Chemosphere xxx (2014) xxx–xxx

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Occurrence and spatial distribution of emerging contaminants in the unsaturated zone. Case study: Guadalete River basin (Cadiz, Spain)

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ARTICLE INFO

Article history:
Received 3 January 2014
Received in revised form 21 April 2014
Accepted 29 April 2014
Available online xxxx

Handling Editor: J. de Boer

Keywords:
Emerging pollutants
Surfactants
Pharmaceuticals
Vadose zone
Soils

ABSTRACT

Irrigation with reclaimed water is becoming a common practice in arid- and semi-arid regions as a consequence of structural water resource scarcity. This practice can lead to contamination of the vadose zone if sewage-derived contaminants are not removed properly. In the current work, we have characterized soils from the Guadalete River basin (SW Spain), which are often irrigated with reclaimed water from a nearby wastewater treatment plant and amended using sludge. Physico-chemical, mineralogical and hydraulic properties were measured in soil samples from this area (from surface up to 2 m depth). Emerging contaminants (synthetic surfactants and pharmaceutically active compounds, or PhACs) were also determined. Synthetic surfactants, widely used in personal care products (PCPs), were found in a wide range of concentrations: 73–1300 μg kg^{-1} for linear alkylbenzene sulfonates (LAS), 120–496 μg kg^{-1} for alkyl ethoxysulfates (AES), 19–1090 μg kg^{-1} for alcohol polyethoxylates (AEOs), and 155–280 μg kg^{-1} for nonylphenol polyethoxylates (NPEOs). The presence of surfactant homologues with longer alkyl chains was predominant due to their sorption capacity. A positive correlation was found between LAS and AEOs and soil organic carbon and clay content, respectively. Out of 64 PhACs analyzed, only 7 were detected occasionally (diclofenac, metoprolol, fenofibrate, carbamazepine, clarithromycin, famotidine and hydrochlorothiazide), always at very low concentrations (from 0.1 to 1.3 μg kg^{-1}).

1. Introduction

Groundwater contamination is often the result of human activities. This is a rising issue as the worldwide population density is increasing and the use of land is becoming more intensive. One of the clearest examples is contamination by pesticides, which are directly applied to crops. These compounds are now frequently measured for monitoring the quality of soils and aquifers (Hildebrandt et al., 2008). There are, however, hundreds of other chemicals that are not considered in routine sampling campaigns and have potential to jeopardize groundwater resources. Among these contaminants, there has been a growing interest over the last decade in pharmaceuticals and personal care products (PPCPs), a wide group that includes therapeutic drugs, antimicrobials, fragrances, sun-screen agents, insect repellents, surfactants and some polymers. PPCPs have been dumped into the environment for as long as humans have been using them, although they have become relevant recently, once the improvement of analytical techniques (e.g., mass spectrometry) has enabled their detection and quantification at trace levels. So far, these substances have been detected in most surface water bodies worldwide (Halling-Sörensen et al., 1998; Heberer, 2002) and, occasionally, in groundwater (Teijón et al., 2010). Available data on the concentrations and distribution of PPCPs in solid matrices, especially sediment and soils, are still scarce (Xu et al., 2009; Perez-Carrera et al., 2010).

Most of the information is related to the fate and behavior of PPCPs in wastewater treatment plants (WWTPs) (Miége et al., 2009) as their effluents are one of the most significant sources of these chemicals to the aquatic environments. These studies show that conventional treatments are not capable of efficiently removing many of these chemicals, especially pharmaceutically active compounds (PhACs). As a consequence, soils can be later contaminated in several ways: (1) using digested sewage sludge or biosolids as fertilizer on agricultural soils, (2) irrigation from treated wastewater, (3) leakages of sewer drains and sewage treatment

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http://dx.doi.org/10.1016/j.chemosphere.2014.04.098
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plants and (4) surface flooding with waters containing appreciable proportions of treated wastewater (Oppel et al., 2004). Other sources include industrial production of pharmaceuticals, residues from hospitals (Thiele-Bruhn, 2003), and the use of antibiotics in animal farms. Later, these contaminated soils are a potential source of surface and groundwater pollution by runoff (Oppel et al., 2004) and leaching (Candela et al., 2007; Xu et al., 2009). Other PPCPs considered in this work, such as surfactants and their degradation products (main ingredients in detergents, cleaning products, shampoos, or lotions), unlike many PhACs, show high removal efficiencies in WWTPs (95–99%) (Matthijs et al., 1999). Their presence in aquatic and terrestrial ecosystems, where they have been detected in a wide range of concentrations (Corada-Fernández et al., 2010, 2013), is mostly related to their extended use and high consumption. In fact, surfactants and their metabolites constitute, by far, the organic contaminants showing the highest concentrations in untreated wastewaters (Kolpin et al., 2002). Other sources include the use of these compounds in pesticide formulations as emulsifiers, dispersing and spreading agents (Carlsen et al., 2002).

The behavior and fate of most PPCPs still remains unclear, especially in soils and aquifers. There are only a few studies focusing on the transport of these compounds from soils to surface waters and groundwater (Oppel et al., 2004; Topp et al., 2008). Due to their wide structural diversity, understanding the different sorption mechanisms of PPCPs in soils is determinant for predicting their mobility and leaching to the groundwater. Their persistence is also another key aspect as the main route for disappearance of PPCPs from contaminated soils is biodegradation. Degradation in soils can be a relatively fast process for some surfactants such as linear alkylbenzene sulfonates (LAS) (half-life = 3–33 d), the most common anionic surfactant (Linear Alkylbenzene Sulfonate, Environmental Risk Assessment, 2013), and pharmaceuticals, but extend over long periods of time for many other PPCPs. As an example, amoxicillin, sulfamethazine and trimethoprim, three antibiotics, show half-lives in soils of 1, 18.6 and 103 d, respectively (Boxall, 2008). Both sorption and degradation processes are also strongly influenced by environmental conditions such as temperature, redox potential, pH, soil type, organic carbon content, clay minerals and soil bacteria (Topp et al., 2008).

The current work has been carried out in the Guadalete River basin (Cadiz, Spain), a region where reclaimed water from WWTPs is occasionally used for irrigation due to water scarcity. Other issues include severe pollution episodes in some areas of the basin due to uncontrolled sewage spills and the use of digested sludge as a fertilizer (Lara-Martín et al., 2008; Corada-Fernández et al., 2010, 2013; Perez-Carrera et al., 2010). Our main objectives were: (a) to assess the occurrence of some selected PPCPs (surfactants and pharmaceuticals) in the unsaturated zone, including both surface and deep soils and (b) to relate their spatial distribution to different sources and the physicochemical properties of the receiving media.

2. Materials and methods

2.1. Study area

The study area is within the Guadalete River basin (SW, Spain) where two unconfined aquifers are located: Jerez de la Frontera and Guadalete alluvial aquifer (Fig. 1). Land use is dominated by agricultural and farmland activities. There is also a significant presence of small villages along the riverside, sources of small uncontrolled sewage spills to the surface waters (Lara-Martín et al., 2008; Corada-Fernández et al., 2011). The main population in the area is a 200,000 inhabitant city, Jerez de la Frontera, located in the northwest part of the basin. Most of the sewage of this city is collected and treated in the WWTP El Portal (Fig. 1) and discharged into the river, although there also some other small settlements dumping untreated wastewater to the main watercourse through a small creek (Salado Stream) (Corada-Fernández et al., 2013).

The region has a mean annual precipitation of 600 mm and a mean annual temperature of 18 °C. Cotton and beetroot are the main crops that irrigated in the area, and only the first type (31 km^2) is irrigated in summer (4–8 mm m^2 d^{-1}) using water from the river and/or the aquifer. Additionally, a fraction of the

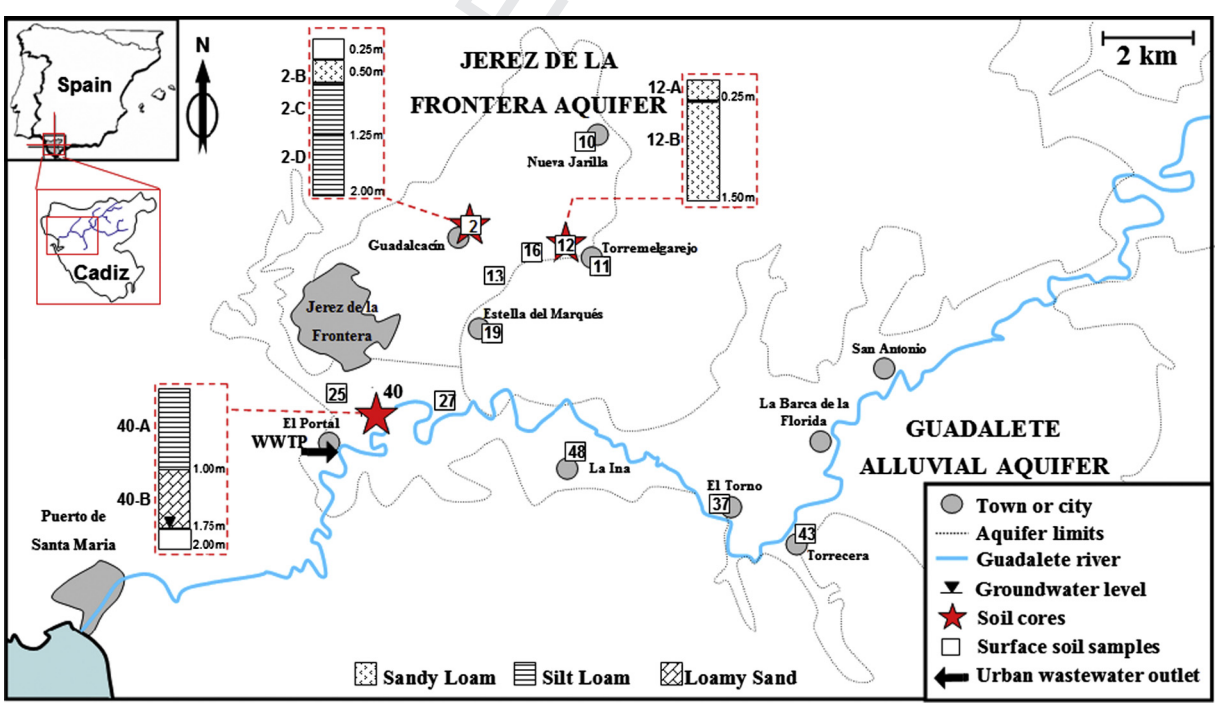

Fig. 1. Map of the Guadalete River basin showing the location of sampling stations and nearby populations. Textural class for the three soil cores is also displayed.

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WWTP effluent (60,000–70,000 m^3 $year^{-1}$) undergoes tertiary treatment (UV disinfection after filtration) and is used for irrigation of the local golf course and/or discharged into the Torrox pond, both locations adjacent to sampling stations 25 and 40. Sludge is composted (4000 tons $year^{-1}$) and used by local farmers as fertilizer, covering a surface up to 10 km^2.

2.2. Unsaturated zone sampling and characterization

The sampling was divided in two campaigns, the first in September 2006 to collect surface soil samples (disturbed, 500 g), and the second in September 2008 to collect soil cores (including disturbed and undisturbed). Note that both years were dry (567 and 476 mm in 2006 and 2008, respectively), especially during the 3 months before the sampling campaigns (40 mm in 2006 and 9 mm in 2008).

Surface soil samples (disturbed, 500 g) were taken from both Jerez de la Frontera and Guadalete aquifers at seven and five different locations, respectively (Fig. 1), in September 2006. Later, and taking into account the results obtained from surface soil samples, and other criteria like land use/cover, disturbed and undisturbed core samples (at intervals of 0.25 m up to 2 m depth) were collected from sampling points 40, 12 and 2, within the Jerez de la Frontera aquifer (Fig. 1), in September 2008. A hand auger drilling equipment (Eijkelkamp®) and stainless steel rings (5 cm length; 5 cm inner diameter), inserted into the soil using a hand-held hammer, were used to this end. All samples were transported and stored after to be carefully wrapped in aluminum foil to avoid photodegradation of some photosensitive PhACs, wrapped hermetically in plastic bag to avoid loss of water content, and kept at 4 °C during their transport to the laboratory using a cooler. All samples were subsequently frozen in the laboratory until their analysis.

Different techniques and standards were used to determine soil physico-chemical properties (grain size distribution, bulk density, saturated hydraulic conductivity, organic carbon content, electric conductivity, pH, cation exchange capacity and clay fraction mineralogy). More information is available in Supplementary Information.

2.3. Determination of PPCPs in soil samples

Analysis of surfactants in soil samples was carried out according to Lara-Martín et al. (2006), whereas determination of pharmaceuticals was performed following the method developed by Jelic et al. (2009). These references include the list of all the chemicals and reagents used during this study, as well as further details about the performance of the different methods. Briefly, 4 different synthetic surfactants – linear alkylbenzene sulfonates (LAS), alcohol ethoxysulfates (AES), nonylphenol ethoxylates (NPEOs), and alcohol ethoxylates (AEOs) – and 64 pharmaceuticals – analgesics and anti-inflammatories, antihypertensives, lipid regulators, antibiotics, psychiatric drugs, and others – were analyzed by liquid chromatography – mass spectrometry (LC-MS) after pressurized liquid extraction (PLE). More information is available in Supplementary Information.

3. Results and discussion

3.1. Distribution of synthetic surfactants in surface soil samples

Fig. 2 shows concentrations of anionic (LAS and AES) and nonionic surfactants (AEOs and NPEOs) in surface soil samples. Values of target compounds ranged from less than 20 μg kg^{-1} to 1200 μg kg^{-1}. Maximum concentrations were measured for LAS (from 290 to 1183 μg kg^{-1}) and AES (from 120 to 496 μg kg^{-1}), two anionic surfactants mainly used in household detergents and personal care products (e.g., shampoos). AEOs and NPEOs, nonionic surfactants mostly used for industrial applications and some specific uses (e.g., wetting agents, dispersers and emulsifiers), were detected at lower concentrations, between 19 and 140 μg kg^{-1}, and between 57 and 280 μg kg^{-1}, respectively. NPEOs were banned for household applications a few years ago in the EU due to the estrogenic properties of their degradation metabolites (Jobling et al., 1996). They were only detected in soil samples from the Guadalete alluvial aquifer, where agriculture and farming are predominant. The main source of NPEOs in this area is probably the application of pesticides to crops as this surfactant is as adjuvant in pesticide formulation (Krogh et al., 2003). Regarding LAS, the most abundant contaminant in soils, maximum concentrations (around 1 mg kg^{-1}) were found at sampling points 25, 19, and 2, within the Jerez de la Frontera aquifer and surrounding urban areas. Here, treated and untreated wastewater is discharged (WWTP El Portal, Fig. 1) and represents the main source of this surfactant. The occurrence of these discharges has been confirmed in previous works reporting highly polluted sediments and surface waters within the same study area (Corada-Fernández et al., 2011, 2013; Lara-Martín et al., 2008, 2010). Briefly, they measured average values for surfactants between 0.1 and 3.7 mg kg^{-1} in surface sediments from Guadalete River, and between 0.2 and 37 mg L^{-1} in surface water. In this study, maximum concentrations for anionic surfactants were observed in two hot spots corresponding to the outlet of WWTP El Portal (89.4 mg kg^{-1}) and a small creek (Salado Stream) that collects untreated wastewater from small villages in rural areas (242.6 mg kg^{-1}) (Corada-Fernández et al., 2011). On the other hand, the highest values for nonionic surfactants were measured by the mouth of the river (14.9 mg kg^{-1}) and were related to industrial and seaport activity in that area (Lara-Martín et al., 2008).

The distribution of organic contaminants in terrestrial environments is affected by their physico-chemical properties, and this is especially relevant for surfactants, which are often sold in commercial formulations as a complex mixture of homologues and ethoxymers (occasionally, formed by more than 100 individual

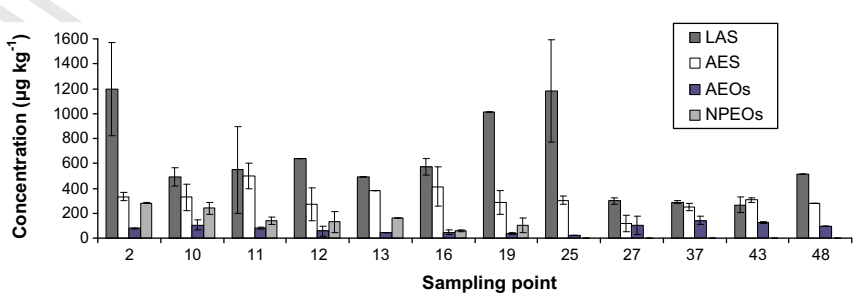

Fig. 2. Surfactant concentrations (μg kg^{-1}) in surface soil samples.

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components) with different solubility and sorption capacity. Fig. 3 shows the average homologue percentages of LAS, AES, and AEOs in surface soil samples. It is noticeable that, for AES and AEOs, only homologues with an even number of carbon atoms (C_{12}, C_{14} and C_{16} for AES, and C_{12}, C_{14}, C_{16} and C_{18} for AEOs) in their alkyl chain were detected. This fact can be explained because most of them are derived from vegetable and/or animal fatty acids instead from petrochemical feedstocks (which contain not only even but also odd-carbon numbered homologues). Differential sorption can be observed by examining the homologue distributions represented in Fig. 3. In general, those homologues having longer alkyl chains have higher sorption capacity on soils. This is especially evident for AEO components, which are usually more hydrophobic than the rest of surfactants. Regarding AES, highlights C_{12} AES, also known as lauryl ether sulfate, which is one of the main ingredients in shampoos, soaps, toothpastes, etc., as it is one of the cheapest and more effective foaming agents. It is the main homologue also in AES commercial mixtures (see data in Supplementary Information respect to the composition of the standard used), the main reason why this homologue is always the most abundant in the environment, in agreement with results reported by Lara-Martín et al. (2005) for these compounds in aquatic systems. Similar trends regarding the homologue distribution of LAS, AEOs, and AES have been previously reported for river and marine sediments (Corada-Fernández et al., 2011; Lara-Martín et al., 2005, 2008) from this and/or nearby sampling areas. Toxicity of these compounds has been addressed in Supplementary Information.

Apart from the physico-chemical properties of their molecules, the distribution and behavior of surfactants may be also correlated to the properties of the environment, which may differ greatly from one sampling area to another. That makes that sorption mechanisms for anionic and non-ionic surfactants on soils and other solid phases (e.g., sludge and sediments) are still not fully understood (Rodríguez-Cruz et al., 2005). Some authors have reported the existence of a positive relationship between sorption coefficients and the organic carbon content in soils (Litz et al., 1987; Fytianos et al., 1998), whereas other have found a similar relationship but considering the clay content and/or specific surface instead (Ou et al., 1996; Brownawell et al., 1997; Shen, 2000). Sorption can occur in multiple ways in the environment as both hydrophobic and hydrophilic moieties in the molecular structure of surfactants can interact with soil surfaces. Table 1S (see Supplementary Information) shows the main physico-chemical and hydraulic properties of surface soil samples in the Guadalete River basin. These soils are characterized by low organic matter content (<2.5%) and low percent of clay (<3.8%). These values, however, are high enough to influence the sorption and, therefore, the distribution of surfactants in the area. LAS concentrations were positively correlated ($r^2 = 0.6$, $p = 0.002213$) with organic matter content in soils (Fig. 4a), suggesting hydrophobic interactions between the alkyl chain of LAS homologues and the organic carbon content in soils (e.g., Litz et al., 1987; Fytianos et al., 1998). No influence of the soil clay content was observed for this surfactant (Fig. 4b) at a *p-value* of 0.05. On the other hand, AEO concentrations in soil did not seem to be affected by the organic carbon content in soil (Fig. 4c) at a *p-value* of 0.05, but were weakly positively correlated ($r^2 = 0.5$, $p = 0.02148$) with the presence of clays in soil (Fig. 4d). This was especially true for those AEO ethoxymers with higher molecular weight, as polar interactions such as hydrogen bonding may occur (Brownawell et al., 1997; Shen, 2000; Krogh et al., 2003).

3.2. Vertical profiles of PPCPs in soils

Three different sampling points (2, 12 and 40) were selected to study the vertical distributions of contaminants in the vadose zone. We considered not only LAS but also the total concentration of surfactants (LAS + AES + NPEO + AEO) in surface soil samples taken in 2006, as well as other criteria like land use/cover, for collection soil core samples later in 2008. We decided to choose the 3 most polluted stations, which were 25, 19 and 2, having a total concentration of surfactants of 1506, 1436 and 1888 μg kg^{-1}, respectively. However, stations 25 and 19 were altered due to construction works after two years, so we decided to sampling station 40 and 12 instead. Station 40 is less than 1 km away from station 25 (Fig. 1), whereas station 12 is the next one having higher levels of LAS (and a total surfactant concentration of 1096 ng g^{-1}) after stations 25, 19 and 2. Fig. 5 shows concentrations of synthetic surfactants, the most commonly detected target compounds, in these soil sediment cores. Surfactant levels ranged from 73 to 1300 μg kg^{-1} for LAS, and from 329 to 1090 μg kg^{-1} for AEOs. Nonylphenol polyethoxylates (NPEOs) were also detected in some samples, although at much lower concentrations than the rest (<200 μg kg^{-1}) probably due to their lower use. According to the USDA textural classification system, the three soil cores were characterized by loamy sand, sandy loam and silt loam textures, with low levels of organic matter (<2%) and a low clay fraction (<4%) (Table 2S, see Supplementary Information). The vertical distribution of surfactants seems to be related to changes in the physicochemical and hydraulic properties of soils. Thus, the maximum values for AEOs were measured in those soil sections with higher clay content, as we could observe in surface soil samples. LAS concentrations decreased with depth, which was also the trend observed for organic carbon content in soil. This decrease in the organic carbon content, combined with an increase in pH, may reduce the sorption capacity of this surfactant on soils. Overall, there was a decrease in the concentration of surfactants towards deeper layers in the soil column, although an exception was observed at sampling point 40, between 1.25 and 1.75 m depth (Fig. 5a), where an increase in the concentrations of LAS and AEOs was detected. This may be related to the presence of the capillary fringe (fully saturated conditions were found at 1.75 m depth). We

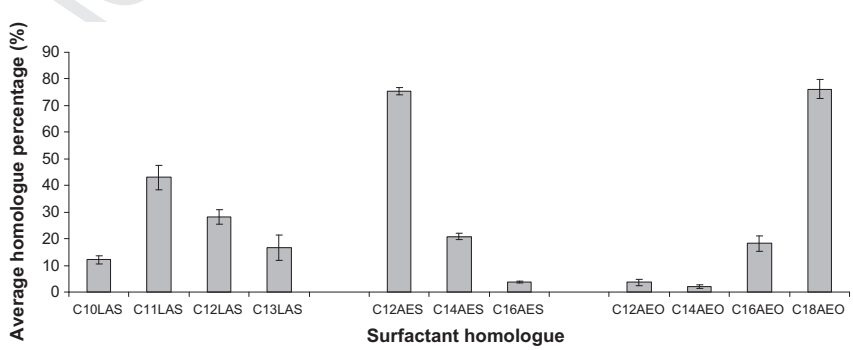

Fig. 3. Average homologue distribution (%) of surfactants in surface soil samples.

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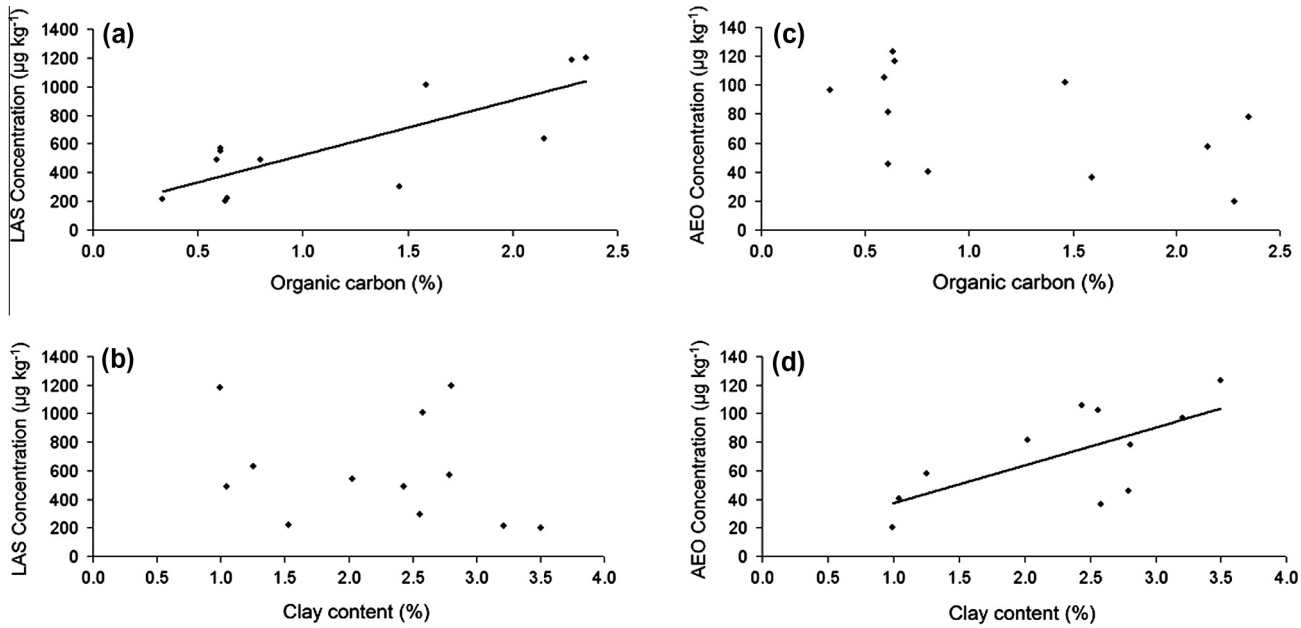

Fig. 4. Concentration of LAS and AEOs (µg kg^{-1}) as a function of organic carbon content (%) (a and c) and clay content (%) (b and d) in soils.

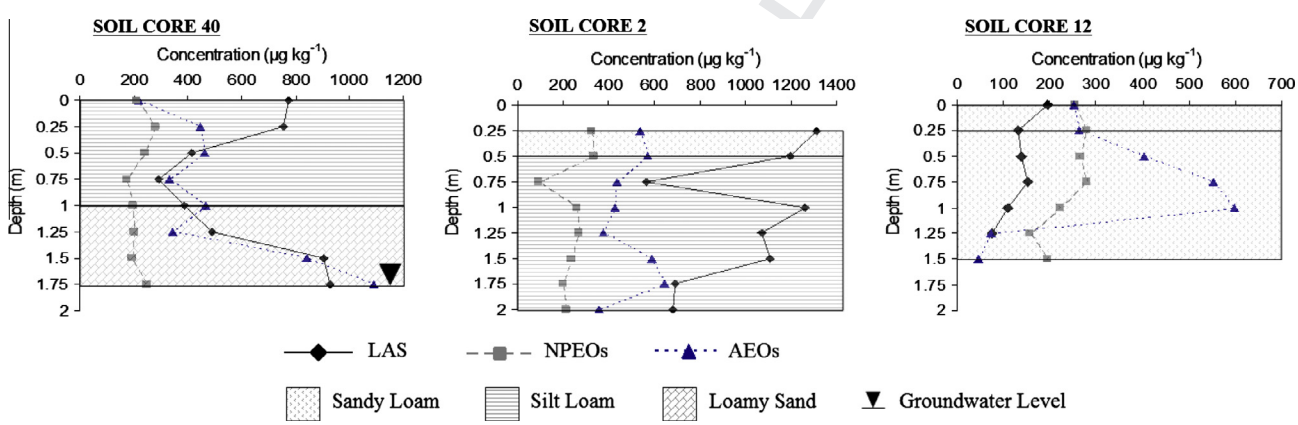

Fig. 5. Vertical concentration profiles (µg kg^{-1}) for selected surfactants in three soil cores: sampling points 40, 2 and 12.

have detected the presence of surfactants and pesticides (data unpublished) at significant concentrations (>1 ppb) in groundwater samples from this sample station. The increase in the concentrations of LAS and AEOs in the capillary fringe is due to their presence in the aqueous phase and later-lower adsorption under saturated conditions. The occurrence of local maximums at different depths (e.g., between 0.75 and 1 m for AEOs in soil core 12, or between 1 and 1.5 m for LAS in soil core 2) was also observed and can be attributed to sporadic inputs of untreated or poorly treated wastewater, as well as to the application of pesticides. Note that untreated sewage dumped into the river sporadically from the WWTP outlet during heavy rains every year, as well as through small creeks collecting wastewater from local farms and cottages (Lara-Martín et al., 2010; Corada-Fernández et al., 2011), and polluted surface waters (concentrations up to 2.8 mg L^{-1} of LAS have been measured), are later used for irrigation. However, which was observed in the soil profiles is the typical mass transport movement in soil media when a pulse of chemical compound (contaminant or a tracer) is applied on the ground surface (Candela et al., 2007), with the possible accumulation in soil deep horizons by the reasons exposed above.

Table 1 shows concentrations of PhACs at specific layers (Table 2S) in the soil, as well as some physicochemical properties (log K_{ow} and pK_a) of these compounds. The selected pharmaceuticals belong to different therapeutical classes – analgesics and anti-inflammatories, antihypertensives, lipid regulators, psychiatric drugs, and antibiotics – and are among the most used. Only 7 out of 64 target compounds (diclofenac, metoprolol, fenofibrate, carbamazepine, clarithromycin, famotidine and hydrochlorothiazide) were occasionally detected at very low concentrations (from 0.1 to 1.3 µg kg^{-1}) in soil samples. Additionally, 5 pharmaceuticals (ketoprofen, acetaminophen, atenolol, clofibric acid and sulfamethazine) were detected in some samples but always below the limits of quantification (<0.1 µg kg^{-1}). The compounds showing the highest concentrations were metoprolol (up to 1.5 µg kg^{-1}), an antihypertensive, and clarithromycin (1.3 µg kg^{-1}), an antibiotic. The rest of pharmaceuticals were always at concentrations lower than 0.4 µg kg^{-1}. Although some of these compounds showed relatively high log K_{ow} values (over 4), such as fenofibrate, ketoprofen and diclofenac, this may be not the best indicator to evaluate the presence of PhACs in terrestrial environments. Many of these chemical can be either in ionic or neutral form depending on the pH of the

Table 1
Chemical properties and concentrations (μg kg^{-1}) of PhACs in three soils cores (12, 40 and 2).

Compound	pK_a	Log K_{ow}	12-A	12-B	40-A	40-B	2-B	2-C	2-D
Ketoprofen	3.12[a]	4.45[a]	–	–	n.q.	n.q.	–	–	–
Diclofenac	4.15[b]	4.51[b]	0.3	0.1	0.2	0.2	–	0.1	0.1
Acetaminophen	9.38[b]	0.46[b]	n.q.	n.q.	–	–	–	–	–
Atenolol	9.6[c]	−0.03[d]	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.
Metoprolol	9.7[b]	1.88[b]	0.5	0.1	0.6	0.6	0.1	1.5	0.6
Clofibric acid	3.46[b]	2.58[b]	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.
Fenofibrate	–	5.19[b]	0.4	0.3	0.4	0.2	0.4	0.4	0.2
Carbamazepine	13.9[b]	2.45[b]	n.q.	n.q.	0.1	0.1	0.1	n.q.	n.q.
Clarithromycin	8.89[c]	–	0.5	0.5	1.3	0.5	0.3	0.6	0.7
Sulfamethazine	7.4[c]	0.89[e]	n.q.	0.1	1.2	n.q.	n.q.	n.q.	n.q.
Famotidine	–	–	0.3	0.2	n.q.	0.2	0.2	0.3	0.3
Hydrochlorothiazide	7.9[c]	−0.07[d]	0.1	0.2	0.2	0.2	0.2	0.2	0.2

Concentration (μg kg^{-1}); –, not detected; n.q., detected, not quantified.
[a] Baccar et al. (2012).
[b] Vazquez-Roig et al. (2010).
[c] Morais et al. (2013).
[d] Chemspider (www.chemspider.com/chemical-structure).
[e] Gong et al. (2012).

soil and, therefore, their sorption capacity may change and better be evaluated by D_{ow} (pH-dependent n-octanol–water distribution ratio) (Wells, 2006). Thus, some of the PhACs identified in this study may show log D_{ow} values that are from similar (0.33–0.34 for acetaminophen) to very different (0.16–0.67 for sulfamethazine) from those for log K_{ow} (Table 1). Additionally, hydrophilic interactions between ionic compounds and soils also occur. It has been observed for AEOs, which were positively correlated to the amount of clays in soil (Fig. 4d), but also for metoprolol and clarithromycin, both positively charged at environmental conditions and the two most predominant PhACs in the sampling area in spite of their relatively low log K_{ow} values (1.88–3.16). This kind of interactions has been previously foreseen from very recent laboratory experiments (Schaffer et al., 2012) and field data from other aquatic systems (Lara-Martín et al., 2014).

Results in Table 1 can be complemented with those from a previous study carried out in the same study area, where 21 surface soil samples were screened for 32 specific PhACs (Perez-Carrera, 2009; Perez-Carrera et al., 2010). Eleven target compounds were detected at concentrations ranging from below limits of detection (0.3–7.1 μg kg^{-1}) up to 24.3 μg kg^{-1}. Omeprazole, used for treating peptic ulcers and not analyzed in the present work, was the most commonly detected pharmaceutical (>50% of soil samples), although we did not include it in this sampling campaign as we used a different analytical methodology (Jelic et al., 2009). The rest of compounds showed a low detection frequency (only 1–2 positive samples) (Perez-Carrera, 2009; Perez-Carrera et al., 2010). As most of the pharmaceuticals detected in the sampling area are only for human consumption, their occurrence in agricultural soils may be related to irrigation of crops with either recycled wastewater (e.g., golf courses) or with river water, which is sometimes mixed with treated/untreated wastewater. Application of sludge from the WWTP El Portal over soils as a fertilizer cannot be discarded as a source either. A few compounds (e.g., sulfamethazine) are also for veterinary use, so they could be released into the environment by disposal of manure residues and/or by leaching from animal excrements (Halling-Sörensen et al., 1998).

4. Conclusions

Data on the occurrence, reactivity and behavior of PPCPs in solid matrices is severely limited in comparison with aqueous matrices. In that sense, this work shows some of the first data available on the areal and vertical distribution of surfactants and pharmaceuticals in sewage affected soils. Their occurrence in the vadose zone can be explained by several sources, including the direct (or indirect) use of treated and untreated wastewater for crop irrigation, the application of sewage sludge and manure residues as fertilizer, and the use of pesticides. Synthetic surfactants were detected in all soil samples, and their distribution was related to the presence of local sewage sources, as well as to the physico-chemical properties of the soils. In this sense, LAS concentrations were positively correlated with organic matter content in soils, suggesting hydrophobic sorption mechanisms. AEO concentrations, on the other hand, were positively correlated with the presence of clays, especially for those ethoxymers having longer ethylene oxide chains. Presence of PhACs in soils was scarce. Only 7 out of 64 compounds analyzed could be measured, most of them showing high log K_{ow} values (>4.45) (e.g., diclofenac, fenofibrate and ketoprofen) or being positively charged at environmental conditions (e.g., atenolol, metoprolol, clarithromycin). Our data suggest a low exposure level for pharmaceuticals in terrestrial environments if we compare their occurrence and concentrations with those measured for surfactants in the same soil samples.

5. Uncited references

Chemspider (xxxx), Jensen and Folker-Hansen (1995). Q3

Acknowledgements

We express our gratitude to J.J. Montes de Oca and J.M. Traverso-Soto for their help during the sampling campaigns and to E. de Miguel (SCCYT UCA) for his technical support with the LC-MS system. Thanks to Dr. Ignasi Queralt from the Laboratory of X-ray Analytical Applications (ICTJA-CSIC) too. This research has been funded by the CICYT project CGL2008-05598 and a FPI fellowship from the Spanish Ministry of Education and Science.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chemosphere.2014.04.098.

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Please cite this article in press as: Corada-Fernández, C., et al. Occurrence and spatial distribution of emerging contaminants in the unsaturated zone. Case study: Guadalete River basin (Cadiz, Spain). Chemosphere (2014), http://dx.doi.org/10.1016/j.chemosphere.2014.04.098