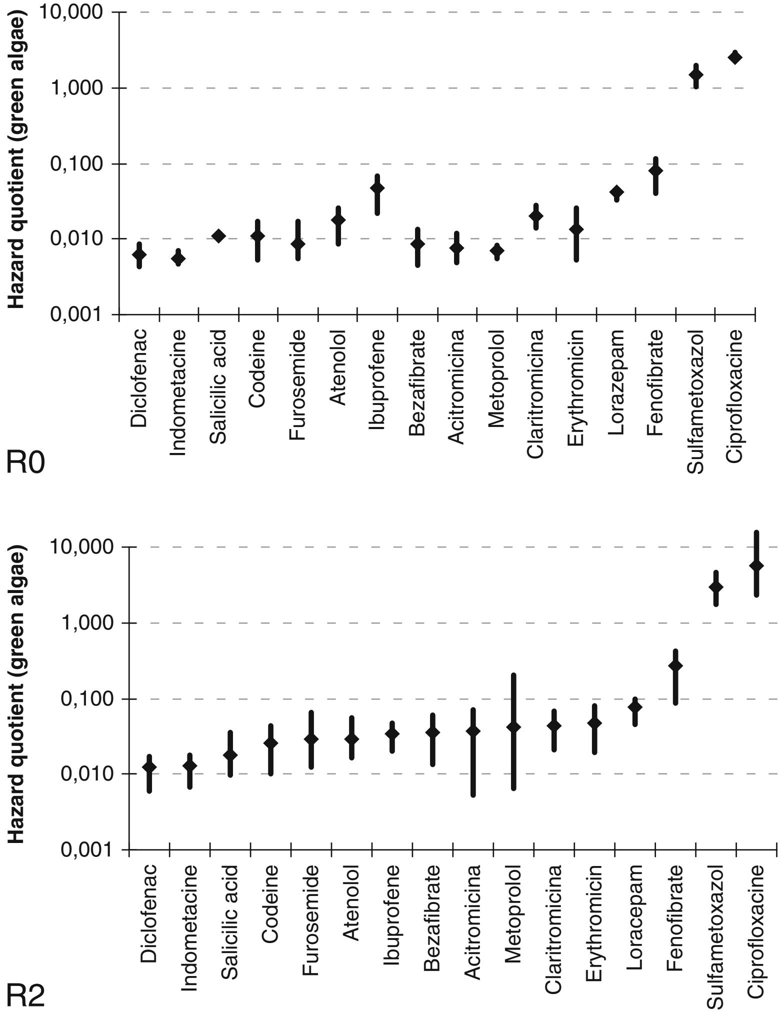

Fig. 4 Hazard quotients calculated with the detected concentration and the calculated toxicity of green algae for selected pharmaceuticals in R0 and R2 sites

Regarding the possibility of augmenting drinking water supplies with reclaimed water, a pair of reports [23, 25] recognize the feasibility of using reclaimed water to supplement drinking-water sources, but recommend adding viruses and protozoa to traditional, bacterial indicators based, microbiological water quality controls in order to better estimate the health risks linked to water-borne infectious diseases.

Pathogens and Fecal Indicators

E. coli, which is the traditional bacterial indicator, spores of sulfite reducing clostridia as potential indicators of oocysts of protozoa, somatic coliphages as potential indicators of viruses, cytopathogenic enteroviruses, and total and infectious *Cryptosporidium* oocysts were determined in sampling points RW1, which is reclaimed water delivered by the treatment plant; RW2 that is reclaimed water discharged in the river after transport upstream through a 15.6 km long pipe, R0, R1 and R2.

Methods used were either the standardized ones or the more sensitive methods available to detect "still alive" indicators and pathogens. Two different tertiary treatments were applied to the secondary effluent of a WWTP (biological-activated sludge) during the follow up of the effect of discharge of reclaimed water in the river. First one included physic-chemical (flocculation), microfiltration (10-μm pore size membranes), UV irradiation (medium pressure lamps) and chlorination; whereas the second one omitted chlorination.

The concentrations of indicators in reclaimed water were significantly different depending on whether the water was chlorinated or not. After chlorination only spores of clostridia were detected. But even in the non-chlorinated reclaimed water the values of indicators were quite low, with the following geometric means per 100 mL: *E. coli* 15 colony forming units (CFU), spores of sulfite reducing clostridia 50 CFU and somatic coliphages 40 plaque forming units (PFU). The cytopathogenic enteroviruses and infectious *Cryptosporidium* numbers were below the detection limit (<0.01 PFU per liter for enterovirus and <0.02 fluorescent foci per liter for *Cryptosporidium*) despite the treatment applied (Fig. 5). *Cryptosporidium* oocysts were still found in some samples regardless of the treatment, but the highest values never reached 1 oocyst per 10 L that is the value required for drinking water by the only regulation that includes [26]. The transport upstream through the pipe did not change significantly the numbers of the three indicators detected in the reclaimed water. The concentrations of indicators and pathogens in the river, upstream the discharge point (R0), were significantly higher than the concentrations in reclaimed water. Geometric means per 100 mL or river water were: *E. coli*, 700 CFU; spores of sulfite reducing clostridia, 1,300 CFU; and somatic coliphages, 7,000 PFU, with the lowest value for each parameter being higher than the higher values in reclaimed water only treated with UV. Low, ranging from 1 to 5 per liter, but measurable values of both studied pathogens were found in the great majority of the samples (Fig. 5). Numbers of indicators and pathogens determined in river water sampled downstream the discharge point (R1) were either significantly lower, *E. coli* and coliphages, or nonsignificantly different, spores of clostridia, enteroviruses and *Cryptosporidium*, than those upstream the discharge point. No significant differences related to the different dilutions between river flow and reclaimed water (3:1 ($Q_{RW2}/Q_{R2} = 0.25$), 2:1 and 1:1 dilutions) were detected. Thus, it can be concluded that the release of reclaimed water in the river does not impair the microbiological quality of the river water used as source water by the Sant Joan Despi Drinking Water Facility.

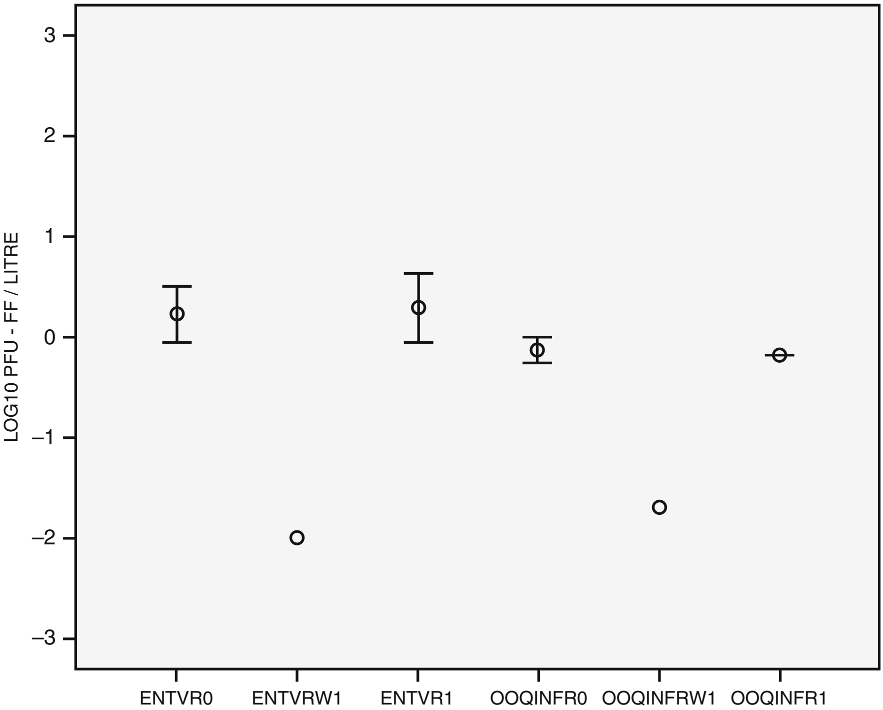

Fig. 5 Log10 values of the concentrations of infectious pathogens (mean values and 95% confidence levels) in reclaimed water (R2 samples) and river water samples (R0 and R1). Values of enteroviruses are expressed as plaque forming units (PFU) (ENTVIR) and infectious *Cryptosporidium* (INFOOQ) as fluorescent foci (FF) per liter

These results indicate that discharging reclaimed water into the river does not increment the microbiological health risks associated to the use of Llobregat river water as source water. Then, in emergency situations, at least from the infectious diseases point of view, the risks of augmenting drinking water supplies with reclaimed water can be satisfactorily and safely managed.

4.2.2 Effects of the Reclaimed Water on the Ecological Status: Macroinvertebrate Community Assemblages and Biomarkers

The reclaimed water discharged into the lower part of the Llobregat River did not produce significant changes in the structure and composition of macroinvertebrate communities [27]. The number of taxa is similar in both sites, before and after the reclaimed water discharge, with some reduction of densities downstream. Some of the differences for biological quality indices analyzed (IASPT, ICM-Star, and IMMi-T) between R0 and R1 were found already before the reclaimed water dumped into the river. The lower Llobregat River already has low water quality and low abundant species even before the discharge of reclaimed water. Biomarkers used in the analysis also indicate a low risk of sublethal contamination due to reclaimed water discharge [27]. Three out of the five biomarkers measured in field collected caddisfly larvae (*H. exocellata*) were affected by the reclaimed water input. However, this seems not to produce any changes in the macroinvertebrate community structure found in the lower Llobregat River, at least in short time.

5 Conclusions

Due to the water scarcity in the catchments' area of the Llobregat River, a Mediterranean river in Catalonia, the Catalan Water Agency designed performed several experiments for the artificial recharge of this River with reclaimed water. In this book chapter, the impact of the reclaimed water on ecology, microbial communities, and chemical contamination [24] during the campaign carried out in fall 2009 is summarized. The concentrations of emerging pollutants detected in this experiment were compared with those obtained in the previous campaign which took place in fall 2008. The water quality was evaluated for priority pollutants, three (physico-)chemical parameters (ammonium concentration, conductivity, and TOC), pharmaceuticals, illicit drugs, and estrogens. In general a null or slight increase of the water quality parameters was observed. Regarding the analyzed pesticides, only one was detected at concentrations higher than the quality threshold for human water supply, although this parameter was reduced once water was treated for urban purposes. Comparing concentrations of pharmaceuticals in river water upstream and downstream of the discharge point of the reclaimed tertiary effluent, a slight increase of concentrations was observed but it was not significant. Concerning illicit drugs and their metabolites, the impact of the discharge into the river was even lower than the one observed for pharmaceuticals. In contrast to the previous campaign (fall 2008), estrogens levels were clearly higher river upstream than downstream. In order to get a better assessment of the relative contribution of the river basin upstream and discharged sewage to the burden of the different micro-contaminants, their respective concentrations and flows should be handled together, especially if one considers the low proportion of the receiving river flow relative to the discharged tertiary effluent. Comparing the calculated loads of emerging pollutants downstream at R0 site to the R2 site (upstream), it was feasible to identify the origin of the overall pollution. While pharmaceuticals and illicit drugs loads were mostly allocated to the effluent, being the relative contribution dependent on the effluent to receiving river dilution ratio, the origin of estrogens was mainly the upstream river (except at the effluent's lowest dilution).

Finally, an evaluation of effects of the reclaimed water on the river water was done. With a theoretical approach, the ecotoxicity risk for pharmaceuticals and illicit drugs was assessed. First, hazard quotients were calculated based on the concentration ranges found and the ecotoxicological data reported in the literature for three reference organisms belonging to different trophic level (fish, dapnids, and algae), as it is recommended by the WFD. Comparing the hazard quotients for the river water upstream and downstream of the discharge point, differences were appreciable but not significant. In general, no relevant risks were identified, with the only exception of pharmaceuticals vs. algae that were likely to occur both in river upstream and downstream. In a similar fashion, estrogenicity was evaluated using EEQs for the estrogenic compounds identified. In the present case, river upstream showed higher estrogenicity than river downstream, attributable to estrone and diethylstilbestrol. An experimental approach, in turn, was used for the evaluation of the effects of the reclaimed water on the microbiological and on the ecological status. Several organisms and biomarkers were used to detect the effects of the wastewater, concluding that the risks of supplementing drinking water supplies with reclaimed water can be satisfactorily and safely managed.

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