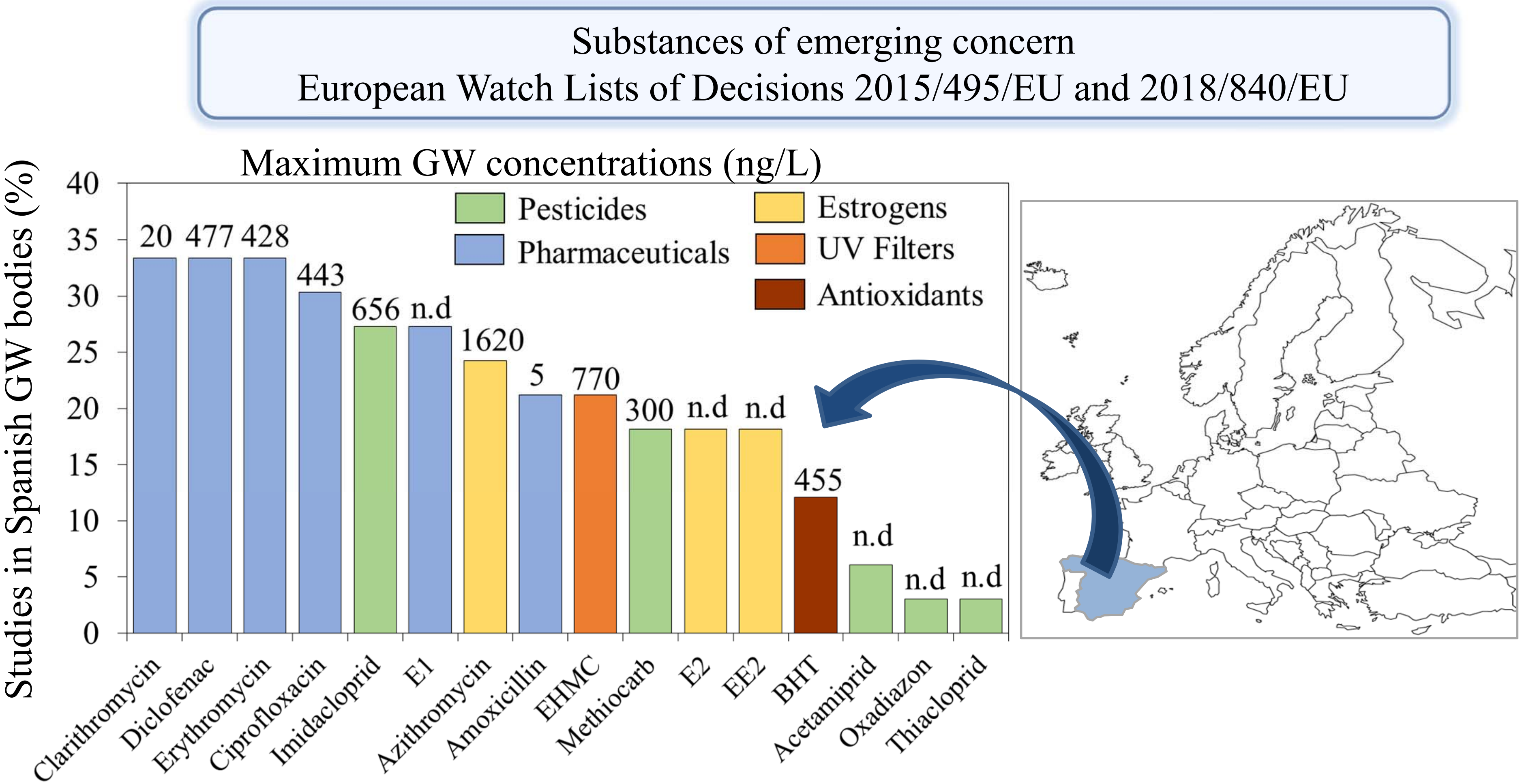
*Graphical Abstract



***Highlights (for review : 3 to 5 bullet points (maximum 85 characters including spaces per bullet point)**

HIGHLIGHTS

- Review on the Watch List substances for EU-monitoring in the groundwater of Spain
- Groundwater is considerably less contaminated than surface and waste waters
- Some substances are eventually detected at high concentrations (>100 ng/L)
- Insufficient data exists to assess the fate of these substances in groundwater
- Groundwater chemical status needed for risk assessment and future regulations

Occurrence, fate and environmental risk assessment of the organic microcontaminants included in the Watch Lists set by EU Decisions 2015/495 and 2018/840 in the groundwater of Spain

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Abstract

This paper aims to review the existing occurrence data in Spanish groundwater (GW) for the emerging organic contaminants (EOCs) defined in the surface water Watch Lists of Decisions 2015/495/EU and 2018/840/EU since these contaminants are likely to reach GW bodies because surface waters show close interaction with GW. These two lists include 20 substances: 9 pesticides (5 neonicotinoids, 2 carbamates, 1 oxadiazole and 1 semicarbazone), 6 pharmaceuticals (diclofenac and 5 antibiotics), 3 estrogens, 1 UV filter (2-ethylhexyl-4-methoxycinnamate, EHMC) and 1 antioxidant (2,6-di-tert-butyl-4-methylphenol, BHT). Most of these substances are usually detected at low ng/L concentration range or not detected in the GW bodies of Spain. However, eventually they are reported at concentrations greater than 100 ng/L (e.g., imidacloprid, methiocarb, diclofenac, macrolide antibiotics, ciprofloxacin, EHMC and BHT). Consequently, it is required to set up drinking water standards, and/or GW threshold quality values because GW is a valuable water resource worldwide. Overall, GW is less contaminated than other water bodies, such as rivers, suggesting that aquifers possess a natural attenuation capacity and/or are less vulnerable than rivers to contamination. Nevertheless, the natural hydrogeochemical processes that control the fate and transformation of these substances during infiltration and in the aquifer have been barely investigated so far.

The concentrations of the target EOCs are used to calculate hazard quotients (HQs) in the Spanish GW bodies as an estimation of their ecotoxicity and in order to compare somehow their chemical quality with respect to those of surface water. Due to the limited ecotoxicity data for most EOCs, HQs can only be calculated for few substances. The results pointed out the risk posed by the anti-inflammatory diclofenac towards

Ceriodaphnia dubia (HQ = 21) and the medium risk associated to the antibiotic erythromycin for *Brachionus calyciflorus* (HQ = 0.46).

Keywords: Emerging organic contaminants, groundwater, monitoring, Spain, European Watch Lists.

1. Introduction

Groundwater (GW) is the largest freshwater resource in the world, accounting for 97% of freshwater available on earth, whereas the remaining 3% is mainly surface water (European Commission, EC, 2006). Hence, it is the main source for water supply in 75% of the EU countries (Tanwar et al., 2014). GW resources are being overexploited and can be used as an alternative resource in many countries for different purposes (e.g., Fram and Belitz, 2011; SPW-DGO3 2016; Jurado et al., 2017). However, anthropogenic activities mainly industrial and/or agricultural, threat GW chemical quality because many contaminants might enter the aquifers.

Currently, there is a growing concern for the emerging organic contaminants (EOCs) because, even at low concentrations (from ng/L to low µg/L), their individual and synergetic effects on ecosystems and human health are largely unknown (Arnold et al., 2014). In the last years, many reviews have compiled data on the occurrence and fate of EOCs in GW accounting for different regions (Carenghini et al., 2015; Lapworth et al., 2012; Postigo and Barceló, 2015; Sui et al., 2015) and specific countries such as Spain (Jurado et al., 2012), Italy (Meffe and de Bustamante, 2014) and UK (Stuart et al., 2012). These reviews demonstrate the widespread contamination of GW by a vast and increasing number of EOCs and, thus, opened the debate about the urgent need to define quality standards for GW.

According to the European Directive 2014/80/EC (EC, 2014), a watch list for GW pollutants such as emerging pollutants should be established on substances posing a risk or potential risk to GW bodies. Recently, a methodology for developing a voluntary GW watch list has been established by the EU GW working group and discussed for per- and polyfluoroalkyl substances and pharmaceuticals (Lapworth et al., 2018) but so far a GW watch list has not been stablished in the European GW Directive. In contrast to GW, surface water watch lists (EC, 2015 and 2018) have already been developed as established by the 2013 amendment (EC, 2013) to the EU Environmental Quality Standards Directive (2008/105/EC) (EC, 2008). The first Watch List of substances for Union-wide monitoring in the field of water policy was defined in the Decision 2015/495/EU (EC, 2015) and, recently, a second Watch List has been proposed by the European Union in the Decision 2018/840/EU (EC, 2018). The substances included in these watch lists are likely to reach GW bodies because surface waters such as rivers show close interaction with GW bodies (e.g., Serra-Roig et al., 2016) and the potential contamination of GW dependent ecosystems such as wetlands, springs and lakes can occur (Eamus et al., 2016; Kløve et al., 2011). Moreover, EOCs can reach GW when river water is used for managed aquifer recharge (Petrie et al., 2015).

Recently, Barbosa et al. (2016) summarized some relevant data on the occurrence and removal of the substances included in the Decision 2015/495/EU in different aqueous matrices (i.e., wastewater, surface water and GW). Here, the work of Barbosa et al. (2016) has been extended to other studies that reported occurrence data of these microcontaminants in the Spanish GW. The present review aims to compile the occurrence data of the 20 EOCs listed in the first and second Watch Lists for European Union monitoring defined in the Decisions 2015/495/EU (20 March 2015) and 2018/840/EU (5 June 2018) in the GW bodies of Spain. The first Watch List includes: 8 pesticides (oxadiazon, methiocarb, triallate and 5 neonicotinoids including imidacloprid, thiacloprid, thiamethoxam, clothianidin and acetamiprid), 4 pharmaceuticals (the non-steroid anti-inflammatory diclofenac and 3 macrolide antibiotics namely azithromycin, clarithromycin and erythromycin), 3 estrogens (the natural hormones estrone (E1) and 17-beta-estradiol (E2) and the synthetic hormone 17-alpha-ethinylestradiol (EE2)), 1 UV filter (2-ethylhexyl-4-methoxycinnamate, EHMC) and 1 antioxidant commonly used as food additive (2,6-di-tert-butyl-4-methylphenol, BHT). Further, in the second Watch List, five substances were excluded from the first Watch List (diclofenac, oxadiazon, triallate, EHMC and BHT) and 3 new substances were included: 2 antibiotics, amoxicillin and ciprofloxacin and the pesticide metaflumizone. The occurrence data of these substances in the GW of Spain were compared with that reported in other studies worldwide. With the development and improvement of GW pollution research, GW risk research is becoming a necessary tool for future local and regional integrated land use planning and GW resource protection planning. Therefore, and as the final part of this review, we estimate the risk posed by the substances detected in the GW of Spain.

2. Occurrence and spatial distribution of EOCs in the GW of Spain.

The occurrence and the spatial distribution of the 20 EOCs included in the Decisions 2015/495/EU and 2018/840/EU (EC, 2015 and 2018) in the GW of Spain are summarized in this section (Fig. 1). A total of 33 studies are included in this review. The number of studies (%) and the reported maximum concentrations are shown in Figures 1 and 2.

2.1 Pesticides

Pesticides are substances intended for preventing, destroying, repelling or mitigating pests (e.g., pathogens, weeds, mollusks, birds, etc). Excessive use of pesticides has prevented harm by pests and improved the product of crops but their widespread use has resulted in the contamination of water resources including surface water and GW, mainly in agricultural areas (Zhao and Pei, 2012).

From the 9 pesticides included in the Watch Lists, only imidacloprid and methiocarb were detected in the GW bodies of Spain. Other three pesticides, oxadiazon and the neonicotinoids thiacloprid and acetamiprid were also investigated but not detected in any sample (Fig. 2 and Table S1 of the Supplementary Material). The most investigated pesticides were imidacloprid (n=9) followed by methiocarb (n=6), acetamiprid (n=2) and thiacloprid and oxadiazon (n=1).

The occurrence of imidacloprid was investigated by Herrero-Hernández et al. (2013, 2017) in surface and GW of the vineyard region of La Rioja (north-central of Spain). To this end, 90 sampling points (78 from GW and 12 from surface water) were monitored over four campaigns (September 2010, March 2011, June 2011, and September 2011). Imidacloprid was detected in all the sampling campaigns at average detection frequency of 9% (ranged from 7% to 18%). As expected, the maximum concentration of 656 ng/L was observed in June 2011 after the application period of insecticides (Table S1 of the Supplementary Material). This value is far above the European GW quality standard set for individual pesticides (100 ng/L). High concentrations of imidacloprid were also found in GW in the surroundings of a solid-waste treatment plant of Castellón (eastern of Spain) that was monitored between 2011 and 2013, along five periods: January 2011, April 2012, December 2012, May 2013 and December 2013. A total of 10 surface water and 23 GW samples were collected. Imidacloprid was generally detected at concentrations below 20 ng/L, but maximum GW concentration reached 120 ng/L. Similarly, Hernández et al. (2008) investigated the occurrence of several pesticides, including imidacloprid and methiocarb, in GW of the Comunidad Valenciana region (eastern of Spain) in two years (2000 and 2003). This area is one of the most important citrus cultivation sites of southern Europe. Despite that, pesticide residues were not frequently detected. Imidacloprid and methiocarb were only found in the first sampling campaign at low detection frequencies (9% and 1%, respectively), and low maximum concentrations (40 and below 25 ng/L, respectively). Other studies conducted in the

GW bodies of the Comunidad Valenciana (Diaz et al., 2013; Hernández et al., 2015; Marín et al., 2009; Valdes-Abellan et al., 2013) and Almería (southeast of Spain) (Chiron et al., 1993; Chiron et al., 1995; Martínez-Galera et al., 1997) assessed the occurrence of some neonicotinoids and methiocarb, but they were barely detected (Table S1 of the Supplementary Material). Only methiocarb was measured in well waters of Almería at concentrations up to 300 ng/L (Chiron et al., 1995). Oxadiazon was investigated but not detected in a GW sample from an agricultural area of Granada (Navalón et al., 2001).

2.2 Pharmaceuticals

The pharmaceuticals included in the Decision 2015/495/EU belong to two different groups: (1) diclofenac is a non-steroidal anti-inflammatory drug (NSAID) used to reduce inflammation and as an analgesic reducing pain in mild to moderate conditions and (2) macrolide antibiotics are employed to prevent and combat respiratory diseases caused by gram-positive pathogens in human and veterinary medicine. Afterwards, two new antibiotics were listed in the Decision 2018/840/EU: (3) amoxicillin is a β-lactam antibiotic and (4) ciprofloxacin belongs to fluoroquinolone antibiotics. Both are used in the treatment of a number of infections and their investigation in GW has recently become a matter of great concern because their widespread use has caused the occurrence of antibiotic resistant bacteria present in the aquifers (Szekeres et al., 2018).

2.2.1 Diclofenac

Diclofenac was one the most investigated EOCs included in the Decision 2015/495/EU in the GW of Spain (n=11) (Fig. 2). Among these studies, six reported the occurrence of diclofenac in GW bodies of Catalonia (northeast of Spain). López-Serna et al. (2013) investigated the occurrence of diclofenac in three different zones of Barcelona: two urbanized areas where GW had oxic conditions and the main source of contamination were losses from sewage system and the shallow aquifer of the Besòs River Delta, where GW has a reducing character and is recharged by the Besòs River. This river receives large amounts of effluents from WWTPs. The highest detection frequency (100%) and high average concentrations (225.2 ng/L) were found in the shallow aquifer of the Besòs Delta, whereas the GW from urbanized areas presented lower detection frequencies (50%) and average concentrations below 1 ng/L. In fact, the average concentration of diclofenac in the aquifer was higher than that found in the Besòs River (225.2 vs. 113 ng/L). The occurrence of diclofenac was also investigated in the low confined aquifer of the Llobregat Delta (northeast of Spain) where tertiary treated wastewater (TWW) was injected through wells to build up a hydraulic barrier against seawater intrusion from 2007 to 2010 (Cabeza et al., 2012; Candela et al., 2016; Teijon et al., 2010). Average GW concentrations of diclofenac were reduced over time from 256 ng/L (March-November 2008; Teijon et al., 2010) to 49 ng/L (March 2007–May 2010 period; Candela et al., 2016) (Table S1 of the Supplementary Material). Candela et al. (2016) reported higher average concentrations in the injected TWW than those determined in the aquifer (182 vs. 49 ng/L). The authors pointed out that the decreased concentrations observed would be associated to the dilution effect in the aquifer rather than to degradation processes. Radjenovic et al. (2008) investigated the removal of diclofenac in a drinking water treatment plant (DWTP) located in the northeast of Spain that is fed from GW wells directly influenced by infiltration from the Besòs River. Diclofenac was measured at average concentrations of 121.5 ng/L, but presented excellent removal rates (R>95%). Finally, Calderón-Preciado et al. (2013) did not detect residues of diclofenac in GW used to irrigate crops. There are other studies focused on GW bodies of the Comunidad Valenciana, but diclofenac was not detected (Hernández et al., 2015; Vazquez-Roig et al., 2012) or the concentrations were not reported (Diaz et al., 2013). Rodríguez-Navas et al. (2013) determined the presence of diclofenac in the aquatic environment of Mallorca Island. The authors identified the reuse of reclaimed wastewater for irrigation as the main contamination source of pharmaceuticals to the aquifer. Leaching from landfills was also pointed out as a minor contributor. Despite these water sources contained diclofenac in concentrations from 22 (landfill) to 298 ng/L (wastewater), it was not detected in GW. Recently, Corada-Fernández et al. (2017) investigated the occurrence of a wide array of EOCs in surface and GW of the Guadalete River basin (Cádiz, southwest of Spain). Only 24 out of 180 chemicals were detected in GW at concentrations below100 ng/L but diclofenac was not detected.

2.2.2 Macrolide antibiotics

Macrolide antibiotics were widely studied but barely detected or even not detected in the GW bodies of Spain (e.g., Corada-Fernández et al., 2017; Hernández et al., 2015; Pérez et al., 2017; Rodríguez-Navas et al., 2013; Valdes-Abellan et al., 2013) (Table S1 of the Supplementary Material). This section thus focuses only on the studies that positively reported the presence of these substances in GW (Boy-Roure et al., 2018; Cabeza et al., 2012; Candela et al., 2016, Estévez et al., 2012; López-Serna et al., 2013) (Table S1 of the Supplementary Material). The most investigated substances were clarithromycin and erythromycin (n=11) followed by azithromycin (n=8). The occurrence of macrolide antibiotics was investigated in different urban aquifers of Barcelona. Azithromycin, clarithromycin and erythromycin were ubiquitous (i.e., frequency of detection 100%) in GW samples of the shallow aquifer of the Besòs River Delta, at average concentration of 15.7, 10.7 and 28.7 ng/L, respectively. These concentrations were lower than those found in the polluted River Besòs, which is the main recharge source of this aquifer, being 133 ng/L for azithromycin, 101 ng/L for clarithromycin and 54.9 ng/L for erythromycin. This observation might indicate the natural attenuation capacity of the shallow aquifer of the Besòs River Delta. Macrolide antibiotics were also present in the aquifers below urbanized areas but at lower average concentrations for clarithromycin (2.6 ng/L) and erythromycin (not detected in any sample). In contrast, azithromycin was found at high average concentrations (190.2 ng/L) and maximum value of up to 1620 ng/L (Table S1 of the Supplementary Material). A somewhat lower concentration but still high was found for erythromycin in the low confined aquifer of the Llobregat River Delta (northeast of Spain), being 427 ng/L (average concentration was 63 ng/L for the period March 2007–May 2010, Candela et al., 2016). Azithromycin and clarithromycin were not detected in this aquifer (Cabeza et al., 2012; Candela et al., 2016). The occurrence of azithromycin and clarithromycin was also investigated in an agricultural region of the Baix Fluvià alluvial aquifer (northeast of Spain), where the main source of pharmaceuticals was manure application. The average concentrations of azithromycin and clarithromycin measured were low, being 0.94 and 0.45 ng/L, respectively. Finally, Estévez et al. (2012) monitored the presence of EOCs in a volcanic aquifer of Gran Canarias Island where a Golf Course has been sprinkled with reclaimed water since 1976. Only erythromycin was detected at low concentrations (maximum concentration of 43 ng/L).

2.2.3 Amoxicillin

Amoxicillin was frequently studied (n=7) but poorly detected in the GW bodies of Spain. This compound was only measured at low concentration (5 ng/L) in the GW of Mallorca Island (Rodríguez-Navas et al., 2013). The rest of investigated GW bodies located in Catalonia (Boy-Roure et al., 2018; Cabeza et al., 2012; Candela et al., 2016; Teijon et al., 2010; Tong et al., 2014a) and Cádiz (Corada-Fernández et al., 2017) were free of this compound (Table S1 of the Supplementary Material).

2.2.4 Ciprofloxacin

The fluoroquinolone antibiotic ciprofloxacin was one of the most reported substances in the GW bodies of Spain (n=10). The maximum concentration of ciprofloxacin was 443 ng/L (average concentration 67.5 ng/L) in the urban aquifers of Barcelona, where the main source of pollution was found to be the leaks from the sewerage system (López-Serna et al., 2013). In the lower confined aquifer of the Llobregat River Delta, ciprofloxacin concentrations were up to 406 ng/L (average concentration 126 ng/L), where TWW-recharge took place (Cabeza et al., 2012; Candela et al., 2016; Teijon et al., 2010). High concentrations of ciprofloxacin were also found in the aquifers of an agricultural area of the Baix Fluvià (northeast of Spain), reaching values up to 298.3 ng/L (average concentration 34 ng/L) (Table S1 of the Supplementary Material). Somewhat lower concentrations were found in the shallow aquifer of the Besòs River delta, ranging from 5.4 to 130 ng/L (average concentration 18.6 ng/L) (López-Serna et al., 2013). The frequency of detection of ciprofloxacin was moderate in the aquifers of the Baix Fluvià and high in the urban aquifers of Barcelona, being 52% and 94% respectively. In the remaining studies where this compound was detected, its frequency of detection was not specified.

Many other studies conducted in the GW bodies in the Comunidad Valenciana region (Diaz et al., 2013; Vazquez-Roig, 2012), Almería (Parilla-Vázquez et al., 2012), Granada (Lombardo-Aguí et al., 2014), Málaga (south of Spain) (Lombardo-Aguí et al., 2014), and Cádiz (Corada-Fernández et al., 2017) investigated the occurrence of ciprofloxacin but it was not detected (Table S1 of the Supplementary Material).

2.3 Steroids

Steroids are either natural (E1 and E2) or synthetic (EE2) hormones, which are biologically active compounds classified as endocrine-disrupting substances (EDCs, Chang et al., 2009). These chemicals have negative effects on ecosystems (e.g., E2 and EE2 cause sex reversal of amphibians and fish) and bioaccumulate in aquatic organisms, reaching human beings through the food chain (Santos et al., 2010).

The most studied substances were E1 (n=9) followed by EE2 and E2 (n=6). Some studies related to these substances were performed in the Llobregat River aquifer where GW mixed with Llobregat River water, is frequently used to produce drinking water in the municipality of Sant Joan Despí (Rodriguez-Mozaz et al., 2004a and 2004b; Farré et al., 2007; Huerta-Fontela et al., 2011). Three recent studies investigated the occurrence of steroids in aquifers of southern Spain (Corada-Fernández et al., 2017; Pintado-Herrera et al., 2014; Valdes-Abellan et al., 2013) and one in the Canary Islands (Estévez et al., 2012). Despite these substances have been widely studied and the low limits of detection (LOD) of the analytical methods (e.g., LOD<1 ng/L, Rodriguez-Mozaz et al., 2004b), the investigated GW bodies of Spain were found to be free of estrogens (Table S1 of the Supplementary Material).

2.4 UV filters

UV filters, also known as sunscreen agents, constitute a heterogeneous group of chemicals used to protect humans and goods from the deleterious effects of UV radiation (Serra-Roig et al., 2016). They are used in a broad range of personal care products (e.g., body lotions, cosmetics, sunscreen and shampoos) and added to polymeric materials to protect them from sunlight-initiated degradation (Gago-Ferrero et al., 2013).

The occurrence of EHMC in the GW bodies of Spain was reported in seven studies (n=7) (Cabeza et al., 2012; Corada-Fernández et al., 2017, Díaz-Cruz et al., 2012; Hernández et al., 2015; Pintado-Herrera et al., 2014; Pitarch et al., 2016; Teijon et al., 2010). This compound was found in the deep confined aquifer of Llobregat River at average concentration of 38 ng/L (Cabeza et al., 2012). It is important to mention that the average concentrations in GW were higher than those of TWW from the Depurbaix facility, which is injected to the deep aquifer of Llobregat in an attempt to control seawater intrusion (38 vs. 3 ng/L and 35.3 vs. 9.5 ng/L, respectively). Díaz-Cruz et al. (2012) reported the highest concentration of EHMC, 770 ng/L, in a well water sample from the Barcelona city aquifer. Recently, Corada-Fernández et al. (2017) investigated the occurrence of EHMC in two GW bodies (Guadalete and Jerez de la Frontera) of the Guadalete river basin (Cádiz), where irrigation with reclaimed water has become a common practice especially during the summer season. Near an urban area in December 2010, high concentrations of EHMC of up to 381 ng/L were found in wells heavily influenced by treated (e.g., wastewater) or untreated (e.g., Salado Stream) waters in Jerez de la Frontera. In contrast, EHMC concentrations were much lower in areas where agriculture is the main land use (i.e., from not detected to 4 ng/L in GW sampling points of Guadalete aquifer). Finally, there are two additional studies that analyzed the presence of EHMC in GW but neither the concentrations nor the limit of detection of the analytical methodologies were provided (Hernández et al., 2015; Pitarch et al., 2016). The frequency of detection of EHMC in GW samples was moderate, ranging from 44% (Corada-Fernández et al., 2017) to 58% (Hernández et al., 2015).

2.5 Antioxidants

BHT is the most commonly used synthetic antioxidant recognized as safe for use in foods containing fats, pharmaceutical, petroleum products, rubber and oil industries (Yehye et al., 2015). The presence of BHT was scarcely investigated (n=4) in the GW of Spain (Cabeza et al., 2012; Calderón-Preciado et al., 2013; Pitarch et al., 2016; Teijon et al., 2010). The occurrence of BHT was reported for the first time in the lower aquifer of the Llobregat River by Teijon et al. (2010) at concentrations that ranged from

62 to 455 ng/L, average value above 130 ng/L (Cabeza et al., 2012) and detection frequencies above 90%. Calderón-Preciado et al. (2013) assessed the presence of BHT in crops irrigated with GW and secondary-treated wastewater from Caldes de Montbui WWTP (close to Barcelona, northeast of Spain). Both irrigation water sources presented concentrations below the limit of quantification (LOQ<192 ng/L). Finally, Pitarch et al. (2016) analyzed the occurrence BHT in GW from Castellón (east of Spain) but the concentrations were not reported (Table S1 of the Supplementary Material).

3. Fate of EOCs in the Spanish aquifers

Eight of the 20 microcontaminants included in this review (the pesticides imidacloprid and methiocarb, the pharmaceuticals azithromycin, ciprofloxacin diclofenac and erythromycin, the antioxidant BHT and the UV filter EHMC) were detected in Spanish GW at concentrations far above 100 ng/L (Fig. 2), suggesting that it is of paramount importance to understand their fate in GW. The latter depends on a number of factors such as the physico-chemical properties of EOCs and the processes occurring in the soil-aquifer system such as filtration, sorption, mixing, biodegradation, etc.

3.1 Physico-chemical properties of EOCs

The physico-chemical properties of a substance drive its mobility in GW. A typical parameter to evaluate the potential of pesticides to leach is the Groundwater Ubiquity Score (GUS) index (Gustafson, 1989). The GUS index is estimated as follows:

$$\mathrm{GUS} = \log(\mathrm{DT50}) \times (4 - \log(K_{oc})) \qquad \textit{Eq. (1)}$$

where DT50 is the soil half-life (i.e., the rate of degradation of a given pesticide) and K_{oc} is the organic soil-water partition coefficient (see Table 1). If the GUS index is <1.8 the pesticides are classified as a "non-leachers", whereas a GUS index >2.8 indicates "probable leachers" (Table 1). Other typical parameters used to assess the mobility of EOCs are the water solubility (S_w) and the octanol–water partition coefficient (K_{ow}), typically expressed as log K_{ow} (Table 2). Generally, EOCs with log K_{ow}>4 are considered hydrophobic and they are ranked as low mobility substances. On the contrary, substances with lower log K_{ow} (log K_{ow}<1, hydrophilic) are expected to be more mobile and substances with log K_{ow} values of 1-4 show medium mobility (Table 2). However, the ionized forms (positively and/or negatively charged substances) of EOCs are controlled by GW pH in the subsurface. Consequently, the log D_{ow} (the pH-dependent octanol-water distribution ratio) is more appropriate to predict the fate of ionizable organic substances in GW (Wells et al., 2006).

Based on the calculations of the GUS index (*Eq. (1)*), clothianidin, imidacloprid and thiamethoxam are likely to be potential leachers to GW since their GUS indexes are above 3 (Table 1). Moreover, their solubilities in water are moderate and the log K_{ow} values indicate that these substances have hydrophilic character (Table 2). Conversely, thiacloprid, acetamiprid, oxadiazon, triallate and metaflumizone are classified as non-leachers. For oxadiazon, thiacloprid, triallate and metaflumizone the GUS index is in agreement with their low solubility and high log K_{ow}, whilst acetamiprid, albeit classified as non-leacher, shows high solubility and log K_{ow}, indicating its moderate hydrophilic character. Despite some of these pesticides are fairly hydrophilic they were not widely detected in Spanish GW bodies. For instance, imidacloprid, which is one of the most investigated pesticides, presented frequencies of detection of 24% in GW samples collected near a solid-waste treatment plant of Castellón (Pitarch et al., 2016) and of 9% in the GW resources of the vineyard region of La Rioja (Herrero-Hernández et al., 2017). So far, the pesticides included in the Watch Lists defined in the Decisions 2015/495/EU and 2018/840/EU have been poorly studied in the GW bodies of Spain.

Concerning pharmaceuticals, the antibiotics amoxicillin and ciprofloxacin have moderate low and high water solubility, respectively, and low log K_{ow} values, suggesting their possible occurrence in GW bodies. Diclofenac and macrolide antibiotics have low (14.8 mg/L) and high solubility (>2800 mg/L), respectively, but their log K_{ow} values suggest that they have low to moderate mobility, respectively (log K_{ow}>2.4, Table 2). Thus, their occurrence in GW bodies at high concentrations is not expectable. However, in urban GW of Barcelona aquifers they presented high detection frequencies (71% for diclofenac, 97% for azithromycin and 100% for clarithromycin) and diclofenac and azithromycin showed average concentrations above 100 ng/L (López-Serna et al., 2013). Therefore, the log D_{ow}, which is a combination of K_{ow} and pK_a, seems more appropriate to understand the mobility of a compound in environmental conditions. Amoxicillin, diclofenac and macrolide antibiotics have ionizable groups at GW pH ranges and, hence, changes in log K_{ow} values can be observed with respect to log D_{ow} (Table 2). The ionizable groups present in amoxicillin are the carboxyl (acidic) and the amino (basic) groups. As the former is more acidic than the latter group, its dissociation is represented by the first equilibrium constant (pK_a=3.23), the second equilibrium constant (pK_a=7.33) resulting from the dissociation of the amino group. Thus, amoxicillin is present in zwitterionic and anionic forms in GW at pH 7.4. Diclofenac has weak acidic properties (pK_a=4, Table 2) and at pH 7.4 the anionic form of diclofenac (i.e., deprotonation of the carboxylic group) might occur in GW. Macrolide antibiotics are weak bases (pK_a ranging from 8.38 to 9.57, Table 2) and are present as cationic and neutral species in GW at pH 7.4. The ionizable forms of these pharmaceuticals result in very different values of log K_{ow} and log D_{ow} for diclofenac (4 vs. 1.1), moderate different values for azithromycin (2.44 vs. 1.23), clarithromycin (3.24 vs. 2.22) and erythromycin (2.6 vs. 1.57) and slightly different values for amoxicillin (-2.31 vs. -2.67) (Table 2).

The steroids E1, E2 and EE2, the UV filter EHMC and the antioxidant BHT have low solubilities in water and high log K_{ow} values, and thus, can be considered hydrophobic substances (Table 2). In fact, none of the estrogens were found in GW bodies of Spain despite they were frequently studied (Fig. 2). However, BHT and EHMC were detected very frequently, >90% and 100%, respectively, in the deep aquifer of the Llobregat River Delta (Cabeza et al., 2012). Similarly, EHMC was also found quite frequently (44%) in the GW of the Guadalete River (Corada-Fernández et al., 2017). This observation might suggest that the physico-chemical properties of EOCs do not always predict properly their mobility and occurrence in GW bodies. In fact, many substances included in the Watch Lists exceeded many times the concentration of 100 ng/L in the GW bodies of Spain for a wide range of log D_{ow} values (Fig. 3 and Table 1 of the Supplementary Material). Thus, other valuable information such as GW residence times, the hydraulic properties and concentration of EOCs in the aquifer recharge sources will help in understanding their fate in GW bodies and might also hint areas with less soil/aquifer remediation potential.

3.2 Adsorption and transformation processes in GW

The occurrence and the fate of EOCs in GW also depend on the geochemical processes (i.e., adsorption, degradation, dilution and transformation processes). GW is less contaminated than other freshwater bodies (e.g., rivers) and, generally presents lower concentrations than influents and effluents from WWTPs, which are the main source of pollution to GW environment. For example, average concentrations of macrolide antibiotics in the shallow aquifer of the Besòs River Delta were much lower than those found in the Besòs River, which is the main contamination source of the aquifer (López-Serna et al., 2013). The concentrations were 16 vs. 133 ng/L for azithromycin, 11 vs. 101 ng/L for clarithromycin and 29 vs. 55 ng/L for erythromycin. Similarly, the average concentrations of diclofenac in the low aquifer of the Llobregat River Delta were also much lower than those observed in the treated wastewater (49 vs. 182 ng/L) infiltrated to avoid seawater intrusion (Candela et al., 2017). These observations might indicate the natural attenuation capacity of the aquifers, however none of the studies that investigated the occurrence of EOCs thoroughly evaluated the processes in which these microcontaminants are involved in GW.

The main processes driving the fate of EOCs in GW are sorption, generally to organic matter and clay minerals, and biological degradation or transformation (Lapworth et al., 2012). Boy-Roure et al. (2018) pointed out that antibiotic transport modeling at a regional scale will most probably be unsuccessful due to difficulties in predicting the coefficients in the sorption equations and the fact that retardation factors vary orders of magnitude, causing some of these contaminants to be rather immobile compared to GW flow. Thus, the characterization of such process at field conditions is not an easy task. For example, biotransformation was investigated by Barbieri et al. (2012) under denitrifying conditions at laboratory scale, where a transient transformation of diclofenac to nitro-diclofenac was observed while nitrite was present in the water. However, biotransformation processes at field scale might be difficult to assess because the concentrations of such contaminants in GW are relatively low (ranging from ng/L to the low µg/L). Absorption processes depend on the ionogenicity of a given substance and the type of surface. Positive charged substances tend to sorb onto negatively charged surfaces such as clays, whilst negative charged substances tends to sorb onto positively charged surfaces such as iron oxides (Valhondo et al., 2015). Neutral substances have affinity for solid organic matter. In GW, the attenuation of these substances occurs mainly through microbial degradation, because adsorption is reversible and only retards the contaminants' transport (Greskowiak et al., 2017). Biodegradation of some microcontaminants is described as redox-dependent process (Burke et al., 2014; Massmann et al., 2008) but the redox state of GW is not described in many field studies. It is therefore clear that EOCs' analysis in the subsurface should be associated to the redox character of GW at field scale.

4. Spanish vs. worldwide GW concentrations of the microcontaminants included in the Watch Lists

In the following the maximum EOC concentrations in the GW bodies of Spain are compared to those reported in studies carried out in other countries (Fig. 4 and Fig. 5). The profile of GW contamination seems to be dominated by pesticides because they were detected at high concentrations in GW (Fig. 4), reaching values close to 9000 ng/L for thiamethoxam (Table S2 of the Supplementary Material). The most investigated pesticides were the neonicotinoids in aquifers of Canada (Government of Quebec, 2011), USA (Huseth and Groves, 2014; Zhao et al., 2011), Brazil (Carbo et al., 2008), France (Lopez et al., 2015); Italy (Fava et al., 2010), Serbia (Dujakovic et al., 2010), and Vietnam (Lamers et al., 2011). Overall, neonicotinoids were found at maximum concentrations of: 8930 ng/L for thiamethoxam, 6310 ng/L for acetamiprid, 6100 ng/L for imidacloprid and 3340 ng/L for clothianidin (Fig. 4). These concentrations are one order of magnitude higher than the maximum concentration found in Spain (656 ng/L). However, lower concentrations were reported for acetamiprid ranging from <20 ng/L to

70 ng/L in a study in France (Lopez et al., 2015) and from <12 ng/L to 20 ng/L for imidacloprid in coastal GW of Long Island (New York, USA, Zhao et al., 2011). Moreover, acetamiprid and imidacloprid were not detected in GW influenced by agriculture in Serbia (Dujakovic et al., 2010) and thiacloprid was not detected in GW of Brazil (Carbo et al., 2008) and Denmark (Brüsch et al., 2017) (Table S2 of the Supplementary Material). The remaining substances were less investigated than neonicotinoids (Fig. 4). Methiocarb was detected at the high concentration of 5400 ng/L in GW of an agricultural zone of the Yaqui Valley (northwest of Mexico) (García de LLasera and Bernal-González, 2001). Oxadiazon and triallate were detected at maximum concentrations of 180 ng/L in Italy (Fava et al., 2010) and 500 ng/L in GW in Canada (Hill et al., 1996) (Table S2 of the Supplementary Material).

The occurrence of pharmaceuticals in GW was more frequently investigated than that of pesticides; however they were detected at lower concentrations (Table S2 of the Supplementary Material). The maximum GW concentrations reported (Fig. 5) are 3050 ng/L for diclofenac (Germany) (Müller et al., 2012), 2380 ng/L for erythromycin (Nebraska, USA) (Bartelt-Hunt et al., 2011), 130.8 ng/L for ciprofloxacin (Cluj-Napoca, Romania) (Szekeres et al., 2018), 42 ng/L for clarithromycin (France) (Lopez et al., 2015) and 23 ng/L for azithromycin (Minnesota, USA) (Erickson et al., 2014). These values are higher than those reported in Spanish GW for diclofenac (3050 vs. 477 ng/L) and erythromycin (2380 vs. 428 ng/L), lower for azithromycin (23 vs. 1620 ng/L) and ciprofloxacin (130.8 vs. 443 ng/L), and similar for clarithromycin (42 vs. 20.5 ng/L) (Fig. 5). Overall, these pharmaceuticals were detected at low concentrations (<50 ng/L) in GW bodies of Germany (15.5 ng/L for diclofenac, Einsiedl et al., 2010), France (24 ng/L for diclofenac, Lopez et al., 2015), USA (23 ng/L for azithromycin, Erickson et al., 2014), Singapore (17 ng/L for diclofenac, Tran et al., 2014), China (0.7 ng/L for clarithromycin and azithromycin, Tong et al., 2014b) and Canada (0.83 ng/L for clarithromycin, Van Stempvoort et al. 2013) (Table S2 of the Supplementary Material). The antibiotic amoxicillin was not detected in the GW of Germany (Sacher et al., 2001), the Netherlands (Kivits et al., 2018) and Tehran (Mirzaei et al., 2018). As for steroids, despite none of the studied substances (E1, E2 and EE2) were found in the aquifers in Spain, they were detected at maximum concentrations above 100 ng/L in GW bodies from the USA (Bartelt-Hunt et al., 2011; Karnjanapiboonwong et al., 2011; Swartz et al., 2006). In contrast, E1 was detected at low levels (<10 ng/L) in French GW bodies (Lopez et al., 2015) and E1 and E2 were not detected in the GW of Mezquita Valley (Mexico, Lesser et al., 2018) (Table S2 of the Supplementary Material). The antioxidant BHT was found at maximum concentrations ranging from 190 ng/L in GW of California (USA, Soliman et al., 2007) to 7000 ng/L in the GW bodies from UK (Stuart et al., 2012) (Fig. 5). Finally, the sunscreen EHMC was rarely studied in GW worldwide since, to the authors' knowledge, it was only investigated in a GW sample collected from Joinville (Santa Catarina, Brazil) but was not detected (Luiz Oenning et al., 2018), which might be due to the high detection limit of the analytical method applied (LOD=4600 ng/L) since the maximum concentration of EHMC in Spanish GW was 770 ng/L.

To summarize, some of the EOCs included in the Watch Lists defined in the Decisions 2015/495/EU and 2018/840/EU (EC, 2015 and 2018), such as the pesticides clothianidin, thiacloprid, methiocarb, oxadiazon and triallate and the UV filter EHMC, were barely studied in GW. Overall, these microcontaminants were not detected or determined at low ng/L level, with the exception of a few aquifers where they reached concentrations of thousands ng/L. Further research must be devoted to investigate the occurrence of EOCs reported at high concentrations in GW since they might pose environmental and health risks. This would help to define threshold values for GW quality assessment and/or drinking water standards of these unlegislated substances in the near future.

5. Environmental risk assessment

The assessment of the ecotoxicological risks associated to the occurrence of the substances from the Watch Lists was performed following the European Agency for the Evaluation of Medicinal Products guidelines (EMEA, 2006), as described in Molins-Delgado et al. (2016). EC50 (50% effect concentration) data for the calculations were obtained from the literature (Boran et al., 2007; Cleuvers, 2003; Ferrari et al., 2003; Isidori et al., 2005; Molins-Delgado et al., 2016; Park and Choi, 2008) (Table S3 of the Supplementary Material). Maximum EOC concentrations in Spanish GW bodies were selected in order to consider the worst-case scenario.

Hazard quotients (HQs) for acute toxicity were estimated for *Daphnia magna, Raphidocelis subcapitata, Vibrio fischeri, Ceriodaphnia dubia, Desmodesmus subspicatus, Brachionus calyciflorus and Oncorhynchus mykiss*. Ecotoxicity data from the literature were available for diclofenac, clarithromycin, erythromycin, amoxicillin, EHMC and methiocarb. The estimated HQ values are listed in Table 3. Most HQs are very low indicating no risk. However the HQ = 21 for diclofenac against *Ceriodaphnia d.* pointed out the high risk posed by this anti-inflammatory compound at GW measured concentrations. Besides, erythromycin showed potential ecological risk (medium-low), with certain margin of safety, for *Brachionus c.* as its associated HQ was 0.46.

6. Conclusions and future prospects

This work reviewed the occurrence of the organic microcontaminants listed in the first and second surface water Watch Lists for European Union monitoring defined in the Decisions 2015/495/EU and 2018/840/EU (EC, 2015 and 2018) in GW bodies of Spain. The most investigated and detected substances were pharmaceuticals such as clarithromycin, diclofenac and erythromycin. In contrast, pesticides were poorly studied since only imidacloprid and methiocarb were detected in the GW of Spain. Moreover, there are no studies that investigated the occurrence of the pesticides triallate, clothianidin, thiamethoxam and metaflumizone in Spanish aquifers. Despite some of the substances such as E1, E2 and EE2 were frequently investigated, they were never detected in the GW bodies of Spain. Some of these substances have been detected at concentrations higher than 100 ng/L in several Spanish GW bodies and thus it is required to set up GW threshold quality values. This is the case of the pesticides imidacloprid (656 ng/L) and methiocarb (300 ng/L), the pharmaceuticals azithromycin (1620 ng/L), diclofenac (477 ng/L), erythromycin (428 ng/L), ciprofloxacin (443 ng/L), the UV filter EHMC (770 ng/L) and the antioxidant BHT (455 ng/L). Note that the values in brackets are the maximum concentration reported in the Spanish GW bodies.

The maximum EOC concentrations measured in Spanish GW were generally much lower than those reported in GW from other countries, reaching values near to 9000 ng/L for thiamethoxam. Nevertheless, it is important to mention that (1) some of these EOCs were not detected or reported at low concentrations (<50 ng/L) in the GW from many countries, and (2) GW is considerably less contaminated than other freshwater bodies (e.g., rivers) indicating the natural attenuation capacity of the aquifers and/or that rivers are more vulnerable to be polluted than GW. The elimination of these microcontaminants in GW is mainly due to microbial degradation since sorption is a reversible process which retards the contaminant transport in the aquifer. There are currently few studies that evaluate the hydrogeochemical processes controlling the fate of EOCs in GW at field scale and thus, further research should be devoted to this relevant topic.

The global EOC contamination loads of the Spanish and the European GW bodies remains largely unknown because most of the studies were site-specific and each of them analyzed different substances. For example, the occurrence of herbicides and insecticides in GW is expected in rural areas where they are applied (e.g., Herrero-Hernández et al., 2017). Similarly, a wide array of pharmaceuticals and personal care products were found in urban aquifers located in densely populated cities such as Barcelona (e.g., López-Serna et al., 2013; Serra-Roig et al., 2016). Thus, the reviewed studies provide a biased picture of the current state of the GW bodies. Water Catchment and/or Federal Agencies are responsible for monitoring groundwater quality and specifically EOCs but, to the authors' knowledge, information about EOCs is not published. These regular monitoring campaigns might give more insight on the real state of GW bodies' contamination. Moreover, it is necessary to design monitoring programmes at regional scale including different land use contexts and a broad range of hydrogeological conditions to assess the spatial and temporal occurrence of these contaminants in each country (e.g., Lopez et al., 2015). This would help to (1) establish drinking water standards of these unlegislated substances, (2) evaluate their environmental risk assessment and (3) select many other polar organic substances frequently found in freshwater resources that are susceptible to be included in future GW Watch Lists.

The compiled concentration in the Spanish GW bodies was used to assess the environmental risk posed by the target EOCs. According to the estimated HQs for diclofenac, clarithromycin, erythromycin, amoxicillin, EHMC and methiocarb, these substances mostly do not pose risk for the aquatic environment in the frame of the described scenarios GW and aquatic organisms tested. However, diclofenac (high, HQ = 21) and erythromycin (medium-low, HQ = 0.46) do pose a risk for *Ceriodaphnia dubia and Brachionus calyciflorus,* respectively.

Appendix A. Supplementary tables associated with this article can be found in the online version.

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Figure captions

Figure 1. Spatial distribution of the studies included in this review.

Figure 2. Number of studies (n=33) that investigated the occurrence of the microcontaminants listed in the Decisions 2015/495/EU and 2018/840/EU in the GW of Spain (%) and maximum GW concentrations (ng/L) reported. n.d= not detected

Figure 3. Maximum concentrations of the microcontaminants listed in the Decisions 2015/495/EU and 2018/840/EU reported in the GW of Spain vs. Log D_{ow} values. Note that the black dashed line represents the concentration threshold of 100 ng/L.

Figure 4. Comparison between the maximum concentrations of pesticides in GW bodies of Spain (black dotes) and in GW worldwide. References: [1] Carbo et al. (2008), [2] Fava et al. (2010), [3] García de Llasera and Bernal-González (2001),[4] Gaw et al. (2010), [5] Government of Quebec, (2011), [6] Hill et al. (1996), [7] Huseth and Groves (2014), [8] Lamers et al. (2011), [9] Lopez et al. (2015), [10] Melo et al. (2012), [11] Zhao et al (2011) and [12] maximum concentration in Spanish GW bodies.

Figure 5. Comparison between the maximum concentrations measured in GW bodies of Spain (black dotes) and in GW worldwide for (a) pharmaceuticals, (b) esteroids and (c) the antioxidant BHT. References: [1] Bartelt-Hunt et al. (2011), [2] Einsiedl et al. (2010), [3] Erickson et al. (2014), [4] Fries and Puttmann (2004), [5] Karnjanapiboonwong et al. (2011), [6] Lopez et al. (2015), [7] Müller et al. (2012), [8] Soliman et al. (2007), [9] Stuart et al. (2012), [10] Swartz et al. (2006) and [11] Szekeres et al. (2018), [12] Van Stempvoort et al. (2013) and [13] maximum concentration in Spanish GW bodies.

Table captions

Table 1. Groundwater Ubiquity Score (GUS) index evaluated for pesticides using the values of the organic Soil Organic Carbon Partition Coefficient (K_{oc}) and the soil half-life (DT50). Data were obtained from the Footprint Pesticide Properties Data Base (available via: http://www.eu-footprint.org/ppdb.html) (Lewis et al., 2016). Missing data from the aforementioned data base is from: [a] Spadotto (2002) and [b] Miranda et al. (2011).

Table 2. Physico-chemical properties of the target substances. [a] Calculated using Advanced Chemistry Development Inc. (© 1998-2018 ChemAxon Ltd.)

Table 3. Hazard quotients (HQ) estimated for selected Watch List substances. Calculation was based on the maximum concentrations reported for the substances in GW from Spain. Toxicity data (EC50 values) were obtained from the literature. References: Boran et al., 2007; Cleuvers, 2003; Ferrari et al., 2003; Isidori et al., 2005; Molins-Delgado et al., 2016; Park and Choi, 2008.

Figure 1

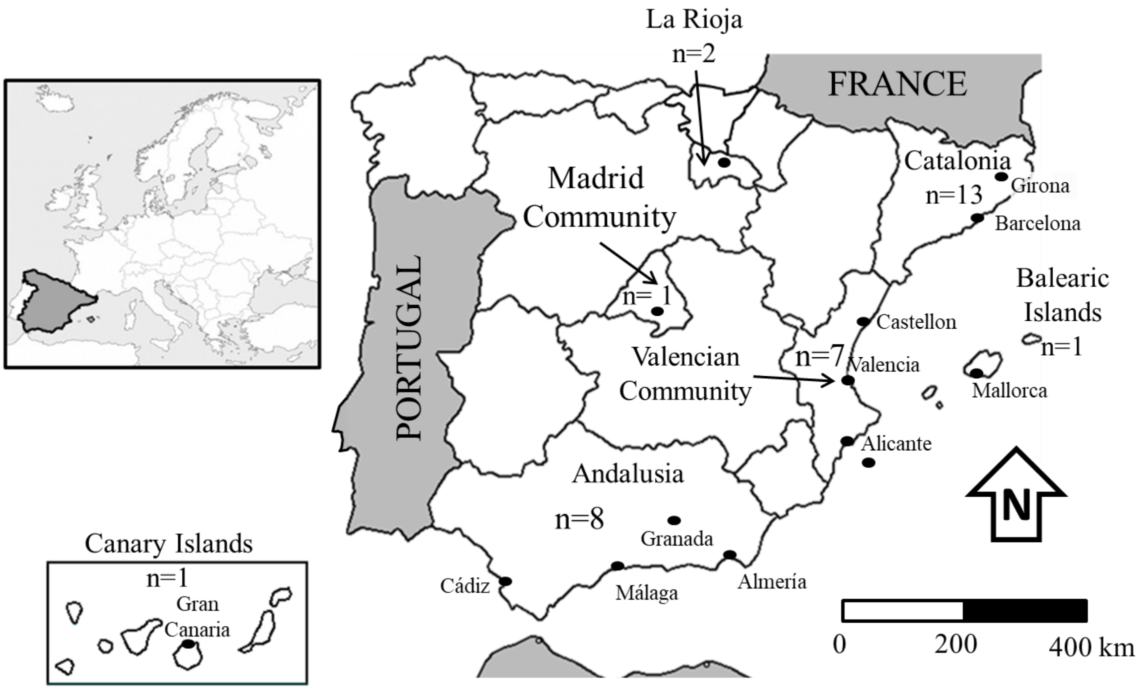

La Rioja
n=2
FRANCE
Catalonia
n=13
Girona
Barcelona
Madrid
Community
n= 1
PORTUGAL
Balearic
Islands
n=1
Castellon
Valencian
Community
n=7
Valencia
Mallorca
Alicante
Andalusia
n=8
Granada
N
Canary Islands
n=1
Gran
Canaria
Cádiz
Málaga
Almería
0
200
400 km

Figure 2

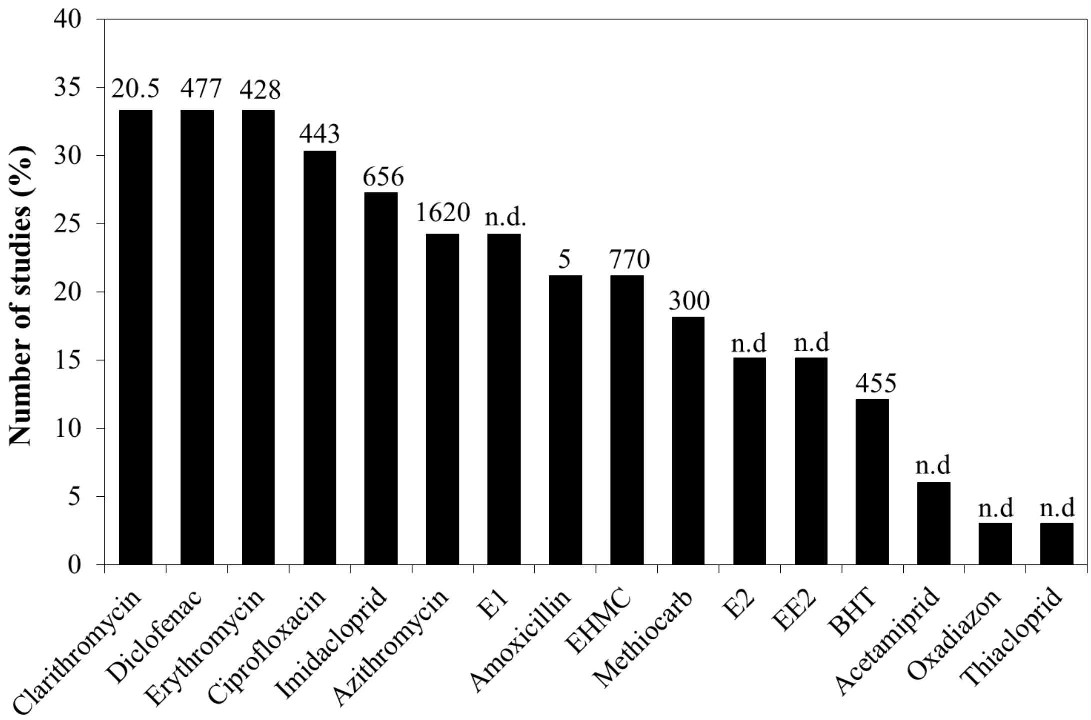

Number of studies (%)
40
35
30
25
20
15
10
5
0
20.5
477
428
443
656
1620
n.d.
5
770
300
n.d
n.d
455
n.d
n.d
n.d
Clarithromycin
Diclofenac
Erythromycin
Ciprofloxacin
Imidacloprid
Azithromycin
E1
Amoxicillin
EHMC
Methiocarb
E2
EE2
BHT
Acetamiprid
Oxadiazon
Thiacloprid

Figure 3

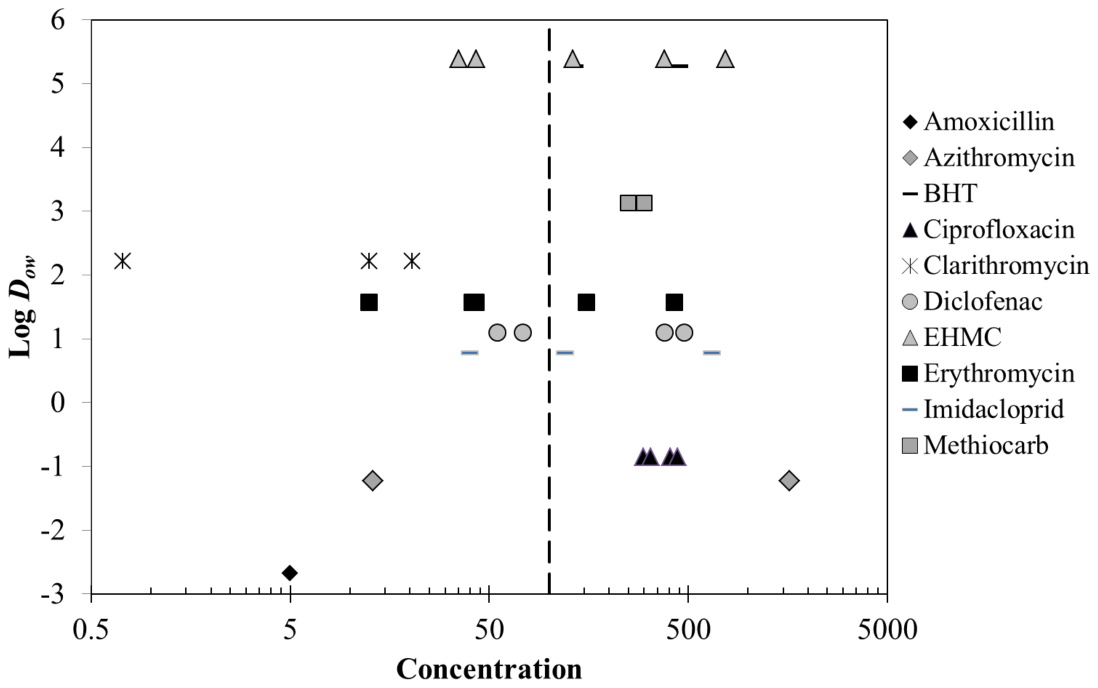
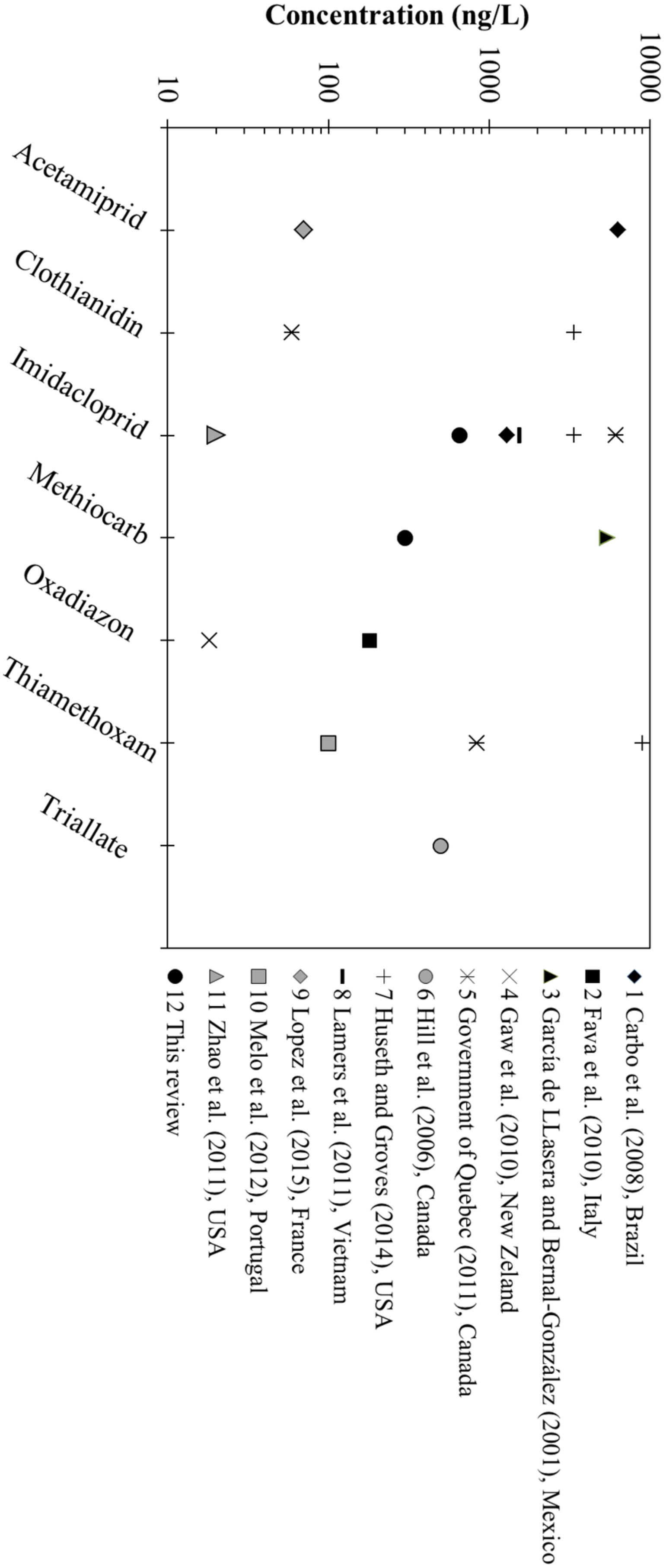
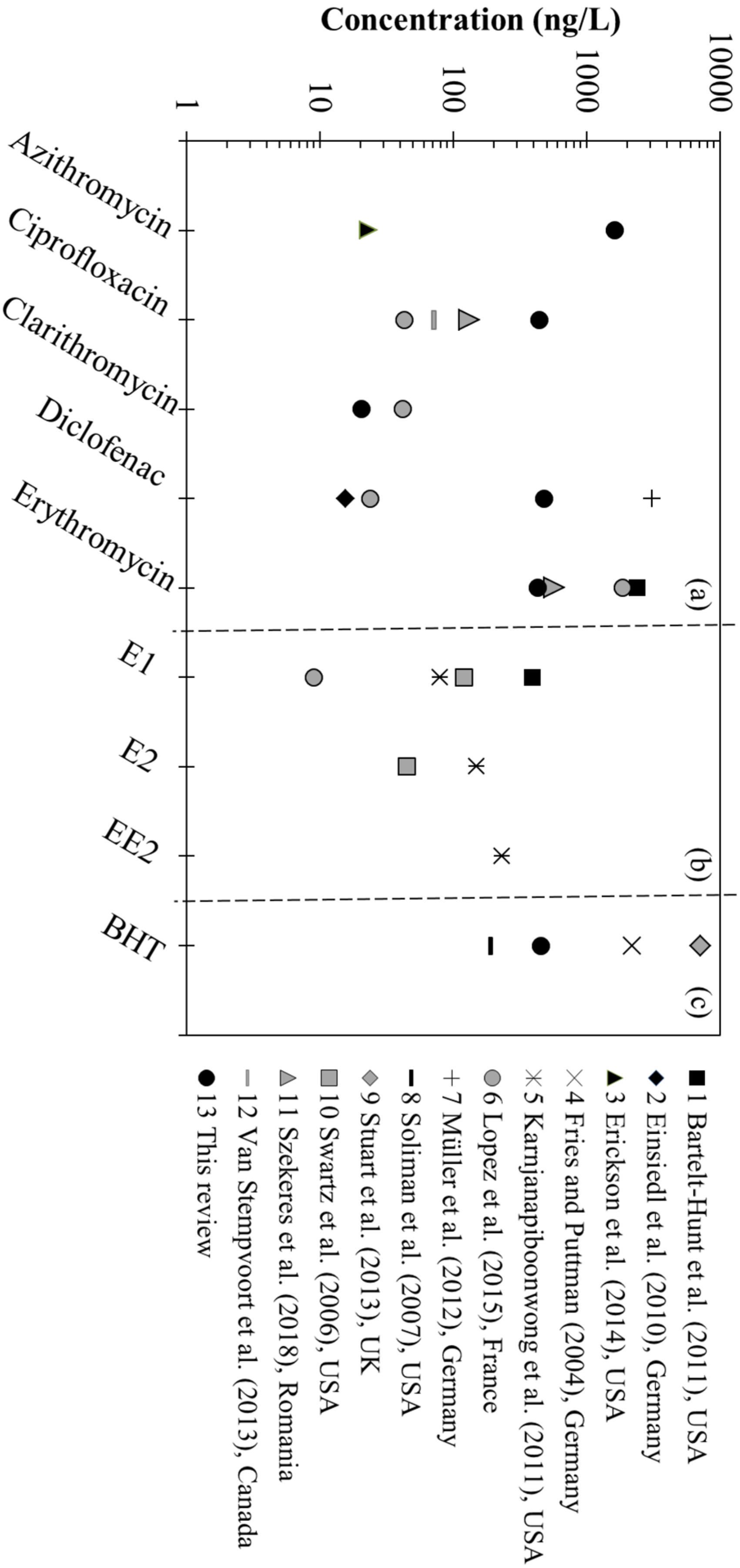

6
5
4
3
2
1
0
-1
-2
-3
Log D_{ow}
0.5
5
50
500
5000
Concentration
Amoxicillin
Azithromycin
BHT
Ciprofloxacin
Clarithromycin
Diclofenac
EHMC
Erythromycin
Imidacloprid
Methiocarb

Figure 4



Concentration (ng/L)
10
100
1000
10000
Acetamiprid
Clothianidin
Imidacloprid
Methiocarb
Oxadiazon
Thiamethoxam
Triallate
1 Carbo et al. (2008), Brazil
2 Fava et al. (2010), Italy
3 García de LLasera and Bernal-González (2001), Mexico
4 Gaw et al. (2010), New Zeland
5 Government of Quebec (2011), Canada
6 Hill et al. (2006), Canada
7 Huseth and Groves (2014), USA
8 Lamers et al. (2011), Vietnam
9 Lopez et al. (2015), France
10 Melo et al. (2012), Portugal
11 Zhao et al. (2011), USA
12 This review

Figure 5



Concentration (ng/L)
1
10
100
1000
10000
Azithromycin
Ciprofloxacin
Clarithromycin
Diclofenac
Erythromycin
E1
E2
EE2
BHT
(a)
(b)
(c)
1 Bartelt-Hunt et al. (2011), USA
2 Einsiedl et al. (2010), Germany
3 Erickson et al. (2014), USA
4 Fries and Puttman (2004), Germany
5 Karnjanapiboonwong et al. (2011), USA
6 Lopez et al. (2015), France
7 Müller et al. (2012), Germany
8 Soliman et al. (2007), USA
9 Stuart et al. (2013), UK
10 Swartz et al. (2006), USA
11 Szekeres et al. (2018), Romania
12 Van Stempvoort et al. (2013), Canada
13 This review

Table 1

Group	Compound	K_{oc} (mg/L)	DT50 (d)	GUS index	Classification
Carbamates	Methiocarb	300 [a]	35	2.35	Transition
	Triallate	3034	46	0.86	Non-leacher
Semicarbazone	Metaflumizone	30714	13.8	-0.56	Non-leacher
Neonicotinoids	Acetamiprid	200	3	0.81	Non-leacher
	Clothianidin	123	121.2	3.98	Leacher
	Imidacloprid	260 [b]	174	3.55	Leacher
	Thiacloprid	615 [b]	18	1.52	Non-leacher
	Thiamethoxam	56.2	39	3.58	Leacher
Oxadiazole	Oxadiazon	3200	165	1.10	Non-leacher

Table 2

Group	Compound	CAS Number	S^a (mg/L)	Log K_{ow} [a]	pKa [a]	Log D_{ow} [a] (charge) (pH=7.4)
Pesticides						
Carbamates	Methiocarb	2032-65-7	185	3.13	14.77	3.13
	Triallate	2303-17-5	21.2	3.8	-	3.8
Semicarbazone	Metaflumizone	139968-49-3	0.015	6.86	11.17	6.86
Neonicotinoids	Acetamiprid	135410-20-7	1820	1.11	4.16	1.11
	Clothianidin	210880-92-5	283	0.54	15.59	0.54
	Imidacloprid	105827-78-9 138261-41-3	267	0.87	6.75	0.78 (+ 1)
	Thiacloprid	111988-49-9	68.7	2.06	1.62	2.06
	Thiamethoxam	153719-23-4	206	1.29	3.01	1.29
Oxadiazole	Oxadiazon	19666-30-9	9.2	5.31	-	5.31
Pharmaceuticals						
NSAID	Diclofenac	15307-86-5	14.8	4.26	4	1.10 (-1)
Macrolide antibiotics	Azithromycin	83905-01-5	18100	2.44	9.57	-1.23 (+ 1.96)
	Clarithromycin	81103-11-9	2830	3.24	8.38	2.22 (+ 0.91)
	Erythromycin	114-07-8	3920	2.6	8.38	1.57 (+ 0.91)
β-lactam antibiotic	Amoxicillin	26787-78-0	16.3	-2.31	3.23 7.22	-2.67 (- 0.61)
Fluoroquinolone antibiotic	Ciprofloxacin	85721-33-1	1610.0	-0.85	5.56 8.68	-0.85 (- 0.02)
Steroids						
	E1	53-16-7	18	4.31	10.33	4.31
	E2	50-28-2	28.1	3.75	10.33	3.74
	EE2	57-63-3	4.4	3.9	10.33	3.9
UV Filters						
	EHMC	5466-77-3	0.8	5.38	-	5.38
Antioxidant						
	BHT	128-37-0	9.1	5.27	11.6	5.27

Table 3

Compound	**HQ** **Species**						
	Daphnia m.	***Raphidocelis s.***	***Vibrio f.***	***Ceriodaphnia d.***	***Desmodesmus s.***	***Brachionus c.***	***Oncorhynchus m.***
Diclofenac	7,0E-03	-	-	**2,1E+01**	6,6E-03	-	-
Clarithromycin	8,0E-04	-	-	1,1E-03	-	1,7E-03	-
Erythromycin	1,9E-02	-	-	4,2E-02	-	**4,6E-01**	-
Amoxicillin	-	-	1,4E-06	-	-	-	-
EHMC	2,3E-01	3,7E-01	-	-	-	-	-
Methiocarb	-	-	-	-	-	-	3,8E-01

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