

## Review

# Occurrence and removal of organic micropollutants: An overview of the watch list of EU Decision 2015/495



Marta O. Barbosa, Nuno F.F. Moreira, Ana R. Ribeiro, Manuel F.R. Pereira, Adrián M.T. Silva\*

Laboratory of Separation and Reaction Engineering – Laboratory of Catalysis and Materials (LSRE-LCM), Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

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## ABSTRACT

Although there are no legal discharge limits for micropollutants into the environment, some regulations have been published in the last few years. Recently, a watch list of substances for European Union-wide monitoring was reported in the Decision 2015/495/EU of 20 March 2015. Besides the substances previously recommended to be included by the Directive 39/2013/EU, namely two pharmaceuticals (diclofenac and the synthetic hormone 17-alpha-ethinylestradiol (EE2)) and a natural hormone (17-beta-estradiol (E2)), the first watch list of 10 substances/groups of substances also refers three macrolide antibiotics (azithromycin, clarithromycin and erythromycin), other natural hormone (estrone (E1)), some pesticides (methiocarb, oxadiazon, imidacloprid, thiacloprid, thiamethoxam, clothianidin, acetamiprid and triallate), a UV filter (2-ethylhexyl-4-methoxycinnamate) and an antioxidant (2,6-di-tert-butyl-4-methylphenol) commonly used as food additive. Since little is known about the removal of most of the substances included in the Decision 2015/495/EU, particularly regarding realistic concentrations in aqueous environmental samples, this review aims to: (i) overview the European policy in the water field; (ii) briefly describe the most commonly used conventional and advanced treatment processes to remove micropollutants; (iii) summarize the relevant data published in the last decade, regarding occurrence and removal in aqueous matrices of the 10 substances/groups of substances that were recently included in the first watch list for European Union monitoring (Decision 2015/495/EU); and (iv) highlight the lack of reports concerning some substances of the watch list, the study of un-spiked aquatic matrices and the assessment of transformation by-products.

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\* Corresponding author.

E-mail address: [adrian@fe.up.pt](mailto:adrian@fe.up.pt) (A.M.T. Silva).

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## 1. Introduction

Water is a valuable resource, crucial to all living organisms and for multiple human activities, such as domestic uses, agriculture and industry. However, several contaminants of emerging concern (CECs) end up in vital aquatic compartments, such as surface water, groundwater and even drinking water, at concentrations between few  $\text{ng L}^{-1}$  and several  $\mu\text{g L}^{-1}$  (Matamoros and Bayona, 2006), with negative impact on water quality. The occurrence of CECs in the environment is reported in thousands of publications during the last decades and reviewed by many authors (Bell et al., 2011; Bu et al., 2013; da Silva et al., 2012; da Silva et al., 2013; Li et al., 2015; Li, 2014; Liu and Wong, 2013; Sima et al., 2014; Zhang et al., 2014a), demonstrating an increasing concern about them. For instance, a series of periodic review articles focused on occurrence, fate, transport and treatment of CECs were published annually since 2007 (Wells et al., 2007) until 2011 (Bell et al., 2011), and then works on occurrence, fate and transport of CECs were reviewed separated from treatment since 2012 (da Silva et al., 2012) until 2015 (Li et al., 2015), due to the significant increase in the number of publications dealing with this particular topic.

CECs can be natural or anthropogenic substances such as pesticides, industrial compounds, pharmaceuticals, personal care products, steroid hormones, drugs of abuse and others (Ribeiro et al., 2015). Sources of CECs include: (i) industrial wastewater; (ii) runoff from agriculture, livestock and aquaculture; (iii) landfill leachates; and (iv) domestic and hospital effluents, from which micropollutants might follow many pathways (Mompelat et al., 2009), as represented in Fig. 1.

The management of industrial effluents resulting from the production of pharmaceuticals, personal care products, pesticides and other compounds, has been properly done in several countries where regulations are already implemented, but more strict regulations are still needed in other regions of the world. The runoff from agriculture and livestock areas is another important source of micropollutants, particularly in the case of pesticides used to improve productivity, as well as steroid hormones and antibiotics used for livestock (Birkett and Lester, 2002; Song et al., 2007). In addition, many contaminants and their intermediates can reach the fields when they are irrigated with treated wastewater and, as consequence, the receiving waters can also contain these substances (Pedersen et al., 2003). Other source of CECs is the leakage from landfills and sewage treatment facilities, industrial waste systems and septic tanks (Matthiessen et al., 2006). The release of effluents from municipal wastewater treatment plants (WWTPs) is other important route for the appearance of micropollutants in the aquatic environment (Tijani et al., 2013), the wastewater treated in these plants mainly resulting from domestic and/or industrial activities, as well as from hospitals.

In fact, most of the conventional WWTPs are not designed to completely eliminate organic compounds at low concentrations, making the treatment processes vulnerable to such problem of pollution (Tijani et al., 2013). In this context, the non-degradable or partially removed compounds in WWTPs are likely to be detected in surface water. In the cases of sewage sludge and soils, micropollutants can desorb and runoff to surface water or undergo direct leaching to groundwater aquifers with consequent contamination of drinking water (Feng et al., 2013).

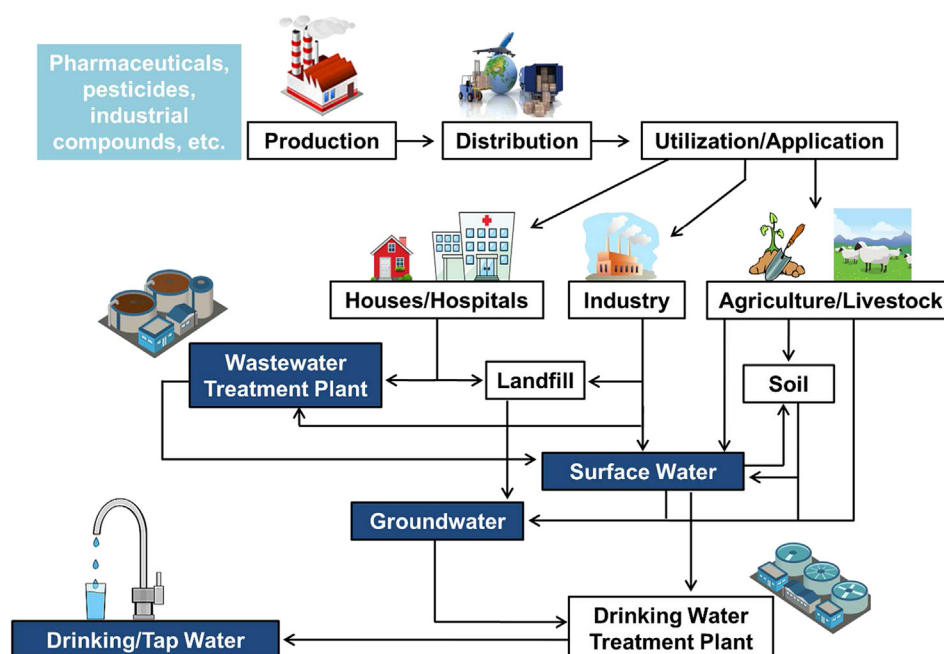


Fig. 1. Representative sources and routes of micropollutants in the environment.

Agricultural reuse of sewage sludge in particular as fertilizer, is a common practice to improve the soil structure and provide nutrients, but can represent a source of environmental contamination (Dichtl et al., 2007). Moreover, sewage sludge solids sourced by wastewater can be considered a sink of hazardous substances (e.g., such as pathogens, heavy metals and organic pollutants) that will accumulate in soils (Dichtl et al., 2007). Due to the increasing concern about human health impacts, land application gained interest to convert sludge into a safer material through the treatment by anaerobic digestion, composting or other biological processes (Zhang et al., 2014b). While composting is a controlled bio-oxidative process that converts sludge into stable and humic like materials, anaerobic digestion occurs in the absence of oxygen and has two main end products, a methane-rich biogas used as renewable energy source and the digested used as fertilizer (Zhang et al., 2014b). Removal of toxic organic contaminants by these processes was reported; however, their complete mineralization is difficult due to the adsorption mechanism and the formation of intermediates (Zhang et al., 2014b).

The fate and distribution of CECs will depend on the  $D_{ow}$ , which is a pH-dependent n-octanol–water distribution ratio that simultaneously considers hydrophobicity and ionogenicity (Wells, 2006, 2007). Although most regulators use octanol–water partitioning coefficient ( $K_{ow}$ ) to evaluate the hydrophobic partitioning, the environmental fate and transport should be based in the parameter  $D_{ow}$ , which is more accurate for ionizable organic compounds.

The contamination of environmental compartments, such as surface water, groundwater and soils, which are continuously interrelated, may cause cumulative negative effects along multi-generational exposure in aquatic organisms and/or affect the human's health by drinking water contamination (Daughton, 2010). A great concern about the occurrence of micropollutants in the aquatic resources and the subsequent effects on humans and biota has been highlighted in the last few years. However, it is difficult to predict which environmental and public health implications may arise from the occurrence of CECs in freshwater ecosystems, since the individual concentrations usually found in the environment are lower than those able to cause direct negative effects (Quinn et al., 2009). For instance, concerning pharmaceuticals, toxicological studies have shown that they might have direct toxicity towards certain aquatic organisms (Crane et al., 2006). The main issues related to the frequent occurrence of recalcitrant compounds are their simultaneous presence as complex mixtures and the long term exposition that can lead to serious chronic effects, as reported by several studies (Kidd et al., 2007; Santos et al., 2010). Their constant but imperceptible effects can gradually accumulate, finally leading to irreversible changes on both wildlife and human beings (Daughton and Ternes, 1999; Jjemba, 2006).

Natural attenuation is a low-cost and simple process comprising physical, chemical and/or biological mechanisms to reduce contaminants concentrations (Khan et al., 2004; Kuppusamy et al., 2016). Volatilization, dispersion, dilution, sorption, photolysis, biodegradation/transformation are the main natural attenuation processes (Khan et al., 2004; Kuppusamy et al., 2016). While volatilization has a minor impact, dispersion and dilution can lead to a significant decrease on the concentrations of contaminants (Gurr and Reinhard, 2006). The dilution can decrease their concentration to levels for which no significant effects are verified for aquatic organisms. Sorption to sediments and suspended solids also reduce the concentration of CECs, but accumulation is enhanced. Indirect or direct photolysis can lead to removal of contaminants, but is highly dependent on the presence of suspended matter and solar radiation. CECs can also be degraded by biodegradation/transformation, by bacterial enzymes (Khan et al., 2004).

The upgrading of the treatment processes for effluents

generated by conventional WWTPs might minimize the discharge of micropollutants into the receiving waters, and can even improve the overall quality status of effluents for possible reuse (Comminellis et al., 2008; De Luca et al., 2013). The design improvement of WWTPs to include advanced treatment technologies, aiming to transform CECs into less harmful compounds or even to mineralize them, is one of the promising strategies to achieve this aim, as recently implemented in Switzerland. Advanced water treatment processes include adsorption (e.g., granular activated carbon (GAC)), membrane and advanced chemical/oxidation technologies (Sudhakaran et al., 2013). Other option is the implementation of natural systems to depurate water, such as riverbank filtration (RBF), aquifer recharge and recovery (ARR) and constructed wetlands (CWs), which are reviewed in the literature (Li et al., 2014; Petrovic et al., 2009; Zhang et al., 2014a) and will not be discussed in this work.

### 1.1. European policy

Although there are no legal discharge limits for micropollutants, some regulations have been published. The Directive 2000/60/EC was the first mark in the European water policy, which set up a strategy to define high risk substances to be prioritized (Directive, 2000). A set of 33 priority substances/groups of substances (PSs) and the respective environmental quality standards (EQS) were ratified by the Directive 2008/105/EC (Directive, 2008). Two years ago, the European Union Directive 2013/39/EU recommended attention to the monitorization and treatment options for a group of 45 PSs (Directive, 2013), meeting the protection of the aquatic compartments and the human health. In that Directive, two pharmaceuticals (the non-steroid anti-inflammatory diclofenac and the synthetic hormone 17-alpha-ethinylestradiol – EE2) and a natural hormone (17-beta-estradiol – E2) were recommended to be included in a first watch list of 10 substances/groups of substances for European Union monitoring, to be launched within two years. In the first quarter of 2015, the watch list of substances for European Union-wide monitoring (as set out in Article 8b of Directive 2008/105/EC) was amended in the Decision 2015/495/EU of 20 March 2015. Besides the abovementioned substances (diclofenac, EE2 and E2), three macrolide antibiotics (azithromycin, clarithromycin and erythromycin) were included, together with other natural hormone (estrone – E1), some pesticides, a UV filter and an antioxidant commonly used as food additive, listed in Table 1. The frequent occurrence of CECs in the environment and the inefficiency of conventional WWTPs to remove such compounds, promoted the amendment of the framework to cover a larger set of hazardous compounds, as well as further recommendations for wastewater treatment steps or even new treatment scenarios. This actions should be implemented by the European Commission and regulated by the European country authorities.

This review aims to summarize some relevant data of occurrence and removal in aqueous matrices of the 10 substances/groups of substances (i.e., a total of 17 organic compounds) enlisted in the first watch list for European Union monitoring, defined in the Decision 2015/495/EU. Studies on the occurrence of the referred substances (3 estrogens, diclofenac, 2,6-di-tert-butyl-4-methylphenol, 2-ethylhexyl-4-methoxycinnamate, 3 macrolide antibiotics, methiocarb, 5 neonicotinoids, oxadiazon and triallate) are shown in Table 1, for different aquatic compartments, namely wastewater, surface water and groundwater. Reports dealing with the removal of these 17 substances, only in real matrices, are overviewed below. The search comprised publications since 2005 (last decade) in Scopus database, using as keywords each substance and the treatments herein reported. Most of the works refer to unspiked aqueous environmental samples treated at lab-, pilot- or

**Table 1**  
List of 10 substances/groups of substances (total of 17 organic compounds) included in the watch list of EU Commission Decision 495/2015, and their occurrence in different aquatic compartments, namely effluents of wastewater (WW), surface water (SW), and groundwater (GW). \*n.a. refers to not available data.

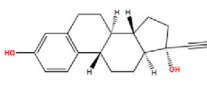
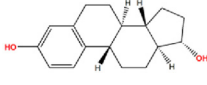
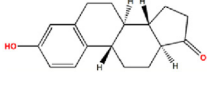
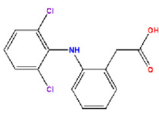
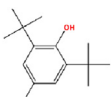
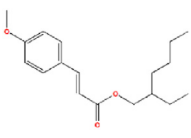
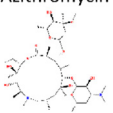
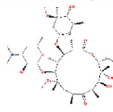
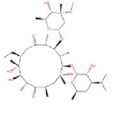
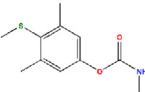
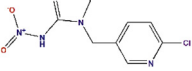
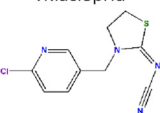
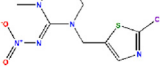
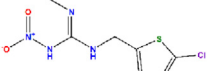
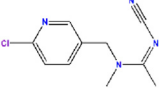
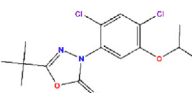
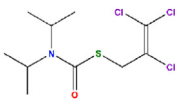
Name of substance/ group of substances	CAS number	(Substance) structure	Concentration (ng L <sup>-1</sup> ) Matrix Locations (number of samples)	Reference
17-Alpha-ethynylestradiol (EE2)	57-63-6		<1–8 WW Korea (n = 120), Germany (n.a.), South Africa (n = 12) 0.2–1.9 SW China (n = 3), Korea (n = 120), Germany (n.a.), France (n = 73) 0.5–230 GW France (n = 73), USA (n.a.)	(Behera et al., 2011; Bolong et al., 2009; Manickum and John, 2014)  (Bolong et al., 2009; Luo et al., 2014; Vulliet and Cren-Olivé, 2011)  (Luo et al., 2014; Vulliet et al., 2008; Vulliet and Cren-Olivé, 2011)
17-Beta-estradiol (E2) Estrone (E1)	50-28-2		<1–88 WW China (n = 3), Korea (n = 120), Sweden (n = 3), UK (n.a.), Germany (n.a.) 0.2–10.1 SW China (n = 3), Korea (n = 120), Germany (n.a.), Japan (n = 517), France (n = 71) 0.3–147 GW France (n = 73), USA (n.a.)	(Behera et al., 2011; Bolong et al., 2009; Nie et al., 2012; Zorita et al., 2009)  (Bolong et al., 2009; Luo et al., 2014; Vulliet and Cren-Olivé, 2011)  (Luo et al., 2014; Vulliet et al., 2008; Vulliet and Cren-Olivé, 2011)
	53-16-7		<1–220 WW China (n = 3), Korea (n = 120), Sweden (n = 3), UK (n.a.), Germany (n.a.) 0.5–69.1 SW China (n = 3), Korea (n = 120), Germany (n.a.), France (n = 71) 0.7–79 GW France (n = 73), USA (n.a.)	(Behera et al., 2011; Bolong et al., 2009; Nie et al., 2012; Zorita et al., 2009)  (Bolong et al., 2009; Luo et al., 2014; Vulliet and Cren-Olivé, 2011)  (Luo et al., 2014; Vulliet et al., 2008; Vulliet and Cren-Olivé, 2011)
Diclofenac	15307-86-5		14.9–4425 WW Spain (n.a.), Italy (n = 3), USA (n.a.), Portugal (n = 4) 0.8–1043 SW Spain (n.a.), Vietnam (n.a.), Costa Rica (n = 86), Greece (n = 30) 1.17–380 GW Spain (n = 30), France (n = 70)	(Al Aukidy et al., 2012; Lara-Martin et al., 2014; Pereira et al., 2015; Prieto-Rodriguez et al., 2012)  (Li, 2014; Spongberg et al., 2011; Stasinakis et al., 2012)  (Li, 2014; Lopez-Serna et al., 2013; Luo et al., 2014)
2,6-di-tert-butyl-4-methylphenol	128-37-0		49–620 SW USA (n = 19), Sweden (n.a.)	(Bendz et al., 2005; Benotti et al., 2009)
2-ethylhexyl-4-methoxycinnamate	5466-77-3		4.7–505 WW China (n = 17), Norway (n = 5) 12–1040 SW Japan (n = 23) 770 GW Spain (n = 7)	(Langford et al., 2015; Li et al., 2007; Tsui et al., 2014)  (Amine et al., 2012)  (Díaz-Cruz et al., 2012)

Table 1 (continued)

Name of substance/ group of substances	CAS number	(Substance) structure	Concentration (ng L <sup>-1</sup> ) Matrix Locations (number of samples)	Reference
Macrolide antibiotics	83905-01-5		0.4–1220 WW Italy (n = 3), Slovakia (n = 3), USA (n.a.), Portugal (n = 4) 0.6–90.8 SW Vietnam (n = 2), China (n = 24)	(Al Aukidy et al., 2012; Birosova et al., 2014; Gibs et al., 2013; Pereira et al., 2015) (Hoa et al., 2011; Tong et al., 2014)
	81103-11-9		0.6–1620 GW Spain (n.a.), China (n = 69) 54–1890 WW Spain (n.a.), Italy (n = 3), Slovakia (n = 3), USA (n.a.) 0.01–778 SW Vietnam (n = 2), Spain (n = 18), China (n = 24)	(Lopez-Serna et al., 2013; Ma et al., 2015; Tong et al., 2014) (Al Aukidy et al., 2012; Birosova et al., 2014; Lara-Martin et al., 2014; Prieto-Rodriguez et al., 2012) (Gracia-Lor et al., 2011; Hoa et al., 2011; Tong et al., 2014) (Lopez-Serna et al., 2013; Tong et al., 2014)
	114-07-8		16–147.9 WW Spain (n.a.), Slovakia (n = 3), USA (n.a.), China (n = 3) 0.28–2246 SW Vietnam (n = 2), Spain (n = 18) 4.8–154.3 GW Spain (n = 121), China (n = 54)	(Birosova et al., 2014; Gibs et al., 2013; Prieto-Rodriguez et al., 2012; Yan et al., 2014b) (Gracia-Lor et al., 2011; Hoa et al., 2011) (Cabeza et al., 2012; Lopez-Serna et al., 2013; Ma et al., 2015)
Methiocarb	2032-65-7		4.73–14.92 WW Spain (n = 55)	(Campo et al., 2013; Masiá et al., 2013)
Neonicotinoids	105827-78-9		2–34.44 WW Spain (n = 55)	(Campo et al., 2013; Masiá et al., 2013)
	138261-41-3		1.1–105 SW Spain (n = 24), USA (n = 35), Greece (n = 89), Portugal (n.a.), Australia (n = 13)	
	111988-49-9		20–400 SW Australia (n = 13)	(Sánchez-Bayo and Hyne, 2014)
	153719-23-4		40–1580 SW Brasil (n.a.), Vietnam (n = 11), Australia (n = 13)	(Chau et al., 2015; da Rocha et al., 2015; Sánchez-Bayo and Hyne, 2014)
	210880-92-5		20–420 SW Australia (n = 13)	(Sánchez-Bayo and Hyne, 2014)
135410-20-7 160430-64-8		20–380 SW Australia (n = 13)	(Sánchez-Bayo and Hyne, 2014)	
Oxadiazon	19666-30-9		4–1440 SW Canada (n = 8)	(Furtula et al., 2006)

(continued on next page)

Table 1 (continued)

Name of substance/ group of substances	CAS number	(Substance) structure	Concentration (ng L <sup>-1</sup> ) Matrix Locations (number of samples)	Reference
Triallate	2303- 17-5		n.a.	n.a.

full-scale, some describing the removal of these substances on spiked environmental matrices, and some including the comparison between the real matrix and ultrapure/deionized water. The first step of sample preparation is usually the filtration of the samples, and the works on occurrence take into account this step in the sample preparation protocol of the analytical method. Before such literature overview, the next sections (1.2, 1.3 and 1.4) present a brief description of the most commonly used conventional and advanced treatment processes.

## 1.2. Treatment by conventional processes

The efficiency of a conventional WWTP varies depending on the characteristics of the pollutant and on the treatment process employed. The main mechanisms for removal of micropollutants occurring during the secondary treatment at WWTPs are biological and/or chemical transformation and sorption (Radjenovic et al., 2009; Verlicchi et al., 2012). The most common employed processes are conventional activated sludge (CAS) and membrane biological reactors (MBRs).

The efficiency of a CAS system depends on the physicochemical characteristics of the substances and on the nature of the microbial community. The most important operational factors affecting the efficiency are the temperature, the hydraulic retention time (HRT) and the sludge retention time (SRT) (Oulton et al., 2010; Petrovic et al., 2009), a higher HRT favoring the removal of more refractory compounds and a higher SRT allowing a higher diversity of microorganisms (Petrovic et al., 2009). The usual SRT in the CAS systems is 7–20 days and the biomass concentration 3–5 kg m<sup>-3</sup>, with a HRT typically ranging from 2 to 24 h (Verlicchi et al., 2012).

MBRs emerged as an alternative to CAS, integrating aerobic biodegradation and membrane separation, modestly more efficient than CAS in the extent of removal of several CECs (Oulton et al., 2010). MBR treatment differs mainly in the SRT that is normally longer (15–80 days) and the commonly higher biomass concentration (8–10 kg m<sup>-3</sup>), HRT being often between 7 and 15 h (Verlicchi et al., 2012). Other important difference is the final stage using ultrafiltration (UF) or microfiltration (MF) membranes to separate the liquid from sludge. Therefore, MBR overcome the constraints of CAS treatment related to the sludge retention and settling characteristics, by applying these membranes to retain the biomass (Petrovic et al., 2009), decreasing the chemical oxygen demand while enhancing the removal of suspended solids and pathogens. Unlike the reports related to CAS, studies focusing on the performance of MBR processes to remove CECs are limited and difficult to compare due to the different operation conditions and target pollutants (Kim et al., 2014). Verlicchi et al. (2012) reviewed extensively the occurrence and removal of pharmaceutical compounds in municipal wastewater, comparing the effectiveness of the secondary treatment by CAS and MBR, with much more studies employing CAS and using generally 24 h composite water samples, avoiding diurnal variability and favoring the inter-studies comparison. Pharmaceuticals and hormones that are now included in the watch list of Decision 495/2015 were referred in that review,

where it was concluded that average removals found in the literature were superior employing MBR than CAS, namely between 26 and 44% for CAS and higher than 60% for MBR, except for azithromycin (Verlicchi et al., 2012).

### 1.2.1. Intermediates formation

Overall, most studies on both CAS and MBR have been focusing on the parent compounds and little attention has been given to the produced intermediates. It is noteworthy that biological or chemical reactions occurring in the secondary clarifiers might lead to the accumulation of metabolites/by-products (Oulton et al., 2010). There are also some compounds (e.g., pharmaceuticals, hormones, drugs of abuse that are excreted by humans and/or animals) that can be found at higher concentrations in the WWTPs effluents than in the respective influents, due to their excretion as conjugates that are broken in the WWTPs. These conjugates are generally metabolized during biological treatment and the parent compound is released, often increasing the concentrations of the parent compounds at the outlet of the WWTPs. For example, E1 can be detected in the secondary effluent of a WWTP at a higher concentration than that found in the raw influent, due to the oxidation of E2 that enters into the WWTP. This fact explains the occasional negative removal efficiencies, sometimes at high extents, with the greatest contribution of the biological transformation (Verlicchi et al., 2012). There are other causes for negative removals occurring during the WWTP treatment. In most cases, the sampling protocol does not consider the HRT and/or SRT and as consequence effluent does not correspond to the same plug of influent (Campo et al., 2013). Sometimes the compounds can be released from particulate matter during treatment (e.g. macrolide antibiotics released from feces particles) (Kim et al., 2014). There are already some reports investigating the occurrence and removal of metabolites and/or intermediates; however, it is crucial to develop more studies on this matter, comprising the parent compounds, the possible by-products and the known metabolites in a broader and more comprehensive approach.

### 1.3. Separation by membrane technologies

Membrane filtration is mostly used for the removal of microorganisms and salts from water/wastewater. The most common membrane technologies include relatively low-pressure systems, such as MF and UF operating at pressures up to 5 and 10 bar, respectively, or high-pressure systems, namely nanofiltration (NF) operating at nearly 50 bar or reverse osmosis (RO) up to 70 bar (or 150 bar for high pressure RO systems) (Coday et al., 2014; Oulton et al., 2010; Peters, 2010). Among these types, the high pressure systems are more suitable for rejection of organic micropollutants, considering the size exclusion mechanism, but larger pores can be employed if electrostatic repulsion or adsorption are the main mechanisms involved in the process (Oulton et al., 2010). The parameters affecting the efficiency of the process include the molecular weight cut-off (MWCO), some membrane properties (e.g., hydrophobicity, surface roughness and charge) and

physicochemical characteristics of the compounds to be rejected (e.g., molecular weight,  $pK_a$ ,  $K_{ow}$  and polarity), among others (Oulton et al., 2010). Regarding the high pressure systems, the main characteristic of NF is the ion selectivity, where monovalent ions can pass through the membrane and multivalent anions are retained (Peters, 2010). The rejection rates are high for organic compounds with molecular weights above 100–200 g mol<sup>-1</sup> (Hillis, 2000). This process is typically applied for dye/color removal, but recent studies focused on the removal of emerging micropollutants from drinking water and wastewater (Baker, 2012). In the case of RO, the organic and inorganic molecules are separated from the feed solution by their molecular weight (normally, less than 200 g mol<sup>-1</sup>), size, charge and inability to permeate the active surface of the RO membrane (Lee et al., 2012). The applications range from the production of ultrapure water, to the desalination of seawater for drinking water production and the treatment of industrial wastewater (Peters, 2010). More recently, RO was also applied for the removal of micropollutants, the process depending on complex interactions (e.g., steric, electrostatic/repulsion and hydrophobic) between the contaminants, the solution and the membrane (Dolar et al., 2012). Among the membrane processes, RO was considered as the ultimate treatment step yielding highest pollutant rejection efficiencies (Theepharaksapan et al., 2011).

Forward osmosis (FO) and membrane distillation (MD) are some alternatives to the membrane processes exclusively based on hydraulic pressure. FO is an osmotically driven membrane process that consists on the osmotic pressure difference between the draw solution and the feed solution. Recently, FO has been more intensively investigated for water/wastewater treatment, as a single treatment or coupled to other membrane processes (Coday et al., 2014; Liu et al., 2015). MD (mainly developed for desalination) is based on a vapor pressure gradient across a porous hydrophobic membrane and can operate under different possible configurations (e.g., direct contact, vacuum, air gap and sweep gas MD) (Drioli et al., 2015; Silva et al., 2015; Wang and Chung, 2015). MD has also been studied to reject organic compounds in water treatment (Alkhubhri et al., 2012) since a complete rejection of inorganic ions and non-volatile substances is theoretically expected.

One of the major disadvantages in this type of processes is the production of a concentrate containing all the retained compounds (Bagastyo et al., 2011; Justo et al., 2014). The disposal of the concentrate can be performed by sewer disposal, evaporation ponds and deep well injection (Umar et al., 2015), but direct discharge to water bodies (oceans, surface and groundwater) is common and constitute potentially serious threat to ecosystems (Justo et al., 2015; Pérez-González et al., 2012). Thus, careful environmental practices are recommended to handle such a concentrated waste before discharging into the aquatic environment (Westerhoff et al., 2009). Different approaches for the treatment of membrane concentrates have been investigated, mainly using AOPs, but also coagulation/flocculation and adsorption with activated carbon were reported (Bagastyo et al., 2011; Justo et al., 2013b, 2014). However, most of these emerging technologies have been developed at laboratory or pilot plant scale (Pérez-González et al., 2012). Good results have been achieved by AOPs for the removal of organic pollutants and persistent compounds, but the cost of these processes can limit their wide implementation at full-scale (Pérez-González et al., 2012; Westerhoff et al., 2009).

#### 1.4. Degradation by advanced oxidation processes (AOPs)

Advanced oxidation processes (AOPs) are conceptually based on the production of highly reactive oxidizing species, such as hydroxyl radicals (HO<sup>•</sup>). AOPs are able to degrade unselectively organic pollutants (Hoigné, 1997) and can be used as pre- or post-

treatment of a biological process. As pre-treatment, the aim of a single or a sequence of complementary AOPs is to obtain a more biodegradable effluent able to be treated by a conventional biological process. AOPs can be used as post-treatment to remove micropollutants and their by-products, ideally yielding as final products CO<sub>2</sub>, H<sub>2</sub>O and inorganic ions, if the aim is the direct discharge in natural water courses. One shortcoming often found in the application of AOPs for wastewater treatment is the frequent presence of radical scavengers in the wastewater, limiting the attack of the radicals to the organic pollutants. Commonly employed AOPs to investigate the treatment of micropollutants in real matrices, include the Fenton and photo-Fenton processes, (catalytic) wet peroxide/air oxidation, (catalytic) ozonation, heterogeneous photocatalysis, electrochemical oxidation or combination of them. For the catalytic processes, different catalysts have been identified as the most active depending on the reaction system, including metal oxides (based on Ti, Cu, Zn, Mn, Fe, Co and Bi, among others), supported noble metals (e.g., Ru, Pt, Pd, Ir and Rh), or even metal-free carbon materials such as activated carbons, carbon xerogels, carbon nanotubes, carbon foams and fibers and graphite (Ribeiro et al., 2015).

Briefly, the Fenton process, based on the Fenton reagent (Fenton, 1894), employs H<sub>2</sub>O<sub>2</sub> and a precursor of iron, generating HO<sup>•</sup> at atmospheric pressure and room temperature. High efficiency, relatively cheap reagents, no need of energy to activate H<sub>2</sub>O<sub>2</sub> and the consequent easy implementation and operation are the advantages of such treatment. Some disadvantages are the generation of a secondary waste (sludge) and the narrow range of optimal pH (2.5–3.0). The photo-assisted Fenton process can be more efficient than Fenton alone, mainly due to the faster regeneration of Fe<sup>2+</sup> (Pastrana-Martínez et al., 2015). Other related options are electro-Fenton, where Fe<sup>2+</sup> is produced from sacrificial cast iron anodes (Nidheesh and Gandhimathi, 2012), or even photo-electro-Fenton (Umar et al., 2010).

The concept of catalytic wet peroxide oxidation is similar to that of the Fenton process, but in this case any catalyst can be used (not only iron species) and slightly higher temperatures (50–70 °C) are typically employed (the operating pressure and temperature dramatically increasing in the case of wet air oxidation).

Regarding ozonation, this process involves the direct attack of ozone (quite selective for electron-rich organic molecules) mainly at low pH and/or indirect reactions through HO<sup>•</sup> more prone at high pH (Ikehata and El-Din, 2004; Munter, 2001). The main handicap of ozonation is the typical low efficiency to mineralize the organic pollutants, while natural organic matter (NOM) and carbonate ions can have a significant interference with the ozone decomposition rate (Saqib et al., 2010). For this reason, different heterogeneous catalysts are under investigation to improve the process (Faria et al., 2008, 2009; Gonçalves et al., 2013; Gonçalves et al., 2010; Orge et al., 2012; Restivo et al., 2012).

Heterogeneous photocatalysis is other process that has been extensively investigated for water/wastewater treatment and is based on the use of wide band-gap semiconductors which generate electrons and holes (and subsequent chain reactions including HO<sup>•</sup>) when irradiated with photons of energy higher than the semiconductor band-gap (i.e.,  $h\nu \geq E_G$ ) (Frank and Bard, 1977; Fujishima and Honda, 1972). TiO<sub>2</sub> is the most widely used reference photocatalyst due to the outstanding activity, photochemical stability, good band gap energy, low cost and relatively low toxicity (Hoffmann et al., 1995; Kabra et al., 2004). The possible use of sunlight and the intrinsic anti-microbial ability of heterogeneous photocatalysis (Marin et al., 2011; McCullagh et al., 2007; Monteiro et al., 2015; Rincón and Pulgarin, 2004) are counterbalanced by its main shortcomings, such as the fast recombination of electron-hole pairs and the limited usage of solar light when bare TiO<sub>2</sub> is

**Table 2**  
Some examples of studies dealing with the removal of E1, E2 and/or EE2. Pollutants included in these studies that are out of the scope of 495/15/EU Decision are not discussed.

Compound	Initial concentration	Treatment and sampling conditions	Concluding remarks	Reference
E1	ng L <sup>-1</sup> level	3 pilot WWTPs, one employing CAS; Average flow rate: 107 dm <sup>3</sup> d <sup>-1</sup> ; SRT 3 d; HRT 7 h; 24 h composite samples; Burlington Skyway municipal WWTP; Ontario, Canada.	Removal efficiency of CAS was greater than 65% for E1.	(Ogunlaja and Parker, 2015)
E2 EE2 E1	14.5 ± 4.5 ng L <sup>-1</sup> n.d. 3.2 ± 4.1 ng L <sup>-1</sup>	Municipal WWTP with biological and chemical treatment; Average flow rate: 20,000 m <sup>3</sup> d <sup>-1</sup> ; Kristianstad; South Sweden.	Removals of 78% and >47% were observed for E1 and E2, respectively.	(Zorita et al., 2009)
E2	10 µg L <sup>-1</sup> (spiked wastewater)	Lab-scale MBR and CAS; Industrial-municipal mixed wastewater before secondary treatment.	E2 was almost completely removed (99%) applying both treatments.	(López-Fernández et al., 2013)
E1 E2 EE2	n.d./n.d.; up to 23.2/21.2 ng L <sup>-1</sup> ; up to 22.2/29.2 ng L <sup>-1</sup> .	WWTPs: CAS or MBR coupled with UF or MF; 24 h composite samples composed by 4 h-aliquots collected by an automatic device; Granada, Spain.	The concentrations after the CAS and MBR treatments were respectively: up to 0.81 and 4.9 ng L <sup>-1</sup> for E2 and up to 6.62 and 6.92 ng L <sup>-1</sup> for EE2. MBR system was shown as good alternative to provide high-quality water for reuse. MBR with MF was more efficient for E2 removal.	(Camacho-Munoz et al., 2012)
EE2	140 ng L <sup>-1</sup> (after primary clarifier)	WWTP with CAS-MF-GAC-ozonation; Average flow rate: 227,000 m <sup>3</sup> d <sup>-1</sup> ; Gwinnett County, GA, USA.	After CAS and MF, the concentration of EE2 decreased by more than 90%. Ozonation oxidized the remaining compounds by more than 60%.	(Yang et al., 2011)
EE2 E1	8.73 ng L <sup>-1</sup> 20.69 ng L <sup>-1</sup>	Pilot-scale combination of MBR and NF or RO; MBR permeate flux: 10.5 L m <sup>-2</sup> h <sup>-1</sup> (constant flux mode); 4-L samples of the influent and effluents of each MBR, NF and RO process.	Removal efficiencies higher than 70% (based on the detection limits) were verified for E1 and EE2 with each treatment process.	(Lee et al., 2008)
E1 E2 EE2	150 µg L <sup>-1</sup> (spiked surface water)	Lab-scale UF prior to NF; NF experiments were conducted at 10 bar and 3.6 cm s <sup>-1</sup> of cross-flow velocity; Surface water from Tagus river, Portugal.	High rejections (higher than 90%) were obtained for E1, E2 and EE2.	(Sanches et al., 2012)
E2 EE2	0.2 µg L <sup>-1</sup> (spiked wastewater)	MF and RO or MF prior to a pilot-scale UV/H <sub>2</sub> O <sub>2</sub> ; LP-UV lamp; H <sub>2</sub> O <sub>2</sub> : 3 mg L <sup>-1</sup> .	Removal of 99% was achieved in both cases.	(James et al., 2014)
E2 EE2 E1	1 mg L <sup>-1</sup> (spiked surface water)	Multi-barrier approach; Lab-scale NF followed by LP-UV ( $\lambda_{\max}$ = 245 nm) or indirect (H <sub>2</sub> O <sub>2</sub> -assisted) LP-UV; H <sub>2</sub> O <sub>2</sub> : 0, 20, 40, 60, 80 or 100 mg L <sup>-1</sup> ; Surface water.	A rejection of 71% was verified using NF (for all the compounds). Direct photolysis led to high E1 removal, while a removal >74% was obtained by indirect (H <sub>2</sub> O <sub>2</sub> ) photolysis. The multi-barrier approach led to higher overall removals (80, 90 and 95% for E2, EE2 and E1, respectively).	(Pereira et al., 2012)
E1 E2 EE2	1.65–3.59 µg L <sup>-1</sup> (treated wastewater from the secondary clarifier)	Pilot plant O <sub>3</sub> , O <sub>3</sub> /UV, O <sub>3</sub> /H <sub>2</sub> O <sub>2</sub> and O <sub>3</sub> /UV/H <sub>2</sub> O <sub>2</sub> ; O <sub>3</sub> : 3.15 g h <sup>-1</sup> ; 5% of ozone in gas mixture.	A removal higher than 99.7% was observed for the 3 estrogens.	(Pesoutova et al., 2014)
E1	3 µg L <sup>-1</sup> – 5 mg L <sup>-1</sup> (spiked wastewater)	Lab-scale O <sub>3</sub> , UV, UV/H <sub>2</sub> O <sub>2</sub> , O <sub>3</sub> /UV, O <sub>3</sub> /H <sub>2</sub> O <sub>2</sub> and O <sub>3</sub> /UV/H <sub>2</sub> O <sub>2</sub> ; Annular reactor (750 mL); LP-UV lamp ( $\lambda_{\max}$ = 253.7 nm); O <sub>3</sub> : 0.33–1.31 mg L <sup>-1</sup> ; H <sub>2</sub> O <sub>2</sub> : 20, 40 and 60 mg L <sup>-1</sup> ; Municipal wastewater (London, OR, Canada).	A complete removal after 30 min was achieved, employing all processes, except for UV (75 min). Ozonation achieved the higher removal rates of E1. Low TOC removal was observed for all the AOPs tested, with the degradation rate decreasing with higher TOC values.	(Sarkar et al., 2014)
E2 EE2 E1	0.035 mg g <sup>-1</sup> (dw) 0.150 mg g <sup>-1</sup> (dw) 0.125 mg g <sup>-1</sup> (dw)	Lab-scale UV, H <sub>2</sub> O <sub>2</sub> and UV/H <sub>2</sub> O <sub>2</sub> ; Reactor with continuous recirculation (800 mL); 75 W LP Hg lamp ( $\lambda_{\max}$ = 253.7 nm); H <sub>2</sub> O <sub>2</sub> : 0.5 mol L <sup>-1</sup> ; pH 3; Spiked waste activated sludge.	E2, EE2 and E1 were removed respectively by 92%, 95% and 97%, after 2 min. UV/H <sub>2</sub> O <sub>2</sub> was more efficient than UV or H <sub>2</sub> O <sub>2</sub> alone. The sludge matrix influenced the degradation rate.	(Zhang and Li, 2014)
EE2	10 mg L <sup>-1</sup> (spiked wastewater)	Catalytic ozonation; O <sub>3</sub> : 20 mg L <sup>-1</sup> ; Catalysts: 5 g of commercial $\gamma$ -Al <sub>2</sub> O <sub>3</sub> or synthesized Co <sub>3</sub> O <sub>4</sub> /Al <sub>2</sub> O <sub>3</sub> ; Ultrapure water and secondary effluents pre-treated to remove its carbonate/bicarbonate content by stripping; Municipal wastewater from a WWTP; Badajoz, Spain.	EE2 was removed in less than 10 min, regardless the matrix or the presence of catalyst. Comparing with single ozonation, catalytic ozonation enhanced the COD and TOC removals, especially in the presence of the Co <sub>3</sub> O <sub>4</sub> /Al <sub>2</sub> O <sub>3</sub> catalyst.	(Pocostales et al., 2011)



Table 2 (continued)

Compound	Initial concentration	Treatment and sampling conditions	Concluding remarks	Reference
EE2 E1	<4.3–7.4 ng L <sup>-1</sup> 1.6–2 ng L <sup>-1</sup>	Pilot-scale ozonation plant; O <sub>3</sub> : 86–153 g Nm <sup>-3</sup> ; O <sub>3</sub> consumption: 0.6 and 0.9 g O <sub>3</sub> g DOC <sub>0</sub> <sup>-1</sup> ; Wastewater; Austria.	The application of 0.6 g O <sub>3</sub> g DOC <sup>-1</sup> increased the removal of these compounds (to not detected).	(Schaar et al., 2010)
E2 EE2 E1	10–250 ng L <sup>-1</sup> (spiked river water)	Ozonation; O <sub>3</sub> : 3–4 mg L <sup>-1</sup> ; River water.	High removal (98–99%) after 10 min was achieved by ozonation process for all estrogens.	(Westerhoff et al., 2005).
EE2 E2 E1	391.4 ± 59.3 ng L <sup>-1</sup> 110.4 ± 55.4 ng L <sup>-1</sup> 20.2 ± 3.3 ng L <sup>-1</sup>	Lab-scale photolytic ozonation, ozonation and photocatalysis; O <sub>3</sub> flow rate: 150 Ncm <sup>3</sup> min <sup>-1</sup> ; O <sub>3</sub> : 50 g Nm <sup>-3</sup> ; MP Hg vapor lamp (UV/Vis λ > 300 nm); TiO <sub>2</sub> photocatalyst: 0.5 g L <sup>-1</sup> load; Urban wastewater from the secondary treatment of a WWTP; North of Portugal.	Complete removal by photocatalytic ozonation was achieved for all estrogens, while EE2 was not completely removed using ozonation (77.2% only) and E1 was not completely removed using photocatalysis (61.8% only).	(Moreira et al., 2015)
EE2	2.0 μM (spiked surface water)	Quartz photolysis tubes (1.4 cm i.d. × 20 cm) at a 45° angle were used in photodegradation experiments; Lake water from Lake Quinsigamond.	EE2 showed very high resistance to microbial degradation while rapid photodegradation under sunlight irradiation occurred (half-life of 23 h).	(Zuo et al., 2013)

AOP, advanced oxidation process; CAS, conventional activated sludge; COD, chemical oxygen demand; DOC, dissolved organic carbon; dw, dry weight; GAC, granular activated carbon; HRT, hydraulic retention time; LP, low pressure; MBR, membrane biological reactor; MF, microfiltration; MP, medium pressure; n.a., not available; n.d., not detected; NF, nanofiltration; RO, reverse osmosis; SRT, sludge retention time; TOC, total organic carbon; UF, ultrafiltration; WWTP, wastewater treatment plant.

employed (i.e. only the UV fraction, near 3–5% of the overall spectrum) (Andreozzi et al., 1999). A recent approach is the hybridization of photocatalysis with membrane processes, with emphasis in the preparation of new filtration membranes with photocatalytic properties (Athanasakou et al., 2015; Pastrana-Martinez et al., 2015).

Sonolysis, supercritical water oxidation, γ-ray irradiation, microwaves and pulsed electron beam are less commonly applied AOPs (Ribeiro et al., 2015).

## 2. The watch list: occurrence and removal

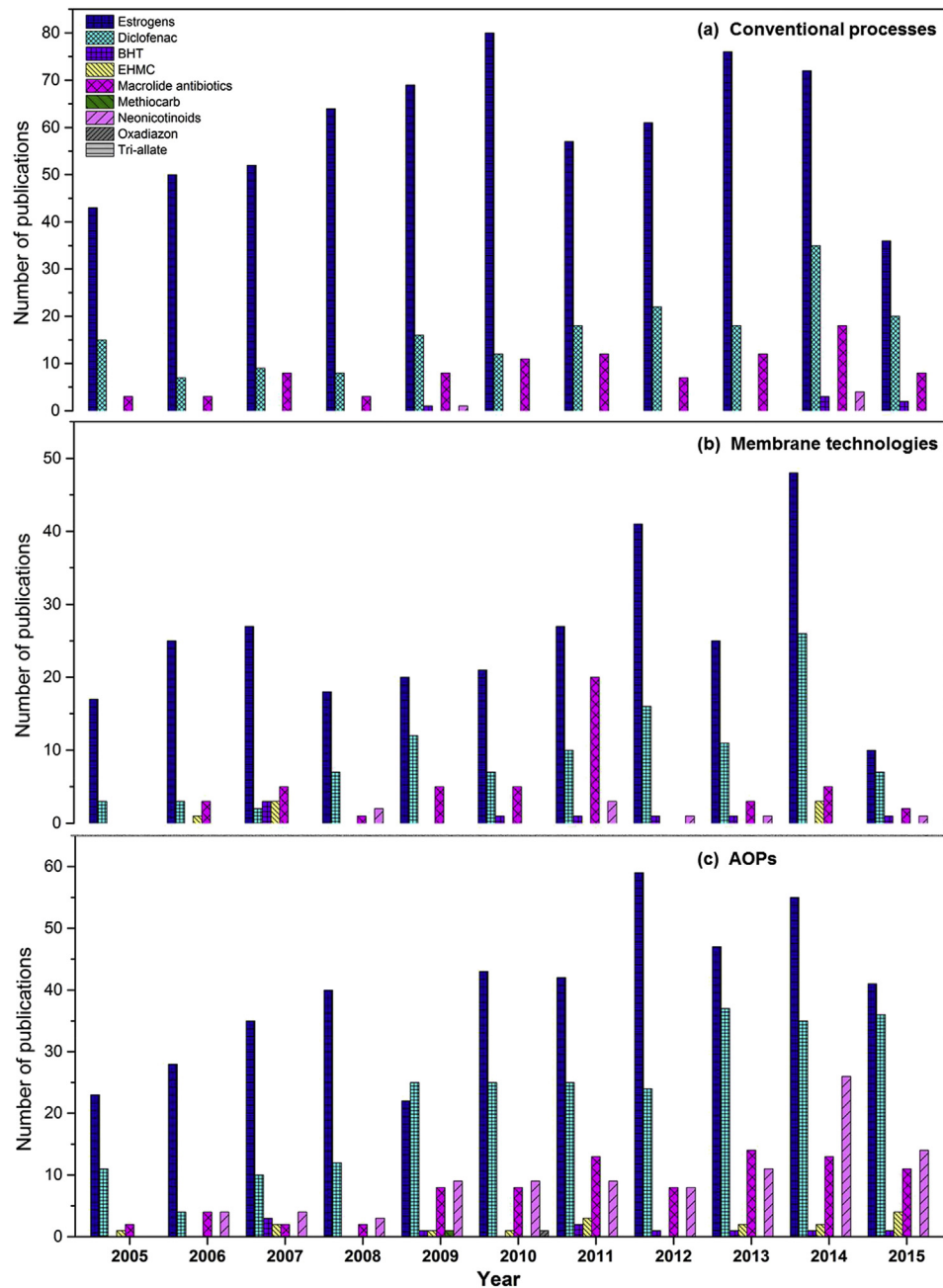
This section aims to overview the substances and group of substances of the watch list for European Union monitoring, defined in the Decision 2015/495/EU, regarding their occurrence in aqueous matrices as well as their removal by using the above-mentioned treatments. Scopus database was used and the keywords were the name of each substance and the following treatments: CAS, MBR (conventional processes); RO, MF, UF, NF, FO or MD (membrane technologies); and UV- and peroxide-based, Fenton-based, heterogeneous photocatalysis or ozonation-based processes (AOPs). The studies selected for this review were performed using realistic matrices. Considering the huge amount of literature available for estrogens (EE2, E2 and E1) and for diclofenac, only some examples of studies related to treatment processes for these particular substances (Tables 1 and 2) are included in this review.

### 2.1. EE2, E2 and E1

Steroid hormones include highly active biological compounds able to induce the therapeutic effect at very low doses. Within this group, estrogens are the most usually found in the aquatic environment, existing either as natural or synthetic substances and acting as endocrine-disrupting compounds (EDCs) (Barreiros et al., 2016; Rocha et al., 2008). Estriol, E1 and E2 are natural estrogens mainly excreted from humans whereas EE2 is the most used oral contraceptive, also excreted by humans, causing injurious effects to the ecosystems such as feminization of male fishes, DNA and immunity alterations (Li, 2014). The effects of EDCs toward animals

are well reported, for example, a 7-year experiment was developed (Kidd et al., 2007) and it was concluded that the chronic exposure of fathead minnow to 5–6 ng L<sup>-1</sup> of EE2 led to feminization of male fish and altered oogenesis in females. Some studies suggested that the effect of EDCs exposure on human health includes a decrease in male sperm count, an increase in testicular, prostate, ovarian and breast cancers and reproductive malfunctions (Joffe, 2001). The major concern is related to fetuses and newborn babies, because of their higher vulnerability (Sharpe and Irvine, 2004). Recently, Kabir et al. (2015) reviewed extensively the mechanism of action and harmful effects of EDCs on human health; and Futran Fuhrman et al. (2015) highlighted the EDCs risk assessment, namely issues related to long-term and combined exposure, transgenerational and mixture effects. Due to the potential deleterious effects that can arise from their release into the environment, their occurrence is well described and reviewed by several authors (Khanal et al., 2006; Li, 2014; Teske and Arnold, 2008). Table 1 summarizes some studies on the occurrence of E1, E2 and EE2 (concentration, matrix and location), which are frequently found in water matrices, namely wastewater, surface and groundwater, at ng L<sup>-1</sup> levels.

The removal of these hormones are reported in several studies (Fig. 2), varying depending on the processes (Table 2). Biological treatments coupled with membrane processes are reported as effective mean for elimination of these types of compounds (Camacho-Munoz et al., 2012). As example, more than 90% of EE2 was removed in an advanced wastewater reclamation plant employing a biological treatment and MF (Yang et al., 2011). Few studies were developed using other membrane technologies to remove E1, E2 and EE2 (Table 2), being highly removed by NF and/or RO (Cheng et al., 2010; Lee et al., 2008). AOPs are promising to remove this type of pollutants, with ozonation having the highest efficiency (Table 2). Data regarding these compounds can be consulted in article reviews that have been published in the last few years and that already encompass a significant amount of information dealing with their removal from water (Basile et al., 2011; Jung et al., 2015; Kaplan, 2013; Liu et al., 2009; Luo et al., 2014; Yu et al., 2013). Concerning the studies on the removal of the substances of the watch list, it can be concluded that E1, E2 and EE2 were the most studied in the last decade, employing all the types of processes herein referred (Fig. 2).



**Fig. 2.** Number of publications dealing with the removal of the 10 substances/groups of substances included in the first watch list for European Union monitoring (Decision 2015/495/EU). The search comprised publications since 2005 in Scopus database, using as keywords each substance and the treatments reported in the previous sections, namely (a) conventional processes (CAS or MBR); (b) membrane technologies (RO, MF, UF, NF, FO or MD); and (c) AOPs (UV- and peroxide based, Fenton based, heterogeneous photocatalysis or ozonation-based processes). In this particular search, any type of matrix (realistic and non-realistic) was considered.

## 2.2. Diclofenac

Regarding the non-steroidal anti-inflammatory drug (NSAID) diclofenac, it is considered harmful to several species at environmental concentrations, as indicated by [Vieno and Sillanpää \(2014\)](#), who overviewed its occurrence, fate and transformation processes during treatment in WWTPs. Diclofenac is often detected in WWTP influents and effluents, surface water and groundwater. [Table 1](#) describes some studies on its occurrence in these aquatic compartments, with diclofenac found up to  $4.4 \mu\text{g L}^{-1}$ . Information concerning the removal of diclofenac can be checked in article reviews that have been published in the last few years and which

already included systematized data of its removal from water ([Barra Caracciolo et al., 2015](#); [Cherik et al., 2015](#); [Fatta-Kassinos et al., 2011](#); [Petrie et al., 2013](#); [Ziylan and Ince, 2011](#)). Diclofenac can be partially adsorbed on sludge and is usually poorly biodegradable, which means low removal rates during biological wastewater treatment ([Table 3](#)) ([Vieno and Sillanpää, 2014](#); [Zhang et al., 2008](#)). Membrane technologies to remove diclofenac have been used, but more research is needed ([Table 3](#)). Concerning AOPs, some studies dealing with heterogeneous photocatalysis and/or photo-Fenton are described in [Table 3](#), with a moderate diclofenac removal, most using a pilot compound parabolic collector (CPC) plant and a high reaction time. Ozonation as single process, or

**Table 3**

Some examples of studies dealing with removal of diclofenac. Pollutants included in these studies that are out of the scope of 495/15/EU Decision are not discussed.

Initial diclofenac concentration	Treatment and sampling conditions	Concluding remarks	Reference
Up to 12.7 ng L <sup>-1</sup> (CAS); up to 38 ng L <sup>-1</sup> (MBR).	WWTP with CAS or MBR coupled to UF or MF; 24 h composite samples composed by 4 h aliquots collected by an automatic device; Granada, Spain.	Mean removal rates were between 54 and 71% for MBR and approximately 79% for CAS.	(Camacho-Munoz et al., 2012)
30 mg L <sup>-1</sup> (spiked surface water)	Photocatalysis and solar photolysis; Advanced lab-scale reactor immersion-well (UV-RS-1) made of Pyrex glass (cut-off <290 nm); Solution volume: 400 mL; MP Hg vapor lamp: TQ 150 W Heraeus, Germany; TiO <sub>2</sub> load: 0.1 g L <sup>-1</sup> ; pH 6.2.	Water quality showed high influence in the treatment efficiency. For river water, solar photolysis showed higher removal compared to TiO <sub>2</sub> photocatalysis, with 66% and 82% diclofenac removal for photocatalysis and direct sunlight, respectively.	(Kanakaraju et al., 2014)
0.05 µg L <sup>-1</sup> (spiked surface water)	Kagithane Drinking Water Treatment Plant; Flow rate: 700,000 m <sup>3</sup> d <sup>-1</sup> ; Lab-scale NF; MF: cross-flow rate of 3 L min <sup>-1</sup> and water flux of 137 L m <sup>-2</sup> h <sup>-1</sup> ; Raw water sources: Terkos Lake and Alibeyköy Dam.	Diclofenac overall rejection was approximately 61%.	(Vergili, 2013)
220 ng L <sup>-1</sup> (after primary clarifier)	WWTP with CAS-MF-GAC-ozonation; Average flow rate: 227,000 m <sup>3</sup> d <sup>-1</sup> ; Gwinnett County, GA, USA.	Diclofenac was removed by CAS, between 51 and 80%, achieving the LOQ.	(Yang et al., 2011)
WWTP1: 507 ng L <sup>-1</sup> ; WWTP2: 1450 ng L <sup>-1</sup> .	WWTP1: parallel CAS and MBR serving 28,000 inhabitants and treating 5544 m <sup>3</sup> d <sup>-1</sup> by CAS and 7237 m <sup>3</sup> d <sup>-1</sup> by MBR; WWTP2: CAS serving 100,000 inhabitants and treating 20,846 m <sup>3</sup> d <sup>-1</sup> ; 24 h composite samples; Lede, Belgium.	Removal was not observed in both treatments of WWTP1 employing parallel CAS and MBR. Almost no removal occurred in WWTP2, with 1391 ng L <sup>-1</sup> in the effluent of CAS.	(Vergeynst et al., 2015)
Up to 2400 ng L <sup>-1</sup>	15 WWTPs designed for 6850 to 756,000 population equivalents; Flow rates: 349–140,000 m <sup>3</sup> d <sup>-1</sup> ; Discharge points: main Portuguese rivers and Atlantic Ocean; 24 h composite influent and effluent samples; Portugal.	Concentration of diclofenac was quantified up to 670 ng L <sup>-1</sup> in the effluent. The mean removal of this substance was 45.6%.	(Pereira et al., 2015)
Up to 0.49 µg L <sup>-1</sup>	4 WWTPs impacted by effluents from mid-size hospitals, corresponding to a WWTP inflow between 1 and 30%; Flow rates: 1300–103,000 m <sup>3</sup> d <sup>-1</sup> ; WWTP 1/3 – SBR and UV-tertiary treatment; WWTP 2 – CAS; WWTP 4 – oxidation ditch activated sludge process; 24 h composite samples; New York, USA.	WWTP 2 and 4, employing CAS or oxidation ditch activated sludge, were more efficient than the others for the removal of diclofenac.	(Oliveira et al., 2015)
Up to 6.34 ng L <sup>-1</sup>	4 WWTPs; Chongqing, China; 2 WWTPs: anaerobic/anoxic/oxic (A/A/O) activated sludge process; 1 WWTP: CAST; 1 WWTP: OD.	Although diclofenac was quantified up to 4.7 ng L <sup>-1</sup> , the removal was not assessed due to its detection in some cases, below than LOQ.	(Yan et al., 2014a)
n.a.	MBR pilot plant in continuous operation (ca. 1% of diurnal hospital sewage); 2 h composite influent and effluent samples; Luxembourg.	Diclofenac was removed at an extent between 40 and 50%. UV was evaluated as post-treatment; degradation was improved by applying H <sub>2</sub> O <sub>2</sub> .	(Kohler et al., 2012)
6.01 ng L <sup>-1</sup>	4 <sup>th</sup> largest WWTP in China, serving 1,540,000 equivalent inhabitants; 600,000 m <sup>3</sup> d <sup>-1</sup> . CAST followed by chlorination; Grab samples collected according to the residence time in each treatment; Southwest China.	The removal obtained after secondary treatment was 41.8% for diclofenac. Chlorination led to a reduction of 8.6%.	(Yan et al., 2014b)
361–911 ng L <sup>-1</sup>	Pilot-scale MF followed by RO; MF: flow rate of 2 m <sup>3</sup> h <sup>-1</sup> and flux of 323 L m <sup>-2</sup> h <sup>-1</sup> ; Residence time 3 min; RO: flow rate of 1 m <sup>3</sup> h <sup>-1</sup> and permeate flux of 34 L m <sup>-2</sup> h <sup>-1</sup> ; Residence time 50 min; Treated effluent; Girona, Spain.	High removal of diclofenac was observed. RO reduced the concentration of diclofenac in the MF permeate to levels below the limit of detection.	(Rodriguez-Mozaz et al., 2015)
57–131 ng L <sup>-1</sup>	Pilot-scale NF and RO; NF: Water flux between 12 and 62 L m <sup>-2</sup> h <sup>-1</sup> , depending on the type of membranes; RO: Water flux of 23.5 L m <sup>-2</sup> h <sup>-1</sup> ; Treated effluent; Sydney, Australia.	RO was the most efficient treatment for the rejection of diclofenac, reaching concentrations lower than 5 ng L <sup>-1</sup> .	(Shanmuganathan et al., 2015)
104.1 ng L <sup>-1</sup>	Pilot-scale UF followed by a RO; UF permeate flux: 227 m <sup>3</sup> d <sup>-1</sup> ; RO permeate flux: 82 m <sup>3</sup> d <sup>-1</sup> ; Ansan, Gyeonggi-do, Korea.	Concentration of diclofenac considerably decreased by UF (permeate concentration: 69.7 ng L <sup>-1</sup> ). RO completely removed diclofenac.	(Chon et al., 2013)

(continued on next page)

Table 3 (continued)

Initial diclofenac concentration	Treatment and sampling conditions	Concluding remarks	Reference
750 ng L <sup>-1</sup>	Pilot-scale NF; Flux: 1–2 L m <sup>-2</sup> h <sup>-1</sup> ; 24 h composite sample; Giessen, Germany.	Diclofenac decreased by at least 65%.	(Röhricht et al., 2010)
605 ng L <sup>-1</sup>	2-L reactors at 25 °C; UV/H <sub>2</sub> O <sub>2</sub> : 3 LP Hg lamps ( $\lambda_{\max}$ = 254 nm); H <sub>2</sub> O <sub>2</sub> consumed ranged from 0.04 to 0.72 mg H <sub>2</sub> O <sub>2</sub> mg TOC <sup>-1</sup> ; Ozonation: 10 g O <sub>3</sub> Nm <sup>-3</sup> ; RO concentrates from a municipal WWTP	UV/H <sub>2</sub> O <sub>2</sub> exhibited higher performance than ozone in the removal of diclofenac, which had one of the lowest initial observed kinetic constants probably due to the matrix effects on the process.	(Justo et al., 2013a)
935 ng L <sup>-1</sup>	2-L reactors at 25 °C; UV/H <sub>2</sub> O <sub>2</sub> : 3 LP Hg lamps ( $\lambda_{\max}$ = 254 nm); H <sub>2</sub> O <sub>2</sub> consumed ranged from 0.01 to 0.90 mg H <sub>2</sub> O <sub>2</sub> mg TOC <sup>-1</sup> ; RO concentrates from a municipal WWTP in a coastal area of Catalonia, Spain.	Diclofenac was completely decomposed by UV, after the first minutes of treatment; it was also removed by UV/H <sub>2</sub> O <sub>2</sub> and ozonation process.	(Justo et al., 2014)
283 ng L <sup>-1</sup>	Biological activated carbon (BAC) process to treat municipal wastewater RO concentrate; Lab scale during 320 days of operation; BAC, combined UV/UV/H <sub>2</sub> O <sub>2</sub> –BAC and ozone–BAC.	54% of diclofenac was removed by the BAC filter. The integration of the UV/H <sub>2</sub> O <sub>2</sub> or the ozonation processes was necessary to obtain a complete removal of diclofenac.	(Justo et al., 2015)
>750 ng L <sup>-1</sup>	Photocatalysis in a pilot-scale CPC plant under natural solar irradiation; TiO <sub>2</sub> load: 20 mg L <sup>-1</sup> ; Effluents of the biological treatment of El Ejido WWTP; Almería, Spain.	Complete diclofenac removal was achieved after 480 min.	(Prieto-Rodriguez et al., 2012)
671–4941 ng L <sup>-1</sup>	Photo-Fenton in a pilot-scale CPC plant; Fe <sup>2+</sup> : 5 mg L <sup>-1</sup> ; pH: 3 and 10; H <sub>2</sub> O <sub>2</sub> : 50 mg L <sup>-1</sup> ; Complexing agents (humic acid and ethylenediamine-N,N'-disuccinic acid); Effluents of the secondary treatment in a municipal WWTP; Almería, Spain.	Diclofenac was removed by 97% in the photo-Fenton process (pH 3), after 50 min. Photo-Fenton with humic acids at neutral pH resulted in a longer treatment time required to reach a similar degradation.	(Klamerth et al., 2013)
≈70 ng L <sup>-1</sup>	Bench-scale UV and UV/H <sub>2</sub> O <sub>2</sub> ( $\lambda_{\max}$ = 254 nm); H <sub>2</sub> O <sub>2</sub> : 7.8 mg L <sup>-1</sup> ; Volume and HRT: 35 L and 5 min, respectively; Capacity: 10 m <sup>2</sup> d <sup>-1</sup> ; Municipal WWTP; Japan.	A complete removal of diclofenac was observed for both processes.	(Kim et al., 2009)
10 µg L <sup>-1</sup> (spiked surface water)	UV/H <sub>2</sub> O <sub>2</sub> in a pilot plant with three parallel reactors with MP, LP or dielectric barrier discharge UV lamps. Pre-treated surface water (by coagulation, flocculation and sedimentation in a natural reservoir, micro-straining and dual layer rapid sand filtration) from Meuse River (Netherlands), spiked with a mixture of 15 compounds.	The degradation of diclofenac was higher than 80%.	(Lekkerkerker-Teunissen et al., 2013)
n.a.	Sulfate radical based homogeneous photo-Fenton involving peroxymonosulfate as oxidant, ferrous iron (Fe(II)) as catalyst and simulated solar irradiation as light source; Biologically treated domestic wastewater effluents;	PMS/Fe(II)/UV–Vis advanced oxidation system using simulated solar irradiation has demonstrated better kinetic performances over TiO <sub>2</sub> /UV–Vis system for diclofenac.	(Ahmed et al., 2014)
0.1 mg L <sup>-1</sup> (spiked wastewater)	Heterogeneous photocatalysis and Photo-Fenton; Pilot-scale CPC solar plant at the Plataforma Solar de Almería (Spain); A: Photo-Fenton (pH 2; 5 mg L <sup>-1</sup> of Fe <sup>2+</sup> ; 50 mg L <sup>-1</sup> of H <sub>2</sub> O <sub>2</sub> ; 5 mg L <sup>-1</sup> of TiO <sub>2</sub> ); B: no pH adjustment; 50 mg L <sup>-1</sup> of H <sub>2</sub> O <sub>2</sub> ; 5 mg L <sup>-1</sup> of Fe <sup>2+</sup> (demineralized water); 5, 15 and 55 mg L <sup>-1</sup> of Fe <sup>2+</sup> (standard freshwater); 5 mg L <sup>-1</sup> of Fe <sup>2+</sup> (standard fresh water without NaHCO <sub>3</sub> ).	Solar TiO <sub>2</sub> photocatalysis showed complete diclofenac degradation. 20–50% of degradation in demineralised water was achieved in the dark (Fenton process) and photo-Fenton was the most effective treatment with a complete removal observed after 20 min. In standard fresh water, diclofenac was removed by Fenton process.	(Klamerth et al., 2009)
0.276 µg L <sup>-1</sup>	Heterogeneous photocatalysis: Solardetox Acadus-2006 CPCs with 3.0 m <sup>2</sup> irradiated surface and 24 L of irradiated volume; TiO <sub>2</sub> load: 0.2 g L <sup>-1</sup> ; Effluent of a WWTP from the South East of Spain.	High diclofenac removal (≈88%) was observed after 3 h of treatment (below LOQ) applying solar TiO <sub>2</sub> photocatalysis.	(Bernabeu et al., 2011)
10 mg L <sup>-1</sup> (spiked wastewater)	Catalytic ozonation; O <sub>3</sub> : 20 mg L <sup>-1</sup> ; Catalysts: 5 g of commercial $\gamma$ -Al <sub>2</sub> O <sub>3</sub> or synthesized Co <sub>3</sub> O <sub>4</sub> /Al <sub>2</sub> O <sub>3</sub> ; Ultrapure water and secondary effluents pre-treated to partially remove its carbonate/bicarbonate content by stripping; Wastewater from a municipal WWTP; Badajoz, Spain.	Diclofenac was removed in less than 10 min, regardless the matrix or the presence of catalyst. Comparing with single ozonation, catalytic ozonation enhanced the COD and TOC removals, in particular with a Co <sub>3</sub> O <sub>4</sub> /Al <sub>2</sub> O <sub>3</sub> catalyst.	(Pocostales et al., 2011)

Table 3 (continued)

Initial diclofenac concentration	Treatment and sampling conditions	Concluding remarks	Reference
30–80 mg L <sup>-1</sup> (spiked wastewater)	UVA, O <sub>3</sub> , O <sub>3</sub> /UVA, O <sub>3</sub> /TiO <sub>2</sub> , O <sub>3</sub> /UVA/TiO <sub>2</sub> ; O <sub>3</sub> : 5–30 g m <sup>-3</sup> ; HP Hg lamp; TiO <sub>2</sub> load: 0.5 and 2.5 g L <sup>-1</sup> ; Ultrapure water and urban wastewater from a municipal WWTP; Badajoz, Spain	Complete removal of diclofenac was verified by applying photocatalytic ozonation within 6 min (60–75% TOC reduction after 60 min, regardless the water matrix used). Photocatalytic ozonation showed the lowest ozone consumption compared to the other ozonation processes.	(Aguinaco et al., 2012)
30 mg L <sup>-1</sup> (spiked surface water)	Single ozonation and catalytic ozonation; O <sub>3</sub> : 10 g m <sup>-3</sup> ; pH = 7; Catalysts: 1 g L <sup>-1</sup> of lab-prepared Mn–Ce–O or a commercial (N-150) catalyst; Synthetic effluent and river water collected from Mondego River; Portugal.	The catalysts had no significant effect on diclofenac removal when compared with single ozonation. However, both catalysts increased the COD removal per mg of ozone applied.	(Martins et al., 2015)
n.a.	Bench-scale photolysis; 150 W MP Hg lamp, which emits radiation between 200 and 450 nm; Municipal wastewater of secondary effluent of a biological WWTP; Portugal.	The degradation rate constants obtained for diclofenac in a filtered wastewater matrix were lower than in a pure water matrix.	(Salgado et al., 2013)
2.5 mg L <sup>-1</sup> (spiked wastewater)	Lab-scale TiO <sub>2</sub> photocatalysis; 125 W black light fluorescent lamp (300–420 nm); Catalyst load: 0.2–0.8 g L <sup>-1</sup> ; Urban WWTP effluent.	TiO <sub>2</sub> photocatalysis showed a high removal of diclofenac (≈98%).	(Rizzo et al., 2009)
100 µg L <sup>-1</sup> (spiked wastewater)	Solar photo-Fenton in a pilot-scale solar CPC reactor; H <sub>2</sub> O <sub>2</sub> dose = 0–50 mg L <sup>-1</sup> ; Fe <sup>2+</sup> = 5 mg L <sup>-1</sup> ; Municipal wastewater.	Diclofenac was completely removed (<LOQ) after 34 min.	(Klamerth et al., 2010)
464.8 ± 64.7 ng L <sup>-1</sup>	Lab-scale photolytic ozonation, ozonation and photocatalysis; O <sub>3</sub> : 50 g Nm <sup>-3</sup> ; O <sub>3</sub> flow rate: 150 Ncm <sup>3</sup> min <sup>-1</sup> ; MP Hg vapor lamp (UV/Vis λ > 300 nm); TiO <sub>2</sub> photocatalyst: 0.5 g L <sup>-1</sup> load; Urban wastewater from the secondary treatment of a WWTP; North of Portugal.	For all processes, the complete removal was achieved.	(Moreira et al., 2015)
13.5–52.0 µg L <sup>-1</sup> (spiked wastewater)	Lab-scale ozonation; O <sub>3</sub> : 5.5–8.5 mg L <sup>-1</sup> ; O <sub>3</sub> flow rate: 0.39 Ndm <sup>3</sup> min <sup>-1</sup> ; Urban wastewater samples from the secondary clarifier of two WWTPs from West-Alcalá and Alcázar de San Juan; Spain.	High diclofenac removal (>90%) was observed.	(Rodríguez et al., 2012)
970–2300 ng L <sup>-1</sup>	Pilot-scale ozonation plant; O <sub>3</sub> : 86–153 g Nm <sup>-3</sup> ; O <sub>3</sub> consumption: 0.6 and 0.9 g O <sub>3</sub> g DOC <sub>0</sub> <sup>-1</sup> ; Municipal wastewater; Austria.	The application of 0.6 g O <sub>3</sub> g DOC <sub>0</sub> <sup>-1</sup> increased the removal of diclofenac (to values < LOQ).	(Schaar et al., 2010)
5–20 mg L <sup>-1</sup> (spiked wastewater)	UV-A/TiO <sub>2</sub> photocatalysis: 9 W lamp; Catalyst load: 50–1600 mg L <sup>-1</sup> ; H <sub>2</sub> O <sub>2</sub> = 0.07–1.4 mM; Treated municipal effluent from Limassol; Cyprus.	UV-A/TiO <sub>2</sub> was efficient for the degradation and mineralization of diclofenac in treated municipal effluents.	(Achilleos et al., 2010)

BAC, Biological activated carbon; CAS, conventional activated sludge; CAST, cyclic activated sludge technology; COD, chemical oxygen demand; CPC, compound parabolic collector; DOC, dissolved organic carbon; GAC, granular activated carbon; HRT, hydraulic retention time; LOQ, limit of quantification; LP, low pressure; MP, medium pressure; MBR, membrane biological reactor; MF, microfiltration; n.a., not available; n.d., not detected; NF, nanofiltration; OD, oxidation ditch; RO, reverse osmosis; SBR, Sequential Batch Reactor; TOC, total organic carbon; UF, ultrafiltration, WWTP, wastewater treatment plant.

combined with photolysis and/or photocatalysis, has been widely investigated showing a high performance for diclofenac removal. Overall, diclofenac is the second most studied substance of the watch list in the last 10 years, employing all the types of processes (Fig. 2).

### 2.3. 2,6-di-tert-butyl-4-methylphenol

The anti-oxidant 2,6-di-tert-butyl-4-methylphenol (BHT) has been used as a common anti-oxidant to preserve and stabilize the freshness, nutritive value, flavor and color of food and animal feed products, since the 1950s (Fries and Püttmann, 2002; Tombesi and Freije, 2002). BHT can also improve the stability of pharmaceuticals and cosmetics and increase the durability of rubber and plastics. Approximately 40 countries allow the use of BHT as a direct or

indirect food additive (Fries and Püttmann, 2002). The use of BHT as a food additive does not appear to pose a public health risk. However, in the natural environment, BHT is degraded biologically to 3,5-di-tert-butyl-4-hydroxybenzaldehyde (BHT-CHO), reported by generating peroxides in mice and rats and inducing cellular DNA damage (Fries and Püttmann, 2004). The occurrence of the anti-oxidant BHT in the aquatic environment has been demonstrated (Table 1), with studies conducted in Sweden (Bendz et al., 2005) and USA (Benotti et al., 2009) reporting the presence of BHT in surface water up to 620 ng L<sup>-1</sup> and 49 ng L<sup>-1</sup>, respectively. In other studies, BHT was detected in wastewater (between 22 and 258 ng L<sup>-1</sup>) (Fries and Püttmann, 2004), whereas higher values were quantified in surface water (up to 1560 ng L<sup>-1</sup>) and groundwater (up to 2156 ng L<sup>-1</sup>) in Greece and Germany (Fries and Püttmann, 2002, 2004; Papadopoulou-Mourkidou et al., 2001).

**Table 4**  
Studies dealing with removal of 2-ethylhexyl-4-methoxycinnamate (EHMC). Pollutants included in these studies that are out of the scope of 495/15/EU Decision are not discussed.

Initial EHMC concentration	Treatment and sampling conditions	Concluding remarks	Reference
n.a.	5 WWTPs equipped with different treatment levels: preliminary screening, primary sedimentation, secondary treatment; UV-disinfection, chlorination, sand filtration and RO; 24 h composite or grab samples, depending on the plant; Hong Kong.	Removal of EHMC varied depending on the season in the range of 30–50%.	(Tsui et al., 2014)
Up to 234 ng L <sup>-1</sup>	Ozonation: nominal capacity of 3000 m <sup>3</sup> h <sup>-1</sup> ; 5 L glass reactor operating in semi-batch mode, at a temperature of 25 °C and pH 8.5; WWTP located in Madrid, which treats a mixture of domestic and industrial wastewater.	The UV filter EHMC was completely refractory to ozone.	(Rosal et al., 2010)
23.6 ± 8.1 ng L <sup>-1</sup>	UV, visible light, photocatalysis (visible light), O <sub>3</sub> ; 15 W LP Hg vapor lamp (λ <sub>max</sub> = 254 nm); Xe 150 Xe-arc lamp with spectral emission in the visible region; Photocatalyst: ceria-doped TiO <sub>2</sub> at 0.5 g L <sup>-1</sup> ; O <sub>3</sub> : 22 g Nm <sup>-3</sup> ; Mixture of domestic and industrial wastewater from the secondary clarifier of a 3000 m <sup>3</sup> h <sup>-1</sup> WWTP placed in Alcalá de Henares; Madrid, Spain	EHMC was removed up to 50% after 15 min of UV-photolysis, mainly during the first 2 min. Visible light Xe-lamp driven photolysis led to an EHMC removal near 20% after 15 min. Removal was not enhanced, applying visible light Ce/TiO <sub>2</sub> photocatalysis. EHMC was not significantly removed by ozone.	(Santiago-Morales et al., 2013)

n.a., not available; LP, low pressure; RO, reverse osmosis; WWTP, wastewater treatment plant.

Additional data are needed to support assessments of human health risks associated with the exposure to this compound in the aquatic environment and to establish possible pathways of removal in aquatic systems. Considering the lack of studies on its removal (Fig. 2), it is urgent to study its elimination from water matrices.

#### 2.4. 2-ethylhexyl-4-methoxycinnamate

Organic UV filters are chemical filters used in many personal care products, alone or in formulations containing a physical filter like ZnO or TiO<sub>2</sub> nanoparticles (Kaiser et al., 2012a). Their occurrence in the environment has been described in several papers that have been given a great attention to the aqueous matrices. These CECs reach the environment by two pathways, wash off from skin or through wastewater or swimming pool water. Organic UV filters are likely to be present in sediments (Kaiser et al., 2012b), where they might induce toxicological effects. Their known estrogenic effects on biota and humans was recently reviewed by Ramos et al. (2015), who highlighted not only the recognized *in vivo* and *in vitro* estrogenic activity to fish and mammals, but also other non-estrogenic hormonal targets in such organisms. The UV filter 2-ethylhexyl-4-methoxycinnamate (EHMC), included in the watch list for Union-wide monitoring, is an EDC and was reported at concentrations levels of hundreds of μg kg<sup>-1</sup> in diverse organisms including macroinvertebrates and fish (Kaiser et al., 2012a). Lake and rivers sediments are well characterized regarding this contaminant, which is usually present at μg kg<sup>-1</sup> levels (Kaiser et al., 2012a, 2012b; Langford et al., 2015). This compound was also detected up to 260 ng L<sup>-1</sup> in tap water from Barcelona (Spain), one of the most frequently found of a group of five UV filters included in that study (Díaz-Cruz et al., 2012). Little is known about the removal of EHMC in the aquatic environment (Table 4, Fig. 2), only three studies reporting its removal. The removal of EHMC varied (30–50%), depending on the respective treatment applied at the WWTP and season (Tsui et al., 2014). This UV filter was refractory to ozonation, without any degradation being observed after 15 min (Rosal et al., 2010) or after 22 min, but could be removed by UV treatment (Santiago-Morales et al., 2013).

#### 2.5. Macrolide antibiotics

Among the different classes of pharmaceuticals present in the environment, particular importance has been given to antibiotics,

which are the most often discussed pharmaceuticals due to their potential role in the development of resistant mechanisms by bacteria (Xekoukoulotakis et al., 2010). Macrolide antibiotics, such as clarithromycin, azithromycin and erythromycin are widely used in human and veterinary medicine, as well as in aquaculture, for the purpose of preventing or treating serious infections induced by pneumococci, staphylococci and streptococci (Lange et al., 2006; Xekoukoulotakis et al., 2010). The conventional municipal WWTPs do not fully eliminate these drugs, which are found in WWTP effluents (Lange et al., 2006) and in other aquatic systems (Gracia-Lor et al., 2011; Hoa et al., 2011; Lopez-Serna et al., 2013; Tong et al., 2014). These antibiotics have been extensively detected in wastewater, surface and groundwater in several countries at ng L<sup>-1</sup> levels, with some studies reporting antibiotics at several μg L<sup>-1</sup> (Table 1). For instance, azithromycin, erythromycin and clarithromycin were found in effluents of a WWTP in Slovakia at ng L<sup>-1</sup> levels (Birosova et al., 2014). Clarithromycin and erythromycin were reported in surface water in Spain and Vietnam (Gracia-Lor et al., 2011; Hoa et al., 2011). Lopez-Serna et al. (2013) also reported the occurrence of the three macrolide antibiotics in groundwater (Spain) in the range 1.6–1620 ng L<sup>-1</sup>.

Elimination of this class of antibiotics in the environment has been reported in the last decade, for all the types of processes here discussed (Fig. 2). Biological treatments occurring at WWTPs are normally insufficient to remove such recalcitrant pharmaceuticals (Table 5). The combination of biological with advanced treatments can be fruitful, as example MBR and RO led to elimination rates above 99% (Dolar et al., 2012) for the macrolides included in the watch list. Hence, advanced methods should be applied to deal with this environmental concern. Membrane technologies alone are not enough for the complete removal of such micropollutants (Table 5). Studies reported in the literature employing AOPs for the removal of this type of antibiotics in environmental samples are focused only on photocatalysis (Bernabeu et al., 2011; Xekoukoulotakis et al., 2010), revealing a lack of knowledge regarding the efficiency of other AOPs to remove this compounds in real scenarios. In fact, some studies with other AOPs were already published considering these compounds, but not using real matrices and, thus, they are out of the scope of the present review; for instance, UV/TiO<sub>2</sub> and ozonation were studied for the removal of clarithromycin and erythromycin, ozonation apparently being more effective for the parent compounds (complete degradation), while catalytic ozonation improving the mineralization of erythromycin

**Table 5**

Studies dealing with removal of macrolides (azithromycin, clarithromycin and erythromycin). Pollutants included in these studies that are out of the scope of 495/15/EU Decision are not discussed.

Compound	Initial concentration	Treatment and sampling conditions	Concluding remarks	Reference
Erythromycin	2600 ng L <sup>-1</sup> (after primary clarifier)	WWTP with CAS-MF-GAC-ozonation; Average flow rate: 227,000 m <sup>3</sup> d <sup>-1</sup> ; 24 h composite samples; Gwinnett County, GA, USA.	Erythromycin was recalcitrant to the biological treatment, but it was removed at an extent of 74% by GAC adsorption. Ozonation oxidized the remaining compounds by more than 60%.	(Yang et al., 2011)
Azithromycin Clarithromycin Erythromycin	118 ng L <sup>-1</sup> 2020 ng L <sup>-1</sup> 49 ng L <sup>-1</sup>	MBR coupled to RO; Coastal WWTP Castell-Platja d'Aro, Spain.	The combination of MBR and RO led to removal rates above 99% for the target pollutants, with RO showing removal rates always higher than 99%. MBR removed 75–85% of the antibiotics, and the remaining non-degraded macrolides were removed by RO.	(Dolar et al., 2012)
Azithromycin Clarithromycin Erythromycin	232.5–876.9 ng L <sup>-1</sup> >0.1 µg L <sup>-1</sup> 4.11–42.01 ng L <sup>-1</sup>	WWTP1 with secondary treatment (anaerobic/anoxic/oxic (A/A/O) treatment + moving bed biofilm reactor (MBBR) + secondary clarifier) and tertiary treatment (rotary fiber disc filters (RDFDs)). WWTP2 with secondary treatment (C-Orbal OD process + secondary clarifier) and tertiary treatment (UV disinfection and RDFDs); 24 h composite wastewater samples at different sampling points; Wuxi City, Jiangsu Province, China.	Removal efficiencies were generally higher in the WWTP1 employing the A/A/O-MBBR process than those obtained by the conventional WWTP2 adopting the C-Orbal OD process, except for clarithromycin. The type of biodegradation process was the predominant factor in this study, the better performance being obtained with WWTP1.	(Yuan et al., 2015)
Erythromycin	0.2 µg L <sup>-1</sup>	1 WWTP serving 500,000 population equivalent, with an industrial inlet lower than 10% of the total load; with biological treatment, final clarification and tertiary treatment by phosphorus precipitation; 2 h composite influent and effluent samples, during 24 h Nancy, France.	No elimination was reported for erythromycin in the liquid phase. This antibiotic was also not adsorbed on the particulate matter or the sludge.	(Pasquini et al., 2014)
Azithromycin, Clarithromycin Erythromycin	406–611 ng L <sup>-1</sup> 785–941 ng L <sup>-1</sup> 164–210 ng L <sup>-1</sup>	1 WWTP equipped with MBR and UV treatment, serving 24,000 inhabitants; Membrane modules made of hollow-fiber membranes; Average flow rates: 8800 m <sup>3</sup> d <sup>-1</sup> ; 24 h composite influent and effluent samples; Canada.	The degraded fraction of azithromycin was approximately 49% and that of erythromycin was negligible. Clarithromycin was not removed during MBR treatment, being even formed during treatment.	(Kim et al., 2014)
Azithromycin	up to 719 ng L <sup>-1</sup>	15 WWTPs, designed for 6850 to 756,000 population equivalents; Average flow rates: between 349 and 140,000 m <sup>3</sup> d <sup>-1</sup> ; Discharge points: Portuguese rivers and Atlantic Ocean; 24 h composite influent and effluent samples; Portugal.	The concentration of azithromycin in the effluent was up to 200 ng L <sup>-1</sup> , with a mean removal of 94.6%.	(Pereira et al., 2015)
Clarithromycin Erythromycin	up to 0.33 µg L <sup>-1</sup> up to 0.13 µg L <sup>-1</sup>	4 WWTPs impacted by effluents from mid-size hospitals (250–600 beds) corresponding to a WWTP inflow ranging between 1 and 30%; Average flow rates: between 1300 and 103,000 m <sup>3</sup> d <sup>-1</sup> ; WWTP 1/3 – SBR and UV-tertiary treatment; WWTP 2 – CAS; WWTP 4 – OD activated sludge process; 24 h composite samples; New York, USA.	WWTP 2 and 4, employing CAS or OD activated sludge process were more efficient than the others for the removal of clarithromycin and erythromycin.	(Oliveira et al., 2015)
Azithromycin Erythromycin	up to 661.9 ng L <sup>-1</sup> up to 338.2 ng L <sup>-1</sup>	2 municipal WWTPs with anaerobic/anoxic/oxic (A/A/O) activated sludge process, one of them employing a cyclic activated sludge technology (CAST) whereas the other having an OD; Chongqing, China.	WWTP using the OD biological treatment process had the higher efficiency to remove the macrolide antibiotics.	(Yan et al., 2014a)
Clarithromycin Erythromycin	n.a.	MBR pilot plant in continuous operation ca. 1% of diurnal hospital sewage; 2 h composite influent and effluent samples; Luxembourg.	Erythromycin was almost totally removed by MBR, while clarithromycin was removed at extents between 40 and 50%. UV was evaluated as post-treatment, with improved degradation obtained by adding H <sub>2</sub> O <sub>2</sub> .	(Kohler et al., 2012)
Azithromycin Erythromycin	330.27–376.5 ng L <sup>-1</sup> 238.6–275.4 ng L <sup>-1</sup>	4th largest WWTP in China, serving 1,540,000 equivalent inhabitants and treating 600,000 m <sup>3</sup> d <sup>-1</sup> . CAST (anaerobic/anoxic/aerobic (A/A/A) treatment secondary clarifier) followed by chlorination; Grab samples collected according to the residence time in each treatment; Southwest China.	The removal obtained after secondary treatment was 75.6% for azithromycin and 42.8% for erythromycin. Chlorination led to a reduction of 8.0% for azithromycin. Erythromycin was not removed during chlorination.	(Yan et al., 2014b)
Azithromycin Clarithromycin	160–279 ng L <sup>-1</sup> 1129–1570 ng L <sup>-1</sup>	Samples were collected in winter from four WWTP located in Kyoto and Shiga prefecture (Japan); WWTPs employed a wide variety of secondary treatment processes: CAS; anaerobic/anoxic/aerobic (A/A/A) and anoxic/aerobic (A/A).	Removal efficiency of the macrolide antibiotics were higher using CAS (39–83%) and A/A (34–86%) processes than using A/A/A (41–53%) process.	(Ghosh et al., 2009)

(continued on next page)

Table 5 (continued)

Compound	Initial concentration	Treatment and sampling conditions	Concluding remarks	Reference
Clarithromycin	up to 27.4 $\mu\text{g L}^{-1}$	MBR followed by NF and RO; Membrane surface of NF and RO modules: 2.5 $\text{m}^2$ ; Operation: cross flow membranes; NF/RO modules: maximum flux between 20 and 36 $\text{L m}^{-2} \text{h}^{-1}$ ; Hospital wastewater, Germany.	Clarithromycin was completely removed by RO and NF treatments (<LOQ).	(Beier et al., 2010)
Erythromycin	337 $\pm$ 19.2 $\text{ng L}^{-1}$	Pilot-scale UF and RO treatments in sequence; UF flux range of 25–47 $\text{L m}^{-2} \text{h}^{-1}$ ;	High removal rates were achieved after RO (99% for macrolides antibiotics).	(Sahar et al., 2011)
Clarithromycin	377 $\pm$ 30.9 $\text{ng L}^{-1}$	RO flux range of 22–31 $\text{L m}^{-2} \text{h}^{-1}$ ; Municipal WWTP; Tel-Aviv, Israel.		
Azithromycin	187–367 $\text{ng L}^{-1}$	Pilot-scale MF followed by RO; MF: flow rate of 2 $\text{m}^3 \text{h}^{-1}$ and flux of 323 $\text{L m}^{-2} \text{h}^{-1}$ ; Residence time 3 min;	High removals were observed for these pharmaceuticals compounds. Even though the pharmaceuticals were present in the MF permeate at levels higher than 100 $\text{ng L}^{-1}$ , RO filtration reduced their loads to the low $\text{ng L}^{-1}$ range or to below the method LOQ.	(Rodríguez-Mozaz et al., 2015)
Erythromycin	180–191 $\text{ng L}^{-1}$	RO: flow rate of 1 $\text{m}^3 \text{h}^{-1}$ and permeate flux of 34 $\text{L m}^{-2} \text{h}^{-1}$ ; Residence time 50 min; Municipal treated effluent; Girona, Spain.		
Clarithromycin	77 $\text{ng L}^{-1}$	2-L reactors at 25 $^{\circ}\text{C}$ ; UV/H <sub>2</sub> O <sub>2</sub> : 3 LP Hg lamps ( $\lambda_{\text{max}} = 254 \text{ nm}$ ); H <sub>2</sub> O <sub>2</sub> consumed ranged from 0.01 to 0.90 $\text{mg H}_2\text{O}_2 \text{ mg TOC}^{-1}$ ; RO concentrates from a municipal WWTP in a coastal area of Catalonia, Spain.	Clarithromycin was completely removed by ozonation, but it was recalcitrant to UV (removal of 60%) and UV/H <sub>2</sub> O <sub>2</sub> (removal of almost 80%).	(Justo et al., 2014)
Clarithromycin	46 $\text{ng L}^{-1}$	Biological activated carbon (BAC) process to treat municipal wastewater RO concentrate; Lab scale during 320 days of operation; BAC, combined UV/UV/H <sub>2</sub> O <sub>2</sub> –BAC and ozone–BAC.	70% of clarithromycin was removed by the BAC filter. Pretreatment of RO brine with UV/H <sub>2</sub> O <sub>2</sub> or ozonation led to the removal of the pharmaceutical.	(Justo et al., 2015)
Clarithromycin	<750 $\text{ng L}^{-1}$	Pilot-scale photocatalysis: CPC plant under natural solar irradiation; TiO <sub>2</sub> load: 20 $\text{mg L}^{-1}$ ;	Using a low TiO <sub>2</sub> load (29.2 mm photoreactor), the treatment was not effective due to the slow reaction rate; 85% of the pollutants were degraded after 480 min. Increasing the light-path of the reactor, the performance was enhanced (90% of the pollutants removed after 300 min).	(Prieto-Rodríguez et al., 2012)
Erythromycin		Municipal effluents collected downstream of the secondary biological treatment of El Ejido WWTP; Almería, Spain.		
Clarithromycin	$\approx$ 0.0275 $\mu\text{g L}^{-1}$	Pilot-scale photocatalysis: Solardetox Acadus-2006 CPCs; 3.0 $\text{m}^2$ irradiated surface; 24 L irradiated volume;	Removal was high for all the compounds after 3 h of treatment (below LOQ).	(Bernabeu et al., 2011)
Erythromycin	<0.05 $\mu\text{g L}^{-1}$	TiO <sub>2</sub> load: 0.2 $\text{g L}^{-1}$ ; Wastewater.		
Azithromycin	1653.84 $\text{ng L}^{-1}$	O <sub>3</sub> /H <sub>2</sub> O <sub>2</sub> ; O <sub>3</sub> : 24 $\text{g O}_3 \text{ Nm}^{-3}$ ; Gas flow: 0.36 $\text{Nm}^3 \text{h}^{-1}$ ; H <sub>2</sub> O <sub>2</sub> : 0.15 mL of a 30% (w/v) solution; Wastewater from the secondary clarifier from a sewage treatment plant of Alcalá de Henares; Madrid, Spain.	The removal for azithromycin was 89.6% after 5 min.	(Rodríguez et al., 2011)
Clarithromycin	up to 0.1 $\mu\text{g L}^{-1}$	Bench-scale ozonation: at pH 8.5 (original) and at pH 7.0 (adjusted by adding H <sub>2</sub> SO <sub>4</sub> ); O <sub>3</sub> doses ( $\text{g O}_3/\text{g DOC}$ ): 0.25, 0.5, 1.0, and 1.5; H <sub>2</sub> O <sub>2</sub> /O <sub>3</sub> molar ratio = 0, 0.25, and 0.5; 24 h composite samples of hospital wastewater effluents from a pilot MBR; Baden, Switzerland.	The elimination of clarithromycin was efficient when the ratio of O <sub>3</sub> /DOC was higher than 0.5. The LOQ was achieved and the removal was higher than 92% at both pH conditions. The average removal was 80% using a ratio of O <sub>3</sub> /DOC of 0.25.	(Lee et al., 2014)
Azithromycin	n.d.	Ozonation of secondary effluent;	The removal efficiencies of all the target macrolides antibiotics were up to 80%.	(Nakada et al., 2007)
Clarithromycin	228 $\text{ng L}^{-1}$	O <sub>3</sub> : 3 $\text{mg L}^{-1}$ ;		
Erythromycin	150 $\text{ng L}^{-1}$	Samples were collected from a municipal sewage treatment plant; Tokyo.		
Clarithromycin	363–469 $\text{ng L}^{-1}$	Lab-scale UV, UV/H <sub>2</sub> O <sub>2</sub> , solar irradiation, Fenton, solar photo-Fenton; UV-C irradiation ( $\lambda_{\text{max}} = 254 \text{ nm}$ ); H <sub>2</sub> O <sub>2</sub> : 25 $\text{mg L}^{-1}$ ; Fenton: 25 $\text{mg H}_2\text{O}_2 \text{ L}^{-1}$ and 5 $\text{mg Fe}^{2+} \text{ L}^{-1}$ ; Photo-Fenton: 25 $\text{mg H}_2\text{O}_2 \text{ L}^{-1}$ and 5 $\text{mg Fe}^{2+} \text{ L}^{-1}$ ; Municipal wastewater from Vidy WWTP; Lausanne, Switzerland.	From the five different treatments applied, only the UV-based processes were able to remove 80% of clarithromycin. After 30 min of treatment, the oxidation was significant, verified by COD and TOC removals. For the cases of solar light, Fenton and photo-Fenton processes, the degradation rates were lower.	(Giannakis et al., 2015)
Clarithromycin	469 $\text{ng L}^{-1}$	Solar Fenton treatment (natural solar driven oxidation) in a pilot-scale CPC plant; H <sub>2</sub> O <sub>2</sub> : 50 $\text{mg L}^{-1}$ ; Fe <sup>2+</sup> : 5 $\text{mg L}^{-1}$ ; Municipal wastewater from the El Ejido municipal WWTP; Almería, Spain.	Clarithromycin was completely degraded, applying photolytic and solar Fenton experiments, with a removal of 77% at the end of the treatment time (250 min), when present at low concentrations and at low Fenton reagent dosages.	(Karaolia et al., 2014)
Erythromycin	170 $\text{ng L}^{-1}$	Pilot-scale ozonation plant; O <sub>3</sub> : 86–153 $\text{g Nm}^{-3}$ ; O <sub>3</sub> consumption: 0.6 and 0.9 $\text{g O}_3 \text{ g DOC}_0^{-1}$ ; Wastewater; Austria.	The application of 0.6 $\text{g O}_3 \text{ g DOC}^{-1}$ increased the removal of erythromycin (to values < LOQ).	(Schaar et al., 2010)



Table 5 (continued)

Compound	Initial concentration	Treatment and sampling conditions	Concluding remarks	Reference
Azithromycin	139.9 ± 6.2 ng L <sup>-1</sup>	Lab-scale photolytic ozonation, ozonation and photocatalysis; O <sub>3</sub> : 50 g Nm <sup>-3</sup> ; O <sub>3</sub> flow rate: 150 Ncm <sup>3</sup> min <sup>-1</sup> ;	It was verified a complete removal by photocatalytic ozonation for all macrolide antibiotics, while by ozonation only erythromycin was totally eliminated. Photocatalysis was the less efficient process in study.	(Moreira et al., 2015)
Clarithromycin	116.4 ± 2.7 ng L <sup>-1</sup>	MP mercury vapor lamp (UV/Vis λ > 300 nm); TiO <sub>2</sub> photocatalyst: 0.5 g L <sup>-1</sup> load;		
Erythromycin	27.0 ± 2.5 ng L <sup>-1</sup>	Urban wastewater from the secondary treatment of a WWTP; North of Portugal.		
Erythromycin	0.7–0.9 µg L <sup>-1</sup> (spiked wastewater)	Lab-scale ozonation; O <sub>3</sub> : 5.5–8.5 mg L <sup>-1</sup> ; O <sub>3</sub> flow rate: 0.39 Ndm <sup>3</sup> min <sup>-1</sup> ; Urban wastewater samples (spiked) from the secondary clarifier of two treatment plants from West-Alcalá and Alcázar de San Juan; Spain.	High removal of erythromycin (>90%) was observed for both wastewaters studied.	(Rodríguez et al., 2012)

BAC, Biological activated carbon; CAS, conventional activated sludge; CAST, cyclic activated sludge technology; CPC, compound parabolic collector; DOC, dissolved organic carbon; GAC, granular activated carbon; LOQ, limit of quantification; MBR, membrane biological reactor; MF, Microfiltration; n.a., not available; n.d., not detected; OD, oxidation ditch; RFDs, rotary fiber disc filters; RO, Reverse osmosis; SBR, sequential batch reactor; UF, ultrafiltration; WWTP, wastewater treatment plant.

(Derrouiche et al., 2013; Lange et al., 2006).

## 2.6. Methiocarb

Regarding pesticides, their use plays an important role in harvest quality and food protection, providing enormous benefits to increase production, as pests and diseases are usually responsible to damage up to one-third of crops (Herrero-Hernández et al., 2013). As consequence of massive global consumption, pesticides and their degradation products spread through the environment and can contaminate water resources. Surface and groundwater located in intensive agricultural areas are more susceptible to pesticide contamination, which is a major concern if the water is used for human consumption (Masía et al., 2013). The impact of these contaminants in the environment and to the wildlife is demonstrated by several injurious effects, including the enhancement of the incidence of cancer, birth defects, genetic mutations, or other problems such as damage in the liver or in the central nervous system (Dabrowski et al., 2014). The occurrence of pesticides in aquatic compartments and their possible effects to public health are a topic of considerable environmental interest.

Methiocarb (also known as mercaptodimethur, mesurol, 3,5-dimethyl-4-(methylthio)phenyl methylcarbamate) is one of the most commonly used carbamate pesticides worldwide. This pesticide has been applied since 1960s for a variety of invertebrate pests and also as a bird repellent on fruit crops (Altinok et al., 2006; Qiang et al., 2014). The detected concentrations of methiocarb in wastewater and groundwater are generally low (Table 1); however, it poses a serious health threat to aquatic life and humans considering its high toxicity (Qiang et al., 2014). A negative removal of methiocarb was reported in a Spanish sewage treatment plant (Table 6), probably due to the limitations on the sampling procedure, where both HRT (24–72 h) and SRT (7.5–25 days) were not taken into consideration, consequently higher concentrations were found in the effluents than in influents (Campo et al., 2013). Recent studies related to the removal of this compound by advanced treatment options were not found in the literature.

Table 6

Studies dealing with removal of methiocarb. Pollutants included in these studies that are out of the scope of 495/15/EU Decision are not discussed.

Initial methiocarb concentration	Treatment and sampling conditions	Concluding remarks	Reference
3.77–5.74 ng L <sup>-1</sup> (2010); 1.26 –105.31 ng L <sup>-1</sup> (2011).	Sewage treatment plants monitored in the four River Basins of Ebro River; Spain.	The removal of methiocarb was negative. The higher concentrations in effluents than in influents were attributed to the sampling limitations: influent and effluent samples were collected at the same day, without considering the HRT (24–72 h) and SRT (7.5–25 days).	(Campo et al., 2013)

HRT, hydraulic retention time; SRT, sludge retention time.

## 2.7. Neonicotinoids

In the last decade, the neonicotinoid group of insecticides has been one of the most broadly adopted conventional management tools to deal with insect pests of annual and perennial cropping systems. Benefits of the neonicotinoids include flexibility of application, a wide range of active ingredients and broad spectrum activity (Huseth and Groves, 2014; Morrissey et al., 2015). This group includes imidacloprid, thiacloprid, thiamethoxam, clothianidin and acetamiprid, which are extremely toxic to all aquatic arthropods, except water fleas (Sánchez-Bayo and Hyne, 2014). However, as a result of structural differences in the polypeptide subunit containing the neonicotinoid-binding region of the vertebrates' nicotinic acetylcholine receptors, neonicotinoids pose a relatively low risk to fish and mammals (Sánchez-Bayo and Hyne, 2014). Neonicotinoids are systemic insecticides and are applied as seed dressings by sprays, owing to their solubility in water. Therefore, the main sources of this class of herbicides in the environment are the runoff from agriculture areas and leaching into groundwater, with the consequent subsurface discharge into wetlands and other surface water (Morrissey et al., 2015). As a result of their high water solubility and persistence in soil, neonicotinoids cause a threat for water contamination, mainly after storm events that produce runoff pulses (Sánchez-Bayo and Hyne, 2014). Other sources of these compounds are soluble or insoluble fractions transported via snowmelt, decay of treated plants in water bodies, and deposition of treated seeds or soil into water bodies (Morrissey et al., 2015). Recent studies from Spain, Portugal, USA, Australia and other countries (Table 1) have confirmed the occurrence of this group of pesticides in the aquatic ecosystems (Campo et al., 2013; Chau et al., 2015; da Rocha et al., 2015; Gonzalez-Rey et al., 2015; Masía et al., 2013; Papadakis et al., 2015; Sánchez-Bayo and Hyne, 2014).

There is a lack of literature concerning the removal of this class of pesticides in the environment (Fig. 2). The majority of the reports refers to the performance of AOPs, dealing with their degradation at laboratory or pilot-scale conditions and mostly using spiked water or spiked simulated water (Pena et al., 2011). Photolysis,

**Table 7**  
Studies dealing with removal of neonicotinoids (imidacloprid, thiacloprid, clothianidin and acetamiprid). Pollutants included in these studies that are out of the scope of 495/15/EU Decision are not discussed.

Compound	Initial concentration	Treatment and sampling conditions	Concluding remarks	Reference
Acetamiprid	<0.05 $\mu\text{g L}^{-1}$	Pilot-scale photocatalysis: Solardetox Acadus-2006 CPCs 3.0 m <sup>2</sup> irradiated surface; 24 L of irradiated volume; TiO <sub>2</sub> load: 0.2 g L <sup>-1</sup> ; Water taken from the outlet of a WWTP from the South East of Spain.	High removal was obtained for all the emerging contaminants after 3 h of treatment (below LOQ).	(Bernabeu et al., 2011)
Thiacloprid	0.05–0.38 mM (spiked spring water)	Photocatalysis: Lab-scale reactor operated in a circular 'closed-loop' mode; Six 18 W UV lamps ( $\lambda_{\text{max}} = 366 \text{ nm}$ ); ZnO load: 0.5–3.0 g L <sup>-1</sup> ; Thermal water collected from the spring of Kistelek, Hungary.	Very low degradation was verified by direct photolysis. A removal of 86.6% was observed for thiacloprid, with a ZnO load of 2 g L <sup>-1</sup> and pH 6.8. The efficiency of the thiacloprid removal in filtered and un-filtered thermal water was about two times lower than from the distilled water, indicating that the removal was due to the dissolved substances.	(Abramović et al., 2013)
Thiacloprid	0.32 mM (spiked river water)	Lab-scale UV and UV/H <sub>2</sub> O <sub>2</sub> ; 125 W HP Hg lamp (emission bands $\lambda = 304, 314, 335, 366 \text{ nm}$ ) ( $\lambda_{\text{max}} = 366 \text{ nm}$ ); H <sub>2</sub> O <sub>2</sub> concentration: 0–162 mM; pH: 2.8–9; Spiked water from Begej river at Itebej, Serbia.	The removal rate of thiacloprid was influenced by the presence of HCO <sub>3</sub> <sup>-</sup> . Very low degradation rates were observed for single UV and H <sub>2</sub> O <sub>2</sub> . High removal of thiacloprid was achieved after 120 min of UV/H <sub>2</sub> O <sub>2</sub> . The removal rate for natural water was lower compared with distilled water (45 mM H <sub>2</sub> O <sub>2</sub> ) at pH 8.2. However, the removal in natural water adjusted at pH 2.8 was higher than in distilled water due to the naturally occurring photosensitizers, i.e. dissolved organic matter.	(Abramović et al., 2010)
Clothianidin	n.a.	Sulfate radical based homogeneous photo-Fenton involving peroxymonosulfate as an oxidant, ferrous iron (Fe(II)) as a catalyst and simulated solar irradiation as a light source; Biologically treated domestic wastewater effluents.	PMS/Fe(II)/UV–Vis advanced oxidation system using simulated solar irradiation has demonstrated better kinetic performances over TiO <sub>2</sub> /UV–Vis system for clothianidin.	(Ahmed et al., 2014)
Acetamiprid	100 $\mu\text{g L}^{-1}$ (spiked wastewater)	Pilot-scale photocatalysis: CPC; Wastewater of Almería, Spain.	The removal of acetamiprid was poor in the wastewater matrix.	(Jiménez et al., 2015)
Imidacloprid	60 mg L <sup>-1</sup>	Pilot-scale CPC plant (60 L); Fe(III)-EDDS as complexing agent; Spiked tap water from the groundwater well of Plataforma Solar de Almería, Spain.	Photolysis of the complexing agent generated radical species able to act independently of carbonate scavengers that are present in natural water.	(Papoutsakis et al., 2015)

CPC, compound parabolic collector; EDDS, ethylenediamine-N,N'-dissuccinic acid; HP, high pressure; LOQ, limit of quantification; n.a., not available; WWTP, wastewater treatment plant.

photocatalysis and photo-Fenton were applied to study the removal of these compounds from water, photocatalysis being the most applied (Table 7). Studies dealing with real water and other treatment processes should be performed to bring a more realistic overview of the elimination of this group of pesticides. Some other studies with these substances were already published, but not using real matrices and, therefore, they are out of the scope of the present review; for instance the degradation of imidacloprid (Peng et al., 2015; Tang et al., 2011; Wang et al., 2014; Zabar et al., 2012; Zarora et al., 2010), thiamethoxam (Mir et al., 2013; Šojić et al., 2012; Zabar et al., 2012), clothianidin (Zabar et al., 2012) and acetamiprid (Mitsika et al., 2013) were studied with photo-assisted and ozonation processes.

## 2.8. Oxadiazon

The oxadiazole herbicide oxadiazon [5-tert-butyl-3-(2,4-dichloro-5-propan-2-yloxyphenyl)-1,3,4-oxadiazol-2-one] has been habitually used to combat weeds in various agricultural crops such as rice, cotton, soybean, potato, peanut and onion. Oxadiazon is an organic contaminant causing a great environmental concern due to its relatively long half-life (Rahman, 2010). Previous studies on the leaching of oxadiazon in soils indicated that, the strong adsorption of the herbicide to soils reduces the displacement towards the sub-surface layers (Pinilla et al., 2008). However, oxadiazon was found in surface water in Canada (Table 1) at ng L<sup>-1</sup> levels (Furtula et al., 2006). In contrast, the removal of oxadiazon in aquatic matrices is still unknown.

## 2.9. Triallate

Triallate (S-2,3,3-trichloroallyl di-isopropyl thiocarbamate) is a carbamothioate herbicide widely used to control annual and perennial grasses in wheat, barley, legumes and a number of other crops (D'Orazio et al., 1999; Volpe et al., 2004). This pesticide is often used in mixture with other chemicals (chloridazon, isoproturon, metoxuron) and its use, in the last decades, has exceeded 500 tons per year in some European countries (Volpe et al., 2004). Triallate has a high hydrophobic partitioning (Hornsby et al., 1996), therefore it adsorbs to loam and clay soils and is not readily dissolved in water (Bernal et al., 1996). This information indicates that this herbicide is not likely to move through the soil, even though it has a long soil half-life (82 days). Nevertheless, if there is significant moisture and/or low levels of organic matter in the soil, triallate may become desorbed from soil particles (D'Orazio et al., 1999). Leaching and consequent groundwater contamination would be possible in such situations, but Environmental Protection Agency (EPA) suggests that triallate leaching does not cause a threat to the environment, since it is usually used where the water table is relatively low (Kamrin, 1997). A lack of knowledge exists about its occurrence and removal in the aquatic environment due to its chemical nature.

## 3. Conclusions

Despite the considerable amount of studies reported on the occurrence and removal of E1, E2, EE2, diclofenac and macrolide antibiotics (azithromycin, clarithromycin and erythromycin), a lack

of knowledge exists concerning the pesticides (methiocarb, neonicotinoids, oxadiazon and triallate), the UV filter (EHMC) and the antioxidant (2,6-di-tert-butyl-4-methylphenol), which are included in the watch list of Decision 2015/495/EU for European Union monitoring. Thus, more investigation is needed regarding the occurrence and removal of neonicotinoids, EHMC and 2,6-di-tert-butyl-4-methylphenol and the performance of different treatments to remove the substances included in the watch list under realistic conditions. These compounds are usually present at residual concentrations, as mixtures in the different environmental compartments (e.g., municipal wastewater, surface water, groundwater, solid matrices) and comprehensive works considering it are scarce. As shown by different studies, the efficiency of the treatment processes can decrease considerably when realistic water matrices are used instead of simulated ones. For example, the presence of carbonates and bicarbonates can decrease the efficiency of AOPs, principally due to competition by HO<sup>•</sup>. Since multiple factors can affect the efficiency of the treatments, experiments should be performed as close as possible to the real conditions. Additionally, the formation of intermediates should be attempted in this type of studies, considering that the produced by-products might be more toxic and/or persistent than the parent compounds. Toxicological studies are needed to determine the deleterious effects on the ecosystems and human health of parent compounds and by-products formed in real matrices. Considering the scale up of the treatment option, these processes can be expensive both in the implementation and maintenance, therefore it is of major importance to perform cost effectiveness analysis for each of them under a common base of comparison.

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