Environmental Pollution 174 (2013) 305–315

Contents lists available at SciVerse ScienceDirect

Environmental Pollution

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

Occurrence of 95 pharmaceuticals and transformation products in urban groundwaters underlying the metropolis of Barcelona, Spain

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ARTICLE INFO

Article history:
Received 4 September 2012
Received in revised form
30 October 2012
Accepted 24 November 2012

Keywords:
Pharmaceuticals
Transformation products
Metabolites
Urban groundwater
Field scale
Barcelona

ABSTRACT

The present paper presents the occurrence of 72 pharmaceuticals and 23 transformation products (TPs) in groundwaters (GWs) underlying the city of Barcelona, Spain. Thirty-one samples were collected under different districts, and at different depths. Aquifers with different geologic features and source of recharge were included, i.e., natural bank filtration, infiltration from wastewater and water supply pipes, rainfall recharge, etc. Antibiotics were the most frequently found compounds detected at levels reaching 1000 ng L^{-1}. Natural bank filtration from the river that receives large amounts of effluents from waste water treatment plants (WWTPs), turned out being the most influencing source of contamination, thus GW showed high range of compounds and concentrations as high as or even higher than in the river itself. In general, TPs were found at lower concentrations than the corresponding parent compounds, with some exceptions, such as 4OH propranolol and enalaprilat.

1. Introduction

Groundwater (GW) is an important resource of water supply in the world. In Catalonia, GW represents 35% of the water resources, of which 30–35% is used for drinking water, while the rest is used for industrial activities and agriculture supply (García-Galán et al., 2010). In Barcelona metropolitan area GW represents 19% of all the water resources and currently it is extracted for purposes where quality requirements are less stringent than for human consumption, such as municipal services (watering parks, street cleaning, ornamental fountains, etc.), other uses, including industrial (building heating and cooling and car washing, industrial cleaning, etc.), environmental (regeneration of the Vallvidrera reservoir and the Besòs riverbed) and agricultural.

Urban aquifers are especially vulnerable to contamination by a variety of contaminants due to urban activities and industry. Although soil provides a big inertia to quality changes and slows propagation of the contamination, for that same reason, once contaminated, the effects can hardly ever be reverted (García-Galán et al., 2010, 2011). Previous studies showed that aquifers underlying the Barcelona metropolitan area suffer pollution from different sources, including losses from water supply networks, leakage from sewers, seepage from rivers or other surface water (SW) bodies, and seawater intrusion. Emerging contaminants, such as surfactants and their degradation products (i.e. nonylphenol ethoxylates, nonylphenol carboxylates, nonylphenol and linear alkyl benzene sulfonates) were found at high concentrations (μg/L level) in aquifers recharged by the river Besòs showing clear dependence on the sources of recharge or/and pollution containing these substances and groundwater redox conditions (Tubau et al., 2010). Low, but measurable concentrations of drugs of abuse, are also found in zones recharged by a river that receives large amounts of effluents from WWTPs (Jurado et al., 2012).

Pharmaceuticals are another important class of emerging contaminants that can potentially reach GW. The use of pharmaceuticals by the modern society is huge and steadily increasing. They are developed with the intention of performing a biological effect and they may exert their activity at the low ng L^{-1} range (Vulliet and Cren-Olivé, 2011), therefore harmful effects to the ecosystem and humans should be evaluated (Eggen et al., 2010).

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0269-7491/$ – see front matter
http://dx.doi.org/10.1016/j.envpol.2012.11.022

Furthermore, the metabolites and biotic and abiotic transformation products (TPs) of parent pharmaceuticals can remain pharmacologically active.

Only a few studies of presence of pharmaceuticals in urban GWs (e.g., Grujić et al., 2009; Osenbrück et al., 2007; Reinstorf et al., 2008; Schirmer et al., 2011; Strauch et al., 2008; Wolf et al., 2006) can be found in the literature, and in all cases, very few pharmaceuticals were monitored and none of the studies included TPs. Analgesics and antibiotics were the classes more studied, and the levels found ranged from low ng L^{-1} (Standley et al., 2008; Vulliet and Cren-Olivé, 2011), to hundreds of ng L^{-1} (Grujić et al., 2009; Teijon et al., 2010).

In general, TPs are not frequently monitored, and only a few studies reported levels of in GW, i.e., 5 acetylated TPs of sulphonamides surveyed in Catalonia (region Barcelona belong to) (García-Galán et al., 2011), and TPs of phenazone-type compounds in GW in Germany (Massmann et al., 2008a, 2007, 2008b).

The present work studied the presence of 72 pharmaceuticals and 23 of their TPs in GW underlying the city of Barcelona (Spain). Eight of those 23 TPs are pharmacologically active, and another 8 are potentially active as glucuronides or acetylated derivates of active substances. To the knowledge of the authors, this is the first time such a big number of pharmaceuticals, especially TPs, have been studied in GW so far.

2. Material and methods

2.1. Study site

Fig. 1 shows the study area, situated in the North-East of Spain. The analyzed GWs are situated under 136 km^2 of urban realm, which includes Barcelona metropolitan area, where 2.2 million people live. The area is bounded by the Mediterranean Sea and the Collserola Range. Both, Llobregat and Besòs Rivers, close the rectangular zone. The climate is typically Mediterranean with an average rainfall of 600 mm $year^{-1}$.

Samples belong to different aquifers with different lithologies and ages, and can be divided into three groups. First group, located under the district called Poble Sec (PS), belongs to either Barcelona plain (samples labeled as upper depth (u)), or to the underlying confined aquifer (samples labeled as medium depth (m)). Barcelona plain is cropping out and consists of carbonated clays from Pleistocene, Quaternary. The underlying aquifer consists of sandstones, marls and sands from Miocene, Tertiary. Samples featured as (a) contain water from both aquifers, since the screened depth covers both units. See Table 1. The second group of samples is under Mallorca Street (MS), situated midway between Collserola range and the sea. They belong to either the Barcelona plain (samples labeled as upper depth (u)), or to the underlying confined aquifer (samples labeled as medium (m) and low depth (l)). Again, samples typified as (a) contain water from both aquifers since the depth screened covered both groundwater units. The third group of samples was located under Besòs River Delta (BRD). All of them belong to the most superficial unconfined aquifer, composed of gravels, sands, silts and clays from Holocene, Quaternary. Underlying that, there are another two aquifers with the same composition, confined this time, and separated by lutidic units.

Generally, in all aquifers, GW flows seawards, from the mountain range. Several recharge sources have been identified (Vázquez-Suñé et al., 2010). These include: (1) rainfall infiltration in the non-urbanized areas at the highest parts of the city (Collserola range hillside), which is consider as “clean” natural recharge water; (2) seawater intrusion; (3) Besòs River infiltration, which contains a large proportion of effluents from WWTPs, especially during the summer, when precipitations are scarce; (4) losses from the water supply network; (5) losses from the sewage system; and (6) runoff water from the paved areas, which washes away the urban surface and recharges the aquifers through direct infiltration or sewer seepage. A previous study by Jurado et al. (2012), calculates the proportion in which those sources, contribute to the recharge of every area, when the sampling campaign took place. According to that, in MS area, the main contributor to the total recharge is rainfall infiltration (60%), especially in the deepest aquifer (where GRA-2 was sampled), followed by the losses from sewage system (31%) and the losses from the water supply network (9%). In PS area, the main contributors are the losses from sewage system and losses from the water supply network, accounting for 96% (50% and 46%, respectively). The remaining 4% corresponds to rainfall infiltration. Regarding to BRD area, infiltration of water from the Besòs River is the largest contributor to the total recharge, representing 91%, but other contributors are losses from sewage system and water supply network. When considering all the 3 zones as a whole, average proportions are as follows: 21% corresponds to losses from the water supply network, 28% to losses from the sewage system, 18% to rain infiltration, and 33% to recharge from the Besòs River.

The presence of oxidizing species like nitrate, and the absence of ammonium, indicates oxidizing conditions in MS, and especially in PS. In the latter, nitrate was found at concentrations as high as 150 mg/L, along with high levels of dissolved oxygen. In contrast, BRD showed reducing conditions.

2.2. Sample collection

Thirty-one GW samples and one sample from Besòs River were collected during three field campaigns in May 2010 (27 GW and 1 Besòs River), December 2010 (1 GW) and May 2011 (three GW). See Supplementary data 1. Out of the 30 samples,

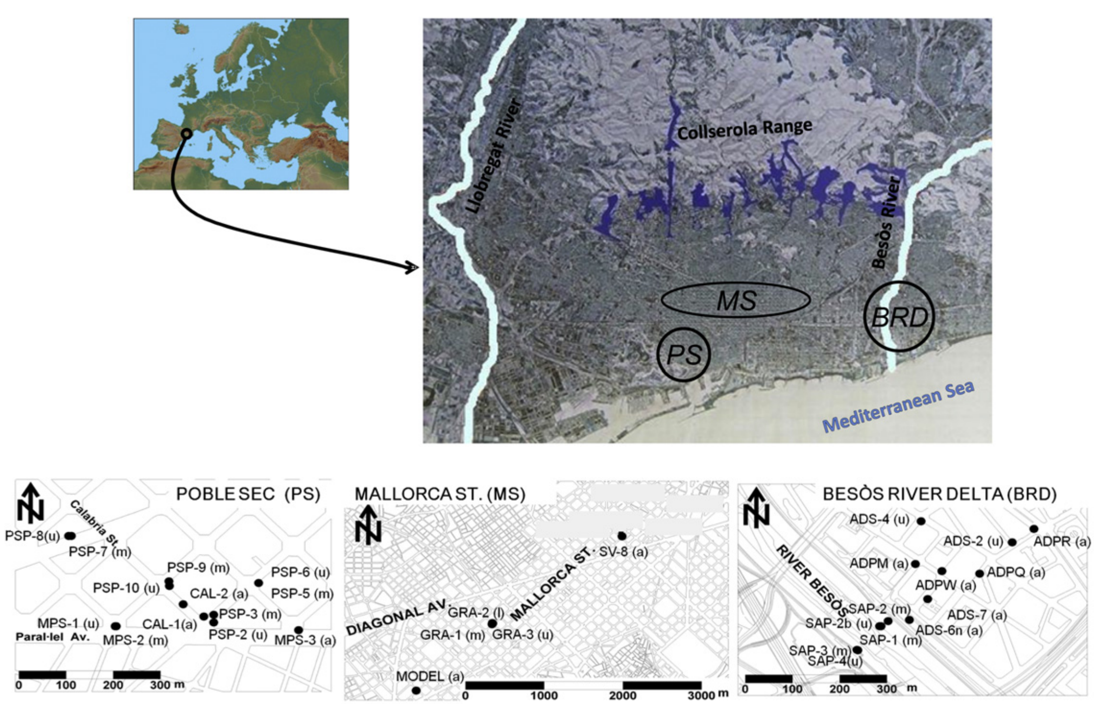

Fig. 1. Sampling map.