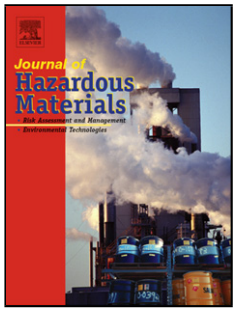

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- Microfiltration and reverse osmosis evaluated in a pilot plant
- Combined study removal of pharmaceuticals and pesticides
- Typical recalcitrant pharmaceuticals in WWTPs eliminated through MF-RO system
- Exploration of reuse possibilities for reclaimed water

Pharmaceuticals and pesticides in reclaimed water. Efficiency assessment of a microfiltration-reverse osmosis (MF-RO) pilot plant.

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Abstract

Water reuse is becoming a common practice in several areas in the world, particularly in those impacted by water scarcity driven by climate change and/or by rising human demand. Since conventional wastewater treatment plants (WWTPs) are not able to efficiently remove many organic contaminants and pathogens, more advanced water treatment processes should be applied to WWTP effluents for water reclamation purposes. In this work, a pilot plant based on microfiltration (MF) followed by reverse osmosis (RO) filtration was applied to the effluents of an urban WWTP. Both the WWTP and the pilot plant were investigated with regards to the removal of a group of relevant contaminants widely spread in the environment: 28 pharmaceuticals and 20 pesticides. The combined treatment by the MF-RO system was able to quantitatively remove the target micropollutants present in the WWTP effluents to values either in the low ng/L range or below limits of quantification. Monitoring of water quality of reclaimed water and water reclamation sources is equally necessary to design the most adequate treatment procedures aimed to water reuse for different needs.

Keywords: Reclaimed Water, Water Reuse, MF-RO Pilot Plant, Pharmaceuticals, Pesticides

Highlights:

- Microfiltration and reverse osmosis evaluated in a pilot plant
- Combined study removal of pharmaceuticals and pesticides

- Typical recalcitrant pharmaceuticals in WWTPs eliminated through MF-RO system
- Exploration of reuse possibilities for reclaimed water

1. Introduction

Public and scientific interest for newly recognized organic micro-contaminants has become an important issue for a number of water utilities. Among these chemicals there is an expanding list of pharmaceuticals, which are being found ubiquitous in the environment in the last years [1-5]. Even though information about the effects of many of these compounds in the environment and in public health is still scarce, applying treatment barriers to avoid their entering in the aquatic environment appears adequate for cautionary reasons. Wastewater treatment plants (WWTP) are indeed major discharge points of pharmaceutical compounds in natural receiving waters since they are unable to efficiently remove most of the pharmaceutical compounds from sewage water [6-8].

The presence of pesticides in the environment is usually linked to diffuse pollution coming from run-off of agricultural fields after their application. However, pesticides and biocides can be also used in urban areas for gardening and other non-crop protection purposes. Due to the input of urban run-off into the sewer lines, the presence of pesticides in urban wastewaters should not be underestimated: some studies have found that urban biocides loads can be found in water in the same range as the most widely-used agricultural pesticides [9-11]. Therefore, evaluation of WWTPs performance regarding elimination of micropollutants such as pharmaceutical products and pesticides is necessary to assess their potential impact in the environment.

The application of newly developed tertiary treatments to produce better quality treated water is attracting the attention of water managers, especially as an opportunity for reusing water for appropriate purposes. As a result, wastewater can be a source of

reusable water but represents also a source of contamination. The challenge of wastewater reuse is to eliminate pathogens and micropollutants that could have negative impacts on human's health, animal's health and the environment [12, 13]. Water reuse is practiced across Northern and Southern Europe although there are no guidelines, best practice or regulations at a EU level other than the Urban Wastewater Directive (91/271/EEC), which states that "*treated wastewater shall be reused whenever appropriate*" to minimize the adverse effect on the environment [14, 15]. In addition, the Water Framework Directive (WFD) (2000/60/EC) refers, under Annex VI (v) to "emission controls" and under Annex VI(x) to "*efficiency and reuse measures inter alia, promotion of water efficient technologies in industry and water saving techniques for irrigation"* [16]. In Spain, the Royal Decree (RD 1620/2007, Annex I) establishes the acceptable values for selected quality parameters that reclaimed water needs to comply depending on the use [17]. The different uses are grouped into five broad categories: urban, agricultural, industrial, recreational, and environmental.

Different technologies can be used for water treatment before water reuse, such as oxidation, activated carbon adsorption, and membrane processes including reverse osmosis (RO) and nanofiltration (NF). Membrane processes are often chosen since they achieve high removals of constituents like dissolved solids, organic carbon, inorganic ions, and regulated and unregulated organic compounds [18]. The use of RO, in particular, allows the use of the treated waters for more exigent purposes. Reverse osmosis processes have proved highly effective at removing a wide range of emerging contaminants [19-21]. However, RO membranes may become fouled or scaled and

consequently shortened in its useful life if feed water quality is not suitable. Therefore a pretreatment step, such as microfiltration, is needed for turbidity reduction, stabilization of the water, microbial control, etc.

In this work, the performance of a pilot wastewater treatment system based on a microfiltration step coupled to a reverse osmosis filtration (MF-RO system) that treated on-site the effluents of a urban wastewater treatment plant was studied. A multi-monitoring approach in the wastewater treatment plant and in the pilot plant included selected pharmaceuticals as emerging environmental contaminants, and a group of pesticides as well-known water contaminants. The main objective of the work was to evaluate the feasibility of the MF-RO system for the removal efficiency of these contaminants and to preliminary assess the applicability of the water obtained for multiple reuse possibilities.

2. Materials and Methods

2.1. Description of the WWTP and the Pilot Plant. Sampling campaign

The municipal WWTP where the pilot plant was installed and fed with the treated effluent is located at Torroella de Montgrí municipality (Girona, Northeastern Spain). Torroella de Montgrí is located 5 Km far from the Mediterranean Sea and has a territorial extension of 6,613 ha and 11,385 inhabitants. Torroella is at the Ter River banks, in the vicinity of its mouth (average flow rate of 25 m^3 s^{-1}). Along its watershed the Ter river collects discharges from metallurgic, pulp mill, textile and tannery industries as well as raw sewage inputs from small adjacent communities [22]. Torroella de Montgrí

municipality also includes the beach resort of L'Estartit, which undergoes important fluctuations in population size during the summer season due to the high tourism activity.

The WWTP of Torroella consists on a primary sedimentation stage to remove grit, fat and grease and a secondary treatment, which is based on activated sludge, with the corresponding nitrogen removal. The total Hydraulic Retention Time (HRT) of the plant is 47 hours (33 hours corresponding to the biologic reactor and 14 hours to the decanter vessel). Although plant is designed to work with 16,500 m^3/day. Input flows during the year ranged from 3584 m^3/day (October) to 6940 m^3/day (August). For water reuse, a tertiary system based on disinfection through high intensity-low pressure UV lamps and chlorination as tertiary treatment is applied. Reclaimed water can be used for field irrigation, especially during the dry season (i.e., June to August) when the river flow is not enough to meet agriculture needs [22]. In addition a pilot plant, which consists of a microfiltration system followed by a RO filtration system (Figure 1), was tested as an alternative tertiary treatment or WWTP effluents. Hollow fiber membranes (1775 fibers; 1.1m long; 1.1 mm diameter;) with a molecular weight cut-off (MWCO) of 500,000 Da (Koch; Romicon; polysulfone) and with 6.2 m^2 surface, were used for the microfiltration unit (module model number: HF 66-43-PM500; module length:1.1 m; module diameter: 127 mm) and were operated at a flux of 14 m^3/h and a flow rate of 2258 L/m^2/h. For reverse osmosis the "spiral wound with tape outwrap" membranes (Koch, TFC®-ULP; polyamide; module model number: 4040ULP; module length:1m; module diameter 99,1 mm) with 7.3 m^2 surface were working at a flux of 8.7 m^3/d and 50 L/m^2/h flow rate) and with water recoveries around 65%. Total suspended solids are eliminated from 5,5-

9.6 mg/L to 1.6-1.7 mg/L through MF and to levels lower than 1 mg/L after RO. Effluent conductivity was not altered by MF whereas through RO it dropped from c.a. 3000 μS/cm to c.a. 150 μS/cm. Membrane fouling and scaling of membranes in the pilot plant was controlled by periodical cleaning using water reverse flow. In addition, chlorine and citric acid were used for a thorough cleaning of the MF membranes whereas sodium hydroxide and citric acid was used for the cleaning of RO membranes. Both, MF and RO membranes were cleaned before the sampling campaign to provide the most optimal working conditions Residence time of the effluent in the MF system is 3 minutes whereas for RO is about 3.2 minutes.

Influent and effluent wastewater from the main WWTP, tertiary effluent (after UV treatment) as well as treated water from different points along the pilot plant were collected and monitored for pharmaceutical products and pesticides during a campaign conducted along various days in summer 2009. In total, seven sampling points were selected (Fig.1): (1) influent of the WWTP, (2) effluent of the WWTP (equivalent to the entrance of the pilot plant), (3) permeate MF (located after the microfiltration system), (4) permeate RO, (5) concentrate RO (residual of the reverse osmosis) and (6) tertiary effluent (after UV treatment in the WWTP).

Two different sampling campaigns were performed where 24h-composite samples of influent wastewater were collected using a portable automatic sampler (Hach Lange Sigma 900) whereas the rest of the samples were collected as grab samples taking into account the corresponding HRT of the corresponding water treatment. Namely, after 47

hours for the WWTP effluent , 3 minutes later for MF filtrate and 3.2 minutes later for RO permeate. Water samples were collected in pre-cleaned amber glass bottles (2.5 L) and transported to the laboratory under cold conditions. Once in the laboratory, samples were well-mixed and filtered through a 0.45 nylon membrane filter (Whatman), and stored in PET bottles at -20ºC until microcontaminant analyses.

2.2. Chemicals

All standards used were of high purity grade (>90%). Details about the standards purchased can be found in supplementary materials section (SM1). Individual stock standard solutions were prepared on a weight basis in methanol at 1 mg/mL and stored in the dark at -20ºC. Two standard solutions were prepared by appropriate dilution of individual stock solutions: a mixture of all pharmaceutical standards and a mixture of pesticides. Further dilutions of mixtures were prepared in methanol–water (25:75, v/v), in the case of pharmaceuticals, and in methanol, in the case of pesticides, and were used as working standard solutions.

HPLC-grade methanol, acetonitrile and water (LiChrosolv) were supplied by Merck (Darmstadt, Germany). Hydrochloric acid 37%, NH4Ac and HAc were from Merck (Darmstadt, Germany). Nitrogen for drying 99.995% of purity was from Air Liquide (Spain).

2.3. Micropollutants analysis

Analysis of micropollutants (pesticides and pharmaceuticals) was performed using a Waters 2690 HPLC system (Milford, MA, USA) coupled to a Quattro triple–quadrupole mass spectrometer from Micromass (Manchester, UK), equipped with an orthogonal electrospray (ESI) ionization source. Two different selected reaction monitoring (SRM) transitions were monitored per compound. To maximize sensitivity, data acquisition was performed under time-scheduled conditions. To compensate for possible matrix effects internal standard calibration was applied using isotopically labeled compounds. Quantification values were corrected by the method recovery values obtained for the different matrices analyzed and that ranged from 40 to 149%.

2.3.1 Analysis of Pesticides

Target pesticides were chosen because of their widespread use and high frequency of detection both in aquatic environments and in WWTPs [11, 23, 24]. Their selection was also based on legal requirements of the EU and information gathered from water authorities. Their analysis, based on automated on-line solid phase extraction-liquid chromatography-tandem mass spectrometry (SPE-LC-MS/MS), was performed according to the method described by [25, 26]. Extraction of the samples was carried out with a sample processor Prospekt-2 (Spark Holland, Emmen, The Netherlands) configured for high sample volumes and connected in series with the LC–MS/MS instrument. On-line SPE was performed with disposable trace enrichment polymeric cartridges: Hysphere Resin GP for pesticides measured in negative ionization mode, and PLRP-s for the pesticides measured in positive ionization mode (both from Spark Holland). The samples (5 mL) were loaded at a flow-rate of 8 mL/min onto the cartridges previously conditioned with 1 mL acetonitrile and 1 mL water (flow-rate 5 mL/min). Subsequent washing of the

cartridges was carried out with 1 mL of HPLC water (flow-rate 5 mL/min). Elution of the target analytes directly onto the chromatographic column was performed with the chromatographic mobile phase.

Chromatographic separation was performed using a reversed-phase Purospher STAR-RP-18e analytical column (125 × 2 mm, 5 μm particle diameter) preceded by a guard column (4 × 4 mm, 5 μm) of the same packing material from Merck (Darmstadt, Germany). On-line elution of the trapped pesticides onto the chromatographic column was performed at 0.2 mL/min with a 45 min gradient starting from 10% acetonitrile in water, increasing to 50% acetonitrile in 5 min, and continuing to 80% in 20 min. During the following 5 min the column was cleaned with 100% acetonitrile, readjusted to the initial conditions in 2 min, and equilibrated for further 13 min.

2.3.2. Analysis of Pharmaceutical products

Target compounds were selected based on their occurrence and ubiquity in the aquatic environment as well as their high human consumption worldwide according to the information found in the literature [27-29]. All target compounds were extracted in one single extraction step according to the method previously published by [30]. In brief, the samples (100 mL of influent, 200 mL of effluent and concentrate RO, and 500 mL of the other water matrices) were passed through Oasis HLB cartridges (60 mg, 3 mL, from Waters Corporation, Milford, MA) previously conditioned with 5 mL of methanol followed by 5 mL of HPLC-grade water. Elution was performed with 2 ×4 mL of methanol at a flow of 1 mL/min. The extracts were evaporated under a nitrogen stream

and reconstituted with 1 mL of methanol–water mixture (25:75, v/v). Chromatographic separation was carried out with the same column used for pesticides under the conditions described in [30] .

3. Results and Discussion

3.1. Occurrence and Removal of Micropollutants in the WWTP

Target pharmaceutical compounds and pesticides were monitored in the influent and after the secondary and the tertiary treatment in the WWTP. Table 1 lists the concentration levels (dissolved fraction) of the selected compounds. The levels found for pharmaceuticals in influent water were similar to those found in other urban WWTPs elsewhere [6, 8, 28]. Acetaminophen (or paracetamol) was the most abundant compound in the raw wastewater, where it reached 237 μg/L; however, concentrations in the μg/L range have been commonly reported for this compound in other European WWTPs, [6, 28] with values as high as, e.g., 492 μg/L [31]. In terms of load at the inlet of the WWTP, acetaminophen was followed by other analgesics and antinflamatory drugs (ibuprofen and ketoprofen), the lipid regulators gemfibrozil and bezafibrate, and the betablocker atenolol. Antibiotics levels ranged between 102 ng/L (for trimethoprim) and 792 ng/L (for azythromycin). Psychiatric drugs were below the method limit of quantification in wastewater except in the case of carbamazepine (214-246 ng/L). Ranitidine was the Histamine H1 and H2 receptor antagonist found at the highest concentration (332 – 436 ng/L).

Despite being the most concentrated pharmaceuticals found in wastewaters, analgesics and antinflamatories are also the compounds with higher removal rates in conventional

WWTPs [32, 33]. Removals in the range 85-100% were achieved for these compounds after conventional treatment in the Torroella WWTP; with the only exception of diclofenac, which increased in concentration. Figure 2 shows the overall removal achieved for most of the contaminants tested, distinguishing between the WWTP and the pilot plant. As shown in Table 1 some compounds like propyphenazone, propanolol, sotalol, carbamazepine and diclofenac were poorly or not removed at all, with concentrations sometimes higher in the effluent than in the influent; for the sake of clarity these compounds have not been included in Figure 2. Increasing pharmaceutical concentrations after wastewater treatment are usually attributed to deconjugation of the corresponding conjugated metabolites by action of glucuronidases during the treatment process and/or to desorption from particles [8, 34]. Diclofenac exhibited up to 50% increase in concentration after passing through the Torroella WWTP (table 1). Similar behavior has been observed in other conventional WWTPs as well as in systems based on membrane bioreactor (MBR) [8, 35-37]. The low removal efficiency for carbamazepine, on the other hand, can be explained by its resistance to biodegradation (carbamazepine was included in the category of "no removal" in the classification scheme for pharmaceutical biodegradation established by Joss et al. [38], though cleavage of glucuronide conjugates by enzymatic processes has also been hypothesized [35, 39]. In the case of the other psychiatric drugs, fluoxetine and paroxetine, removal rates could not be calculated because they were measured (though at low concentrations) in the effluent, but were below their respective limits of quantification (LOQ) in the influent (12 and 4 ng/L for fluoxetine and paroxetine, respectively, versus 3 and 1 ng/L for the same

compounds in the effluent). The LOQ and LOD calculated for each compound in each matrix are listed in Table 2 and Table S1 respectively.

Concerning pesticides, only terbutylazine, diazinon, linuron, mecoprop, bentazone and MCPA were above their respective LOQ in the influents of the WWTP, with values ranging between 8 ng/L for bentazone and 607 ng/L for diazinon (Table 1). Diazinon has also been the compound showing the highest concentration in other studies investigating the occurrence of pesticides in urban wastewaters [9]. Next to its use in agriculture, diazinon has also been used as insecticide in urban areas (e.g., against lice on roses, fish moths in wet rooms etc. [40]. However, diazinon is now a non authorized active substance according to the Decision 2007/393/EC related to the Directive 91/414/EEC (concerning the placing of plant protection products (PPP) on the market) [41]. The deadline for its sale was June of 2008. Tertbutylazine, an authorized active substance until 2021 (Regulation EC No 820/2011), was also found at levels between 163 and 263 ng/L. Terbuthylazine is a triazine herbicide and as such is closely related to the priority pollutants simazine and atrazine. Neither diazinon nor terbutylazine are in the list of priority pollutants established in the Directive 2008/105/EC (or its recent amendment) [42]. However, these compounds are the two most problematic, out of 73 investigated as potential priority pollutants, according to the classification made by Von der Ohe and col. in a recent study [29]. On the other hand, all compounds measured in the influent were substantially reduced in the WWTP effluent (removal rates varied between 50% for mecoprop and 100 % for linuron). However, other pesticides, such as diuron, isoproturon, chlortoluron, simazine and desethylatrazine, not detected in the influent were found in the

effluent as well as in the samples subsequently collected along the treatment process in the pilot plant. Again, the comparatively higher LOQ achieved for many of these pesticides in the influent than in the effluent could be behind some of these data.

After tertiary treatment in the WWTP by means of UV radiation and chlorination some compounds present in the secondary effluent were removed to below quantification or detection limits (e.g. simazine, dimethoate, and 2,4-D) but others still remain at similar concentration (e.g. terbutylazine, diazinon, mecoprop and diuron).

Overall, it was obvious that the WWTP posed a barrier to many pollutants, but could not completely eliminate these compounds. Main forces of elimination of micropollutants in WWTP are transformation processes and sorption into the sludge [43].

3.2. Removal of micropollutants in the pilot plant

The number of WWTPs equipped with membrane technologies such as RO and NF has increased remarkably during the last years, especially in regions where treated wastewater is intended for reuse applications, and/or where higher quality water is desired. The presence of the selected pesticides and pharmaceuticals in the pilot plant was determined before and after microfiltration (points 2 and 3 in figure 1, respectively), before and after RO (points 3 and 4, respectively), as well as in the concentrate resulting from this last step (Table 1). Stand-alone membrane microfiltration hardly made any difference in the concentration of the various target micropollutants found to be present in the secondary WWTP effluent. The operated microfiltration membrane did not allow any retention of the investigated substances. Removal by size exclusion was actually not

expected to be relevant because the MWCO of the MF membranes is in the range of 300.000 g/mol, whereas size of micropollutants was always below 1000 g/mol. Meanwhile, adsorption effects between the membrane surface and the micropollutants could have occurred but they were also discarded, as no removal was observed in this step. Even though MF is not very effective removing micro pollutants it is used as pretreatment for particular matter reduction and water stabilization and therefore to avoid fouling and clogging of the RO membranes, which guarantees optimal conditions for RO work.

Most of the compounds were removed completely or at least to values below the method LOQ after RO filtration. Among the three major factors affecting solute rejection in membranes −electrostatic repulsion, hydrophobic/adsorptive interactions and steric hindrance [18]− the latter seems to play the major role in the removal of the target compounds in the system [44]. Based on this, molecules larger than the MWCO of the membrane cannot permeate through the membrane due to size exclusion [18, 45]. RO should thereby remove those compounds that have molecular weights above approximately 200 g/mol [46]. The investigated target pesticides and pharmaceuticals have a molecular mass between 200 and 450 g/mol, with the exception of the antibiotics erythromycin and azythromycin (734 and 749 g/mol, respectively) and the analgesic acetaminophen (150 g/mol). Therefore, high removal rates were expected at this stage for basically all compounds. Removals between 98% and 100% were indeed observed for the majority of pharmaceuticals. Even though most of the pharmaceuticals were present in the microfiltration permeate at levels higher than 100 ng/L, RO filtration reduced their

loads to the low ng/L range or to below the method LOQs. For the pharmaceuticals and the pesticides that were present in the MF permeate at levels below 100 ng/L and/or close to their LOQ, the calculated removal percentages were lower but the RO process still acted as an effective barrier reducing their levels to just a few ng/L or to non detected. This is the case of the pesticides tertbutylazine, diazinon, MCPA and mecoprop, and the pharmaceutical clofibric acid, that presented RO removals around 70%. As expected, acetaminophen, with a MW lower than the RO cut-off, exhibited much lower removal at the RO step.

Elimination values obtained with RO for the analyzed compounds are similar to those observed in other studies, where removals >98% were obtained for different types of pharmaceuticals [44, 45, 47, 48]. Regarding pesticides, removal percentages for those found in the RO feed water (microfiltration permeate) at high enough concentration were calculated: 67%, 90% and 88% removals were found for diazinon, diuron, and 2,4 D respectively. Kosutic et al. observed removals between 78-99% for MCPA and other pesticides [49], whereas between 97-98% removal was achieved for MCPA and mecoprop with different RO membranes [50]. In summary, the RO filtration proved to pose a physical barrier for the majority of the pollutants, although most of them were still present in the RO permeate at low ng/L values or below LOQs, which are between 0.1 and 20 ng/L (see Table 2). The maximum concentration found in RO permeate was 16.7 ng/L for the pharmaceutical acetaminophen and 13 ng/L for the pesticides diazinon and diuron.

Pressure-driven separation membranes such reverse osmosis represent an outstanding technology to deal with a broad range of organic and inorganic contaminants and constitutes an effective barrier for rejection of these pollutants [45]. This has been confirmed in the present study, with regard to pharmaceuticals and pesticides. However, other studies illustrated that some hydrophobic endocrine disrupting compounds (EDCs) like natural hormones can adsorb to the membrane, thus decreasing rejection since upon saturation the compounds diffuse through the membrane [51]. On the other hand, for the case of recalcitrant compounds such as the antiepileptic drug carbamazepine, the antiinflamatory diclofenac and some betablockers (sotalol and propanolol) physical barriers such as RO are the only means to efficiently remove them from effluents. RO constitutes thus an added value in water treatment for those contaminants that are not well removed in conventional CAS and also in MBR.

3.3. Concentrate from reverse osmosis

The RO system of the pilot plant at Torroella operates with water recoveries around 65%, which generates relatively high volumes of concentrates (up to 7 m^3/day) containing all the retained compounds, salts and other compounds that constitute a potentially serious threat to aquatic ecosystems if discharged to water bodies, and therefore needs a suitable and environmentally friendly management option [52] . In our study concentrations in the µg/L range in the RO concentrate were found for 8 out of the 20 investigated pharmaceuticals (azythromycin, diclofenac, ketoprofen, atenolol, sotalol, bezafibrate, gemfibrozil, and carbamazepine) whereas the highest observed pesticide concentration was considerably lower: 208 ng/L for diuron. Appropriate treatment or disposal of these

RO brines, is therefore a requirement and a challenge for an environmentally friendly management. Acceptable methods of waste disposal typically include discharge to waste treatment facilities, or to an evaporation pond [53]. Other innovative and promising strategies to reduce the organic pollutant load of RO concentrate include advanced oxidation processes such as ozonation, fenton processes, photocatalysis and photooxidation, sonolysis and electrochemical oxidation, although the high cost of some of these technologies may limit their application [52].

3.4. Water Reclamation. Potential applications of reclaimed water

A tertiary treatment based on UV irradiation is in place at the WWTP site and the suitability of the reclaimed water for its application for irrigation was already evaluated and considered good enough in terms of presence of contaminants [22]. In the present study, a comparison between the removal efficiencies of the tertiary treatment (UV) with the removals obtained by the pilot plant with the combined system of membranes was performed. Both tertiary treatments were applied to the effluents of secondary treatment of the conventional WWTP. Figure 3 gathers together the removal data for pharmaceuticals, grouped according to their therapeutic class, through the different treatments evaluated. Psychiatric drugs were not considered since they exhibited negative removal in some treatment steps as already explained in section 3.1. As shown in the figure, UV treatment was not very efficient in terms of removal of pharmaceutical compounds, with removal values very similar to those provided by the microfiltration step alone. Only filtration through the combined MF-RO system in the pilot plant provided quantitative removal for most of the pharmaceuticals (> 97%). As mentioned

before, the pilot plant studied in this work was implemented in the WWTP site in order to review and evaluate the applicability and possibilities of advance treatment based on membrane technology of WWTP effluents for water reclamation. Micropollutants presence can be undesirable residuals in reclaimed water used for irrigation of crop fields intended for human consumption and although almost all the pollutants detected in influent water were also found in the finished (after MF-RO) water; they were at very low concentrations, in the low ng/L range. In the case of pesticides, none of them surpassed the levels set in the European legislation for water intended for human consumption (Directive 98/83/EC) [54]. On the other hand, conductivity of wastewater feeding the WWTP can achieve values of 3000 µS/cm because of users pumping water from wells impacted by marine intrusion in the sewage, and RO can help decrease salinity of WWTP effluents till values below 200 µS/cm thus suitable for agricultural irrigation. On the other hand, paradoxically, the water of the river wouldn't even comply with the Spanish regulations for water reuse in terms of quality as set by the Royal Decree 1620/2007 for agricultural irrigation [17]. To this sense blending the river water with the better quality RO filtrate would first provide a suitable water for field irrigation and would also decrease the demands of the river water, which needs to be used in a great extent for the abstraction of drinking water for the city of Barcelona.

4. Conclusions

The treatment efficiency of a pilot plant equipped with a MF membrane coupled to a RO membrane was preliminary evaluated as an alternative tertiary treatment of WWTP effluents regarding the removal of selected micropollutants. Elimination of most of the

substances was incomplete in the previous conventional WWTP even after existing tertiary treatment based on UV irradiation. In contrast, drastic removal of most of the compounds was achieved through the MF-RO system. All compounds were reduced to levels lower than 16 ng/L (highest value detected in RO permeate). This is especially important for the compounds that were not efficiently removed during conventional WWTP and were thereby still present at high concentrations (in the range of 162-240 ng/L) in the wastewater effluents, as it happened in the case of carbamazepine, diclofenac, atenolol, azythromycin and erythromycin. Reverse osmosis is thus a practical method to reduce concentrations of these recalcitrant compounds drastically (98-99% removal obtained). RO membranes act as a physical barrier that blocks many micropollutants as well as transformation products generated during wastewater treatment and that can also pose an environmental risk. In addition, this physical treatment does not lead to the formation of contaminant byproducts, as in the case of advanced oxidation processes (AOPs) or biological-based treatments, where these transformation products could also be of environmental concern. The most important benefit of water reuse for irrigation purposes of the Torroella WWTP effluents is that irrigation needs from the crop fields in the area, do not need to be covered by River Ter water, which is preferably devoted for the abstraction of drinking water for the city of Barcelona. This is particularly important in periods of water scarcity when the river flow is not enough to cover all the water demands. Water reuse can also help to control over-abstraction in wells, and eventually to increase water availability. Tertiary treatment based on membranes in Torroella de Montgrí pilot plant provided a safe option in order

to obtain higher quality water although their use is not widespread due to their high cost in terms of energy consumption.

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References:

[1] K.K. Barnes, D.W. Kolpin, E.T. Furlong, S.D. Zaugg, M.T. Meyer, L.B. Barber, A national reconnaissance of pharmaceuticals and other organic wastewater contaminants in the United States -I) Groundwater Sci. Total Environ., 402 (2008) 192-200.

[2] B. Ferreira da Silva, A. Jelic, R. Lopez-Serna, A.A. Mozeto, M. Petrovic, D. Barcelo, Occurrence and distribution of pharmaceuticals in surface water, suspended solids and sediments of the Ebro river basin, Spain, Chemosphere, 85 (2011) 1331-1339.

[3] S. Gonzalez, R. Lopez-Roldan, J.-L. Cortina, Presence and biological effects of emerging contaminants in Llobregat River basin: A review, Environ. Poll., 161 (2012) 83-92.

[4] R. Loos, B.M. Gawlik, G. Locoro, E. Rimaviciute, S. Contini, G. Bidoglio, EU-wide survey of polar organic persistent pollutants in European river waters, Environ. Pollut. (2009) 561-568.

[5] V. Osorio, R. Marce, S. Perez, A. Ginebreda, J.L. Cortina, D. Barcelo, Occurrence and modeling of pharmaceuticals on a sewage-impacted Mediterranean river and their dynamics under different hydrological conditions, Sci.Total Environ. 440 (2012) 3-13.

[6] E. Gracia-Lor, J.V. Sancho, R. Serrano, F. Hernandez, Occurrence and removal of pharmaceuticals in wastewater treatment plants at the Spanish Mediterranean area of Valencia, Chemosphere, 87 (2012) 453-462.

[7] A. Jelic, M. Gros, A. Ginebreda, R. Cespedes-Sanchez, F. Ventura, M. Petrovic, D. Barcelo, Occurrence, partition and removal of pharmaceuticals in sewage water and sludge during wastewater treatment, Water Res., 45 (2011) 1165-1176.

[8] S. Zorita, L. Martensson, L. Mathiasson, Occurrence and removal of pharmaceuticals in a municipal sewage treatment system in the south of Sweden, Sci.Total Environ., 407 (2009) 2760-2770.

[9] M. Köck-Schulmeyer, M. Villagrasa, M. López de Alda, R. Cespedes, F. Ventura, D. Barceló, Occurrence and behavior of pesticides in wastewater treatment plants and their environmental impact, Sci.Total Environ., 458-460 (2013) 466-476.

[10] H. Singer, S. Jaus, I. Hanke, A. Lück, J. Hollender, A.C. Alder, Determination of biocides and pesticides by on-line solid phase extraction coupled with mass spectrometry and their behaviour in wastewater and surface water, Environ. Poll., 158 (2010) 3054-3064.

[11] I.K. Wittmer, R. Scheidegger, H.-P. Bader, H. Singer, C. Stamm, Loss rates of urban biocides can exceed those of agricultural pesticides, Sci.Total Environ., 409 (2011) 920-932.

[12] M. Jacob, C. Guigui, C. Cabassud, H. Darras, G. Lavison, L. Moulin, Performances of RO and NF processes for wastewater reuse: Tertiary treatment after a conventional activated sludge or a membrane bioreactor, Desalination, 250 (2010) 833-839.

[13] T. Wintgens, T. Melin, A. SchÃ¤fer, S. Khan, M. Muston, D. Bixio, C. Thoeye, The role of membrane processes in municipal wastewater reclamation and reuse, Desalination, 178 (2005) 1-11.

[14] A.N. Angelakis, B. Durham, Water recycling and reuse in EUREAU countries: Trends and challenges, Desalination, 218 (2008) 3-12.

[15] CEC: Council of the European Communities. Directive 91/271/EEC concerning urban wastewater treatment. Off J Eur Union 1991;L 135/40..

[16] CEC: Council of the European Communities. Directive 2000/60/EEC establishing a framework for the community action in the field of water policy (EEU Water Framework Directive). Off J Eur Union 2000;L 327/1.

[17] Royal Decree 1620/2007, Which sets the legal framework for the reuse of treated wastewater. Spanish Regulations for Water Reuse

[18] C. Bellona, J.E. Drewes, P. Xu, G. Amy, Factors affecting the rejection of organic solutes during NF/RO treatment - a literature review, Water Res., 38 (2004) 2795-2809.

[19] S.A. Snyder, S. Adham, A.M. Redding, F.S. Cannon, J. DeCarolis, J. Oppenheimer, E.C. Wert, Y. Yoon, Role of membranes and activated carbon in the removal of endocrine disruptors and pharmaceuticals, Desalination, 202 (2007) 156-181.

[20] H. Huang, H. Cho, K. Schwab, J.G. Jacangelo, Effects of feedwater pretreatment on the removal of organic microconstituents by a low fouling reverse osmosis membrane, Desalination, 281 (2011) 446-454.

[21] H. Siegrist, A. Joss, Review on the fate of organic micropollutants in wastewater treatment and water reuse with membranes, Water Sci. Technol., 66 (2012) 1369-1372.

[22] D. Calderon-Preciado, C. Jimenez-Cartagena, V. Matamoros, J.M. Bayona, Screening of 47 organic microcontaminants in agricultural irrigation waters and their soil loading, Water Res., 45 (2011) 221-331.

[23] A.C. Gerecke, M. Schärer, H.P. Singer, S.R. Müller, R.P. Schwarzenbach, M. Sägesser, U. Ochsenbein, G. Popow, Sources of pesticides in surface waters in Switzerland: pesticide load through waste water treatment plants-current situation and reduction potential. , Chemosphere 48 (2002) 307-315.

[24] M. Neumann, R. Schulz, K. Schäfer, W. Müller, W. Mannheller, M. Liess, The significance of entry routes as point and non-point sources of pesticides in small streams, Water Res., 36 (2002) 835-842.

[25] A.A. Kampioti, A.C. Borba da Cunha, M.J. López de Alda, B. Damià, Fully automated multianalyte determination of different classes of pesticides, at picogram per litre levels in water, by on-line solid-phase extraction-liquid chromatography-electrospray-tandem mass spectrometry., Anal. Bioanal. Chem., 8 (2005) 1815-1825.

[26] M. Kuster, M.J. Lopez de Alda, C. Barata, D. Raldua, D. Barcelo, Analysis of 17 polar to semi-polar pesticides in the Ebro river delta during the main growing season of rice by automated on-line solid-phase extraction-liquid chromatography-tandem mass spectrometry, Talanta, 75 (2008) 390-401.

[27] P. De Voogt, M.-L. Janex-Habibi, F. Sacher, L. Puijker, M. Mons, Development of a common priority list of pharmaceuticals relevant for the water cycle, Water Sci. Technol., 59 (2009) 39-46.

[28] M. Gros, S. Rodriguez-Mozaz, D. Barcelo, Fast and comprehensive multi-residue analysis of a broad range of human and veterinary pharmaceuticals and some of their metabolites in surface and treated waters by ultra-high-performance liquid chromatography coupled to quadrupole-linear ion trap tandem mass spectrometry, Journal of Chromatography A, 1248 (2012) 104-121.

[29] P.C. Von der Ohe, V. Dulio, J. Slobodnik, E. De Deckere, R. Kühne, R.-U. Ebert, A. Ginebreda, W. De Cooman, G. Schürmann, W. Brack, A new risk assessment

approach for the prioritization of 500 classical and emerging organic microcontaminants as potential river basin specific pollutants under the European Water Framework Directive, Sci.Total Environ., 409 (2011) 2064-2077.

[30] M. Gros, M. Petrovic, D. Barceló, Development of a multi-residue analytical methodology based on liquid chromatography-tandem mass spectrometry (LC-MS/MS) for screening and trace level determination of pharmaceuticals in surface and wastewaters, Talanta, 70 (2006) 678-690.

[31] B. Kasprzyk-Hordern, R. Dinsdale, A. Guwy, Multiresidue methods for the analysis of pharmaceuticals, personal care products and illicit drugs in surface water and wastewater by solid-phase extraction and ultra performance liquid chromatography–electrospray tandem mass spectrometry, Anal. Bioanal. Chem., 391 (2008) 1293-1308.

[32] Collado, N. , S. Rodriguez-Mozaz, M. Gros, A. Rubirola, D. Barceló, J. Comas, I. Rodriguez-Roda, B. G., Pharmaceuticals occurrence in a WWTP with significant industrial contribution and its impact into the river system, Environ. Poll. (accepted).

[33] P. Verlicchi, M. Al Aukidy, E. Zambello, Occurrence of pharmaceutical compounds in urban wastewater: Removal, mass load and environmental risk after a secondary treatment. A review, Sci.Total Environ., 429 (2012) 123-155.

[34] S.K. Behera, H.W. Kim, J.-E. Oh, H.-S. Park, Occurrence and removal of antibiotics, hormones and several other pharmaceuticals in wastewater treatment plants of the largest industrial city of Korea, Sci.Total Environ., 409 (2011) 4351-4360.

[35] M. Clara, S. B, O. Gans, E. Martinez, N. Kreuzinger, H. Kroiss, Removal o selected pharmaceuitclas, fragances and endocrine disrupting compounds in a membane bioreactor and conventional wastewater treatment plants, Water Res., 39 (2005) 4797-4807.

[36] S.D. Kim, J. Cho, I.S. Kim, B.J. Vanderford, S.A. Snyder, Occurrence and removal of pharmaceuticals and endocrine disruptors in South Korean surface, drinking, and waste waters, Water Res., 41 (2007) 1013-1021.

[37] L. Lishman, S.A. Smyth, K. Sarafin, S. Kleywegt, J. Toito, T. Peart, B. Lee, M. Servos, M. Beland, P. Seto, Occurrence and reductions of pharmaceuticals and personal care products and estrogens by municipal wastewater treatment plants in Ontario, Canada, Sci.Total Environ., 367 (2006) 544-558.

[38] A. Joss, S. Zabczynski, A. Göbel, B. Hoffmann, D. Löffler, C.S. McArdell, T.A. Ternes, A. Thomsen, H. Siegrist, Biological degradation of pharmaceuticals in municipal wastewater treatment: Proposing a classification scheme, Water Res., 40 (2006) 1686-1696.

[39] A. Wick, G. Fink, A. Joss, H. Siegrist, T.A. Ternes, Fate of beta blockers and psycho-active drugs in conventional wastewater treatment, Water Res., 43 (2009) 1060-1074.

[40] R. Ashauer, I.K. Wittmer, C. Stamm, B.I. Escher, Environmental risk assessment of fluctuating diazinon concentrations in an urban and agricultural catchment using toxicokinetic-toxicodynamic modeling, Environ. Sci. Technol., 45 (2011) 9783-9792.

[41] Commission Decision 2007/393/EC concerning the non-inclusion of diazinon in Annex I to Council Directive 91/414/EEC and the withdrawal of authorisations for plant protection products containing that substance.

[42] CEC: Council of the European Communities. Directive 2008/105/EC on environmental quality standards in the field of water policy. Off J Eur Union 2008; L 348/84.

[43] T. Urase, T. Kikuta, Separate estimation of adsorption and degradation of pharmaceutical substances and estrogens in the activated sludge process., Water Res., 39 (2005) 1289-1300.

[44] D. Dolar, M. Gros, S. Rodriguez-Mozaz, J. Moreno, J. Comas, I. Rodriguez-Roda, D. Barcelo, Removal of emerging contaminants from municipal wastewater with an integrated membrane system, MBR-RO, J. Hazard. Mater., 239-240 (2012) 64-69.

[45] S. Gur-Reznik, I. Koren-Menashe, L. Heller-Grossman, O. Rufel, C.G. Dosoretz, Influence of seasonal and operating conditions on the rejection of pharmaceutical active compounds by RO and NF membranes, Desalination, 277 (2011) 250-256.

[46] L.D. Sedlak, E.K. Pinkston, Factors Affecting the Concentrations of Pharmaceuticals Released to the Aquatic Environment, Journal of Contemporary Water Research and Education, 120 (2011).

[47] A. Joss, C. Baenninger, P. Foa, S. Koepke, M. Krauss, C.S. McArdell, K. Rottermann, Y. Wei, A. Zapata, H. Siegrist, Water reuse: >90% water yield in MBR/RO through concentrate recycling and CO2 addition as scaling control, Water Res., 45 (2011) 6141-6151.

[48] J. Radjenovic, M. Petrovic, F. Ventura, D. Barcelo, Rejection of pharmaceuticals in nanofiltration and reverse osmosis membrane drinking water treatment, Water Res., 42 (2008) 3601-3610.

[49] K. Kosutic, B. Kunst, Removal of organics from aqueous solutions by commercial RO and NF membranes of characterized porosities, Desalination, 142 (2002) 47-56.

[50] J.A.M.H. Hofman, E.F. Beerendonk, H.C. Folmer, J.C. Kruithof, Removal of pesticides and other micropollutants with cellulose-acetate, polyamide and ultra-low pressure reverse osmosis membranes, Desalination, 113 (1997) 209-214.

[51] K. Kimura, G. Amy, J.r. Drewes, Y. Watanabe, Adsorption of hydrophobic compounds onto NF/RO membranes: an artifact leading to overestimation of rejection, J. Membrane Sci., 221 (2003) 89-101.

[52] A. Perez-Gonzalez, A.M. Urtiaga, R. Ibañez, I. Ortiz, State of the art and review on the treatment technologies of water reverse osmosis concentrates, Water Res., 46 (2012) 267-283.

[53] Recommended Standards for Water Works in: A Report of the Water Supply Committee of the Great Lakes--Upper Mississippi River Board of State and

Provincial Public Health and Environmental Managers, Health Research Inc., Health Education Services Division Albany, 2012.

[54] CEC: Council of the European Communities. Directive 98/83/ EC on the quality of water intended for human consumption. Off J Eur Commun L 330:32-53.

Table and Figure Captions:

Table 1. Occurrence of the target pharmaceuticals a) and pesticides b) along the treatment process in the main and pilot WWTPs (min-max) (ng/L)

Table 2. Limits of Quantification of target pharmaceuticals a) and pesticides b) in different water matrices (ng/L)

Figure 1. Scheme of the pilot plant installed at the wastewater treatment plant in Torroella de Montgrí (NE Spain) and points of sample collection. Hydraulic Retention time WWTPs is 47 hours (33 hours biologic reactor + 14 hours settler). Residence time MF: 3 min. Residence time RO: 50 min

Figure 2. Removal efficiencies (%) of selected pharmaceuticals and pesticides after secondary treatment in the WWTP (bold bars) and after MF-RO treatment in the pilot plant (dashed bars).

Figure 3. Overall removal efficiencies (%) achieved for pharmaceuticals, grouped by class, after conventional secondary treatment in the WWTP (orange line), after secondary plus tertiary treatment (UV lamp) in the WWTP (light green line), after secondary treatment in the WWTP and subsequent microfiltration in the pilot plant (dark green line), and after secondary treatment in the WWTP and subsequent microfiltration plus reverse osmosis in the pilot plant (blue line).

Figure 1. Scheme of the pilot plant installed at the wastewater treatment plant in Torroella de Montgrí (NE Spain) and points of sample collection. Hidraulic Retention time WWTPs is 47 hours (33 hours biologic reactor + 14 hours settler). Residence time MF: 3 min. Residence time RO: 50 min

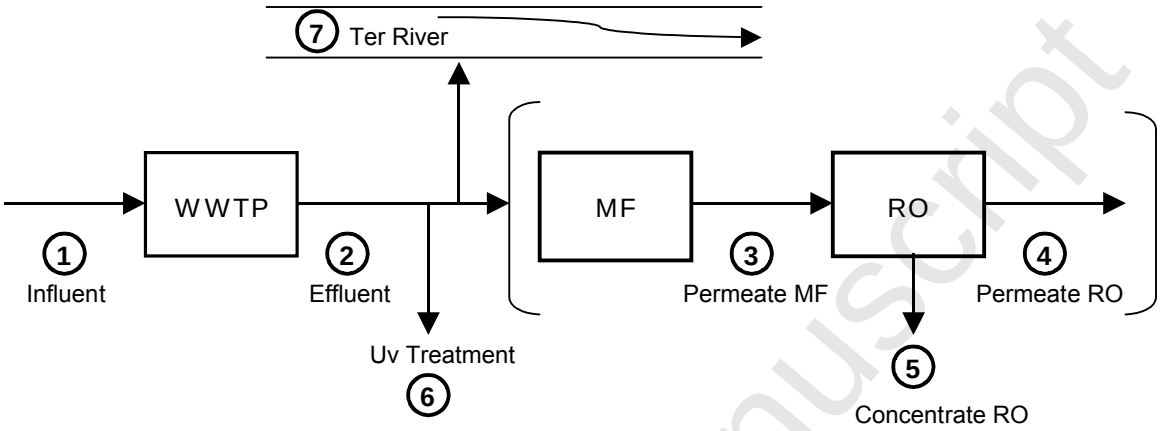

Figure 2. Removal efficiencies (%) of selected pharmaceuticals and pesticides after secondary treatment in the WWTP (bold bars) and after MF-RO treatment in the pilot plant (dashed bars).

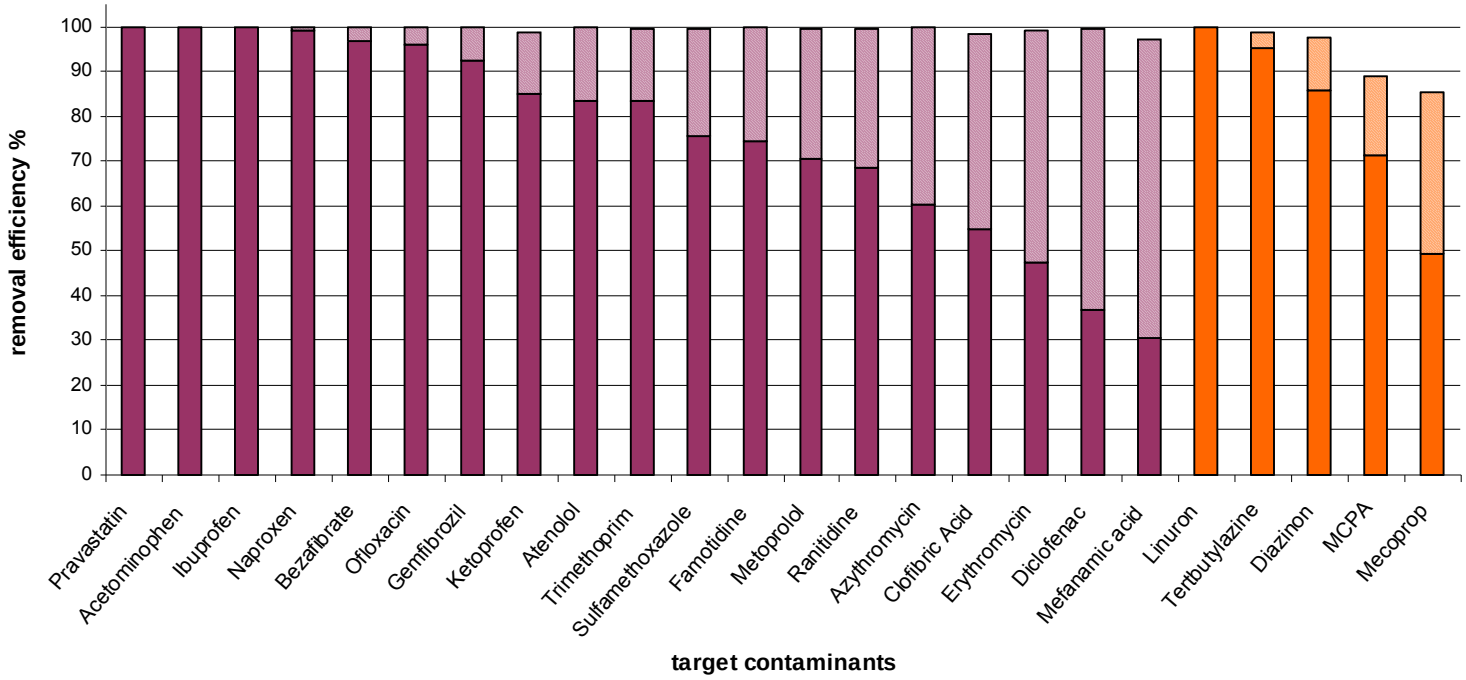

Figure 3. Overall removal efficiencies (%) achieved for pharmaceuticals, grouped by class, after conventional secondary treatment in the WWTP and after the different tertiary treatments tested

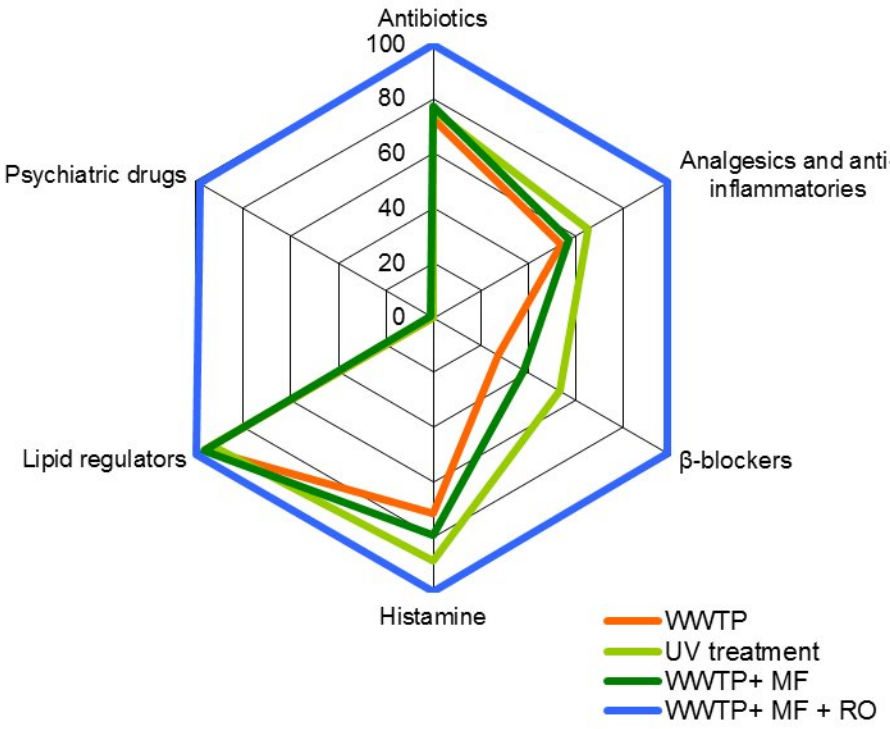

Table 1. Occurrence of the target pharmaceuticals a) and pesticides b) along the treatment process in the main and pilot WWTPs (min-max) (ng/L)

a)	*Pharmaceutical Compounds*	**Influent Wastewater**	**Effluent Wastewater**	**Tertiary Treatment UV**	**Permeate Microfiltration**	**Permeate Reverse Osmosis**	**Concentrate Reverse Osmosis**
Antibiotics	Azythromycin	553 - 792	187 - 367	209 - 266	226 - 246	BLQ - 2.4	1349 - 1460
	Erythromycin	308 - 413	180 - 191	153 - 196	154 - 184	2.5 - 3. 0	548 - 836
	Ofloxacin	343 - 412	10 -21	12 - 14	13 - 19	BLQ	49 - 76
	Sulfamethoxazole	360 - 615	97 - 124	69 - 75	39 - 72	nd - 2.9	364 - 510
	Trimethoprim	102 - 135	14 - 24	10 - 11	12 - 18	nd - 0.9	72 - 74
Analgesics and anti-inflammatories	Acetominophen	179747 - 237455	13 - 36	20 - 23	BLQ - 8	BLQ - 16.7	27 - 44
	Diclofenac	366 - 572	361 - 911	309 - 364	326 - 344	BLQ	1386 - 1523
	Ibuprofen	23127 - 28895	BLQ	nd	nd	nd	nd
	Ketoprofen	787 - 31582	163 - 262	159	82 - 188	BLQ	419 - 1111
	Mefenamic acid	12 - 18	11 - 13	9 - 13	8 - 11	BLQ - 0.8	nd - 21
	Naproxen	888 - 1076	BLQ	nd	nd	nd	BLQ
	Propyphenazone	7 - 13	14 - 17	8 - 9	13 - 14	BLQ - 0.5	55 - 84
Anti-ulcer	Lansoprazole	nd	nd - 2	nd	nd - 1	nd	BLQ
β-blockers	Atenolol	1185 - 1290	169 - 239	112 - 138	162 - 186	1.2 - 4.4	1072 - 1199
	Metoprolol	317 - 321	91 - 101	62 - 70	71 - 85	0.9 - 1.1	314 - 461
	Propanolol	74 - 92	74 - 100	62 - 71	58 - 78	1.2 - 2.9	347 - 363
	Sotalol	337 - 360	432 - 563	288 - 317	411 - 468	1.9 - 7.2	3336 - 3566
Histamine	Famotidine	22 - 26	5 - 8	4 - 6	3.6 - 4.5	nd	21 - 26
	Loratadine	BLQ - 1	BLQ - 1	BLQ	0.4 - 0.6	nd - 0.3	2
	Ranitidine	332 - 436	91 - 152	BLQ	79 - 110	1.0 - 1.6	580 - 746
Lipid regulators	Bezafibrate	848 - 1146	14 - 44	24 - 25	19 -59	nd - 2.2	BLQ - 1291
	Clorifibric acid	nd - 23	6 - 10	BLQ - 4	nd - 3	nd - 0.8	6 - 7
	Gemfibrozil	1076 - 13801	65 - 163	53 - 68	67 - 115	BLQ - 2.9	862 - 1600
	Mevastatin	nd	nd	nd	nd	nd	nd
	Pravastatin	161 - 164	nd - ND	nd	nd	nd	nd
Psychiatric drugs	Carbamezapine	214 - 246	401 - 480	345 - 371	363 - 400	2.4 - 4.7	1694 - 2296
	Fluoxetine	BLQ	BLQ - 19	6 - 7	15 -18	BLQ	64 - 72
	Paroxetine	nd	2 - 4	1.9 -2.1	1.8 - 2.3	nd - 0.3	8 - 14

b)	*Pesticides*	**Influent Wastewater**	**Effluent Wastewater**	**Tertiary Treatment UV**	**Permeate Microfiltration**	**Permeate Reverse Osmosis**	**Concentrate Reverse Osmosis**
Triazines	Atrazine	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ
	Cyanazine	BLQ	nd	nd	BLQ	BLQ	BLQ
	Simazine	nd	BLQ - 4	BLQ	5	2 - 4	BLQ - 9
	Deisopropylatrazine	nd	nd	nd	nd	nd	nd
	Desethylatrazine	nd	nd	nd	5 - 6	BLQ	8 - 9
	Terbutylazine	163 - 263	10	10	9 - 13	BLQ	BLQ - 17
Organophosphates	Diazinon	479 - 607	61 - 93	107	29 - 60	12 - 13	81 - 87
	Dimethoate	BLQ	BLQ -29	BLQ	9 - 20	BLQ	24 - 33
	Fenitrothion	nd	nd	nd	nd	nd	nd
	Malathion	nd	BLQ	nd	nd	nd	nd
Phenylureas	Diuron	BLQ	75 - 101	59	95 - 134	8 - 13	90 - 208
	Isoproturon	BLQ	BLQ	nd	3	3	BLQ - 3
	Linuron	nd-36	nd	nd	nd	BLQ - 1	nd
	Chlotoluron	BLQ	ND	nd	nd - 3	3 - 4	BLQ
Acidic herbicides	Mecoprop	33 - 39	15 - 21	17	19 - 29	5	20 - 59
	2,4D	BLQ	BLQ - 47	BLQ	42 - 45	BLQ	39 - 65
	Bentazon	nd - 8	BLQ	BLQ	2	BLQ - 3	2 - 3
	MCPA	18 - 40	na	9	7 - 10	3	9 - 14
Chloroacetanilides	Alachlor	BLQ	nd	nd	nd	nd	nd
	Metolachlor	nd	nd	nd	nd	nd	nd

n.d., not detected; n.a., not analysed; BLQ: below limit of quantification.

Table 2. Limits of Quantification of target pharmaceuticals a) and pesticides b) in different water matrices (ng/L)

a)	*Pharmaceutical Compounds*	**Inffluent Wastewater**	**Effluent Wastewater**	**Permeate Microfiltration**	**Permeate Reverse Osmosis**	**Concentrate Reverse Osmosis**
Antibiotics	Azythromycin	6.1	3.0	1.3	0.7	5.0
	Erythromycin	32.4	7.0	3.9	1.1	9.7
	Ofloxacin	17.2	7.0	4.6	1.2	9.0
	Sulfamethoxazole	10.0	5.2	2.1	0.7	4.3
	Trimethoprim	5.6	1.9	1.1	0.3	2.8
Analgesics and anti-inflammatories	Acetominophen	51.4	9.6	5.0	0.7	4.8
	Diclofenac	2.3	37.6	22.9	7.6	86.5
	Ibuprofen	1472.6	132.3	149.4	20.1	1047.0
	Ketoprofen	168.8	71.2	29.0	11.5	88.1
	Mefenamic acid	0.6	1.5	1.4	0.3	1.9
	Naproxen	64.4	36.8	14.2	8.6	34.5
	Propyphenazone	4.3	1.5	1.2	0.2	2.3
Anti-ulcer	Lansoprazole	5.9	1.8	1.1	0.5	2.9
β-blockers	Atenolol	8.6	1.8	1.2	0.3	2.5
	Metoprolol	8.9	2.5	1.4	0.5	2.4
	Propanolol	3.9	1.8	0.8	0.4	3.1
	Sotalol	5.7	3.2	2.0	0.5	3.4
Histamine	Famotidine	12.6	3.9	1.5	0.6	4.3
	Loratadine	0.7	0.3	0.2	0.1	0.4
	Ranitidine	6.2	2.0	0.9	0.3	2.0
Lipid regulators	Bezafibrate	78.0	9.6	8.2	1.3	48.7
	Clorifibric acid	5.1	1.9	1.0	0.6	2.6
	Gemfibrozil	0.1	2.4	1.2	0.5	4.9
	Mevastatin	94.9	35.3	19.2	12.6	38.8
	Pravastatin	129.4	43.6	22.4	9.8	60.3
Psychiatric drugs	Carbamezapine	1.2	0.5	0.4	0.1	0.7
	Fluoxetine	11.6	2.9	1.2	1.2	3.6
	Paroxetine	3.5	1.0	0.4	0.3	1.1

b)	Pesticides	Inffluent Wastewater	Effluent Wastewater	Permeate Microfiltration	Permeate Reverse Osmosis	Concentrate Reverse Osmosis
Triazines	Atrazine	34.8	2.6	3.1	4.9	5.0
	Cyanazine	32.4	2.9	2.8	6.0	2.6
	Simazine	61.9	3.3	3.5	1.8	4.9
	Deisopropylatrazine	35.0	47.0	21.4	56.0	41.1
	Desethylatrazine	28.0	4.7	4.8	2.4	6.9
	Terbuthylazine	19.4	8.0	7.8	4.7	17.3
Organophosphates	Diazinon	1.1	0.6	0.9	0.4	0.9
	Dimethoate	2.9	11.0	7.4	5.5	13.2
	Fenitrothion	30.1	37.3	17.5	24.7	18.8
	Malathion	80.4	29.2	62.7	71.0	1595.2
Phenylureas	Diuron	202.5	7.9	13.9	7.2	7.3
	Isoproturon	1.3	1.1	1.0	0.9	2.1
	Linuron	38.2	6.2	10.6	6.1	13.0
	Chlotoluron	33.7	2.0	1.7	1.9	3.2
Acidic herbicides	Mecoprop	11.2	3.9	3.4	2.0	5.1
	2,4D	28.9	22.1	10.7	10.9	15.5
	Bentazon	3.4	2.0	1.5	2.4	2.1
	MCPA	6.7	2.4	2.1	1.8	3.6
Chloroacetanilides	Alaclor	45.0	11.8	11.9	10.9	16.2
	Metolachlor	34.6	22.4	27.3	50.1	28.6