FIRST RESULTS OF PROJECT EMPORE-LIFE15 "DEVELOPMENT OF AN EFFICIENT AND SUSTAINABLE METHODOLOGY FOR EMERGING POLLUTANTS REMOVAL IN WWTPS" (EMPORE-LIFE15 ENV/ES/000598)

Authors: M.A., Bernal-Romero del Hombre Bueno 1 (ma.bernal@ua.es); R., González 2; A. Sánchez 2; J.M., Santos 3; F., Martínez 3; H., García 4; S., Oyonarte 5; F., Bosch 5; M., Company 6; J., Andreu 6; L. Mendes, 1; D. Prats 1

1 Instituto Universitario del Agua y de las Ciencias Ambientales (UNIVERSITY OF ALICANTE, Alicante, Spain)

2 Laboratorios Tecnológicos de Levante, S.L. (LTL, Paterna, Spain)

3 Entidad Pública de Saneamiento de Aguas de la Comunidad Valenciana (EPSAR, Valencia, Spain)

4 Institute for Water Education (UNESCO-IHE, Delft, The Netherlands)

5 Instituto Metalmecánico, Mueble, Madera, Embalaje y Afines (AIDIMME, Paterna, Spain)

6 Engineering and Consultancy Consomar, S.A (CONSOMAR, Paterna, Spain)

Abstract:

The project LIFE15 ENV/ES/000598 "Development of an efficient and sustainable methodology for Emerging Pollutants Removal in WWTPs" aims to demonstrate an innovative, cost-efficient and highly replicable technology for the removal of Emerging Pollutants (EPs) from European Waste Water Treatment Plants (WWTPs). The project is due to last three years (Sep 16-Aug 19). The pilot plant designed and built will be integrated into the WWTP of Benidorm (Spain) where the demonstration will be carried out.

For now, the design and construction of the prototype was carried out. The prototype has a treatment capacity ≈5 m^3/h and it consists of four principal processes: filtration/adsorption by columns, filtration by membrane technology, Electrochemical Advanced Oxidation Processes (EAOPs) and Advanced Oxidation Processes (AOPs). An extensive literature evaluation was conducted analyzing the occurrence of these compounds in European WWTP and in natural water bodies. In addition, a one-year analytical campaign was carried out and the list of targeted pollutants is to be increased from the pre-selected list that includes: a) priority substances regulated by the Directive 2013/39/UE (chlorpyrifos, trifluralin, DEHP, 4-t-octylphenol, diuron and isoproturon); b) EPs listed in the "watch list" of article 8 b of Directive 2013/39/UE (diclofenac, 17-alfa-ethinylestradiol, 17-beta-estradiol and erythromycin); c) EPs not regulated yet (chloramphenicol, carbamazepine, 2-(p-isobutylphenyl) propionic acid, fluoxetine, estrone, sulfamethoxazole, ketoprofen, AMPA, glyphosate and estriol). A set of indicators was selected to monitor the environmental and socio-economic impact of the proposed methodology.

1 INTRODUCTION

The implementation of the Water Framework Directive (WFD) raises a number of shared technical challenges for the Member States. The aim to reach good ecological status in every water body in Europe is far to be reached. Within this context, emerging contaminans (ECs) is one of the key topics to be addressed in the following years.

Directive 2013/39/EU (article 26) defines ECs as "*pollutants currently not included in routine monitoring programmes at Union level but which could pose a significant risk requiring regulation, depending upon their potential ecotoxicological and toxicological effects and on their levels in the aquatic environment*". This term includes a wide variety of compounds, such as pharmaceutical products, flame retardants, personal care products and pesticides, among others. Nowadays, wastewater treatment plants (WWTPs) are not designed for the treatment of this kind of substances. For this reason, most of them are not removed neither altered in the water line and finally reach the aquatic media affecting wildlife and consequently being introduced into the food chain with the associated health effects.

LIFE-EMPORE aims to demonstrate an innovative, cost-efficient and highly replicable technology for the removal of emerging contaminants from European WWTPs.

A pilot plant is due to be designed and integrated into the BWWTP, located in the Valencian Community (Spain). The developed technology will potentially be replicated and used throughout the European Union. The prototype will consist of four principal processing units: filtration/adsorption by columns, filtration by membrane technology, Electrochemical Advanced Oxidation Processes (EAOPs) and Advanced Oxidation Processes (AOPs). This units will be distributed in three levels of treatment.

The LIFE project is co-financed by the LIFE Programme of the European Commission, which Laboratorios Tecnológicos de Levante S.L. coordinating and leading the project. The other beneficiaries are: IHE Delft, Entidad Pública de Saneamiento de Aguas Residuales de la Comunidad Valenciana (EPSAR), University of Alicante, AIDIMME Technology Institute on Metal-Processing, Wood, Furniture and related industries, and CONSOMAR S.A. The total project budget is 1.783.824 €. The project is due to last 36 months, from September 2016 to August 2019. The execution of the project is distributed in actions.

This article focuses on explaining and summarizing the first actions carried out in EMPORE project.

1.1 Objectives

- ✓ To demonstrate that the selected combination of technologies is able to reduce the concentration below Directive 2013/39/UE threshold of the following priority ECs: chlorpyrifos, trifluralin, Di(2-ethylhexyl)phthalate (DEHP) and 4-t-octylphenol.
- ✓ To demonstrate that the selected combination of technologies is able to reduce the concentration in a 99% of their original concentration of the following ECs included in the watch list of DIRECTIVE 2013/39/UE: diclofenac, 17-a-ethinylestradiol and 17-b-estradiol.
- ✓ To demonstrate that the selected combination of technologies is able to reduce the concentration of the following pharmaceutical pollutants in 99% of their original concentration: carbamazepine, ibuprofen, fluoxetine and chloramphenicol and estrone.
- ✓ To evaluate the occurrence of ECs in Europe.
- ✓ To design, construct and set-up a mobile DEMO plant able to reduce the listed ECs.
- ✓ To characterise the ECs and their yearly variability for the Benidorm WWTP, henceforth BWWTP.
- ✓ To analyse the feasibility of the technologies for the ECs removal.
- ✓ To assess the environmental state before and after treatment in BWWTP according to different organoleptic, physical and chemical parameters.
- ✓ To assess the socio-economic impact of the implementation of the demonstration plant for EC removal in the local economy and also in other European regions with similar pollution problems.
- ✓ To transfer the project results to other identified Europe places with a similar situation regarding ECs.
- ✓ To disseminate between stakeholders the benefits of using EMPORE technologies for the reduction of ECs presence in European WWTPs.

2 FIRST RESULTS AND CONCLUSIONS

2.1 Action A1: European emerging pollutant characterization

During A1, an extensive literature evaluation was conducted analysing the occurrence of ECs, their sources, their path into the environment, the different classes of ECs, their occurrence in WWTPs and in natural water bodies, and their effects on ecosystems.

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

The ECs can undergo transformation processes or remain unchanged. Biodegradation will depend both on their bioavailability, and on the presence of microorganisms capable of degrading these compounds. ECs, once incorporated into the aquatic environment, can bio-accumulate within organisms or in trophic chains, accumulate in the sediments, or can follow a degradation process.

According to information collected by Norman Network (Norman), more than 500 ECs have been reported in the aquatic environment in Europe, both in surface and groundwater. The information related to the occurrence of ECs in Europe was summarized in the form of a matrix organized by the occurrence of 532 ECs per country (26 countries were analysed). The occurrence of ECs significantly differed among Europe both in terms of the types of compounds present in the water courses, as well as their reported concentrations; the occurrence of these compounds was strongly influenced by the number of studies carried out at each specific country in Europe looking at the occurrence of a specific set of ECs.

In table 1, it is shown a summary of the European mapping considering the 8 pharmaceutical substances initially proposed in EMPORE project.

Table 1 European mapping of ECs. Red: ECs evaluated and detected at environmentally relevant concentrations. Green: ECs evaluated and non-detected at environmentally relevant concentrations. White: no available data. Source: Network Norman.

Substance	Austria	Belgium	Bulgaria	Croatia	Cyprus	Czech Rep.	Denmark	Finland	France	Germany	Greece	Hungary	Int. Waters	Italy	Netherlands	Norway	Portugal	Romania	Serbia	Slovakia	Slovenia	Spain	Sweden	Switzerland	Ukraine	UK
Diclofenac	R	R	R	R		R			R	R	R	R		R	R		R	R	R	R	R	R	R	R		
Ibuprofen	R	R	R	R		R			R	R	G	R		R	R		R	R	R	R	R	R	R	R		
Chloramphenicol	G		G	G						G		G			R			G				R	G			
Carbamazepine	R	R	R	R		R			R	R		R		R	R		R	R	R	R	R	R	R	R		
Fluoxetine									R	R					R		G					R	R			
Estradiol	R		G	G					R	R		G			G			G		G	R		R			
Estrone	G	R	R	G		G			R	G		R		R	R			R	R	R	R					R
Ethinylestradiol		G							G	R				G	R						G		R			G

It can be observed that the presence of diclofenac, ibuprofen and carbamazepine was evaluated in 19 European countries, included Spain (data not available for: Cyprus, Denmark, Finland, Norway, Ukraine, UK and International Waters). Diclofenac and ibuprofen were detected at environmentally relevant concentrations in the 19 countries, carbamazepine in 18. Thus, their presence in the European surface and groundwaters is quite widespread.

Chloramphenicol, 17-a-ethinylestradiol and fluoxetine were evaluated only in 9, 8 and 6 countries, respectively. These three substances were detected at environmentally relevant concentrations in: a) chloramphenicol: Netherlands and Spain; b) 17-a-ethinylestradiol: Germany, Netherlands and Sweden; c) fluoxetine: France, Germany, Netherlands, Spain and Sweden.

Hormones 17-b-estradiol and estrone were evaluated in 11 and 15 countries, respectively. Estradiol was detected at environmentally relevant concentrations in 5 countries (Austria, France, Germany, Slovenia and Sweeden) and estrone in 11 countries (Belgium, Bulgaria, France, Hungary, Italy, Netherlands, Romania, Serbia, Slovakia, Slovenia and UK).

The priority substances trifluralin, DEHP and 4-t-octylphenol were not included in the European mapping. Priority substance chlorpyrifos was included in the list but there was not available data.

WWTPs are not specifically designed for the removal of emerging contaminants. Different wastewater treatment technologies exhibited a different removal effect on certain ECs. The removal performance of a particularly technology can be linked to the physical/chemical properties of the target EC. However, the physical/chemical properties of these compounds considerably differ among the entire range of ECs; therefore, there is not a single wastewater treatment technology capable of removing the entire range of ECs. Thus, a combination of technologies is required.

The presence of ECs in the influent to a WWTP can vary appreciably from one plant to another. Several factors must be considered: origin (urban, industrial or agricultural), climate, seasonal variability, population habits, regulation and use of social drugs, among others. These factors will be analysed during the development of the EMPORE project.

2.2 Action B1: Characterization of water samples

The main objective of action B1 is to quantify the pre-selected pollutants present at the inlet and output of BWWTP. In addition, the action aims to study the seasonal variability of the concentration of ECs in the wastewater received by BWWTP. It dares saying that the city of Benidorm is a reference tourist destination in Spain, whose population fluctuates considerably especially during Christmas, Easter and summer seasons. The increase on water consumption during these periods increases the discharge of wastewaters, and thus, it is supposed the quality and composition of the wastewater received by BWWTP varies during the different seasons.

Initially, EMPORE members obtained the BWWTP access permissions (action A2). Then, the Annual Analytical Campaign of the influent and effluent of BWWTP (action B1) started in November 2016 and was carried out until December 2017. The campaign lasted a year, with an integrated sampling of weekly frequency. 108 samples were taken (54 from influent and 54 from effluent, respectively) by means of two automatic samplers and a BWWTP Database was created gathering all the analytical results. Analytical techniques used to carry out the samples characterization were gas chromatography with mass spectrometry detection (GC-MS/MS) as well as liquid chromatography with the same detection method (HPLC-MS/MS). Preconcentration methodologies to the compounds prior to the quantification step were carried out by Stir Bar Sorptive Extraction (SBSE) and Solid Phase Extraction (SPE), both integrated online in their corresponding analytical instruments.

The initial list of compounds analysed included priority substances (chlorpyrifos, trifluralin, octylphenol and DEHP), first watch list substances (diclofenac, 17-a-ethinylestradiol and 17-b-estradiol) and other ECs (chloramphenicol, carbamazepine, ibuprofen, fluoxetine and estrone). It was decided to add some new analytes either because they were degradation products of the compounds under analysis or because they had similar properties and they were consumed in an equal form by population. From the results was concluded that it is was not necessary to continue with the simazine, atrazine, pentachlorobenzene, tributyl tin, brominated diphenylether, terbutryn, terbuthylazine, imazalil, orthophenylphenol and thiabendazole analysis, either because they were not detected in the influent nor in the effluent of the treatment plant or because their removal recoveries were enough to constitute them interest pollutants. Another reason is that despite having obtained negative elimination yields for them, the obtained concentrations were generally below their quantification limits, so the obtained results were not conclusive (ea. imazalil case). Diuron and isoproturon were definitively included in the list of pollutants under analysis due to the suspicion that variable and intermittent results can be obtained along the different samples and to the possible adverse effects that can imply their discharge to inland surface waters.

In general, lower concentrations were obtained for several compounds belonging to the industrial or agricultural origin pollutants, whereas it was not the same in the pharmaceutical origin pollutants case. One possible explanation for this phenomenon may be that ECs with industrial and/or agricultural origin are mostly regulated in water legislation whereas those with pharmaceutical origin are not. Another possible explanation is simply the location of the treatment plant; Benidorm is the tourism reference destination in Spain, so it seems logical to think that the changing population that resides there consumes different types of drugs that arrive to the treatment plant under study through the wastewater. Thus, the list of ECs was modified, including: priority substances (chlorpyrifos, trifluralin, octylphenol, DEHP, diuron and isoproturon), first watch list substances (diclofenac, 17-a-ethinylestradiol, 17-b-estradiol and erythromycin) and other ECs (chloramphenicol, carbamazepine, ibuprofen, fluoxetine, estrone, sulfomethoxazole, ketoprofen, AMPA, glyphosate and estriol).

The priority substance chlorpyrifos was mostly detected in the influent of BWWTP at concentrations (average concentration 0.25 ± 0.30 $\mu g \cdot L^{-1}$) higher than the concentration limit allowed in Directive 2013/39/EU, despite it is legislated precisely because of the harmful effects it can cause on health and environment. During summer, the concentration of this pollutant considerably increased in the inlet of BWWTP (figure 1). Priority substance DEPH, was detected in several samples at high concentrations (average concentration 4.5±4.1 $\mu g \cdot L^{-1}$), superior than the limit value allowed in Directive 2013/39/EU. Diuron was detected in several samples, its average concentration was 0.09±0.06 $\mu g \cdot L^{-1}$. Octylphenol was detected in three samples (average concentration 0.11±0.01 $\mu g \cdot L^{-1}$), all of them in March, at concentrations higher than the concentration limit allowed in Directive 2013/39/EU. Priority substances trifluralin and isoproturon were not detected in any sample.

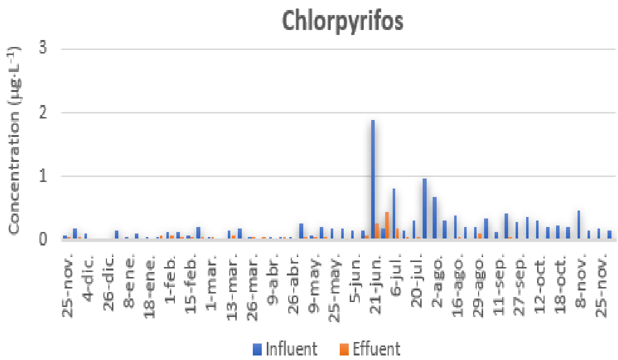

Figure 1 Seasonal influent and effluent variation of chlorpyrifos.

1st watch list substances diclofenac (figure 2), 17-b-estradiol and erythromycin were detected in the influent of Benidorm WWTP with average concentrations of 1.60±1.70 $\mu g \cdot L^{-1}$, 0.068±0.060 $\mu g \cdot L^{-1}$ and 0.20±0.25 $\mu g \cdot L^{-1}$, respectively. 17-a-ethinylestradiol was not detected in any sample; it dares saying that these substances are metabolized in the human body, excreted in the form of estrone and other metabolites.

Chloramphenicol was barely detected in the influent of BWWTP. The highest concentration of chloramphenicol detected was 0.013 $\mu g \cdot L^{-1}$. Its appearance in the influent of BWWTP is mainly due to the foreign population, who can bring this type of medication as part of their luggage. The pilot plant will be designed with the aim of exporting these new technologies to other parts of Europe, fact that justifies its inclusion as indicator.

Ibuprofen was detected in the influent of BWWTP; its average concentration was 32.70 ±31.92 $\mu g \cdot L^{-1}$. The average concentration of carbamazepine (figure 2), fluoxetine, estrone (figure 2), sulfamethoxazole, ketoprofen (figure 2), AMPA, glyphosate and estriol were 0.37±0.49 $\mu g \cdot L^{-1}$, 0.18±0.28 $\mu g \cdot L^{-1}$, 0.048±0.057 $\mu g \cdot L^{-1}$, 0.71±1.05 $\mu g \cdot L^{-1}$, 2.4±2.1 $\mu g \cdot L^{-1}$, 3.2±9.4 $\mu g \cdot L^{-1}$, 0.31±0.40 $\mu g \cdot L^{-1}$ and 0.45±0.27 $\mu g \cdot L^{-1}$, respectively. High concentrations of ketoprofen and AMPA were detected.

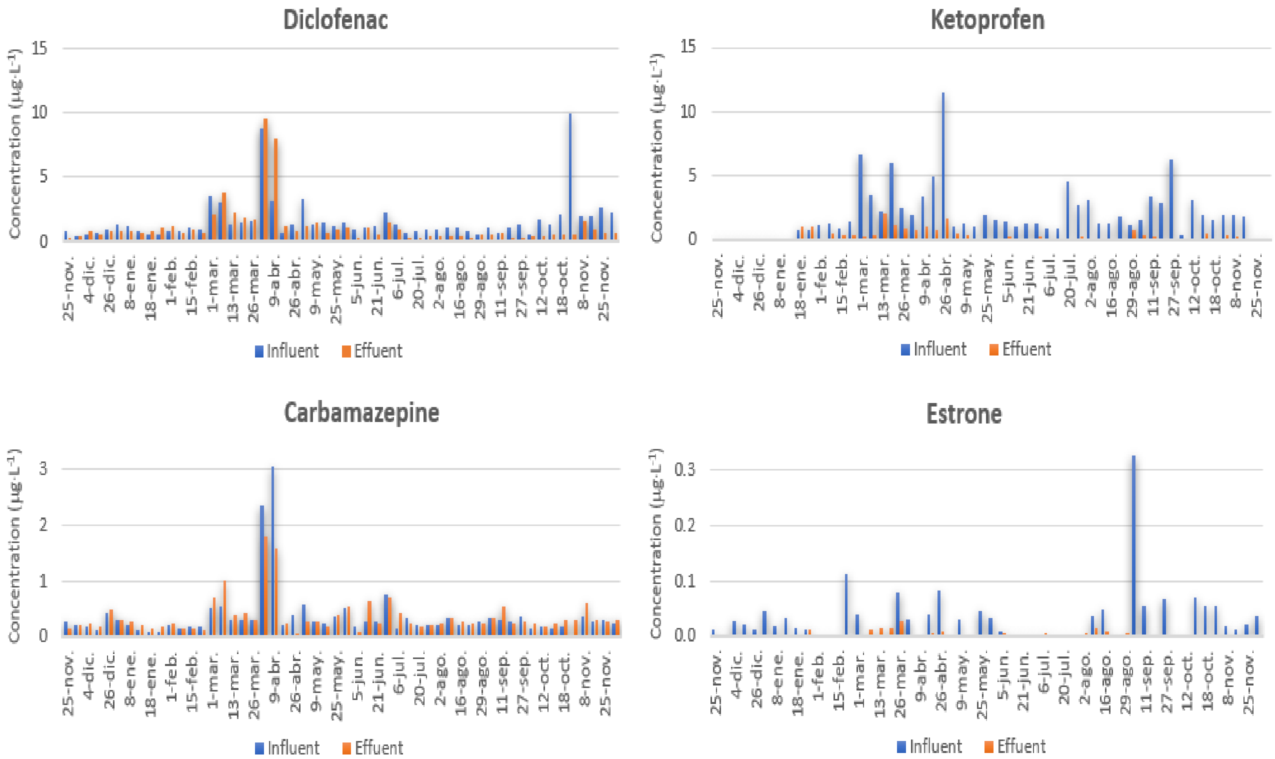

Figure 2 Seasonal influent and effluent variation of pharmaceutical products.

The priority substance DEPH was detected in few samples of the secondary effluent at an average concentration of 2.4±1.2 $\mu g \cdot L^{-1}$, value above the limit value allowed in Directive 2013/39/EU. The average concentration of chlorpyrifos was also above the limit value, 0.07±0.08 $\mu g \cdot L^{-1}$. Priority substance diuron was detected in several samples, its average concentration was 0.08±0.05 $\mu g \cdot L^{-1}$, below the limit value allowed in Directive 2013/39/EU. Priority substances trifluraline, octylphenol and isoproturon were not detected in any sample.

1st watch list substances diclofenac, 17-b-estradiol and erythromycin were detected in the secondary effluent of BWWTP with average concentrations of 1.13±1.64 $\mu g \cdot L^{-1}$, 0.015±0.010 $\mu g \cdot L^{-1}$ and 0.22±0.31 $\mu g \cdot L^{-1}$, respectively. Diclofenac is well-known to very resistant to biological treatment. 17-a-ethinylestradiol was not detected in any sample.

Chloramphenicol was barely detected in the secondary effluent of BWWTP. The highest concentration of chloramphenicol detected was 0.008 $\mu g \cdot L^{-1}$. The average concentration of carbamazepine, fluoxetine and ibuprofen in the secondary influent was 0.36±0.31 $\mu g \cdot L^{-1}$, 0.12±0.09 $\mu g \cdot L^{-1}$ and 0.42±0.80 $\mu g \cdot L^{-1}$ respectively. Carbamazepine, as diclofenac, is very resistant to biological treatment. On the contrary, the conventional treatment efficiently removed ibuprofen.

Estrone, sulfamethoxazole, ketoprofen, AMPA and glyphosate were detected in the secondary effluent with average concentrations of 0.011±0.010 $\mu g \cdot L^{-1}$, 0.23±0.24 $\mu g \cdot L^{-1}$, 0.53±0.47 $\mu g \cdot L^{-1}$, 4.21±6.58 $\mu g \cdot L^{-1}$ and 0.57±0.42 $\mu g \cdot L^{-1}$, respectively. Estriol was detected in few samples at concentrations below its quantification limit (LOQ).

In general, pharmaceutical products were the most abundant compounds in the influent of BWWTP. The concentration of many pharmaceutical products (ea. diclofenac, carbamazepine, ketoprofen, ibuprofen, among others) considerably increased during Easter holidays and Fallas festival (March-April 2017). On the other hand, the concentration of the pesticide chlorpyrifos increased in summer.

2.3 Action B2: Design and implementation of the pilot plant

In action B2, the prototype plant was designed for a hydraulic capacity of ~ 5 $m^3 \cdot h^{-1}$. It was necessary to define the following points: a) selection of proven technologies for removing ECs from water (membranes filtration, adsorption by activated carbon, advanced oxidation processes and electrochemical oxidation processes); b) sequential distribution of the technologies from softest to more aggressive; c) design of a versatile DEMO plant.

The designed plant consists of three principal treatment levels as it is shown in figure 3.

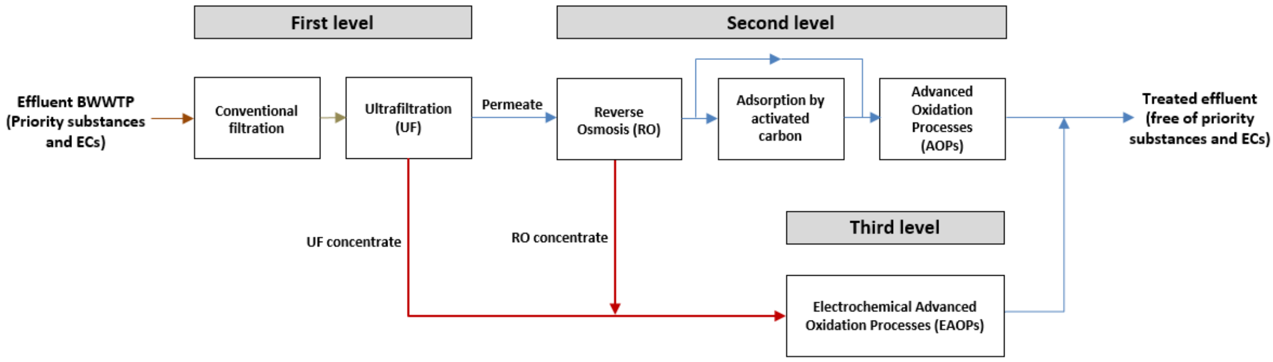

Figure 3 Conceptual scheme.

Action B3 consisted of the following activities: acquisition of the main equipment, instruments and control elements; assembly of the units, pipes and electrical connections in a container (7000 mm x 2500 mm x 2500 mm); transport of the DEMO plant to BWWTP; and verification tests and start-up.

The three treatment levels are described below:

a) First level: conventional filtration and ultrafiltration

The effluent of the secondary treatment of BWWTP is stored in a tank and driven to the first level of the plant by means of a multistage vertical pump. This level aims to progressively reduce the content of suspended solids and colloidal matter. The first unit is a vertical pressure filter with crystal filler. The crystal filler (model FCR-779, Hidrowater) reduces better biofouling than other typical fillers (ea. sand, anthracite) and provides an effective filtration of 3-5 μm. Its objective is to remove suspended particles and turbidity to prepare the water for the ultrafiltration treatment. The effluent from this filter is driven to an automatic mesh pre-filter (model Odismatic 851D02M-P, Copersa) that will ensure protection of UF membranes against solids.

The UF unit aims to remove colloids and organic matter. UF consists of 3 hollow fiber membranes (model SFP 2660, Dow) that work in parallel providing a total filter area of 99 m^2 (33 m^2 per membrane). The pore size is 0.03 μm. The unit operates with filtration – backwash cycles of 25 minutes - 3 minutes. It is necessary to supply air (21 $Nm^3 \cdot h^{-1}$ at 0.5 bar) during the backwash by means of an oil-free rotary vane pump (model FAPS 25, Mapner). The UF effluent is stored in a tank; previously, an ultraviolet lamp (model AMN-550, Aguas del Mare Nostrum) disinfects it to protect RO membranes against biofouling. The UF system also includes a dosage system of sodium hypochlorite, sodium hydroxide and hydrochloric acid for the chemically enhanced backwash (CEB) and clean in peace (CIP) operation.

b) Second level: reverse osmosis followed by advanced oxidation processes (AOPs)

The UF effluent is driven to the second level. A multistage vertical pump impulses the effluent to the RO system. Firstly, the UF effluent is driven to a cloth filter (5 μm filtration) that will ensure protection of RO membranes against solids (model Cintropur NW32, Setasa S.L). The software ROSA (Dow) was used to design the RO system. The configuration is 1 pass of permeate and 2 stages (the concentrated of the first stage is fed to the next stage). The overall conversion is ~70% without recirculation. The configuration requires 24 RO spiral membranes for brackish water (model BW30-4040 4" Dow). Membranes are distributed in 6 pressure vessels. Each pressure vessel contains 4 membranes connected in series (model PRO-4-300-EP-4, Arisawa). The first stage consists of two lines (each one includes two pressure tubes in series). The concentrates of the first stage are driven to the second stage that consists of one line with two pressure tubes in series. The RO system operates at an inlet pressure of 10 bar. The objective of this step is to remove ECs and dissolved salts. The RO system also includes a dosage system of anti-fouling and sodium bisulphite, as pre-treatment.

The RO permeate (3.5 $m^3 \cdot h^{-1}$) can be directly driven to advanced oxidation processes (AOPs). Two batch reactors operate alternatively to carry out the corresponding treatments: a) ozone (O_3); b) ozone combined with ultraviolet light (O_3/UV); c) ozone combined with hydrogen peroxide (O_3/H_2O_2); and d) ultraviolet light combined with hydrogen peroxide (UV/H_2O_2). The AOPs unit includes: two UV lamps (model Dulcodest UV-C 45D/9/1", Prominent), an ozone generator to provide 7 $g \cdot h^{-1}$ O_3 (model GZO7, OzonoSistem) and a dosage system of sodium hydroxide, hydrochloric acid and hydrogen peroxide. By means of a centrifugal pump and a system of electrovalves, the effluent is recirculated in the AOPs system. When UV is applicated, the effluent is previously driven to a cloth filter (50 μm filtration) (model Cintropur NW25, Osmofilter). When O_3 is applied, once the water is treated, the effluent is driven to an activated carbon filter (Clack TC, Osmofilter) to remove O_3 surplus. The treated effluent is assumed to be free of ECs and it is discharged into the basin.

c) Third level: electrochemical advanced oxidation processes (EAOPs)

Electrochemical advanced oxidation processes (AOPs) are substantially applied to remove the ECs present in the concentrates of the membrane operations (1.5 $m^3 \cdot h^{-1}$). Two electrochemical reactors operate in parallel treating the effluent from the pumping tanks. By means of a centrifugal pump and a system of electrovalves, the effluent is recirculated in the EAOPs system for 50 minutes. Each reactor has a set of 5 anode electrodes (doped diamond with boron-BDD) and 5 cathode electrodes (steel). It is possible to combine the electrochemical treatment with UV radiation by means of a UV lamp (model Dulcodest UV-C 45D/9/1", Prominent). When UV is applicated, the effluent is previously driven to a cloth filter (50 μm filtration) (model Cintropur NW25, Osmofilter). The system also includes a dosage system of sodium hydroxide and hydrochloric acid. The treated effluent is assumed to be free of ECs and it is discharged into the basin.

The plant is automatically operated by means of a SCADA. The main screen of the SCADA shows the flow diagram of the pilot plant (figure 4). The pilot plant contains network analysers and a GPRS alarm system.

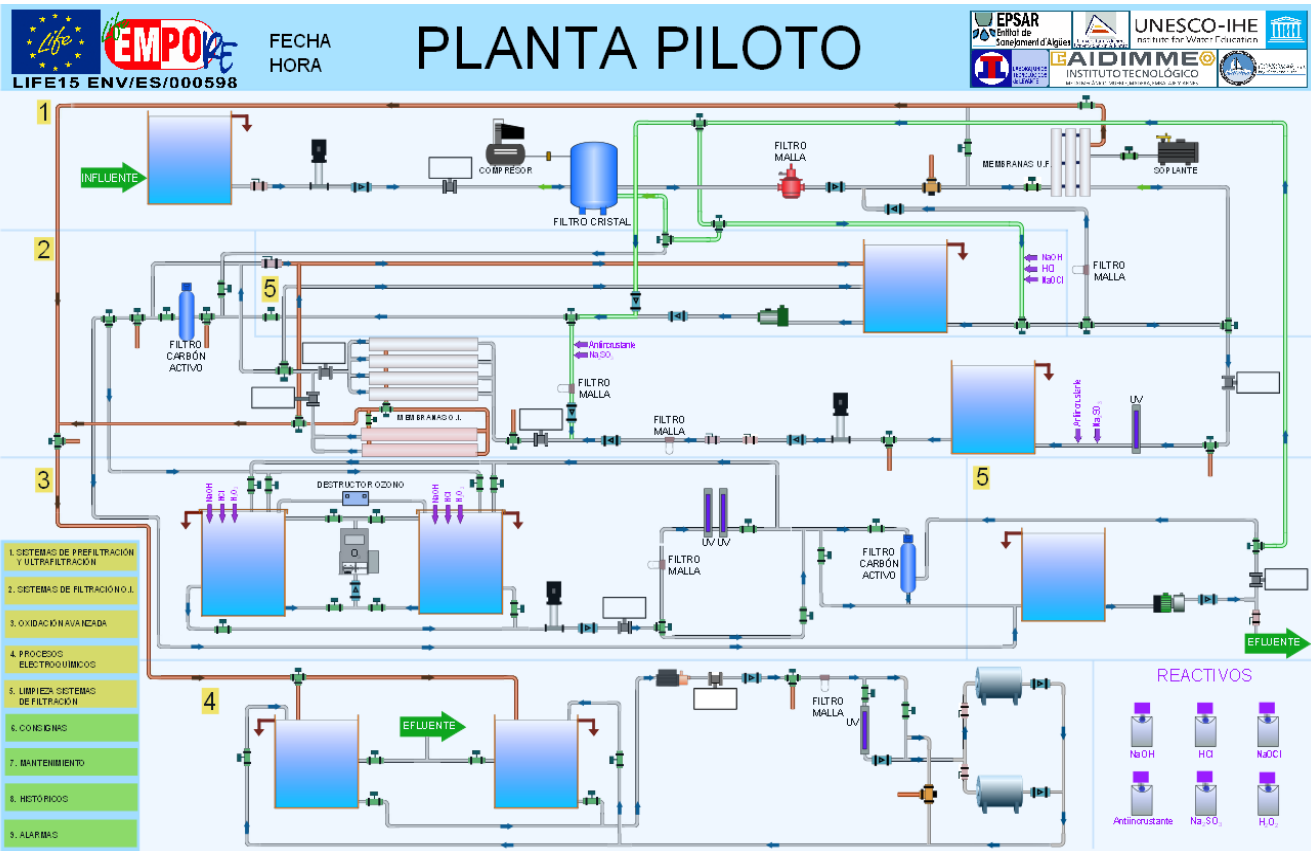

Figure 4 SCADA: screen 1- General process.

2.4 Action C1: Monitoring of the impact of ECs removal

Water reuse is an accepted practice in several European countries, especially in Spain, where the risks of water scarcity have enhanced the reuse of treated wastewater for agricultural, industrial and urban uses. According to Angelakis et al. (2007), irrigation is the dominant application of reclaimed water in Spain. It dares highlighting the case of Benidorm, city located in the region "La Marina Baja" of the Valencian Community (Spain). Benidorm supports a system of integral management of water that comprises, between other actions, the regulation of underground water in the reservoirs of Guadalest and Amadorio, water that is used for the supply of the city of Benidorm. The underground regulated water belongs, by means of administrative concession, to cooperatives of irrigators, who yield the natural water to a regulatory organism in exchange for receiving treated wastewater for its reuse in irrigation. An improvement in the quality of the treated water in Benidorm WWTP would impact on its social acceptation on the part of the user cooperatives.

ECs are rarely monitored in conventional WWTPs, fact that hinders the development of regulatory quality standards and monitoring strategies for reuse schemes. A water quality index (WQI) summarizes a complex water quality data (physical, chemical and/or biological parameters) into a single value to express the data in a simplified form. In general, there are many publications on the application of WQI to assess water quality considering general parameters, such as chemical oxygen demand, pH, dissolved oxygen, conductivity, among others. However, the use of these indexes to assess water quality considering the presence and concentration of ECs has hardly been studied. Some indexes are: Canadian Water Quality Index (CWQI), US National Sanitation Foundation's Water Quality Index (NSFWQI), Weighted Arithmetic Water Quality Index Method (WAWQI), Oregon Water Quality Index (OWQI), among others.

During the first months of action C1 "Monitoring of the impact of ECs removal", a set of indicators and the protocols to obtain them were developed to monitor the environmental impact of the technologies proposed. The indicators finally included in the document "LIFE EMPORE INDICATOR LIST" are: a) concentration of each EC – indicators 1.3-01 to 1.3-20; b) WQI related to the presence and concentration of ECs – indicator 1.3-21; c) WQI related to general parameters – indicator 1.3-22.

- Indicator 1.3-21:

The dimensionless CWQI was selected to monitor the water quality during the demonstration period. The CWQI is a recognized index, used for example in the World Health Organisation's Drinking Water Quality Guidelines (WHO, 2004). The CWQI compares observations to a benchmark. This index quantifies for one station, over a predetermined period, the number of parameters that exceed a benchmark, the number of records in a dataset that exceed a benchmark, and the magnitude of exceedance of the benchmark (Rickwood and Carr, 2007). Water quality is ranked by relating the CWQI to one of the following categories.

Table 2. Categories according to the CWQI.

CLASSIFICATION	CWQI	DESCRIPTION
Excellent	95 - 100	All measurements are within objectives virtually all of the time
Good	80 - 94	Conditions rarely depart from desirable levels
Fair	65 - 79	Conditions sometimes depart from desirable levels
Marginal	45 - 64	Conditions often depart from desirable levels
Poor	0 - 44	Conditions usually depart from desirable levels

20 variables (concentration of each EC) and the following objective values have been considered: a) Maximum Allowable Concentration (MAC) in the Directive 2013/39/EU for priority substances; b)2 times the quantification limit of each EC for the other substances. During the demonstration period, weekly samples will be taken and the index will be determined for: a) influent and effluent of the DEMO plant; b) influent and effluent of each level of treatment. In addition, a modification of the CWQI that penalizes according to the nature of the ECs has been proposed and named WQIEC (factor affecting excursions).

Both indexes, CWQI and WQIEC, were monthly calculated for samples from the influent and effluent of BWWTP during the characterization campaign (action B1); their evolution is shown in figure 5.

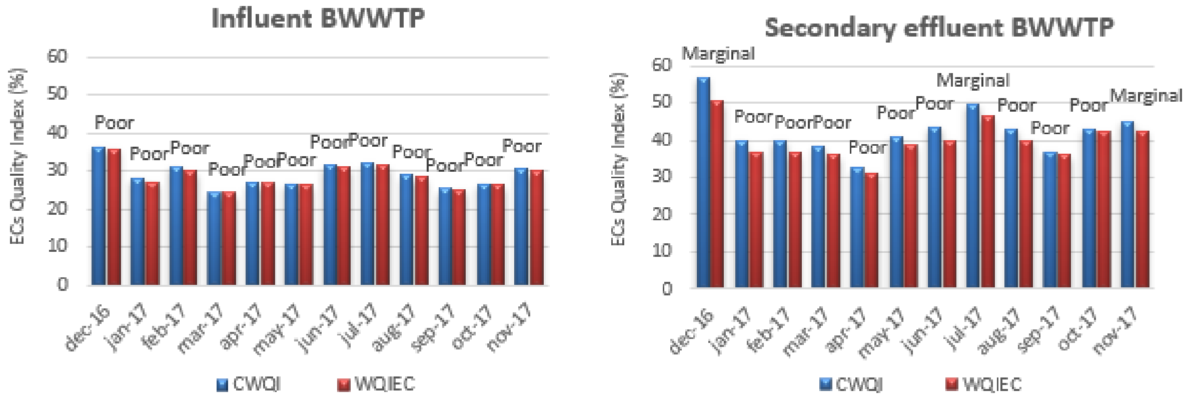

Figure 5 Evolution of the quality of the influent and effluent of BWWTP according to indicator 1.3-21.

For the influent, the monthly mean for CWQI and WQIEC was 28.3 and 27.9, respectively. According to the categories showed in table 2, the quality of the influent was always poor. As it was commented in action B1, some substances were not detected such as trifluralin or isoproturon, whereas the concentration of other ECs (ibuprofen, ketoprofen, chlorpyrifos and DEPH, among others) departed from desirable levels. The concentration of many ECs, especially pharmaceutical products, considerably increased in March, decreasing the quality of the influent (CWQI~24). The population of Benidorm temporarily increased during Easter holidays and Fallas festivals due to the arrival of tourists. In that season, it is common the use of pharmaceutical products to recover from colds. The quality increased during summer months (CWQI~29-32), two factors could contribute: a) dilution effect due to the remarkable increase in the production of urban wastewater; b) decrease in the consumption of some drugs during summer.

For the secondary effluent, the monthly average was 42.4 and 39.7 for CWQI and WQIEC, respectively. The conventional treatment carried out in BWWTP achieved to decrease the concentrations detected in the influent for some compounds (ea. Ibuprofen, hormones); however, it was poor efficient for carbamazepine and diclofenac, among others. Despite the increase on the index, the quality of the secondary effluent was poor during the period monitored, evidencing the need to apply tertiary treatments.

- Indicator 1.3-22: related to the general characterization of water

Water that is highly turbid, highly coloured or that has a strange taste and odour or that possesses high conductivity could lead the consumer to believe that the water is unsafe and/or inadequate for irrigation or other uses. The dimensionless CWQI has been selected to monitor the water quality during the demonstration period considering the parameters: total suspended solids (SS), conductivity, turbidity and pH. The benchmarks selected are: conductivity = 2500 $\mu S \cdot cm^{-1}$ at 20 ºC; pH = 6.5 – 9.5; SS = 20 $mg \cdot L^{-1}$; and turbidity = 5 NTU. weekly samples will be taken, and the index will be determined for: a) influent and effluent of the DEMO plant; b) influent and effluent of each level of treatment.

The quality of the secondary effluent of BWWTP was registered during 2016 and 2017. The monthly mean values in 2016 were: pH (7.45 ± 0.15), conductivity (3042 ± 245 $\mu S \cdot cm^{-1}$), turbidity (8.22 ± 3.21 NTU) and suspended solids (10.48 ± 8.84 $mg \cdot L^{-1}$). Conductivity and turbidity were generally exceeded. The monthly mean values in 2017 were: pH (7.82 ± 0.14), conductivity (2913 ± 178 $\mu S \cdot cm^{-1}$), turbidity (2.40 ± 1.01 NTU) and suspended solids (13.44 ± 5.64 $mg \cdot L^{-1}$). Conductivity always exceeded the objective value.

The index has been four-monthly calculated for samples from the secondary effluent of BWWTP (figure 6). The indicator values in 2017 (during action B1) were: a) January – March: CWQI = 55 Marginal; b) April – May: without data; c) June – August: CWQI = 54 Marginal; d) September – November: CWQI = 57 marginal. The quality of the secondary effluent improved in 2017 with respect to 2016. The index indicates the quality of the secondary effluent was marginal (low quality).

The values of both indicators 1.3-21 and 1.3-22 calculated in action B1 evidence the direct discharge of the secondary effluent to the Benidorm basin is not recommended.

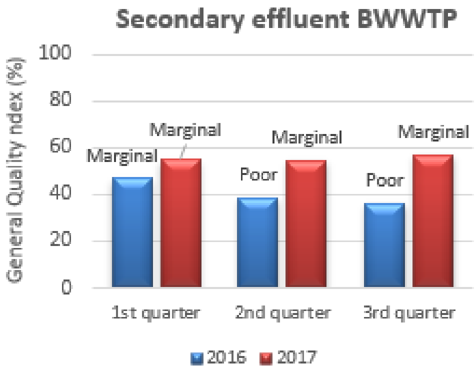

Figure 6 Evolution of the quality of the effluent of BWWTP according to indicator 1.3-22.

2.5 Action C2: Monitoring the socio-economic impact of emerging contaminants removal

In the first stage of action C2, a set of indicators has been selected to monitor the socio-economic impact of ECs removal. Table 3 shows the list of indicators for action C2.

Table 3 Indicators for action C2 in "LIFE EMPORE INDICATOR LIST".

Indicator	Description	Information obtained
12.1.1	Number of entrances in the website	Interest aroused by the project
12.1.2	Register of the number of events/exhibitions in which the members of the Project have been invited to promote the technologies proposed in the plant	
12.1.3	Survey about the acceptation of the water used for irrigation	Social acceptation of treated water
13.1	Networking and other professional training or education	Dissemination of EMPORE results
15.5	Incorporation of the proposed technologies in advanced tertiary treatments for removal of ECs	Incorporation of the proposed technologies in public or private companies.
16.1	Tendencies change about the availability of treated water free of ECs for reuse	Production of water free of ECs
15.1	Running cost/operating costs during the project and expected in case of continuation/replication/transfer after the project period	Costs

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