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Review

Emerging organic contaminants in groundwater in Spain: A review of sources, recent occurrence and fate in a European context

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HIGHLIGHTS

- ► Emerging organic contaminants (EOCs) are reviewed in groundwater in Spain.
- ► These include pesticides, pharmaceuticals and drugs of abuse.
- ► Groundwater is considerably less contaminated than other water bodies.
- ► There is insufficient information to assess the fate of EOCs in the aquifers.
- ► Establishment of environmental threshold value to protect groundwater quality.

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ABSTRACT

This paper reviewed the presence of emerging organic contaminants (EOCs) that have been found in the groundwater in Spain in both, rural and urban areas. The list of compounds included pesticides, pharmaceutical active compounds (PhACs), selected industrial compounds, drugs of abuse (DAs), estrogens, personal care products and life-style compounds. The main sources of pollution and possible pathways have been summarised in this review. EOCs are likely to enter to the aquifer mainly through the effluents of waste water treatment plants (WWTPs) and are present in groundwater at concentrations of ng/L to μg/L. The most studied compounds in Spanish groundwater were pesticides followed by industrial compounds and PhACs. It is important to mention that compared to other water bodies, such as rivers, groundwater is considerably less contaminated, which may be indicative of the natural attenuation capacity of the aquifers. However, some EOCs have sometimes been detected at higher concentration levels in the aquifer than in the rivers, indicating the need for further research to understand their behaviour in the aquifers. For a wide array of compounds, their maximum concentrations show values above the European groundwater quality standard for individual pesticides (0.1 μg/L). Therefore, to preserve groundwater quality against deterioration it is necessary to define environmental groundwater thresholds for the non-regulated compounds.

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1. Introduction

High population growth coupled with industrial and agricultural activities may result in both an increased demand for water and the generation of wastewater. According to directive 2006/118/EC, groundwater is the largest body of fresh water in the European Union, but it is also the most sensitive. Groundwater may suffer pollution from many sources, including water leakage from sewer and septic systems, seepage from rivers and application of fertilizers and agrochemicals, among others (Foster, 2001; Vàzquez-Suñé et al., 2010). As a result, a wide range of organic pollutants can be found in aquifers posing a risk to groundwater quality (Wolf et al., 2004). Thus, a proper assessment of groundwater quality requires the identification of such pollutants.

Among the different organic pollutants, emerging organic contaminants (EOCs) are of particular concern for several reasons. First, different classes of EOCs such as pharmaceuticals, drugs of abuse, surfactants and personal care products have been detected in waste water treatment plant (WWTP) effluents (Petrovic et al., 2003; Radjenovic et al., 2007; Boleda et al., 2009; Martínez Bueno et al., 2012). Consequently, WWTP effluents may be the main source of pollution for groundwater due to the continuous entrance of EOCs into the aquatic environment. Second, research has provided growing evidence that many EOCs are endocrine disruptor compounds (EDCs) (Liu et al., 2008). EDCs are found in a wide range of products, including plastic bottles, detergents, flame retardants, food, toys, cosmetics, pesticides, etc. and are thought to have adverse developmental and reproductive effects in both humans and wildlife (Campbell et al., 2006). Third, EOCs may be toxic and persistent and, despite being detected in low concentrations, may produce potentially harmful effects on ecosystems and human health (Jones-Lepp et al., 2004; Postigo et al., 2008; Reungoat et al., 2010), not to mention that the degradation products (DPs) of some compounds such as alkylphenols are even more toxic than the parent products (Soares et al., 2008).

To tackle the aforementioned problems it is necessary to define groundwater quality standards. To date, legislation on groundwater contamination by organic contaminants has only affected pesticides. The environmental quality standards for both individual substances, including their relevant metabolites and degradation and reaction products (0.1 μg/L) and for the sum (0.5 μg/L), have been established (European Parliament and Council of the European Union, 2006).

Most EOCs research has focused on both surface and waste waters. Groundwater has been much less studied. In the last decade, there have been some reviews on the occurrence and/or fate of specific EOCs such as pharmaceuticals in aquatic environments (Heberer et al., 2002; Mompelat et al., 2009) and EDCs (Campbell et al., 2006; Liu et al., 2008; Silva et al., 2012). Similarly, recent reviews have included a vast array of EOCs in freshwater sources (Murray et al., 2010; Pal et al., 2010), such as the Llobregat River Basin (González et al., 2012) and in waste waters (Bolong et al., 2009; Muñoz et al., 2009). Díaz-Cruz and Barceló (2008) reviewed priority and emerging organic micropollutants in different water resources intended for aquifer artificial recharge. But there is a lack of comprehensive reviews concerning a wide range of EOCs in groundwater. Only Stuart et al. (2012) reviewed the risk of emerging contaminants in the UK groundwater and Lapworth et al. (2012) summarised the sources, fate and occurrence of EOCs in the groundwater of Europe, the Middle East, North America and Asia. Here, we have extended the work of Lapworth et al. (2012) to other studies that have reported the occurrence of EOCs in Spanish groundwater.

In this paper, we review the presence of EOCs in the groundwater of Spain and evaluate the potential sources of contamination, the occurrence and the fate of such EOCs. Among the organic contaminants found in groundwater, we analyse pharmaceutically active compounds (PhACs), selected industrial compounds, drugs of abuse (DAs), estrogens, personal care products and life-style compounds. We have also addressed pesticides trying to focus on the more polar ones and transformation products. Special attention has been paid to the most frequently detected compounds and they have been compared with other studies carried out across Europe.

2. Identification of the potential sources of contamination

Groundwater pollution can be classified as point and non-point (or diffuse) source pollution. Point source pollution refers to contamination from discrete locations that can be easily identified with a single discharge source. Examples include municipal sewage treatment plant discharges, industrial discharges, accidental spills and landfills, among others (Lerner, 2008). In contrast, non-point source pollution is caused by pollution over a broad area and often cannot be easily identified as coming from a single or definite source. Agriculture is the main non-point polluter of groundwater in irrigated areas where fertilizers and other agrochemicals are applied (Chowdary et al., 2005). Similarly, runoff from urban and agricultural areas and leakage from urban sewage systems are non-point sources of pollution (Trauth and Xanthopoulos, 1997; Vàzquez-Suñé et al., 2007a). Since non-point source compounds are usually applied over large areas, they may have a larger impact on the groundwater quality

Table 1
Sources and possible pathways of EOCs in Spanish groundwater.

Source of pollution	Groups EOCs	Pathways into groundwater	Reference
Urban areas	Pesticides PhACs Industrial compounds DAs	Loss from sewage system Loss from water supply system Urban run-off	Latorre et al. (2003); Díaz-Cruz et al. (2008); García-Galán et al. (2010b and 2010c); Postigo et al. (2010); Tubau et al. (2010); Köck-Schulmeyer et al. (2012); Jurado et al. (2012).
Rural areas	Pesticides PhACs Industrial compounds	Wastewater discharges Surface run-off Leaching processes Recharge in non-urbanised areas	Garrido et al. (2000); Lacorte et al. (2002); Carabias-Martínez et al. (2000,2002 and 2003); Latorre et al. (2003); Arráez-Román et al., (2004); Sánchez-Camazano et al. (2005); Hildebrandt et al. (2007 and 2008); Köck-Schulmeyer et al. (2012).
Industrial areas	Industrial compounds PhACs	Industrial discharges Leaching processes	Latorre et al. (2003); García-Galán et al. (2010b and 2010c).
Rivers	Pesticides PhACs DAs Estrogens Life-style compounds	Infiltration of river water to the aquifer	López-Roldán et al. (2004); Rodriguez-Mozaz et al. (2004a and 2004b); Kampioti et al. (2005); Radjenovic et al. (2008); Huerta-Fontela et al. (2008 and 2011); Boleda et al. (2009); Tubau et al. (2010); Jurado et al. (2012).

than point sources. Table 1 summarises the different sources of pollution and pathways into groundwater. It is necessary to identify the different pollution pathways to assess and reduce the introduction of contaminants into groundwater. Upon identification, effective reduction measures can be adopted to prevent the contamination of groundwater by EOCs.

3. Occurrence and concentrations of EOCs in the groundwater of Spain

Research on EOCs in Spanish groundwater is reviewed in this section. A total of 33 studies have been included as a part of this review and their spatial extent is shown in Fig. 1. Table S1 summarised the reported EOCs including the number of studies and the maximum concentrations found in the cited sources for each compound (see supplementary information Table S1 for details).

Water Catchment Agencies are responsible for monitoring groundwater quality and specifically EOCs. But, to the author's knowledge, information about EOCs is not published. In some cases the information can be found in their web services but data are not compiled and interpreted in a public report. Yet, some of the data have been published in scientific journals and have been included in this review.

3.1. Pesticides

Pesticides are substances or mixtures of substances intended for preventing, destroying, repelling or mitigating pests. Pesticides are often categorised into four main classes according to the type of pest they control: herbicides; fungicides; insecticides and bactericides. We have addressed pesticides trying to focus on the more polar ones and transformation products. Note that less studied pesticides have also been summarised in Table S1.

3.1.1. Studies

Garrido et al. (2000) carried out a survey to study the quality status of 13 different hydrological units and analysed 19 organophosphorous and 7 triazine herbicides. Similarly, 10 years later, Postigo et al. (2010) and Köck-Schulmeyer et al. (2012) studied the occurrence of 22 pesticides in different aquifers of Catalonia where agricultural practices are significant. The presence of pesticides in

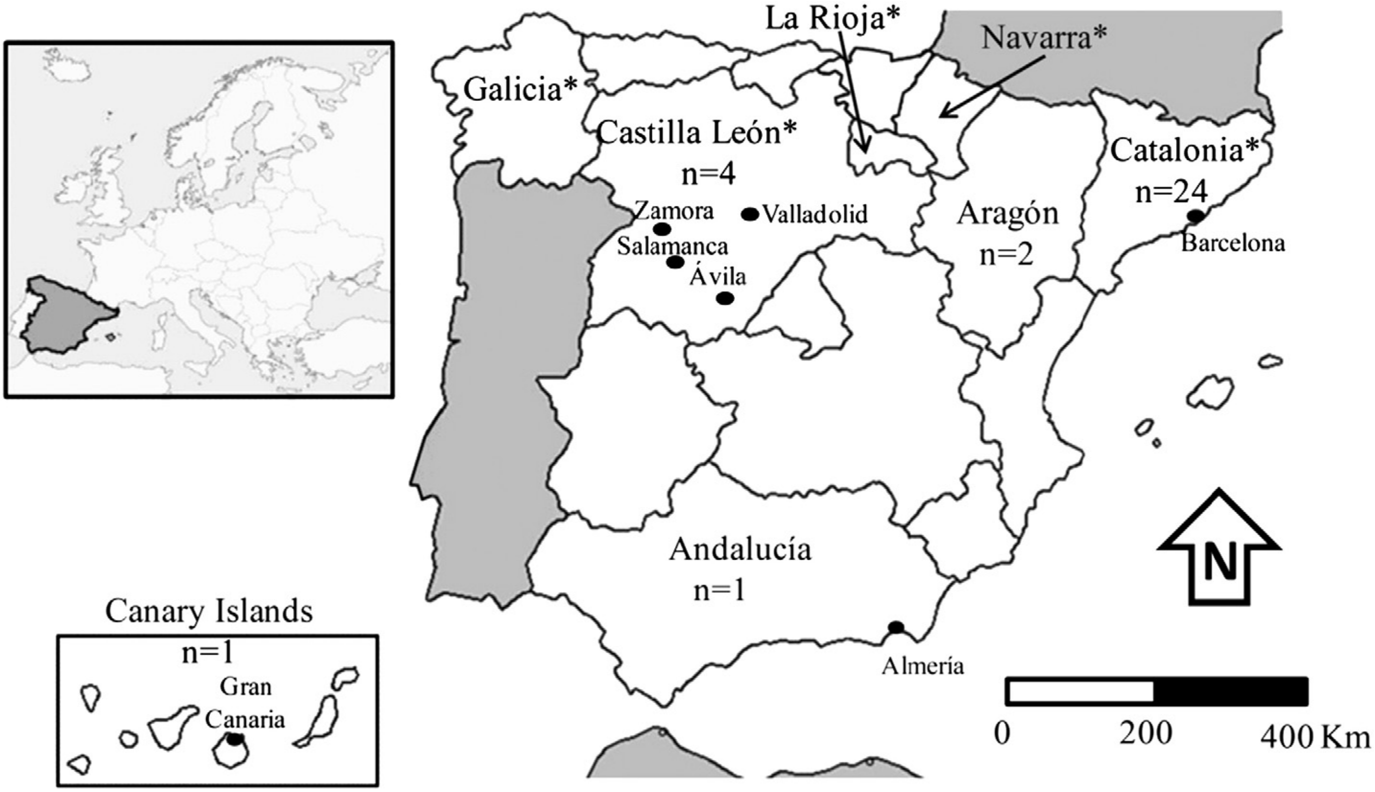

Fig. 1. Spanish map with the spatial distribution of the EOCs studies included in this review. Note that the studies of Hildebrandt et al. (2007 and 2008) have been located in the Aragón region (n = 2) but their spatial extention also include Castilla León, Galicia, Navarra, la Rioja and Catalonia regions (*). The study of Bono-Blay et al. (2012) has not been included because groundwater samples were collected all around Spain.

groundwater of the Llobregat area has also been widely studied (Quintana et al., 2001; López-Roldán et al., 2004; Rodriguez-Mozaz et al., 2004a; Kampioti et al., 2005; Teijon et al., 2010) in 2000, 2002, 2003 and 2007–2008, respectively. Triazine herbicides, phenylureas and organophosphorous herbicides have been the most studied pesticides in the Llobregat basin. García-Galán et al. (2010a) analysed 9 triazine herbicides in groundwater samples collected in the province of Barcelona in March 2007.

In some regions of Spain, the occurrence of specific pesticides has been studied according to the crops that are present in the agricultural areas. Sánchez-Camazano et al. (2005) analysed atrazine and alachlor in the Castilla León region, where corn crops are concentrated in four provinces (Salamanca, Avila, Zamora and Valladolid). Besides, in the area of Salamanca and Zamora in the same Castilla-León region, Carabias-Martínez et al. (2000 and 2003) studied the pollution due to currently used herbicides (ureas, triazines, amides) in the Guareña and Almar River basins. The main crops in the area are cereals followed by sunflower. Hildebrandt et al. (2007 and 2008) investigated the impact of atrazines, anilides and organosphosphorous herbicides in the aquifers of the Duero (in Castilla León region), the Ebro (in la Rioja, Navarra, Aragón and Catalonia regions) and the Miño (in Galicia region) River basins (Fig. 1), where there are extensive areas of vineyards even though corn crops dominate. Finally, Arráez-Román et al. (2004) found carbamate insecticides used for agriculture in greenhouses in Almería (Andalucía region, SE Spain). The occurrence of pesticides has been recently studied in the Canary Islands (Gran Canaria) by Estévez et al. (2012). They screened the occurrence of several pesticides, including atrazines, organophosphorous insecticides, ureas and anilides, among others, in groundwater used for both irrigation and water supply purposes. In the same line, Bono-Blay et al. (2012) evaluated the presence of pesticides on groundwater intended for bottling.

The study of Belmonte Vega et al. (2005) has not been included in this review because they analysed different compounds in both groundwater and surface bodies but results did not differentiate between matrices.

3.1.2. Concentrations and spatial distribution

In the aforementioned studies performed across Spain, the most ubiquitous compounds were: the triazine herbicides atrazine, simazine, the atrazine transformation product desethylatrazine (DEA), terbuthylazine (TBA) and terbutryn, the phenylureas isoproturon and diuron and the anilide alachlor (Fig. 2). The maximum individual concentrations have been observed for the anilides alachlor (9.95 μg/L) and metolachlor (5.37 μg/L), malathion (3.5 μg/L), atrazine (3.45 μg/L), chlorfenvinphos (2.5 μg/L), dimethoate (2.3 μg/L), DEA (1.98 μg/L), chlortoluron (1.7 μg/L), simazine (1.69 μg/L); parathion-methyl (1.5 μg/L), TBA (1.27 μg/L) and linuron (1.01 μg/L). Many others, such as prometryn, the atrazine transformation product desisopropylatrazine (DIA), azinphos-ethyl, chlorpyrifos, fenitrothion and tributyl phosphate presented concentrations higher than 0.5 μg/L. Consequently, the environmental quality standard of 0.1 μg/L set for individual pesticides in groundwater by the EU directive 2006/118/EC was surpassed in several cases. The studies carried out in groundwater bodies from Catalonia showed high concentrations for some of these pesticides. Garrido et al. (2000) found high concentrations (exceeding 0.1 μg/L) of organophosphorous (malathion, parathion-methyl, fenitrothion, chlorfenvinphos, diazinon and dimethoate) and triazines (atrazine, prometryn and simazine) in groundwater samples collected from Catalonia between 1997 and 1998. Fenitrothion, diazinon and dimethoate, were found at lower concentrations 10 years later but atrazine and simanize, were found at similar concentrations (Postigo et al., 2010). This might indicate that: (1) organophosphorous insecticides are currently less applied but atrazine is still used despite being banned in the European Union in 2007 (Köck-Schulmeyer et al., 2012) or (2) atrazine is more persistent than organophosphorous insecticides in the aquifer. Postigo et al. (2010) also reported considerably high concentrations of the ureas linuron, diuron and chlortoluron. It is important to mention that the triazines atrazine, simazine and TBA presented decreasing concentrations over time in groundwater of the River Llobregat. As an example, atrazine concentrations in groundwater samples collected near the Sant Joan Despí waterworks were 0.025 μg/L in 2000, from 0.007 μg/L to 0.014 μg/L in 2002 and, 0.0023 μg/L in 2003. In the Ebro River catchment (NE-Spain), pesticide concentrations in groundwater were much higher than in the River Llobregat area but triazines also decreased in concentration over time. Hildebrandt et al. (2007 and 2008) reported high concentrations of some triazines in groundwater (1.42 μg/L, 1.25 μg/L, 0.79 μg/L and 0.54 μg/L for atrazine, DEA, DIA and simazine, respectively) and metolachor (0.26 μg/L) from samples collected in 2000–2001. However, in 2004 triazines concentrations decreased dramatically while metolachlor presented higher

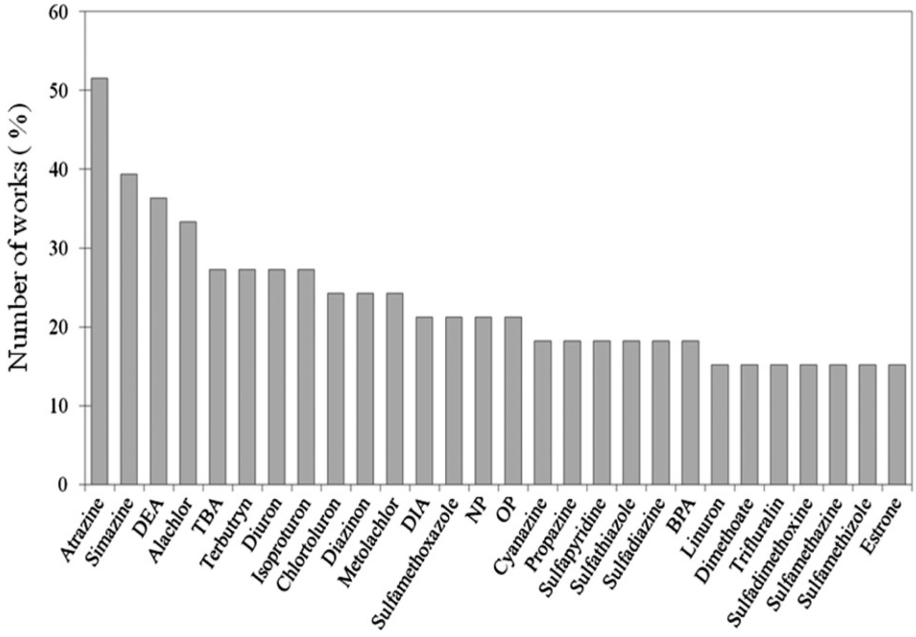

Fig. 2. Most studied EOCs in the groundwater of Spain (%). The number of studies (n) performed was 33 and pesticides are by far the most reported compounds, followed by industrial compounds, PhACs and estrogens. Note that the represented compounds are reported in n ≥ 5 (15%).

concentrations with a maximum concentration of 5.37 μg/L. The latter was detected at very low concentrations (0.0033 μg/L) in the River Llobregat area (Kampioti et al., 2005). In central Spain (Castilla León region), triazine concentrations did not display a clear trend. Sánchez-Camazano et al. (2005) evaluated the inputs of atrazine in groundwater in 1997–1998 and reported concentrations from 0.04 μg/L to 3.45 μg/L while, in the same period, Carabias-Martínez et al. (2000) found lower concentrations, ranging from 0.02 to 0.22 μg/L in 1998 and 0.16 μg/L in 1999 but found high concentrations of chlortoluron (0.4 to 1.7 μg/L). One year later (2000–2001), atrazine concentrations increased significantly, varying from 0.76 to 1.67 μg/L. These observations are related to the land use. High concentrations of atrazine were reported when corn was the main crop whereas high concentrations of chlortoluron were found when other cereal crops dominate. In the NW of Spain (the River Miño basin) only high concentrations of DEA and metalaxil were reported. In contrast, Canary Islands presented very low values of triazines (<0.01 μg/L) and only chlorpyrifos-ethyl exceeded 0.1 μg/L (up to 0.29 μg/L). Another group of pesticides found in groundwater in the South of Spain are carbamates but concentrations reported were always below the prescribed concentration established for individual pesticides in groundwater by the Directive 2006/118/EC.

To sum up, a wide range of pesticides has been studied in the groundwater of Spain over the last 10 years. The most studied pesticides have been triazines (atrazine > simazine > DEA > TBA = terbutryn > DIA) followed by phenyl urea herbicides (diuron = isoproturon > chlortoluron > linuron), anilides (alachlor > methachlor) and organophosphorous herbicides (diazinon > dimethoate). Out of the 80 pesticides that have been studied, 61 were reported in less than four studies and 30 were not detected in any groundwater sample (see Table S1).

3.2. Pharmaceuticals

The PhACs found in groundwater have been divided in the following therapeutic groups: analgesic and anti-inflammatories, lipid regulators and cholesterol lowering statin drugs, psychiatric drugs, histamine receptor antagonists, tetracyclines, macrolides, fluoroquinolines, β-lactams, sulfonamides and other antibiotics, β-blockers, β and α agonist, barbiturates, diuretics, antidiabetics, anti-cancer, cardiac agents, contrast media agents, angiotestin agents, antifungals, dyspepsia drugs, anaesthetics, anthelmintics and antiseptics (see Table S1).

3.2.1. Studies

Sulfonamide antibiotics (SAs) and their degradation products have been the most frequently reported group of PhACs in groundwater from Catalonia (Díaz-Cruz et al., 2008; García-Galán et al., 2010b, 2010c and 2011), mainly in rural areas but also in urban areas. Radjenovic et al. (2008) studied pharmaceuticals detected in the groundwater of the River Besòs aquifers (NE Spain) which are used as inflow to a drinking water treatment plant. The compounds analysed were analgesics and anti-inflammatory drugs such as ketoprofen, diclofenac, acetaminophen, mefenamic acid and propyphenazone, β-blockers such as sotalol and metoprolol, the antiepileptic drug carbamazepine, the antibiotic sulfamethoxazole, the lipid regulator gemfibrozil, the diuretic hydrochlorothiazide and the antidiabetic glibenclamide. Similarly, Huerta-Fontela et al. (2011) studied the occurrence of 48 PhACs in the raw water intended for drinking water production in the Llobregat area (South of Barcelona city), where groundwater is combined with treated surface water to improve the quality of the finished water. Jurado et al. (2012) studied the psychiatric drugs alprazolam, lorazepam and diazepam in the aquifers of the Besòs River Delta and Barcelona Plain. Finally, Teijon et al. (2010) and Estévez et al. (2012) investigated the occurrence of a wide variety of PhACs (around 80 in both studies) in groundwater from the area of Llobregat and from the Canary Islands, respectively, including analgesics and anti-inflamatories, psychiatric drugs and SAs, among others (Table S1).

3.2.2. Concentrations and spatial distribution

In general, PhACs have been detected in lower concentrations than pesticides. Out of 161 PhACs investigated, 84 have never been detected (see Table S1). The most studied compounds (n ≥ 4) have been in descending order sulfamethaxole > sulfapyridine = sulfadiazine = sulfathiazole > sulfadimethoxine = sulfamethizole = sulfamethazine > sulfamethoxypyridazine = sulfisoxazole = sulfamerazine = N4-acetylsulfamethazine = carbamazepine. The maximum individual concentrations have been for sulfacetamide (3461 ng/L), hydrochlorothiazide (2548 ng/L), sulfamerazine (744.7 ng/L), iopromide (687 ng/L), gemfibrozil (574 ng/L), sulfanitran (568.8 ng/L), diclofenac (477 ng/L) and sulfamethazine (446 ng/L). Several compounds such as iopamidol, codeine, ibuprofen, ketoprofen, mepivacaine, naproxen, propyphenazone, carbamazepine, nifuroxazide, furosemide, sulfamethoxazole, sulfapyridine, sulfaquinoxaline, benzalkonium chloride, N-acetyl-4-amino-antipiryne (4-AAA), N-formyl-4-amino-antipiryne (4-FAA), venlafaxime and atenolol have also been detected at concentrations above the reference threshold of 100 ng/L. We have chosen this reference threshold because it is the quality standard set for individual pesticides in groundwater by the EU directive 2006/118/EC.

As commented before, SAs have been widely studied in Catalonian aquifers over the last five years. The occurrence of some of these compounds seems to follow similar pattern. Sulfadimethoxine, sulfamethazine and sulfamethoxazole were repeatedly present in groundwater. In contrast, sulfamethiazole was infrequently detected. Livestock waste in rural areas could contribute to the occurrence of sulfadimethoxine and sulfamethazine because these two SAs are generally used in veterinary practices. In contrast, sulfamethoxazole, which is mainly used in humans, was found more often than expected in groundwater from rural areas (García-Galán et al., 2010c) and presented the highest concentrations and detection frequencies in urban aquifers (Díaz-Cruz et al., 2008; García-Galán et al., 2010c). Sulfamethoxazole was also present in groundwater samples from the Llobregat River Delta area. Its high occurrence could be attributed to contamination from both point sources (WWTP discharges into the rivers) and a diffuse source (losses from sewage systems) in densely populated areas. Apart from SAs, X-ray contrast media (iopamidol and iopromide), psychiatric drugs (carbamazepine, phenytoin and velafaxine), cardiac agents (hydrochlorothiazide and diltiazem), analgesics (4-AAA, 4-FAA, ibuprofen, codeine and diclofenac), fluoroquinolone antibiotics (ofloxacyn), β-blockers(acebutolol, atenolol, metoprolol, propanol and sotalol), angiotensin agents (irbesartan and valsartan) and antihistaminics (salbutamol) were also detected in groundwater of the Llobregat area (Boleda et al., 2009; Teijon et al., 2010; Huerta-Fontela et al., 2011). Comparatively, fewer compounds were detected in the Besòs aquifers (North of Barcelona city), including analgesics (acetaminophen, ketoprofen, propyphenazone, mefenamic acid and diclofenac), cholesterol lowering statin drugs (gemfibrozil), psychiatric drug (carbamazepine), β-blockers (metoprolol and sotalol) and antidiabetics (glibenclamide) (Radjenovic et al., 2008).

3.3. Industrial compounds

This category includes surfactants such as alkylphenol polyethoxylates (APEOs), which are used in a variety of industrial and domestic products (cleaning products, degreasers and detergents) and bisphenol A (BPA) and phthalates, mainly used to make plastics.

3.3.1. Studies

These compounds have been detected in rural groundwater as a result of agronomic practices and also in urban aquifers. Lacorte et al.

(2002) and Latorre et al. (2003) reported the presence of the APEOs degradation products (DPs) nonylphenol (NP) and octylphenol (OP) and of BPA in agricultural areas of Catalonia. These agricultural areas are located near large cities with heavy industrial activity. At Sant Joan Despí waterworks, located in the Llobregat River area (South of Barcelona), López-Roldán et al. (2004) studied the presence of the di (2-ethylhexyl) phthalate (DEHP), NP, OP and phenols such as 2,4 dichlorophenol, 4-chloro-3-mehylphenol, 4-chloro-2-methylphenol and 4-tert-butylphenol in groundwater. In the same area, BPA was monitored by Rodriguez-Mozaz et al. (2004a). Tubau et al. (2010) investigated the occurrence of surfactants, including linear alkylbenzene sulfonates (LAS) and APEOs DPs in Barcelona's urban groundwater. Sánchez-Avila et al. (2009) found that groundwater from the Maresme area (North of Barcelona) was contaminated by the phthalate dimethyl phthalate (DMP), the APEO DP nonylphenol monoethoxylate (NP_1EO) and BPA due to a wastewater leak. In the rest of Spain, there was little research about the industrial compounds. Bono-Blay et al. (2012) presented a study that evaluated the presence of phthalates, alkylphenols and BPA in groundwater resources intended for bottling and Hildebrandt et al. (2007) evaluated the presence of BPA, NP and OP in agricultural areas of the Ebro Basin.

3.3.2. Concentrations and spatial distribution

In general, industrial compounds have seldom been studied in groundwater samples. The most studied compounds have been NP, OP and BPA. The highest maximum individual concentrations have been observed for nonylphenol dicarboxylate (NP_2EC, 11.24 μg/L), DEHP (5.67 μg/L), NP (5.28 μg/L), LAS (5.06 μg/L), nonylphenol monocarboxylate (NP_1EC, 2.46 μg/L), OP (1.8 μg/L), BPA (1.5 μg/L) and diethyl phthalate (DEP, 1.12 μg/L). The maximum concentrations of APEOs DPs and LAS have been found in the aquifers of Barcelona, which reflects not only the industrial part of the city, but also a high sampling density. In this area, LAS are the surfactants most used at present and APEOs, which were banned in the 1990s, have also been detected in WWTPs (González et al., 2004) and in the River Besòs (Tubau et al., 2010). In the Maresme area (North of Barcelona), only NP_1EO (0.45 μg/L) was detected whereas NP and OP were not detected (Sánchez-Avila et al., 2009). Among the 6 phthalates analysed only DMP was detected and BPA was found at concentrations of 0.12 μg/L and 0.78 μg/L, respectively. In Llobregat River Delta aquifers, NP and OP were detected at considerably high concentrations (1.61 μg/L and 0.37 μg/L, respectively), but the highest concentration corresponded to the phthalate DEHP (5.67 μg/L). In contrast, BPA was detected at very low concentrations in Llobregat groundwater (0.007 μg/L). Groundwater of the Ebro River basin was free of BPA and NP and OP was detected at low concentrations (0.15 μg/L) (Hildebrandt et al., 2007).

3.4. Drugs of abuse

DAs include a long list of chemicals that are used with non-therapeutic purposes.

3.4.1. Studies

Little research is available about the presence of DAs and their metabolites in groundwater. DAs have been studied in a well used for pumping at a Spanish drinking water treatment plant (DWTP) located in NE Spain (Boleda et al., 2009; Huerta-Fontela et al., 2008). The first comprehensive study that has specifically addressed the contamination of aquifers by DAs was developed in the Barcelona aquifers by Jurado et al. (2012). DAs have also been reported in the aquifers of Canary Islands (Estévez et al., 2012).

3.4.2. Concentrations and distribution

Thirteen of the 23 DAs analysed in groundwater have not been detected either in Barcelona or in Canary the Islands (see Table S1). Cannabidiol and ethylamphetamine were detected at the Canary Islands aquifer but the frequency of detection and the concentrations of the DAs measured were not specified, so the following results are based on Barcelona studies. Only trace concentrations of methadone (0.5 ng/L) and EDDP (2.3 ng/L) were reported in the River Llobregat aquifers (Boleda et al., 2009). In Barcelona urban groundwater, the most frequently detected DAs were methadone (86%) and ecstasy (or MDMA) (64%). The highest values of concentrations corresponded to methadone (68.3 ng/L), cocaine (60.2 ng/L) and MDMA (36.8 ng/L). The largest number of detected DAs (opiods, cocaininc compounds and amphetamines) was found in a zone recharged by the River Besòs, which receives large amounts of effluents from WWTPs (total concentrations of 200 ng/L in some sampling points). Whereas, the urbanised areas presented fewer DAs and at lower concentrations. It is interesting to note that identified DAs correlate with social class. Jurado et al. (2012) found cheap DAs (e.g. ecstasy) in groundwater from working class quarters, whereas cocaine was found in the groundwater of more affluent neighbourhoods.

3.5. Life-style compounds

A few studies reported the presence of nicotine and its metabolite cotininine and caffeine and its metabolites methylxanthine, paraxanthine, theophylline and theobromine and also caffeine c13. They were studied in Llobregat delta area (Huerta-Fontela et al., 2008; Teijon et al., 2010) and in Canary Islands (Estévez et al., 2012). Caffeine and Nicotine were frequently detected in aquifers of Gran Canaria (both 100%) and also in Llobregat River Delta (77.4% and 71.7%, respectively). However, in the same area, neither nicotine nor caffeine was detected in groundwater intended to improve raw water quality in a DWTP. Other compounds detected, at lower percentages, were theobromine and theophylline (50% each in Canary Islands) and paraxanthine (6% in Llobregat area). Neither caffeine c13 nor methylxanthine and cotinine were detected in groundwater. The maximum concentrations were for caffeine (505.5 ng/L), theobromine (252.5 ng/L), paraxanthine (147 ng/L) and nicotine (144 ng/L).

3.6. Estrogens and related compounds

Estrogens are a group of steroid compounds named for their importance in the estrous cycle and function as the primary female sex hormone. Some of the studies related to estrogens were developed in the River Llobregat aquifers in the municipality of Sant Joan Despí (Rodriguez-Mozaz et al., 2004a and 2004b; Farré et al., 2010; Huerta-Fontela et al., 2011). Farré et al. (2010) have also studied 3 isoflavones. Regarding the rest of Spain, only Estévez et al. (2012) studied the presence of the estrone in groundwater. The most studied compounds were the three major naturally occurring estrogens estrone (E1), estradiol (E2) and estriol (E3) and the synthetic estrogen Ethynyl Estradiol (EE). However, none of the compounds reported in the aforementioned studies were detected in the groundwater samples.

3.7. Personal care products

Personal care products are mainly used for beautification and in personal hygiene. These compounds were only reported by Teijon et al. (2010) in the groundwater of the Llobregat aquifers where polycyclic musks (galaxolide and tonalide), sunscreens (ethylhexyl methoxycinnamate), bacteriocide and antifungal agents (triclosan), among other compounds were found (see Table S1). Only 3 of them were reported in groundwater at significantly high detection frequencies. The most detected was galaxolide (98%), followed by the antioxidant BHT (92.3%), and the sunscreen ethylhexyl methoxycinnamate (50%). The maximum concentrations were for BHT and galaxolide, 455 ng/L and 359 ng/L, respectively.

4. Assessment of the fate of EOCs in Spanish aquifers

Many EOCs have been found in Spanish groundwater at concentrations higher than 100 ng/L (Fig. 3), highlighting the need to understand their fate in aquifers. The fate of EOCs in groundwater depends both on the physico-chemical properties of the contaminant and on the aquifer, notably the redox potential. The former tends to control mobility, the latter degradability (Christensen et al., 2001; Barbieri et al., 2011).

4.1. Physico-chemical properties of EOCs

Among contaminants properties, the octanol–water partition coefficient (K_{ow}) and the water solubility (S_w) are valuable parameters. The octanol–water partition coefficient is usually expressed as log K_{ow}. It measures how hydrophilic (log $K_{ow}<4$) or hydrophobic (log $K_{ow}>4$) an EOC is. Hydrophobic EOCs tend to bioaccumulate and usually have a high adsorption capacity especially onto organic matter (Choi et al., 2005; Jones-Lepp and Stevens, 2007). Conversely, EOCs with low log K_{ow} values tend to have high S_w and both lower bioaccumulation potential and soil/sediment adsorption coefficients (Silva et al., 2012). However, care must be taken because log K_{ow} does not always correlate with adsorption capacity onto mineral sediments (de Ridder et al., 2010).

Concerning pesticides, another relevant parameter used in many studies (Hildebrandt et al., 2007; Postigo et al., 2010; Bono-Blay et al., 2012; Köck-Schulmeyer et al., 2012) is the Groundwater Ubiquity Score (GUS) index (Gustafson, 1993). The GUS index is used to assess the leachability capacity of a pesticide indicating its intrinsic mobility. If GUS is higher than 2.8, the pesticide will likely be a “leacher”. If GUS is less than 1.8, the pesticide will be a “non-leacher”. Table 2 summarises the GUS index for pesticides and the physico-chemical properties (log K_{ow} and S_w) of most of the EOCs plotted in Fig. 2. Note that some PhACs, DAs, industrial compounds and life-style compounds ($n\geq3$) are also included (Table 2). The pesticides' profile is dominated by the presence of triazines. Despite being fairly hydrophobic some of them were widely detected in groundwater samples (e.g. 80%, 64%, 56% and 56% for simazine, atrazine, DEA and diuron, respectively in the study developed by Köck-Schulmeyer et al. (2012) and 89% and 87% for alachor and atrazine in the study performed by Sánchez-Camazano et al. (2005)). In contrast, the other triazines, phenylureas, organophosphorous and anilide pesticides were less frequent or not detected at all. For instance, cyanazine and fenitrothion were detected in less than 5% of the samples (Postigo et al., 2010).

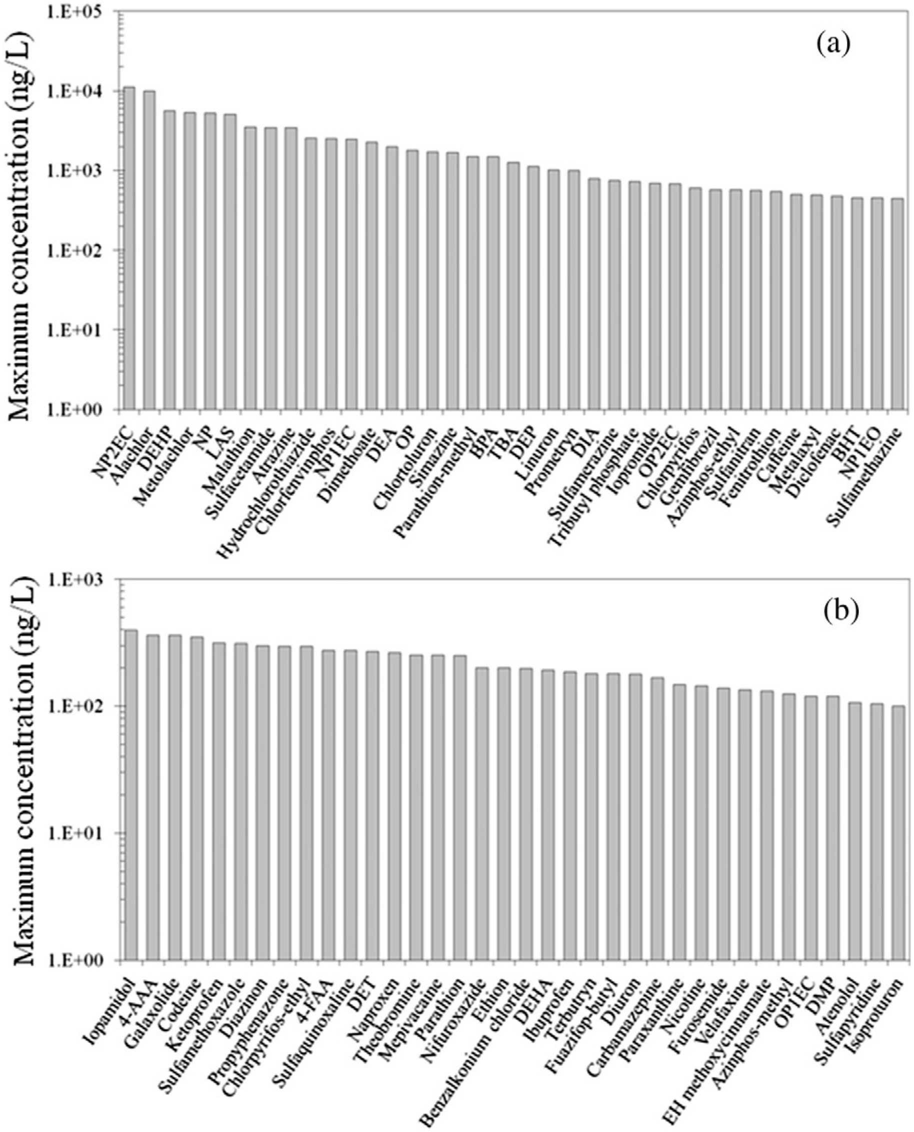

Fig. 3. Maximum EOCs concentrations in the groundwater of Spain (ng/L). (a) Concentrations are higher than 400 ng/L and (b) Concentrations range from 100 ng/L to 400 ng/L.

Table 2
Physicochemical properties and CAS number of the most reported EOCs. Values of water solubility (S_w) and log K_{ow} were extracted from SRC Inc. (2011).

Group of EOCs	Class	Compound	n	CAS	log K_{ow}	S_w (mg/L)	GUS[a]
Pesticides	Triazines	Atrazine	17	1912-24-9	2.61	34.7	3.75
		Simazine	13	122-34-9	2.18	6.2	3.35
		DEA	12	6190-65-4	1.51	3,200	3.54
		TBA	9	5915-41-3	3.21	8.5	3.07
		Terbutryn	9	886-50-0	3.74	25	
		DIA	7	1007-28-9	1.15	670	
		Cyanazine	6	21725-46-2	2.22	170	2.07
		Propazine	6	139-40-2	2.93	8.6	
	Ureas	Diuron	9	330-54-1	2.68	42	1.83
		Isoproturon	9	34123-59-6	2.87	65	2.07
		Chlortoluron	8	15545-48-9	2.41	70	2.79
		Linuron	5	330-55-2	3.2	75	2.03
	Organophosphorous	Diazinon	8	333-41-5	3.81	40	1.14
		Dimethoate	5	60-51-5	0.78	25,000	1.05
		Chlorfenvinphos	4	470-90-6	3.81	124	
		Fenitrothion	4	122-14-5	3.3	38	0.64
	Dinitroanilines	Trifluralin	5	1582-09-8	5.34	0.184	
	Anilides	Alachlor	11	15972-60-8	3.52	240	2.19
		Metolachlor	8	51218-45-2	3.13	530	3.32
PhACs	SAs	Sulfamethoxazole	7	723-46-6	0.89	610	
		Sulfapyridine	6	0144-83-2	0.35	268	
		Sulfathiazole	6	72-14-0	0.05	373	
		Sulfadiazine	6	68-35-9	−0.09	77	
		Sulfadimethoxine	5	122-11-2	1.63	343	
		Sulfamethazine	5	57-68-1	0.89	1,500	
		Sulfamethizole	5	144-82-1	0.54	1,050	
		Sulfamerazine	4	127-79-7	0.14	202	
		Sulfamethoxypyridazine	4	080-35-3	0.32	147	
		Sulfisoxazole	4	127-69-5	1.01	300	
		N4-acetylsulfamethazine	4	100-90-3	1.58	1,150	
	Psychiatric drugs	Carbamazepine	4	298-46-4	2.45	17.7	
		Diazepam	3	439-14-5	2.82	50	
	Lipid regulators	Gemfibrozil	3	25812-30-0	4.77	10.9	
	Cardiac agents	Hydrochlorothiazide	3	58-93-5	−0.07	722	
	Analgesics	Acetaminophen	3	103-90-2	0.46	14,000	
		Codeine	3	76-57-3	1.19	9,000	
		Ketoprofen	3	22071-15-4	3.12	51	
		Mefenamic acid	3	61-68-7	5.12	20	
		Propyphenazone	3	479-92-5	1.94	3 E+06	
	β-blockers	Atenolol	3	29122-68-7	0.16	13,300	
		Metoprolol	3	37350-58-6	1.88	16,900	
		Propranolol	3	525-66-6	3.48	61.7	
		Sotalol	3	3930-20-9	0.24	5,510	
		Salbutamol	3	18559-94-9	0.64	14,100	
Industrial compounds	Surfactants	NP	7	84852-15-3	5.92	5,000	
		OP	7	140-66-9	5.28	5	
	Phenols	BPA	6	80-05-7	3.32	120	
	Phthalates	DEHP	3	117-81-7	7.6	0.27	
DAs	Opioids	Methadone	4	76-99-3	3.93	48.5	
		Heroin	3	561-27-3	1.58	600	
		Morphine	3	57-27-2	0.89	149	
	Cocainic compounds	Cocaine	3	50-36-2	2.3	1,800	
		Benzoylecgonine	3	519-09-5	−1.32	88,300	
	Cannabinoids	THC	3	1972-08-3	7.6	2,800	
	Amphetamines	Amphetamine	3	300-62-9	1.76	28,000	
Estrogens		Estrone	5	53-16-7	3.13	30	
		Estriol	4	50-27-1	2.45	441	
		Ethinyl Estradiol	4	057-63-6	3.67	11.3	
Estrogens		Estradiol	3	50-28-2	4.01	3.6	
		Caffeine	3	058-08-2	−0.07	21,600	
Life-style compounds		Nicotine	3	054-11-5	1.17	1 E+06	

[a] Köck-Schulmeyer et al. (2012).

Linuron, chlortoluron and dimethoate were not detected in groundwater samples from the Llobregat area (Kampioti et al., 2005). These frequencies of detection are more in accordance with the GUS index than the physico-chemical properties of the pesticides. Most of the frequently detected compounds (mainly triazines) have GUS indexes higher than 3. Conversely, fenitrothion, dimethoate and cyanazine are non-leacher pesticides (GUS index$<$1.8, Table 2).

With regards to PhACs and DAs, few compounds are expected to present hydrophobic behaviour (log $K_{ow}>4$ and low solubility). These compounds are the β-blocker propanolol, the analgesics ketoprofen and mefenamic acid, the lipid regulator gembifrozil and the cannabinoid THC. The remaining PhACs and DAs, according to their physico-chemical properties (Table 2), should present more hydrophilic behaviour being more frequently detected in the aquatic environment. In fact, some PhACs and in particular carbamazepine, have been qualified as suitable markers for anthropogenic influence in the aquatic environment (Clara et al., 2004; Müller et al., 2012) since it is highly recalcitrant towards elimination in water/sediment (Löffler et al., 2005).

Industrial compounds (NP, OP and DEHP) as well as both natural and synthetic estrogens have moderately low S_w and high log K_{ow}

values and hence can be considered moderately hydrophobic compounds (Table 2). Estrogens have also been found to sorb in aquifer sediments. According to Ying et al. (2003) their soil sorption coefficients, expressed as log K_{oc}, range from 3.3 to 3.7. Therefore, it is not surprising that they have not been detected in groundwater in Spain. Finally, caffeine and nicotine showed hydrophilic behaviour with considerably high water solubility (Table 2).

4.2. Transformation and degradation processes

The concentration of EOCs in aquifers is affected by numerous processes, including concentration at the source, dilution, adsorption and degradation. Most studies are motivated by testing of pollution hypotheses. Therefore, they provide a biased picture of the actual state of groundwater bodies. In addition to the tendency to sorb onto both organic and inorganic solids, many EOCs are removed from water by transformation (e.g. Barbieri et al., 2012) or degradation, especially if the water has undergone a broad range of redox states (e.g. Christensen et al., 2001; Barbieri et al., 2011). This, together the long residence time of water in aquifers, suggests that the most EOCs will tend to disappear. Unfortunately most studies do not reflect the redox state of water or its age. Old groundwaters are indeed free of EOCs (e.g. Teijon et al., 2010), but this may reflect that EOCs had not been in use at the time of recharge. It is therefore clear that (1) EOCs analyses should be associated to groundwater studies in order to understand the representatively of observations, and (2) further research on degradation and transformation processes is needed to assess the long term fate of EOCs in groundwater.

4.3. River-groundwater interaction

Rivers are usually heavily polluted because of the effluents of WWTPs, industries and agriculture runoff. Understanding the interactions between groundwater and surface water is a key issue to assess the fate of EOCs in the aquifers, especially in heavily pumped aquifers, where rivers are the main source of groundwater recharge. This is certainly the case at the River Llobregat (Vàzquez-Suñé et al., 2007b). There are some studies where the concentrations of some EOCs in the river (Llobregat and Besòs) can be compared with those of the aquifers (Quintana et al., 2001; López-Roldán et al., 2004; Rodriguez-Mozaz et al., 2004a; Kampioti et al., 2005; Tubau et al., 2010; Huerta-Fontela et al., 2011; Jurado et al., 2012). In general, the concentrations in the surface waters were higher than in the aquifers accounting for a wide array of pesticides, PhACs, DAs and selected industrial compounds (Fig. 4). These should indicate natural attenuation capacity in the aquifer due to physical processes, such as sorption and dilution and biochemical processes. However, some compounds presented higher maximum concentration in the aquifer, such as the pesticides simazine, isoproturon, metolachlor, DEA, propanil, cyanazine, TBA and molinate, the industrial compounds NP, OP, NP_2EC and DEHP and the DAs methadone (METH) and ecstasy (MDMA). Note that none of the PhACs presented higher concentration in the aquifer than in the river. This fact suggests that further research is needed to understand the behaviour of the EOCs in the aquifers.

5. Spain–European groundwater EOCs concentrations

It is not easy to establish criteria to compare the occurrence of EOCs in Spanish groundwater with the rest of European groundwater. There are several studies concerning EOCs all over Europe but each of them have analysed different compounds. We decided to establish a comparison of the maximum concentrations detected and taking into account the most recent works performed in European countries. We used the study performed by Loos et al. (2010) to compare the maximum concentrations of EOCs because it is the unique representative work that has monitored polar organic pollutants in European groundwater. In total, 59 selected organic compounds (PhAcs, pesticides, steroids, life-style compounds and industrial compounds) were analysed in 164 samples from 23 European countries. Out of the 59 organic compounds analysed in their survey, 33 have been included in this review. The maximum concentrations detected in the groundwater of Spain and in the Pan-European survey for selected pesticides, PhACs, industrial compounds and life-style compounds are plotted in Fig. 5. In general, Spanish groundwater presents higher maximum concentrations than the Pan-European groundwater survey. The highest concentrations detected in the European survey were for NP_1EC (11,316 ng/L), bentazone (10,550 ng/L), NP (3850 ng/L), ketoprofen (2886 ng/L) and BPA (2299 ng/L). The profile of groundwater contamination seems to be dominated by industrial compounds (the APEOs DPs NP and OP and BPA) because they show high maximum concentrations in Spain and the European countries' aquifers. Pesticides

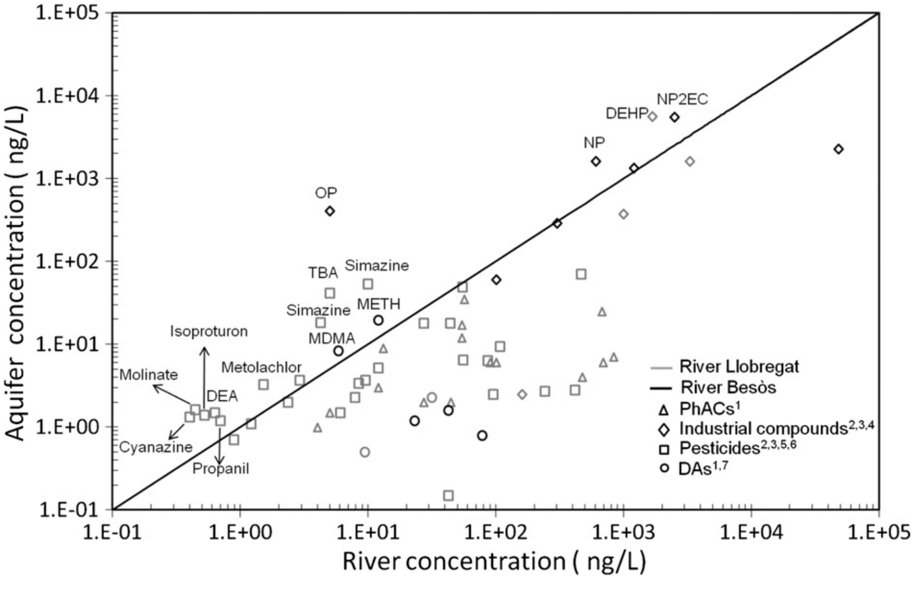

Fig. 4. Measured concentrations of some EOCs in the Rivers Llobregat (grey) and Besòs (black) versus the concentrations reported in the aquifers of Barcelona. Note that aquifer concentrations are consistently much lower than surface waters for a wide array of compounds, suggesting the natural attenuation capacity of the aquifer. [1] Boleda et al. (2009), [2] López-Roldán et al. (2004),[3] Rodriguez-Mozaz et al. (2004a),[4] Tubau et al. (2010), [5] Quintana et al. (2001), [6] Kampioti et al. (2005) and [7]Jurado et al. (2012).

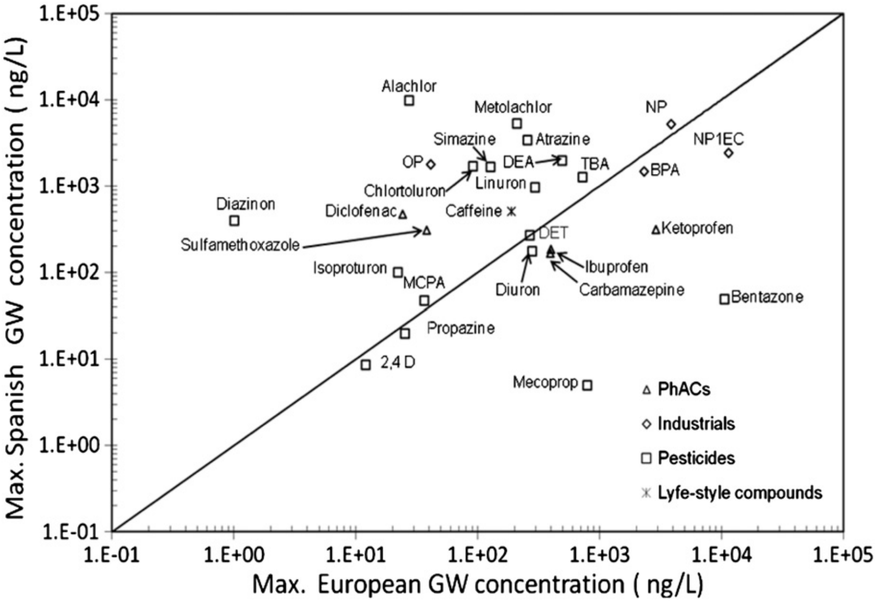

Fig. 5. Maximum concentration of some EOCs in the groundwater (GW) of Spain versus the maximum concentration reported in the study of Loos et al. (2010). The EOCs include PhACs, pesticides, industrial compounds and life-style compounds.

(mainly atrazine and its metabolite DEA, simazine and TBA and its transformation product desethylterbuthylazine (DET)) also contribute to groundwater contamination.

There are some comprehensive monitoring surveys of individual EOCs in Europe. Pesticide compounds have recently been studied in groundwater in Portugal (Silva et al., 2006; Andrade and Stigter, 2009), France (Morvan et al., 2006; Baran et al., 2007), the UK (Lapworth et al., 2006), Italy (Guzzella et al., 2006), Norway (Haarstad and Ludvigsen, 2007) and the Netherlands (ter Laak et al., 2012). The presence of PhACs in European groundwater has been reported in Germany (Osenbrück et al., 2007; Ternes et al., 2007; Strauch et al., 2008; Reinstorf et al., 2008; Wolf et al., 2012), France (Rabiet et al., 2006; Vulliet and Cren-Olivé, 2011) and the UK (Stuart et al., 2012). Hormones and industrial compounds have been less studied than pesticides and PhACs. Hormones and industrial compounds have been reported in Austria (Hohenblum et al., 2004) and the latter also in Germany (Osenbrück et al., 2007; Strauch et al., 2008; Reinstorf et al., 2008) and the UK (Stuart et al., 2012; Lapworth et al., 2012). Personal care products and life-style compounds have been reported in Germany (Osenbrück et al., 2007; Ternes et al., 2007; Strauch et al., 2008; Reinstorf et al., 2008) and the UK (Stuart et al., 2012; Lapworth et al., 2012). The life-style compound caffeine has also been found in France (Rabiet et al., 2006). DAs, to the author's knowledge, have only been studied in the aquifers of Spain (Boleda et al., 2009; Huerta-Fontela et al., 2008; Estévez et al., 2012; Jurado et al., 2012). A comparison of the maximum concentrations reported in all the aforementioned studies allows us to distinguish between Spain and other European countries. This is shown in Fig. 6 for pesticides (only medium to polar compounds) and in Fig. 7 for the remaining EOCs reviewed. The lowest maximum pesticide concentrations were for mecocrop and molinate (both in Spain, at concentrations of 5 ng/L) whilst the highest maximum concentration were for molinate (Portugal, 59.46 μg/L) and bentazone (Norway, 20 μg/L). It must be noted that the maximum concentrations for most of these pesticides were higher in European than in Spanish groundwater. With regards the remaining EOCs, plotted in Fig. 7, maximum concentrations for PhACs were difficult to compare since the studies carried out in each country addressed different compounds. For instance, carbamazepine has been widely studied in Germany but, in general, studies covering a wide variety of PhACs in European countries are scarce and some of the compounds studied have not been detected in Spanish groundwater. For example, diatrizoate, clofibric acid and fenofibrate have not been reported in any groundwater sample in Spain but they have been measured in German (Wolf et al., 2012) and French groundwater (Vulliet and Cren-Olivé, 2011). Meanwhile, the highest maximum groundwater concentrations for industrial compounds have mainly been detected in Spain. There are two exceptions, nonylphenol diethoxylated (NP_2EO), which has been not detected, and BPA, which highest maximum concentration has been found in the UK (Stuart et al., 2012; Lapworth et al., 2012). The personal care product galaxolide has presented its maximum concentration in Spain (Teijon et al., 2010). As regards to life-style compounds, the highest maximum concentrations of caffeine (4.5 μg/L) and nicotine (8.07 μg/L) have been found in the UK aquifers (Stuart et al., 2012; Lapworth et al., 2012). None of the studied estrogens have been found in Spanish aquifers but some of them have been detected in groundwater from the rest of Europe at low concentrations (up to 10 ng/L).

In summary, it is interesting to note that most EOCs are usually detected at low ng/L concentrations or not detected at all in groundwater throughout Europe. While an increasing number of individual compounds are found at μg/L concentrations.

6. Conclusions

This work has reviewed the occurrence of various EOCs reported in Spain's groundwater. These include pesticides, PhACs, industrial compounds, DAs, estrogens, life-style compounds and personal care products. The major point source of pollution of these EOCs in groundwater corresponded to the effluents of WWTPs, which is largely a consequence of the motivation of the studies. The contamination profile seems to be dominated by industrial compounds, followed by pesticides and PhACs. The most relevant compounds contributing to Spanish groundwater contamination with individual concentration higher than 1000 ng/L are, in descending order, NP_2EC, alachlor, DEHP, metolachlor, NP, LAS, malathion, sulfacetamide, atrazine, hydrochlorothiazide, chlorfenvinphos, NP_1EC, dimethoate, DEA, OP, chlortoluron, simazine, parathion-methyl, BPA, TBA, DEP and linuron. Moreover, another 53 EOCs have been reported at concentrations between 100 and 1000 ng/L. Nevertheless, it is important to mention that compared to surface water bodies, such as rivers,

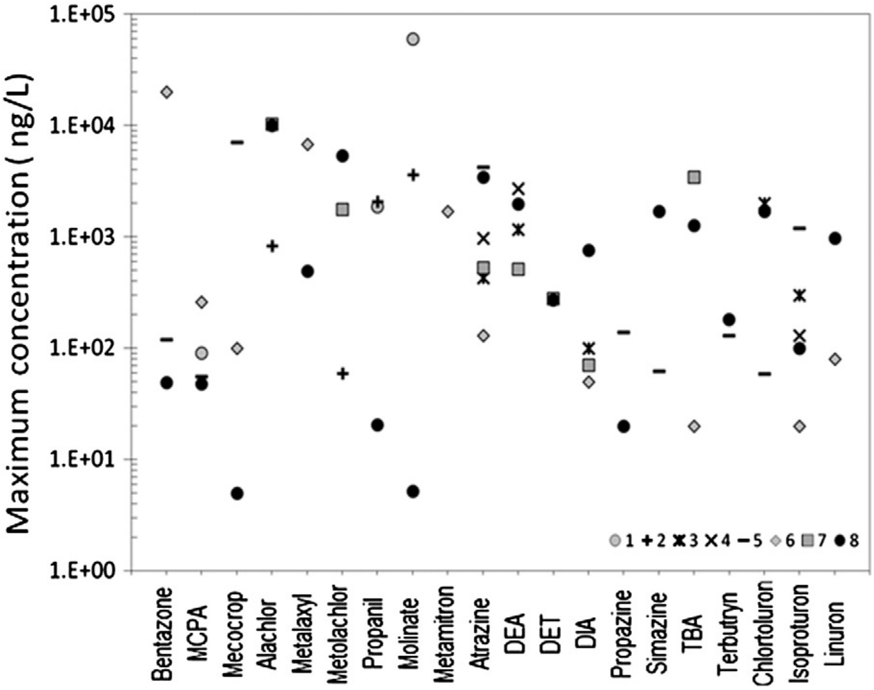

Fig. 6. Maximum Spanish groundwater concentrations versus maximum European groundwater concentrations for some pesticides. References: [1]Silva et al. (2006),[2] Andrade and Stigter (2009),[3] Morvan et al. (2006),[4] Baran et al. (2007),[5] Lapworth et al. (2006),[6] Haarstad and Ludvigsen (2007) and [7] Guzzella et al. (2006). Note that black dots (8) are the maximum Spanish groundwater concentrations of pesticides summarised in Table S1.

groundwater is considerably less contaminated, indicating the natural attenuation capacity of the aquifers. However, some EOCs, namely, simazine, TBA, isoproturon, metolachlor, DEA, propanil, cyanazine, molinate, OP, NP, NP_2EC, DEHP, methadone and ecstasy, have sometimes been detected at higher concentrations in the aquifer than in the corresponding river. This might reflect the persistence of some organic compounds that were banned long ago, which is the case of industrial surfactants, and indicates the need for further research to understand their behaviour in the aquifers. The presence of some of these EOCs in groundwater from other European countries has also

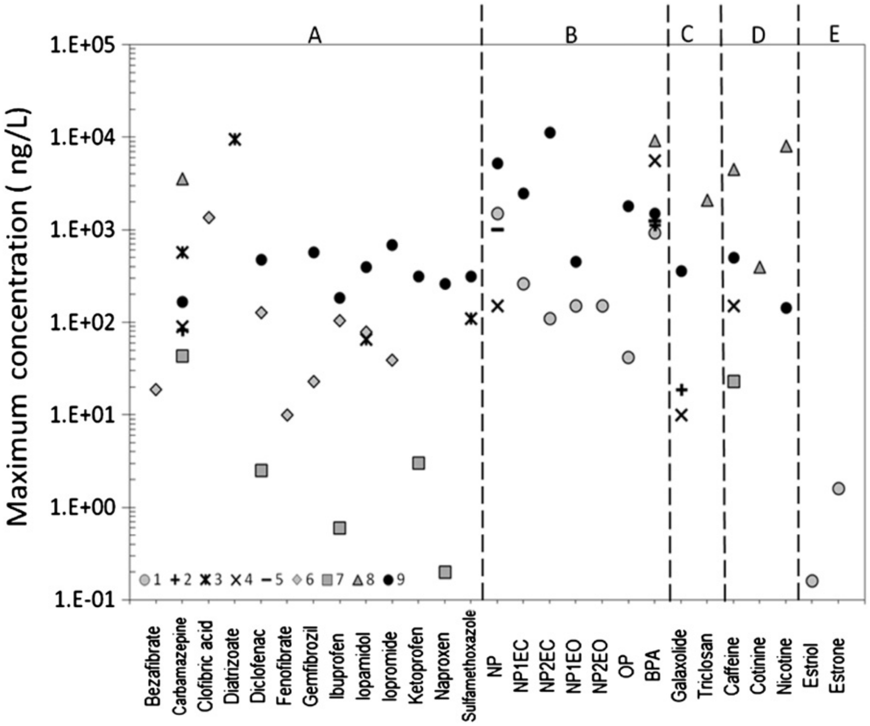

Fig. 7. Maximum Spanish groundwater concentrations versus maximum European groundwater concentrations for (A) PhACs, (B) industrial compounds, (C) personal care products, (D) life-style compounds and (E) estrogens. References: [1] Hohenblum et al. (2004),[2] Osenbrück et al. (2007),[3] Ternes et al. (2007), [4] Strauch et al. (2008),[5] Reinstorf et al. (2008),[6] Wolf et al. (2012),[7] Rabiet et al. (2006) and [8] Stuart et al. (2012). Note that black dots (9) are the maximum Spanish groundwater concentrations of the aforementioned EOCs summarised in Table S1.

been reported with an increasing number showing individual concentration in the μg/L range. Consequently, proper assessment of groundwater quality against deterioration requires the investigation of a wide variety of compounds, of the processes they undergo in groundwater and perhaps the establishment of environmental quality criteria for a large number of contaminants such as PhACs, estrogens, DAs and life-style compounds.

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References

Andrade AIASS, Stigter TY. Multi-method assessment of nitrate and pesticide contamination in shallow alluvial groundwater as a function of hydrogeological setting and land use. Agric Water Manag 2009;96:1751–65.

Arráez-Román D, Segura-Carretero A, Cruces-Blanco C, Fernández-Gutiérrez A. Determination of aldicarb, carbofuran and some of their main metabolites in groundwater by application of micellar electrokinetic capillary chromatography with diode-array detection and solid-phase extraction. Pest Manag Sci 2004;60:675–9.

Baran N, Mouvet C, Negrel P. Hydrodynamic and geochemical constraints on pesticide concentrations in the groundwater of an agricultural catchment (Brevilles, France). Environ Pollut 2007;148:729–38.

Barbieri M, Carrera J, Sanchez-Vila X, Ayora C, Cama J, Kock-Schulmeyer M, et al. Microcosm experiments to control anaerobic redox conditions when studying the fate of organic micropollutants in aquifer material. J Contam Hydrol 2011;126(3–4):330–45. http://dx.doi.org/10.1016/j.jconhyd.2011.09.003.

Barbieri M, Carrera J, Ayora C, Sanchez-Vila X, Licha T, Nodler K, et al. Formation of diclofenac and sulfamethoxazole reversible transformation products in aquifer material under denitrifying conditions: batch experiments. Sci Total Environ 2012;426:256–63. http://dx.doi.org/10.1016/j.scitotenv.2012.02.

Belmonte Vega A, Garrido Frenich A, Martinez Vidal JL. Monitoring of pesticides in agricultural water and soil samples from Andalusia by liquid chromatography coupled to mass spectrometry. Anal Chim Acta 2005;538:117.

Boleda MR, Galceran MT, Ventura F. Monitoring of opiates, cannabinoids and their metabolites in wastewater, surface water and finished water in Catalonia, Spain. Water Res 2009;43(4):1126–36.

Bolong N, Ismail AF, Salim MR, Matsuura T. A review of the effects of emerging contaminants in wastewaters and options for their removal. Desalination 2009;239:229–46.

Bono-Blay F, Guart A, de la Fuente B, Pedemonte, Pastor MP, Borrell A, Lacorte S. Survey of phthalates, alkylphenols, bisphenol A and herbicides in Spanish source waters intended for bottling. Environ Sci Pollut Res 2012. http://dx.doi.org/10.1007/s11356-012-0851-y.

Campbell CG, Borglin SE, Green FB, Grason A, Wozei E, Stringfellow WT. Biologically directed environmental monitoring, fate, and transport of estrogenic endocrine disrupting compounds in water: a review. Chemosphere 2006;65:1265–80.

Carabias-Martínez R, Rodríguez Gonzalo E, Fernández Laespada ME, Sánchez San Román FJ. Evaluation of surface- and ground-water pollution due to herbicides in agricultural areas of Zamora and Salamanca (Spain). J Chromatogr A 2000;869:471–80.

Carabias-Martínez R, Rodríguez-Gonzalo E, Herrero Hernandez E, Sánchez-San Román FJ, Prado-Flores G. Determination of herbicides and metabolites by solid phase extraction and liquid chromatography. Evaluation of pollution due to herbicides in surface and ground waters. J Chromatogr A 2002;950:157–66.

Carabias-Martínez R, Rodríguez-Gonzalo E, Fernández-Laespada ME, Calvo Seronero L, Sánchez-San Román FJ. Evolution over time of the agricultural pollution of waters in an area of Salamanca and Zamora (Spain). Water Res 2003;37(4):928–38.

Choi KJ, Kim SG, Kim CW, Kim SH. Effects of activated carbon types and service life on removal of endocrine disrupting chemicals: amitrol, nonylphenol, and bisphenol-A. Chemosphere 2005;58:1535–45.

Chowdary VM, Rao NH, Sarma PBS. Decision support framework for assessment of non-point source pollution of groundwater in large irrigation projects. Agric Water Manage 2005;75:194–225.

Christensen TH, Kjeldsen P, Bjerg P, Jensen D, Christensen JB, Baun A, et al. Biogeochemistry of landfill leachate plumes. Appl Geochem 2001;16(7):659–718.

Clara M, Strenn B, Kreuzinger N. Carbamazepine as a possible anthropogenic marker in the aquatic environment: investigations on the behaviour of carbamazepine in wastewater treatment and during groundwater infiltration. Water Res 2004;38(4):947–54.

de Ridder DJ, Villacorte L, Verliefde ARD, Verberk JQJC, Heijman SGJ, Amy GL, et al. Modeling equilibrium adsorption of organic micropollutants onto activated carbon. Water Res 2010;44:3077–86.

Díaz-Cruz MS, Barceló D. Trace organic chemicals contamination in ground water recharge. Chemosphere 2008;72(3):333–42.

Díaz-Cruz MS, García-Galán MJ, Barceló D. Highly sensitive simultaneous determination of sulfonamide antibiotics and one metabolite in environmental waters by liquid chromatography–quadrupole linear ion trap-mass spectrometry. J Chromatogr A 2008;1193(1–2):50–9.

Estévez E, Cabrera MC, Molina-Díaz A, Robles J, del Pino Palacios-Díaz M. Screening of emerging contaminants and priority substances(2008/105/EC) in reclaimed water for irrigation and groundwater in volcanic aquifer(Gran Canaria, Canary islands, Spain). Sci Total Environ 2012. http://dx.doi.org/10.1016/j.scitotenv.2012.06.031.

European Commission (EC). Directive 2006/118/EC of the European Parliament and the Council of 12th of December 2006 on the protection of ground water against pollution and deterioration. Off J Europ Union 2006;L 372/19. 27/12/2006.

Farré M, Kuster M, Brix R, Rubio F, López de Alda M, Barceló D. Comparative study of an estradiol enzyme-linked immunosorbent assay kit, liquid chromatography–tandem mass spectrometry, and ultra performance liquid chromatography–quadrupole time of flight mass spectrometry for part-per-trillion analysis of estrogens in water samples. J Chromatogr A 2010;1160:166–75.

Foster S. The interdependence of groundwater and urbanization in rapidly developing cities. Urban Water 2001;3:185–92.

García-Galán MJ, Díaz-Cruz MS, Barceló D. Determination of triazines and their metabolites in environmental samples using molecularly imprinted polymer extraction, pressurized liquid extraction and LC–tandem mass spectrometry. J Hydrol 2010a;383:30–8.

García-Galán M, Garrido T, Fraile J, Ginebreda A, Díaz-Cruz MS, Barceló D. Simultaneous occurrence of nitrates and sulfonamides antibiotics in two ground water bodies of Catalonia (Spain). J Hydrol 2010b;383:93-101.

García-Galán MJ, Díaz-Cruz Silvia M, Barceló D. Determination of 19 Sulfonamides in Environmental Waters by Automated On-line Solid-Phase Extraction–Liquid Chromatography–Tandem Mass Spectrometry (SPE–LC–MS/MS); 2010c.

García-Galán MJ, Garrido T, Fraile J, Ginebreda A, Diaz Cruz MS, Barceló D. Application of fully automated online solid phase extraction-liquid chromatography electrospray-tandem mass spectrometry for the determination of sulfonamides and their acetylated metabolites in groundwater. Anal Bioanal Chem 2011;399(2):795–806.

Garrido T, Fraile J, Niñerola JM, Figueras M, Ginebreda A, Olivella L. Survey of ground water pesticide pollution in rural areas of Catalonia (Spain). Int J Environ Anal Chem 2000;78(1):51–65.

González S, Petrovic M, Barceló D. Simultaneous extraction and fate of linear alkylbenzene sulfonates, coconut diethanol amides, nonylphenol ethoxylates and their degradation products in wastewater treatment plants, receiving coastal waters and sediments in the Catalonian area (NE Spain). J Chromatogr A 2004;1052:111–20.

González S, López-Roldán R, Cortina JL. Presence and biological effects of emerging contaminants in Llobregat River basin: a review. Environ Pollut 2012;161:83–92.

Gustafson DI. Pesticides in drinking water. New York: van Nostrand Reinhold; 1993.

Guzzella L, Pozzoni F, Giuliano G. Herbicide contamination of surficial groundwater in Northern Italy. Environ Pollut 2006;142:344–53.

Haarstad K, Ludvigsen GH. Ten years of pesticide monitoring in Norwegian ground water. Ground Water Monit Rem 2007;27:75–89.

Heberer T, Reddersen K, Mechlinski A. From municipal sewage to drinking water: fate and removal of pharmaceutical residues in the aquatic environment in urban areas. Water Sci Technol 2002;46:81–8.

Hildebrandt A, Lacorte S, Barcelo D. Assessment of priority pesticides, degradation products, and pesticide adjuvants in groundwaters and top soils from agricultural areas of the Ebro river basin. Anal Bioanal Chem 2007;387:1459–68.

Hildebrandt A, Guillamón M, Lacorte S, Tauler R, Barceló D. Impact of pesticides used in agriculture and vineyards to surface and ground water quality (North Spain). Water Res 2008;42:3315–26.

Hohenblum P, Gans O, Moche W, Scharf S, Lorbeer G. Monitoring of selected estrogenic hormones and industrial chemicals in groundwaters and surface waters in Austria. Sci Total Environ 2004;333:185–93.

Huerta-Fontela M, Galceran MT, Ventura F. Stimulatory drugs of abuse in surface waters and their removal in a conventional drinking water treatment plant. Environ Sci Technol 2008;42:6809–16.

Huerta-Fontela M, Galceran MT, Ventura F. Occurrence and removal of pharmaceuticals and hormones through drinking water treatment. Water Res 2011;45(3):1432–42.

Jones-Lepp TL, Stevens R. Pharmaceuticals and personal care products in biosolids/sewage sludge: the interface between analytical chemistry and regulation. Anal Bioanal Chem 2007;387:1173–83.

Jones-Lepp TL, Alvarez DA, Petty JD, Huckins JN. Polar organic chemical integrative sampling and liquid chromatography–electrospray/ion-trap mass spectrometry for assessing selected prescription and illicit drugs in treated sewage effluents. Arch Environ Contam Toxicol 2004;47:427–39.

Jurado A, Mastroianni N, Vazquez-Suñe E, Carrera J, Tubau I, Pujades E, et al. Drugs of abuse in urban groundwater. a case study: Barcelona. Sci Total Environ 2012;424:280–8. http://dx.doi.org/10.1016/j.scitotenv.2012.02.074.

Kampioti AA, Borbada Cunha AC, López de Al da MJ, Barceló D. Fully automated multianalyte determination of different classes of pesticides, at picogram per litre levels in water, by on-line solid-phase extraction-liquid chromatography-electrospray-tandem mass spectrometry. Anal Bioanal Chem 2005;382(8):1815–25.

Köck-Schulmeyer M, Ginebreda A, López de Alda M, Barceló D. Fate and risks of polar pesticides in groundwater samples of Catalonia. The handbook of environmental chemistry; 2012. p. 375–94. http://dx.doi.org/10.1007/698_2011_132. Volume 20/2012.

Lacorte S, Latorre A, Guillamon M, Barceló D. Nonylphenol, octyphenol and bisphenol A in groundwaters as a result of agronomic practices. Analysis, toxicity and biodegradation of organic pollutants in groundwater from contaminated land, landfills and sediments. Sci World J 2002;2:1095–100. http://dx.doi.org/10.1100/tsw.2002.219.

Lapworth DJ, Gooddy DC, Stuart ME, Chilton PJ, Cachandt G, Knapp M, et al. Pesticides in groundwater: some observations on temporal and spatial trends. Water Environ J 2006;20:55–64.

Lapworth DJ, Baran N, Stuart ME, Ward RS. Emerging contaminants: a review of occurrence, sources and fate in groundwater. Environ Pollut 2012;163:287–303.

Latorre A, Lacorte S, Barceló D. Presence of nonylphenol, octyphenol and bisphenol A in two aquifers close to agricultural, industrial and urban areas. Chromatographia 2003;57:111–6.

Lerner DN. Diffuse pollution of groundwater in urban areas. BHS 10th National Hydrology Symposium, Exeter, UK; 2008.

Liu Z, Kanjo Y, Mizutani S. Removal mechanisms for endocrine disrupting compounds (EDCs) in wastewater treatment d physical means, biodegradation, and chemical advanced oxidation: a review. Sci Total Environ 2008. http://dx.doi.org/10.1016/j.scitotenv.2008.08.039.

Löffler S, Römbke J, Meller M, Ternes TA. Environmental fate of pharmaceuticals in water/sediment systems. Environ Sci Technol 2005;39:5209–18.

Loos R, Locoro G, Comero S, Contini S, Schwesig D, Werres F, et al. Pan-European survey on the occurrence of selected polar organic persistent pollutants in ground water. Water Res 2010;44:4115–26.

López-Roldán P, López de Alda MJ, Barceló D. Simultaneous determination of selected endocrine disrupters (pesticides, phenols and phthalates) in water by in-field solid-phase extraction (SPE) using the prototype PROFEXS followed by on-line SPE (PROSPEKT) and analysis by liquid chromatography–atmospheric pressure chemicalionisation–mass spectrometry. Anal Bioanal Chem 2004;378:599–609.

Martínez Bueno MJ, Gomez MJ, Herrera S, Hernando MD, Agüera A, Fernández-Alba AR. Occurrence and persistence of organic emerging contaminants and priority pollutants in five sewage treatment plants of Spain: Two years pilot survey monitoring. Environ Pollut 2012;164:26-273.

Mompelat S, Lebot B, Thomas O. Occurrence and fate of pharmaceutical products and by-products, from resource to drinking water. Environ Int 2009;35:805–14.

Morvan X, Mouvet C, Baran N, Gutierrez A. Pesticides in the groundwater of a spring draining a sandy aquifer: temporal variability of concentrations and fluxes. J Contam Hydrol 2006;87(3–4):176–90.

Müller B, Scheytt T, Asbrand M, Mross de Casas A. Pharmaceuticals as indictors of sewage-influenced groundwater. Hydrogeol J 2012. http://dx.doi.org/10.1007/s10040-012-0852-4.

Muñoz I, Gómez-Ramos MJ, Agüera A, Fernández-Alba AR, García-Reyes JF, Molina-Díaz A. Chemical evaluation of contaminants in wastewater effluents and the environmental risk of reusing effluents in agriculture. TrAC, Trends Anal Chem 2009;28:676–94.

Murray KE, Thomas SM, Bodour AA. Prioritizing research for trace pollutants and emerging contaminants in the freshwater environment. Environ Pollut 2010;158: 3462–71.

Osenbrück K, Gläser HR, Knöller K, Weise SM, Möder M, Wennrich R, et al. Source and transport of selected organic micropollutants in urban groundwater underlying the city of Halle (Saale), Germany. Water Res 2007;41:3259–70.

Pal A, Gin AY-C, Reinhard M. Impacts of emerging organic contaminants on freshwater resources: review of recent occurrences, sources, fate and effects. Sci Total Environ 2010;408:6062–9.

Petrovic M, Gonzalez S, Barcelo D. Analysis and removal of emerging contaminants in wastewater and drinking water. Trends Anal Chem 2003;22:685–756.

Postigo C, Lopez de Alda MJ, Barceló D. Analysis of drugs of abuse and their human metabolites in water by LC-MS2: a non-intrusive tool for drug abuse estimation at the community level. TrAC Trends Anal Chem 2008;27(11):1053–69.

Postigo C, López de Alda MJ, Barceló D, Ginebreda A, Garrido T, Fraile J. Analysis and occurrence of selected medium to highly polar pesticides in groundwater of Catalonia (NE Spain): an approach based on on-line solid phase extraction–liquid chromatography–electrospray-tandem mass spectrometrydetection. J Hydrol 2010;383:83–92.

Quintana J, Marti I, Ventura F. Monitoring of pesticides in drinking and related waters in NE Spain with a multiresidue SPE-GC-MS method including an estimation of the uncertainty of the analytical results. J Chromatogr A 2001;938:3-13.

Rabiet M, Togola A, Brissaud F, Seidel J-L, Budzinski H, Elbaz-Poulichet F. Consequences of treated water recycling as regards pharmaceuticals and drugs in surface and ground waters of a medium-sized Mediterranean catchment. Environ Sci Technol 2006;40:5282–8.

Radjenovic J, Petrovic M, Barceló D. Analysis of pharmaceuticals in wastewater and removal using a membrane bioreactor. Anal Bioanal Chem 2007;387:1365–77.

Radjenovic J, Petrovic M, Ventura F. Rejection of pharmaceuticals in nanofiltration and reverse osmosis membrane drinking water treatment. Water Res 2008;42(14): 3601–10.

Reinstorf F, Strauch G, Schirmer K, Gläser HR, Möder M, Wennrich R, et al. Mass fluxes and spatial trends of xenobiotics in the waters of the city of Halle, Germany. Environ Pollut 2008;152:452–60.

Reungoat J, Macova M, Escher BI, Carswell S, Mueller JF, Keller J. Removal of micropollutants and reduction of biological adverse effects in a full scale reclamation plant using ozonation and activated carbon filtration. Water Res 2010;44(2): 625–37.

Rodriguez-Mozaz S, Lopez de Alda MJ, Barcelo D. Monitoring of estrogen, pesticides and bisphenol A in natural waters and drinking water treatment plants by solid-phase extraction–liquid chromatography–mass spectrometry. J Chromatogr A 2004a;1045:85–92.

Rodriguez-Mozaz S, López de Alda MJ, Barceló D. Picogram per liter level determination of estrogens in natural waters and waterworks by a fully automated on-line solid phase extraction-liquid chromatography-electrospray tandem mass spectrometry method. Anal Chem 2004b;76(23):6998–7006.

Sánchez-Avila J, Bonet J, Velasco G, Lacorte S. Determination and occurrence of phthalates, alkylphenols, bisphenol A, PBDEs, PCBs and PAHs in an industrial sewage grid discharging to a Municipal Wastewater Treatment Plant. Sci Total Environ 2009. http://dx.doi.org/10.1016/j.scitotenv.2009.03.016.

Sánchez-Camazano M, Lorenzo LF, Sánchez-Martín MJ. Atrazine and alachlor inputs to surface and groundwaters in irrigated corn cultivation areas of Castilla-León region, Spain. Environ Monit Assess 2005;105(2005):11–24.

Silva E, Batista S, Viana P, Antunes P, Serôdio L, Cardoso AT, et al. Pesticides and nitrates in groundwater from oriziculture areas of the 'Baixo Sado' region (Portugal). Int J Environ Anal Chem 2006;86:955–72.

Silva CP, Otero M, Esteves V. Processes for the elimination of estrogenic steroid hormones from water: a review. Environ Pollut 2012;165:38–58.

Soares A, Guieysse B, Jefferson B, Cartmell E, Lester JN. Nonylphenol in the environment: a critical review on occurrence, fate, toxicity and treatment in wastewaters. Environ Int 2008;34:1033–49.

SRC Inc. 2011. http://www.syrres.com/what-we-do/databaseforms.aspx?id=386. Accessed 28 May 2012.

Strauch G, Möder M, Wennrich R, Osenbrück K, Gläser HR, Schladitz T, Müller C, Schirmer K, Reinstorf F, Schirmer M. Indicators for assessing anthropogenic impact on urban surface and groundwater. J Soils Sediment 2008;8:23–33.

Stuart M, Lapworth D, Crane E, Hart A. Review of risk from potential emerging contaminants in UK groundwater. Sci Total Environ 2012;416:1-21.

Teijon G, Candela L, Tamoh K, Molina-Díaz A, Fernández-Alba. Occurrence of emerging contaminants, priority substances (2008/105/CE) and heavy metals in treated wastewater and groundwater at Depurbaix facility (Barcelona, Spain). Sci Total Environ 2010;408:3584–95.

ter Laak TL, Puijker LM, van Leerdam JA, Raa KJ, Kolkman A, de Voogt P, van Wezel AP. Broad target chemical screening approach used as tool for rapid assessment of groundwater quality. Sci Total Environ 2012;427–428:308–13.

Ternes TA, Bonerz M, Herrmann N, Teiser B, Rasmus Andersen H. Irrigation of treated wastewater in Braunschweig, Germany: an option to remove pharmaceuticals and musk fragrances. Chemosphere 2007;66:894–904.

Trauth R, Xanthopoulos C. Non-point pollution of ground-water in urban areas. Water Res 1997;31(11):2711–8.

Tubau I, Vázquez-Suñé E, Carrera J, González S, Petrovic M, López de Alda MJ, et al. Occurrence and fate of alkylphenol polyethoxylate degradation products and linear alkylbenzene sulfonate surfactants in urban ground water: Barcelona case study. J Hydrol 2010;383(1–2):102–10.

Vàzquez-Suñé E, Sanchez-Vila X, Carrera J. Introductory review of specific factors influencing urban groundwater, an emerging branch of hydrogeology, with reference to Barcelona, Spain. Hydrogeol J 2007a;13(3):522–33. http://dx.doi.org/10.1007/s10040-004-0360-2.

Vázquez-Suñé E, Capino B, Abarca E, Carrera J. Estimation of recharge from floods in disconnected streameaquifer systems. Ground Water 2007b;45(5):579–89.

Vàzquez-Suñé E, Carrera J, Tubau I, Sánchez-Vila X, Soler A. An approach to identify urban groundwater recharge. Hydrol Earth Syst Sci Discuss 2010;7(2):2543–76.

Vulliet E, Cren-Olivé C. Screening of pharmaceuticals and hormones at the regional scale, in surface and groundwaters intended to human consumption. Environ Pollut 2011;159:2929–34.

Wolf L, Held I, Eisworth M, Hotzl H. Impact of leaky sewers on groundwater quality. Acta Hydrochim Hydrobiol 2004;32(4):1-13.

Wolf L, Zwiener C, Zemann M. Tracking artificial sweeteners and pharmaceuticals introduced into urban groundwater by leaking sewer networks. Sci Total Environ 2012;2012:430,8-430,19.

Ying GG, Kookana RS, Dillon P. Sorption and degradation of selected five endocrine disrupting chemicals in aquifermaterial. Water Res 2003;37:3785–91.