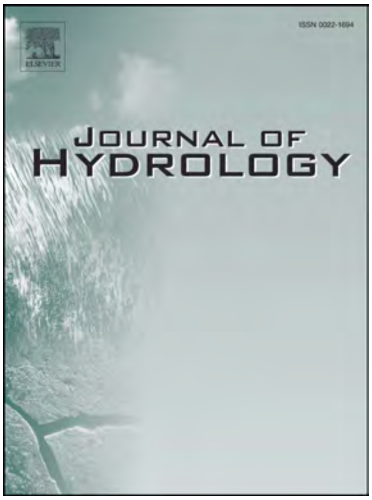

Research papers

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Occurrence of pharmaceuticals and personal care products in the urban aquifer of Zaragoza (Spain) and its relationship with intensive shallow geothermal energy exploitation

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Abstract

A steady increase in the consumption of pharmaceuticals and personal-care products worldwide is increasing their occurrence in the biosphere. The current study describes the abundance of 42 selected emerging organic contaminants (EOCs), including human and veterinary antibiotics, UV-filters and analgesics in the groundwater of the urban aquifer of Zaragoza (Spain), which is affected by intensive exploitation of shallow geothermal resources. The presence of groundwater heat pump systems in the aquifer studied offered the opportunity to study the occurrence of EOCs in relation to groundwater temperature and other physicochemical effects derived from this technology. Analysis of the data obtained allowed us to identify statistically significant relationships between the presence of EOCs and temperature, as well as other physicochemical and geochemical properties of groundwater. The results obtained suggest that temperature is a minor factor controlling the degradation of the organic compounds analysed compared to the oxygen input from groundwater heat pump systems which is possibly increasing the aerobic redox conditions, thus preventing the degradation of organic pollutants. Intensive use of shallow geothermal resources therefore seems to contribute in the prevalence of such compounds in the aquifer close to geothermal systems.

Keywords: Personal care products, UV filters, antibiotics, shallow geothermal, urban groundwater, field study

1. Introduction

In many places, groundwater is a major source of water for humans, but also for rivers and wetlands, and thus, it has a strong influence on both human development and wildlife habitats (Scozzari and Dotsika, 2015). The use of vast quantities of synthetic compounds in agriculture, industrial manufacturing processes, households, animal husbandry, and human healthcare has resulted in their continuous widespread occurrence in aquatic and terrestrial environments (Leung et al., 2012; Liu and Wong, 2013). The release of synthetic organic pollutants was not identified in the environment until the development of sensitive analytical methods capable of detecting their typically parts-per-trillion ($ng \cdot L^{-1}$) concentration levels in complex environmental matrices (Petrovic and Barceló, 2006). The development of highly sensitive and powerful analytical instrumentation has created (Noguera-Oviedo and Aga, 2016) considerable interest in the compounds known as emerging organic contaminants (EOCs) within the scientific community. Interest in EOCs stems from the fact that many of these organic contaminants pose a potential adverse threat to ecological and human health, even at low concentrations (Campbell et al., 2006; Liu et al., 2009; Postigo et al., 2008; Reungoat et al., 2010; Swartz et al., 2006). Occurrence of EOCs in groundwater has been described and reviewed all over the world (Lapworth et al., 2012) highlighting the widespread contamination of groundwater resources (102-104 ng·L-1) by a large variety of emerging contaminants resulted from anthropic activity. In the United States, 65 types of EOCs in groundwater samples were analysed from 47 groundwater sites susceptible of contamination across the country, identifying 35 of the 65 EOCs studied at least once in 81% of the locations (Barnes et al., 2008). A pan-European reconnaissance of EOCs in groundwater analysed 54 compounds in samples from 164 locations, finding a median number of detections per site of 12 compounds (Loos et al., 2010). In Spain, the occurrence of EOCs is manly related to the point source of pollution corresponding to the effluents of wastewater treatment plants (WWTPs) and the contamination profile is dominated by industrial compounds followed by pesticides and pharmaceuticals (PhACs) (Jurado et al., 2012). A national-scale assessment of EOCs involving 2650 sites in the United Kingdom found clear differences in EOCs between land-use types, particularly for urban-industrial and natural land-use, with the urban industrial type presenting the overall highest concentrations (Manamsa et al., 2016; Stuart et al., 2012). Moreover, this national-scale study also concluded that differences in EOCs within important aquifers are less likely related to aquifer flow mechanisms and land-use controls by topography. In Italy, a total of 20 EOCs studies have been performed (Meffe and de Bustamante, 2014) showing the importance of EOC metabolites in the microbial processes controlling EOCs environmental fate. In Africa, the number of EOCs studies are still limited. The first study was located in Zambia (Sorensen et al., 2015)) and showed a general absence of personal care products (PCPs), life-style compounds and PhACs, probably related to the limited use of products containing EOCs in the developing countries. In France, a national screening of 411 EOCs was performed at 494 groundwater sites, finding that 44% of the targeted compounds were found to be present at least in one sampling point (Lopez et al., 2015). Finally, in Switzerland, EOCs studies focus, among others, on the occurrence of EOCs in river-groundwater interaction (Epting et al., 2017b). We can conclude from these reviews that the knowledge on spatial and temporal variability of a vast number of EOCs in groundwater is still limited. Furthermore, the majority of national and regional studies are biased towards contaminated sites involving waste water point sources, while the risk of groundwater pollution from more diffuse sources, such as urban sewage leakage, is poorly characterized (Lapworth et al., 2012). EOCs and their metabolites and transformation products include a vast array of compounds such as PhACs , PCPs, drugs of abuse, pesticides, engineered nano-materials, etc. The PhACs input into urban aquifers has been associated with river bank filtration of polluted surface water, urban waste water infiltration (Gros et al., 2013; Jurado et al., 2014a; Jurado et al., 2014b), and water supply pipes and rainfall recharge, resulting in maximum concentrations above 100 ng L^{-1} in groundwater (López-Serna et al., 2013). PhACs encompass different therapeutic groups, including antibiotics, analgesic and anti-inflammatories, antifungals, psychiatric drugs, lipid regulators, cholesterol-lowering statin drugs, etc. Much attention has been given to occurrence of veterinary PhACs such as tetracyclines and quinolones, and their sorption in soils (Tolls, 2001), as they are highly mobile compounds with the potential to leach into the groundwater, ultimately reaching surface waters. Sulfonamides in manure from treated animals, as well as nitrates, can reach groundwater when applied to the soil (García-Galán et al., 2010), thus affecting its denitrification processes (Ahmad et al., 2014). These compounds can also be transported or degraded in groundwater, depending on the existent redox conditions (Barbieri et al., 2011). Antibiotics reaching groundwater have caused changes in human microbiomes, which can lead to potential hazards for human health (Baran et al., 2011). Although sulfonamides could be ubiquitous in aquifers, the lack of legislation setting up risk environmental levels hinders the establishment of a definitive qualitative assessment for groundwater samples containing these compounds (García-Galán et al., 2011).

On the other hand, chemicals employed in PCPs, such as sunscreen lotions, perfumes, cosmetics, shampoos, insect repellents, and other products, are intended for external application onto the skin, and are ultimately washed away, ending up in the waste water collection system in their unchanged form (Teijon et al., 2010; Ternes et al., 2004). As such, chemicals employed in PCPs ultimately accumulate in the environment, as they are not completely degraded in WWTPs. PCPs have been shown to have a potential impact on aquatic wildlife, bacteria, and/or mammalian cells at low concentrations (Gago-Ferrero et al., 2013a). To date, few data on PCPs concentrations in groundwater have been collected, and such data are limited to ultraviolet-filters (UVFs) in concentrations up to 0.1 μg L^{-1} (Hopkins and Blaney, 2016; Jurado et al., 2014a; Serra-Roig et al., 2016).

Although some pioneer studies have been published, the detection, degradation under different redox conditions (Jurado et al., 2014b; Rodríguez-Escales and Sanchez-Vila, 2016), transport (Martínez-Hernández et al., 2014), and groundwater risk assessment (Molins-Delgado et al., 2016) of PCPs in groundwater has not yet been comprehensively studied and discussed (Hopkins and Blaney, 2016).

The current research in this field is related to the need to define the environmental quality standards in Europe for EOCs, which is still in development. Only pesticides are regulated (EC, 2006), with maximum concentrations of 0.1 and 0.5 μg·L^{-1} for individual substances (including metabolites and by-products) and the total sum, respectively. Therefore, the almost inexistent regulations for drinking water, environmental quality standards, or groundwater threshold values for many EOCs will require further understanding of their occurrence and fate, in order to address the legal regulatory framework regarding these EOCs in the coming decades (Lapworth et al., 2012).

On the other hand, shallow geothermal energy resources in urban areas are increasingly being exploited (Lund and Boyd, 2016). Groundwater heat pump systems (GWHP systems) technology is widely and directly used for heat exchange. Basically, these systems pump up groundwater, and heat from buildings on the surface is exchanged with the extracted groundwater, and usually returned to the same aquifer it was obtained from. Previous research indicated that changes in the quality and chemical composition of groundwater affected by the operation of these systems is mainly a consequence of gas exchange with the atmosphere (CO_2 and O_2) during the injection process, and temperature changes (Abesser, 2010; Banks, 2012; Bonte, 2015; EPA, 1997; Jaudin, 1988). Nevertheless, studies on the changes in EOCs induced by these systems has not been previously conducted to our knowledge. In this context, the urban alluvial aquifer of Zaragoza city (Spain) has been extensively monitored over the last 10 years to study the heat plumes generated by 65 GWHPs injecting heated groundwater (Epting et al., 2017a; García-Gil et al., 2016). The existent geothermal monitoring network in this city covers more than 31 piezometers, and represents an opportunity to evaluate, among other physicochemical and geochemical properties, the effect of temperature variations at a city scale on the occurrence of most important EOCs. The enhancement of aerobic redox conditions and the pH increase induced by shallow geothermal exploitation in Zaragoza has already been documented (García-Gil (García-Gil et al., 2016; Garrido Schneider et al., 2016), thus allowing us to hypothesize that geothermal exploitation activity could prevent the bioprocessed degradation of EOCs (Barbieri et al., 2011), and result in a relative increase of their concentrations within thermal plumes occurring in the groundwater body. Thus, the aims of this study were to (1) investigate the spatial distribution and concentration of 32 antibiotics, 8 UVFs, and 2 nonsteroidal anti-inflammatory drugs in an urban groundwater body and (2) analyse the statistical differences in their concentration/occurrence in relation to heat plumes arising from intensive shallow geothermal exploitation. To address these questions, the chemical analysis of groundwater samples allowed obtaining the EOCs content distribution in the urban aquifer of Zaragoza. Two main approaches were taken to understand the occurrence of EOCs and find a possible relationship between them and shallow geothermal activities. The first approach consisted in analysing cadastral maps and the hydrogeological regime of the city studied to identify plausible sources of contamination. On the other hand, a statistical approach using Mann–Whitney U test allowed explaining the presence and absence of the different types of EOCs in terms of differences in mean values of the physicochemical, geochemical and hydrogeological parameters studied. Moreover, correlations were calculated to show whether and how strongly EOCs were related to these parameters. Finally, presence and absence of EOCs explained by parameters proved to be controlled by geothermal expiation (e.g. groundwater temperature) were used to provide evidence of an existing relationship between geothermal activity and occurrence of some of the EOCs studied.

2 Study site

The city of Zaragoza is located in the central area of the Ebro River Basin (Spain), which has a semi-arid climate, with an average precipitation of approximately 300 mm per year, and a yearly average temperature of 14.9 ºC. The metropolitan area of Zaragoza is underlain by a shallow unconsolidated aquifer composed of siliceous and carbonate grain-supported gravels, underlain by an Oligo-Miocene sub-horizontal gypsum and marl substratum (Fig. 1). The unconsolidated nature of the aquifer, together with a thickness up to 60 m, results in a high transmissivity urban aquifer ranging from $3 \cdot 10^2$ up to $4 \cdot 10^3$ $m^2 \cdot day^{-1}$. Groundwater resources of the city are mainly used (68% of the demand) for air-conditioning of buildings by means of shallow geothermal installations (Garrido et al., 2012). A total of 65 groundwater heat pumps (GWHP) systems, with a total installed heat power of 110 MWt, involving 176 wells interacting with urban groundwater, are currently in use (Garrido et al., 2012). Using a calibrated and validated 3D groundwater flow and heat transport model of the urban alluvial aquifer of Zaragoza, groundwater flow and heat plumes generated by GWHPs were reproduced numerically (Epting et al., 2017a; Garcia-Gil et al., 2014) (Fig. 2). The numerical model used in these studies involved hydraulic head and groundwater temperature high resolution monitoring datasets obtained from a piezometer network in the city of Zaragoza. Furthermore, GWHPs implemented in the model used upscaled daily effective values of pumping rates and captation/injection temperatures recorded every 15 minutes (Muela Maya et al., 2018) from 32 real exploitation systems. Thermographs obtained from piezometers located downgradient from injection wells of GWHPs were used during the inverse method technique (Carrera and Neuman, 1986) application in the estimation of hydraulic and thermal aquifer parameters. The calibration process also incorporated prior information from aquifer test analysis (Criollo et al., 2016).

EOCs studies in this area are limited to studies on surface waters. The river Ebro at its pass through the city of Zaragoza has showed contents of PhACs in the range of 200 to 450 ng·L-1 (Gros et al., 2011). Other organic pollutants such as PCBs, DDTs and other endocrine-disrupting compounds have been found in carps (Lavado et al., 2006).

3 Methods

3.1 Groundwater sampling

Since 2007, the Geological Survey of Spain (IGME), in collaboration with the local water management administrator (CHE), has been monitoring the exploitation of shallow geothermal resources in the city of Zaragoza. The geothermal monitoring network constructed and utilized in this work comprises 17 fully penetrating-screened PVC piezometers specifically constructed for this purpose (involving a total of 650 linear meters), 10 partially-penetrating piezometers managed by the City Council, and 18 groundwater wells. The network covers homogeneously the whole metropolitan area of Zaragoza (52.5 km2), with the average distance between piezometers ranging from 0.9 to 1.5 km. The monitoring network is refined towards the historic quarter of the city in the right margin of the river Ebro, where the distance between piezometers ranges between 90 and 400 m. In this study, 25 samples were collected for geochemical analysis (spectrophotometry and ICP-MS) and EOCs analysis (on-line-SPE-LC-MS/MS). Sample collection was undertaken in October/November 2016. Detailed spatiotemporal distribution of groundwater sampling is provided as supplementary material (Fig. S1). Major and trace elements have been analysed in this groundwater monitoring network for several years showing a very stable geochemical composition over time (Garrido Schneider et al., 2016) which allows us to ensure the temporal representability of the samples taken. Groundwater sampling was performed following USGS protocols and standard procedures (Wilde, 2008). Record keeping of field personnel was maintained for each sampling location to permanently document field activities, measurements and instrument calibration. Field measurements were executed so that bias from data-collection activities were minimized and a checklist for groundwater site setup and well-sampling preparations was followed. Using a Grundfos SQE submersible pump, a flow rate of 7 m3h-1 was maintained for a minimum of 20 minutes in each sampling site to accurately represent the physical and chemical properties of water in the aquifer. The pump intake was located at 0.9 m below static water surface and at a minimum distance above the top of the screened interval of 10 times the well diameter. A needle valve was used as a flow-regulating valve to control the flow rate from the rising main. The volume of groundwater pumped in this procedure ensured the removal of three well volumes of standing water while monitoring the water level and the stabilization of field measurements. During pumping, a flow-through cell was coupled to minimize any gas exchange with the atmosphere during *in situ* measurements of electrical conductivity (EC), temperature (T), and pH, conducted using portable meters (CRISOM pH25/CH35/OXI45). Total alkalinity (TALK) was determined in the field by volumetric titration (0.1 N H2SO4) (HACH AL-AP) from filtered (0.45 µm pore size filters) groundwater samples. Complete stabilisation of physicochemical parameters was required for groundwater sampling. The stabilisation criteria for field direct measurements were ± 0.2 ºC, ± 3 percent, ± 0.1 pH unit for T, EC and pH, respectively. The values reported for each sampling site consisted in the median of the final five readings. Several aliquots were collected in each sample site as follows:

First, non-filtered 500 ml aliquots were used for EOCs analysis, with one sample collected from each sampled point, and aliquots were stored in a pre-cleaned amber glass bottle with a PTFE cap liner to avoid photodegradation. Glass bottle containers were stored at 3 °C, and taken to the laboratory at the end of the sampling day. Samples were vacuum-filtered using a 1 µm glass fibre filter (Whatman, Fairfield, CT, USA), and then passed through a 0.45 µm nylon membrane (Teknokroma, Barcelona, Spain), and stored at -20 ºC in the dark until analysis.

Second, water samples for inorganic chemical analysis were stored in polyethylene terephthalate (PET) containers, and filtered in the field using 0.45 µm pore size cellulose membrane filters (MF-Millipore™). Two 100 mL aliquots were collected using HDPE bottles, including an un-acidified one for major anions, and an acidified one with HNO_3 (1.6 N) at pH < 2 for trace metals. The samples were refrigerated, and stored at 3 °C until chemical analysis.

3.2 EOCs analysis

3.2.1 Standards and reagents

The target compounds analysed and their acronym are listed in Table I. BP3, BP1, 4HB, 4DHB, Et-PABA, UV-P and DMBZT were of the highest purity (> 99%), and were obtained from Sigma–Aldrich (Steinheim, Germany). DHMB (99%) was sourced from Merck (Darmstadt, Germany). Sulfonamide metabolites AcSPY and AcSDZ were purchased from Toronto Research Chemicals (Toronto, ON, Canada). Selected sulfonamides (Table I) were purchased from Sigma–Aldrich. The remaining antibiotics standards of high purity grade (> 90%) were purchased from Sigma–Aldrich. KET was purchased from Fluka (Seelze, Germany). High performance liquid chromatography-grade solvents (water, acetone, methanol, and acetonitrile), as well as formic acid (98% purity) were provided by Merck. N_2 and Ar of 99.995% purity were purchased from Air Liquide (Barcelona, Spain). Glass fibre (1 mm) and nylon membranes (0.45 mm) were obtained from Whatman International Ltd (Maidstone, England). Individual stock standard solutions, as well as the isotopically labelled internal stock standard solution were prepared on a weight basis in MeOH at 200 $mg \cdot L^{-1}$. The solutions were stored in the dark at -20 ºC. Working solutions were prepared daily by appropriate dilution of the mixture stock standard solution in MeOH. Stock standard solutions were prepared in MeOH at 1 mg $m \cdot L^{-1}$ and stored at -2 °C until use. For all compounds, standard solutions of the mixtures were prepared in MeOH. Standard mixtures used as spiking solutions for preparation of the aqueous calibration standards always contained < 0.1% of MeOH.

3.2.2 Analytical methods

Analysis of the selected EOCs and their transformation products was carried out at the Spanish Council of Scientific Research (CSIC). Analyses were performed by on-line solid phase extraction coupled to liquid chromatography-tandem mass spectrometry (on-line-SPE-LC-MS/MS), following a fully automated method previously described by Gago-Ferrero et al. (2013b). Liquid chromatography coupled to tandem-mass spectrometry (LC–MS/MS) allows performing simultaneous analysis of several EOCs and their transformation products with a wide range of physicochemical properties. The advantages of LC-MS/MS above Atomic Absorption Spectroscopy (AAS) are mainly the extremely low detection limits accomplished (low ppt level), the highly automatized platforms and the multi-element analysis. Moreover, when using high-resolution mass spectrometers (HRMS), exact mass calculation and identification of unknown compounds are provided. LC-MS/MS is the technique of choice for the determination of EOCs and their transformation products, while inductively coupled plasma-mass spectrometry (ICP-MS) or even inductively coupled plasma-mass spectrometry optical emission spectrometry (ICP-OES) are the adequate ones for the analysis of metals. Using on-line-SPE-LC-MS/MS, samples previously spiked with deuterated surrogate standards were pre-concentrated and purified using an automated on-line SPE-LC instrument Symbiosis^{TM} Pico from Spark Holland (Emmen, The Netherlands). On-line SPE pre-concentration and purification of all samples, aqueous standard solutions, and blanks were performed by loading 5 mL of the corresponding solutions through a PLRP-s cartridge previously conditioned with MeOH, acetonitrile, and HPLC grade water. The trapped analytes were eluted to the LC column with the chromatographic mobile phase. To ensure selectivity of the analytical method, a minimum of three identification points for positive identification of the analytes and retention time variations were obtained, in accordance with the European Council Directive 2002/657/EC, and specifically described in previous works (García-Galán et al., 2010; García-Galán et al., 2011).

3.3 Geochemical analysis of groundwater

Groundwater aliquots collected for geochemical analysis were analysed at the National Geological Survey Laboratories (IGME). Diverse spectrometric techniques were used, including spectrophotometry (ALLIANCE Integral Plus) for SO_4, NO_3, SiO_2, HCO_3 and Cl; AAS (flame operation, VARIAN FS-220) for Na, K, Mg, Ca and Fe; and ICP-MS (LECO Renaissance) for trace metals Ag, Al, As, B, Ba, Be, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Se, Th, Tl, U, V and Zn. The accuracy and precision of the analytical methods were verified against certified reference waters (SRM 1643, APG 4073, and others, e.g., control samples of the Water Research Centre's AQUACHECK international programme). Chemical oxygen demand (COD) was also measured with standard methods (Wilson, 1959).

3.4 Statistical analysis

The occurrence and fate of EOCs in aquifers in porous mediums depends on different factors, including, among others, the physicochemical and geochemical properties of groundwater. Statistical variables considered in this work are: pH, EC, TALK, COD, unsaturated zone thickness (UZ), sampled temperature of groundwater (T), maximum temperature of groundwater throughout the year (T_{MAX}), minimum temperature of groundwater throughout the year (T_{MIN}), amplitude of groundwater temperature oscillation throughout the year (T_{AMP}) and major, minor, and trace metals described in subsection 3.3. Physicochemical variables are closely related to the stability and mobility of EOCs. For example, variations in pH control the protonation/deprotonation reactions (Tolls, 2001), temperature affects the degradation of antibiotics (Doi and Stoskopf, 2000), dissolved oxygen in groundwater can change aerobic biodegradation rates of EOCs (Al-Rajab et al., 2010; Barbieri et al., 2011), and thickness of the unsaturated zone is related to the potential degradation of EOCs (Sopilniak et al., 2018). On the other hand, major and trace elements such as NO3 and Se have been related to incidental or induced infiltration of sewage water (Dávila Pórcel et al., 2012), therefore qualifying as suitable markers of anthropogenic influence in the aquifer environment. Moreover, antibiotics may affect the natural microbial denitrification process (Ahmad et al., 2014; García-Galán et al., 2010). Other variables such as organic matter contents, GUS index (Gustafson, 1993), water age or distance to surface water bodies have not been considered in this study and these have also a great importance in adsorption processes (Jones-Lepp and Stevens, 2007), leachability capacity, degradation and mixing processes, respectively.

First, to understand the occurrence of EOCs, mean differences of the different parameters were compared between presence and absence of the different types of target compounds. To do so, a Mann–Whitney U test was conducted, as the samples did not meet the assumption of normality (checked with Kolmogórov-Smirnov (K-S) test). Subsequently, correlations between EOCs contents and the variables described were calculated with Spearman's rank correlation (ρ), as the assumption of normality was violated and Pearson's *r* could not be used. Statistical significance was established at *p*-values under 0.05. In some relevant cases, a tendency to significance (*p*-values between 0.05 and 0.08) was considered for discussion. All the statistical analyses were performed using SPSS Statistics version 20.0 software (IBM; Armonk, New York, USA).

4 Results and discussion

4.1 Occurrence and spatial distribution of target EOCs in the urban groundwater of Zaragoza

The concentration of the target EOCs analysed in the groundwater samples collected are provided in Fig. 3. In addition, the ranges and maximum concentration, together with their detection frequency are summarised in Table I. At least one EOC was detected in 12 of the 25 sampled points, i.e., 48% of the measured points contained at least one of the EOCs studied. This is a relatively low frequency compared to other studies performed in urban areas (Sui et al., 2015) and could be explained by hydrogeological features of the urban aquifer studied, where its highly transmissivity and porosity results in an effective mixing process of recharged groundwater (Garcia-Gil et al., 2014) in which EOCs appear diluted in comparison with other less-transmissive urban aquifers in the same climatic zone (Jurado et al., 2012). Specifically, PCPs (UVFs) were found in 12% of the monitoring points sampled, and PCPs occurred at concentrations below 29.6 ng·L^{-1}. In addition, PCPs were found in 19% of the monitoring points containing EOCs, and 6% of the measured mass diluted in the aquifer corresponded to these compounds. Where PCPs were detected, DMBZT was the most commonly found compound (50%), but it occurred at a lower concentration than BP1 and BP3. In terms of mass diluted in groundwater (percentage of the sum of concentrations), the three compounds were equally distributed. Antibiotics, on the other hand, were the most commonly found EOCs (36%) in the aquifer studied. However, it should be noted that sulfonamides are widely used in veterinary activities and their metabolites were not detected, even though 17 sulfonamide family members were analysed (Table I). Still, antibiotics were the most commonly found EOCs group (56%) in the aquifer. Moreover, antibiotics represented 93% of the total measured EOCs mass dissolved in the aquifer. This was due to the high frequency and concentration of TET and OXY, whose maximum observed concentrations were 269 and 400 ng·L^{-1}, respectively. When antibiotics were detected, the most frequently found compound was TET, representing 76% of the total measured antibiotics mass diluted in the aquifer. OXY was only found in 9% of the cases in which antibiotics were detected, but was the second compound in terms of measured mass dissolved in the aquifer studied (21%). The rest of the ATB compounds represented less than 4% of measured antibiotics mass dissolved. The other therapeutic group of target compounds, NSAIDs, was detected more frequently (25%) than PCPs, but their lower concentrations (< 5.9 ng·L^{-1}) explain why they comprised the lowest total measured EOCs mass dissolved in the aquifer (1%). This low concentration of NSAIDs can be explained by the fact that KET and MFA analgesics are PhACs that display hydrophobic behaviour (Jurado et al., 2012), and therefore they tend to bio-accumulate, and have high adsorption capacity on organic matter (Jones-Lepp and Stevens, 2007). MFA was detected three times more frequently than KET, but in terms of mass, both compounds were almost equally distributed (54 and 46%, respectively).

Fig. 4 shows the spatial distribution of the target EOCs found, and the relative proportion of each compound for all the points sampled in the city of Zaragoza. On the left margin of the Ebro River (Northern side), EOCs were detected in 37% of the observation points. On the other hand, on the right margin (Southern side), EOCs were found in 53% of the sampled points. This discovery can be explained not only by the higher number and density of inhabitants on the right margin of the Ebro River, but also by the presence of an older sewerage network system. The samples collected from observation points close to the Ebro River (< 163 m) were all affected by EOCs, which can be related to river-aquifer interactions (Barceló and Petrovic, 2011). No EOCs were detected at monitoring points located 348 to 590 m (GS-55/52/50/04/11) away from the Ebro River, except at monitoring point GS-11.

The latter monitoring point corresponds to a pumping well for irrigation proposes, which was sampled after the pumping season and, therefore, the surface water from the Ebro River could have been mixed with the pumped water, thus generating EOCs contamination. The Huerva River has a very low hydraulic connection with the urban alluvial aquifer studied. The Gállego River, on the other hand, is well connected to the aquifer, but no EOCs were detected in the GS-72 piezometer, located 270 m from the river. No EOCs were detected in the monitoring points located in the historic quarter of the city (GS-50/04) even when these were located in a highly populated area where old buildings dominate. This might be due to the sewage system of this area undergoing a major programme of sewerage extension and rehabilitation in 2012.

4.2. Possible recharge sources of detected PCPs and PhACs

The semi-arid climate in the metropolitan area of Zaragoza involves a potential evapotranspiration larger than the low existent rainfall (< 300 mm·year^{-1}). If the anthropogenic sealing of soils in urban areas is also considered, the surface recharge of the aquifer considered would be very limited (García-Gil et al., 2014). Therefore, EOCs input to the aquifer is expected to be related to leakages from mains and sewage systems, with the latter containing WWTP influents. These EOCs and other contaminants pathways into the aquifer as a diffuse pollution process (non-point source) is generally documented in urban aquifers worldwide (Sui et al., 2015; Trauth and Xanthopoulos, 1997; Vázquez-Suñé et al., 2005). In the city of Zaragoza, detailed cadastral maps showing water-level contour maps in the proximities of the observation points that contained higher EOCs contents allowed us to identify possible sources of contamination (Fig. 5), depending on groundwater flow paths. All observation points close (< 150 m) to the most important hospital centres of Zaragoza were affected by antibiotics (Fig. 5A/B/C/E), except for GS-6, where only NSAIDs were detected. Previous studies have collected wastewater from hospital effluents and identified those as an important source of antibiotics (Coutu et al., 2013; Rodriguez-Mozaz et al., 2015; Santos et al., 2013). The fact that antibiotics are found primarily close to hospital centres in Zaragoza reinforces the idea that these infrastructures act as point-source of antibiotics contamination. Hospital effluent leakages in broken side sewers prior to the inlet into the main city sewerage system may constitute a potential entry path into groundwater. However, the presence of a hospital centre is not a requirement to find antibiotics, as GS-11 had the highest concentration of TET, and the nearest health centre is more than 500 m away from this observation point. The latter point is located within a park (Fig. 5G) and close to three swimming pools, which could explain the presence of UVFs from swimming pool leakages. The relationship between the proximity of swimming pools and the presence of UVFs was also observed in sampling points GS-16 and GS-3. Sample point GS-49 was located down-gradient from a swimming pool, but no UVFs were detected (Fig. 5I), indicating that swimming pools leakages are not necessarily occurring, or do not necessarily contain such compounds, for instance if it is an indoor swimming pool. NSAIDs could be related to hospital centres (Fig. 5E) or university campuses (GS-1).

4.3. Differences in groundwater parameters explaining occurrence of EOCs

Physicochemical properties of the groundwater are a first order factor in the determination of the fate of EOCs during their circulation towards discharge areas. A paired-samples Mann-Whitney U test was conducted to compare physicochemical parameter mean values from the group of samples containing EOCs with respect to the ones not containing EOCs (Fig. 6). Additionally, all Mann-Whitney U coefficients calculated are provided as supplementary material Table S2. As such, we concluded that there was a higher pH in the groundwater samples that contained UVFs. The acid-base reactivity (pK_a values) of many of the EOCs were in the range of pH values encountered in the aquifer (Tolls, 2001). Therefore, it can be inferred that UVFs are subject to protonation/deprotonation reactions, and that their mobility depends on the pH of groundwater. At circumneutral pH levels, UVFs may be adsorbed onto the solid matrix of the porous medium, and at a higher pH, UFVs would be mobilized. Furthermore, there were tendencies showing higher concentrations of HCO_3 due to its ion dependency on pH. The occurrence of antibiotics was related to a positive increase in NO_3 contents in groundwater. NO_3 is a common tracer of sewage water (Wakida and Lerner, 2005). Although nitrates were ubiquitous in groundwater beneath the city, antibiotics were only detected when high nitrate concentrations were found. This could be interpreted as sampled points containing high nitrate contents being close to major sewer leakages, where antibiotics could be detected, since they would not be diluted or/and degraded. This provides evidence for the hypothesis that antibiotics originate from the sewage network, as has been documented in other cases (López-Serna et al., 2013). A small tendency was found associating the presence of antibiotics with an increase in minimum annual temperature of groundwater. The effect of temperature on the time needed to degrade antibiotics by hydrolysis and epimerization was evaluated (Doi and Stoskopf, 2000), indicating that one-half values of the pseudo-first order rate degradation model are reduced from 41 to 19 h, and from 116 to 63 h for XY and TET when changing the temperature from 35 to 22 ºC (pH = 7). These results would in principle lead us to expect the absence of antibiotics in GWHPs heat plumes, but this was not observed in the field. Rather, antibiotics were detected in heat plumes where the minimum temperature throughout the year was higher. Thus, the mechanisms preserving antibiotics, which are enhanced by shallow geothermal activity, acquire a higher importance than the temperature effect in degradation rates of these compounds. NSAIDs occurrence was related to statistically significant higher temperatures and maximum temperatures over the year. These results suggest that the hydrophobic behaviour of NSAIDs analysed could be altered due to temperature variations, and the magnitude of adsorption capacity at temperatures higher than 20 ºC could be reduced, thus increasing their prevalence in the aquifer media. NSAIDs were also related to a tendency to find lower Ba contents in groundwater, and statistically significantly related to higher Mo contents in groundwater. Finally, total EOCs occurrence in general was significantly related to higher groundwater temperatures. EOCs also showed a tendency for a positive relationship with higher minimum groundwater temperatures over the year. Both results concur in relating the shallow geothermal exploitation activity with the presence of EOCs. The exact geochemical mechanisms explaining this relationship are unclear. We can only speculate on whether EOCs contents are related to GWHPs activity enhancing EOCs desorption, accepting it is an endothermic process, or if there is an increase in dissolved oxygen due to gas exchange with the atmosphere, which prevents anoxic degradation of EOCs by microorganisms. In addition, the increase in dissolved oxygen in the aquifer related to GWHPs activity has been previously documented (Garrido Schneider et al., 2016), and the relationship between anaerobic redox conditions and the removal of EOCs from aquifers has been studied experimentally, and numerically reproduced, alluding to biotic processes (Barbieri et al., 2011). Therefore, the input of oxygen into the aquifer enhanced by GWHPs activity (inappropriate isolation of pumped groundwater) may prevent the removal of EOCs through microbes acting more efficiently under anaerobic conditions. Furthermore, this attenuation in the removal of EOCs from aquifers by microorganisms could be slowed down even more if the groundwater content in microorganisms decreases. Such a decrease in bacterial counts in heat plumes has been recently documented for pathogenic bacteria

(García-Gil et al., 2018). Therefore, this referenced study supports the link established between EOCs occurrence and shallow geothermal energy systems in the present work.

Presence of EOCs was also related to positively increased Cr and Se. The increase of Cr mobility with Eh is well known (Guertin et al., 2016), and the increase of dissolved oxygen due to GWHP systems invoked above could also explain this observation. In addition, metal ions have been confirmed to be an important factor influencing the degradation of antibiotics due to the formation of complexes of antibiotics with co-existing metal ions in aqueous solution (Zhang et al., 2014b).

4.4 Correlations of EOCs contents with groundwater parameters

Spearman's rank correlation coefficients (ρ) were calculated to determine the relationship between the compounds analysed, and physicochemical and geochemical parameters measured in the field. Spearman's correlation coefficients and linear models describing correlations are provided as supplementary material (Tables S3 and S4, respectively). A significant positive correlation between UVFs, antibiotics and total EOCs contents and pH was found ($\rho = 0.439$, 0.423 and 0.473, respectively, $p < 0.05$). These results are consistent with those of other studies on the effect of pH in antibiotics retention/degradation and transport in saturated porous media (Cheng et al., 2000; Zhang et al., 2014a). DMBZT compounds had a tendency to decrease as the unsaturated (vadose) thickness increased ($\rho = -0.384$, $p = 0.058$). DMBZTs is used as anticorrosive agent in many daily use products, such as dishwasher detergents, which make them to be found very frequently and at high concertation levels in waste waters form urban origin (Mizukawa et al., 2017). Antibiotics correlated significantly with pH ($\rho = 0.439$, $p = 0.028$). This relationship is probably related to the degradation of antibiotics being associated with hydrolysis and epimerization, which are both pH-dependent mechanisms (Hussar et al. 1968). Only NSAIDs correlated significantly with temperature, maximum temperature, and temperature amplitude over the year (ρ = 0.471, 0.461 and 0.435, respectively, $p < 0.05$). According to previous research, this correlation would be expected to be negative due to the mesophilic behaviour of dominant NSAID-biodegrading microorganisms (Al-Rajab et al., 2015; Carr et al., 2011; Topp et al., 2008). A possible explanation for this result may be related to the increase of dissolved oxygen in groundwater during the heated water injection process (higher temperatures) of GWHPs, since NSAIDs compounds are readily amenable to aerobic biodegradation in soil (Al-Rajab et al., 2010). A strong positive correlation was detected for TET and antibiotics in general, and both had a correlation coefficient of ρ = 0.47 ($p = 0.016$), which is a logical correlation since TET are the dominant antibiotic. Correlation tendencies between total EOCs and NO_3 were also found (ρ = 0.387, $p = 0.056$), probably due to a common source of contamination. Finally, NSAIDs correlated positively with Mo (ρ = 0.435, $p = 0.038$), and total EOCs were correlated positively with Se (ρ = 0.416, $p = 0.049$). High contents of trace metals in groundwater affect bacteria metabolism (Stolz et al., 2006), which may also affect their capacities for biodegradation of EOCs.

Fig. 7 summarizes graphically the most relevant Spearman's correlation coefficients of EOCs with physicochemical and geochemical properties of the aquifer. Best-fitting polynomial regression models were plotted to show identified data trends in samples where EOCs were detected. Fig. 7A illustrates the sensitivity of antibiotics to pH values and, if only TET values are considered (red circles), an exponential regression function is found. Loftin et al. (2008) investigated the effects of pH on the degradation of TET and OXY (the most commonly found antibiotics in this study), and a change in pH from 7 to 9 resulted in a 115-hour increase in the half-lives of the pseudo-first-order degradation model fitted for both antibiotics. This pH effect on the increase of time necessary to degrade (hydrolysis and epimerization) to one-half of the initial concentration of antibiotics would have resulted in an increase of their concentration, as shown in Fig. 7A. Antibiotics were found also to correlate with NO_3 contents (Fig. 7B). In this case, if samples with pH below 7.3 are chosen, a second order polynomial regression model could be fitted indicating that the increase in antibiotics at relatively low pH is limited compared to higher pH values, where antibiotics occurred at the highest concentrations. The findings of the current study have not corroborated significant differences in antibiotics due to COD changes in the aquifer as indicator of organic matter, which have been observed to affect their degradation rates in previous studies (Doi and Stoskopf, 2000). Nevertheless, since different antibiotics with different chemical-physical properties are considered as a whole in this study, it has to be noted that these results cannot therefore be extrapolated to all antibiotics in similar environments. NSAIDs (Fig. 7C) showed an increase in concentration with temperature, reaching the highest values in groundwater clearly affected by heat plumes, since the background temperature of the aquifer is 17 ºC, and the heat island effect produced is limited to 1 to 3 ºC (García-Gil et al., 2015). These observed phenomena could be related to physical adsorption (exothermic process), where temperature simply prevents formation of intermolecular forces (Van der Waals forces) between the sorbent and the surface of the solid matrix. In this case, an increase in temperature would destroy the low interaction between adsorbent and adsorbate molecules by thermal agitation, thus preventing NSAIDs from being retained in the solid matter, and making them available in resident groundwater (Fraissard, 1997). Lastly, Fig. 7D shows that, although correlation between total EOCs and Se (considering all samples) presented a positive association, if highest Se and total EOCs concentration samples were selected, an important decrease of EOCs with increase of Se is observed. This behaviour could be related to rich Se recharging sources of EOCs.

5. Conclusions

We conducted a city scale study evaluating the occurrence of EOCs in an urban alluvial aquifer affected by intensive shallow geothermal activity. Target compounds were detected in 48% of the sampled points. Antibiotics (except sulfonamides) were the most frequently found EOCs, followed by analgesics and PCPs. The maximum concentration of total EOCs was 0.5 $\mu g \cdot L^{-1}$. Detailed cadastral maps, together with water-level contour maps of the city studied, allowed us to link observation points with higher EOCs contents with plausible sources of contamination, such as hospital centres, recreational areas, and polluted surface waters hydraulically well connected to the urban aquifer investigated. By means of statistical analyses, we found that the PCPs mobility in the aquifer was significantly related to groundwater pH. Antibiotics correlated significantly with nitrate, which is used as a common tracer of sewage water, suggesting this was the most probable source. In relation to shallow geothermal exploitation, the statistical analysis showed that, not only occurrence of EOCs is significantly related to higher groundwater temperatures, but also antibiotics were significantly increased in the observation points affected by heat plumes compared to those unaffected by thermal plumes, thus providing experimental evidence of a relationship between this shallow geothermal activity and EOCs. The results of this research support the idea that mechanisms involved in both degradation and sorption of emerging organic contaminants probably take place in the investigated urban aquifer, although more research is needed to elucidate such mechanisms. Two parallel processes cause degradation of EOCs: (1) bioprocesses induced by microbes dependent on redox conditions and (2) chemical processes as a function of temperature, pH, and metal contents. Temperature was not found to trigger degradation of the organic compounds analysed, since only samples collected from heat plumes contained them. Possibly, increases in ground temperature change trace metal contents in groundwater, preventing their transformation by forming metal complexes of the existing emerging organic contaminants. In addition, the oxygen input from groundwater heat pump systems possibly increases the aerobic redox conditions, thus preventing the degradation of organic pollutants. Taken together, these results suggest that intensive shallow geothermal energy exploitation might not enhance emerging organic contamination. However, in the alluvial aquifer investigated, it seems that the geothermal exploitation activity is partly participating in the prevalence of such compounds in the aquifer.

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Figure and Table captions

Fig. 1. Metropolitan area of Zaragoza in the central sector of the Ebro River basin (Spain).

Fig. 2. Spatial distribution of the geothermal monitoring network, sampled points and geothermal pumping-injection wells in the alluvial aquifer of Zaragoza (Spain).

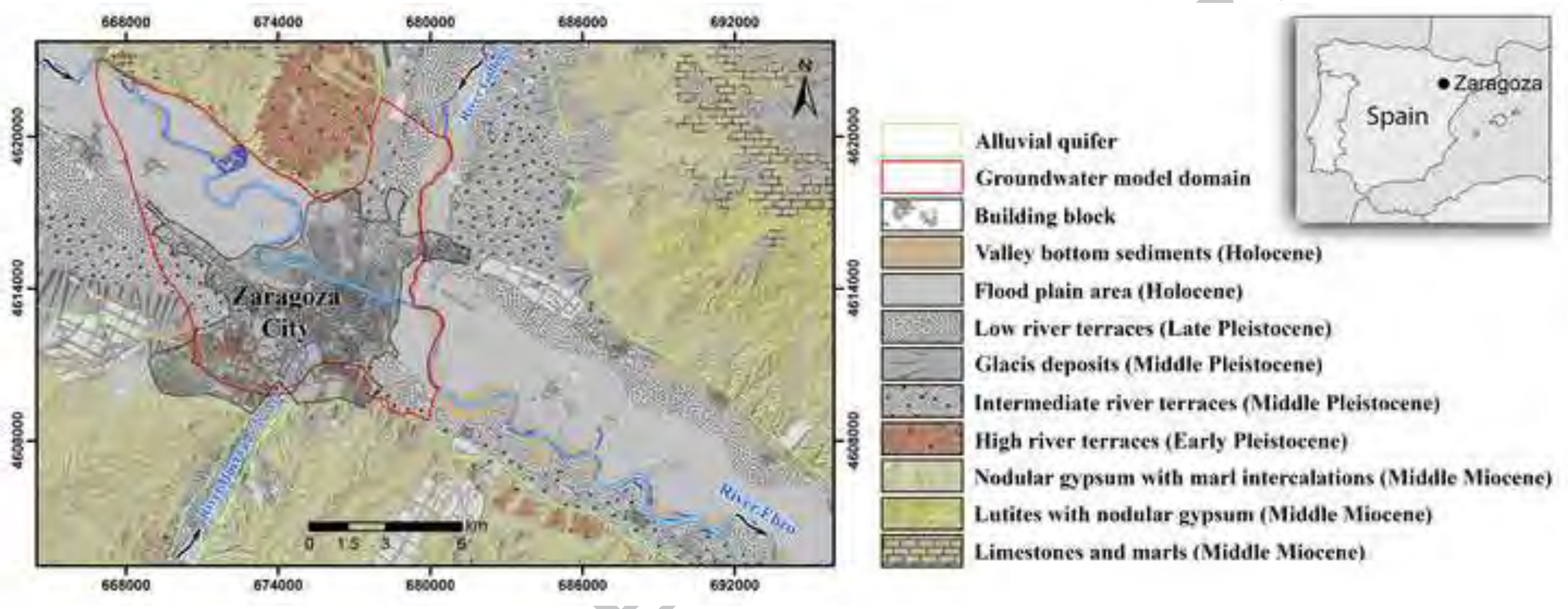
Fig. 3. Detected levels of target PCPs and PhACs in the urban alluvial aquifer of Zaragoza. Percentage of each EOC compound of and each group of EOCs are represented against total concentrations of total EOCs group (A) and total EOCs (B), respectively. Percentages are expressed in terms of mass of measured total EOCs in the aquifer and in terms of detected frequency of the compound-group of EOCs in the aquifer studied.

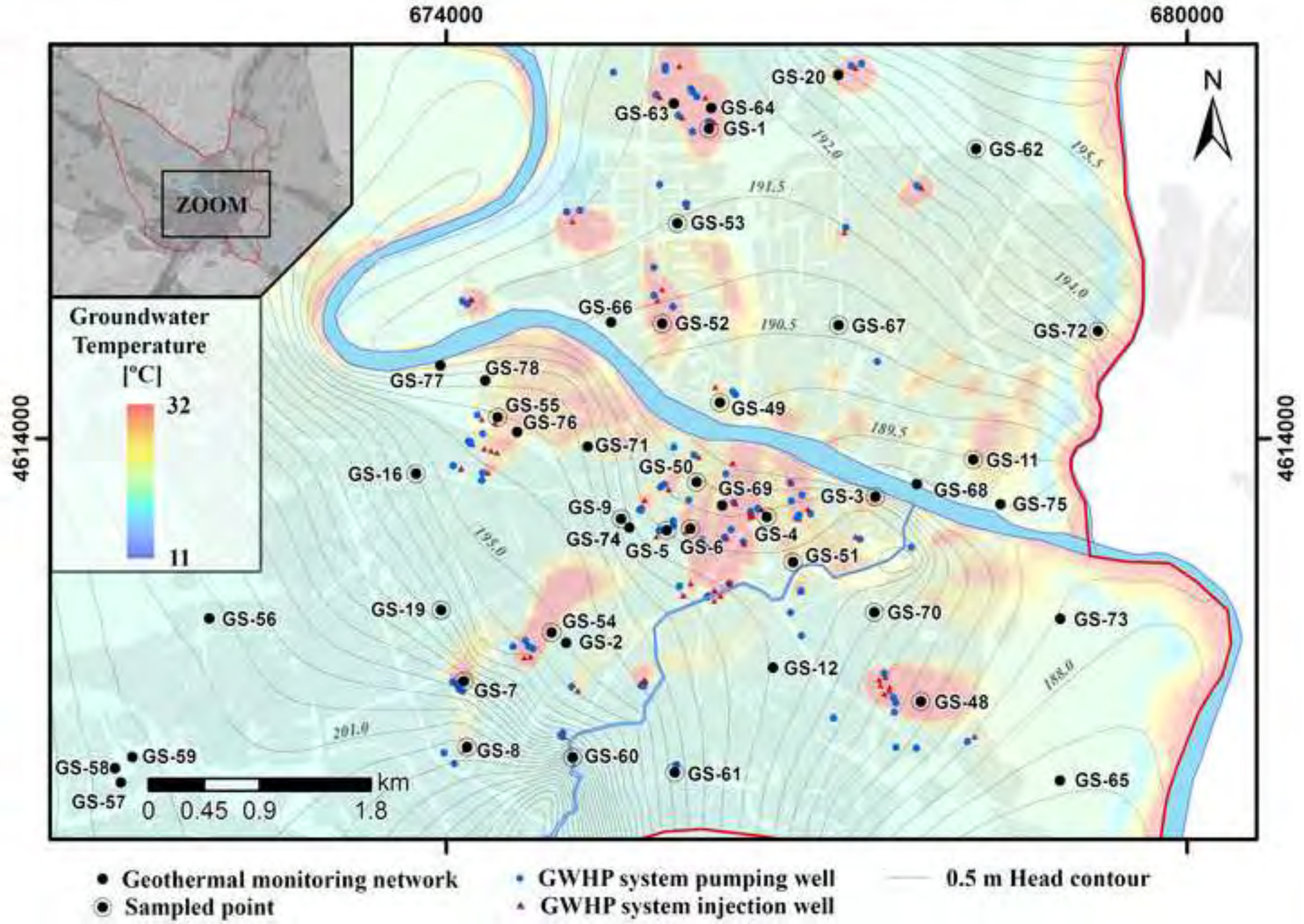
Fig. 4. Spatial distribution of target PCPs and PhACs in the urban alluvial aquifer of Zaragoza. Samples with no target compounds detected are represented with black circles.

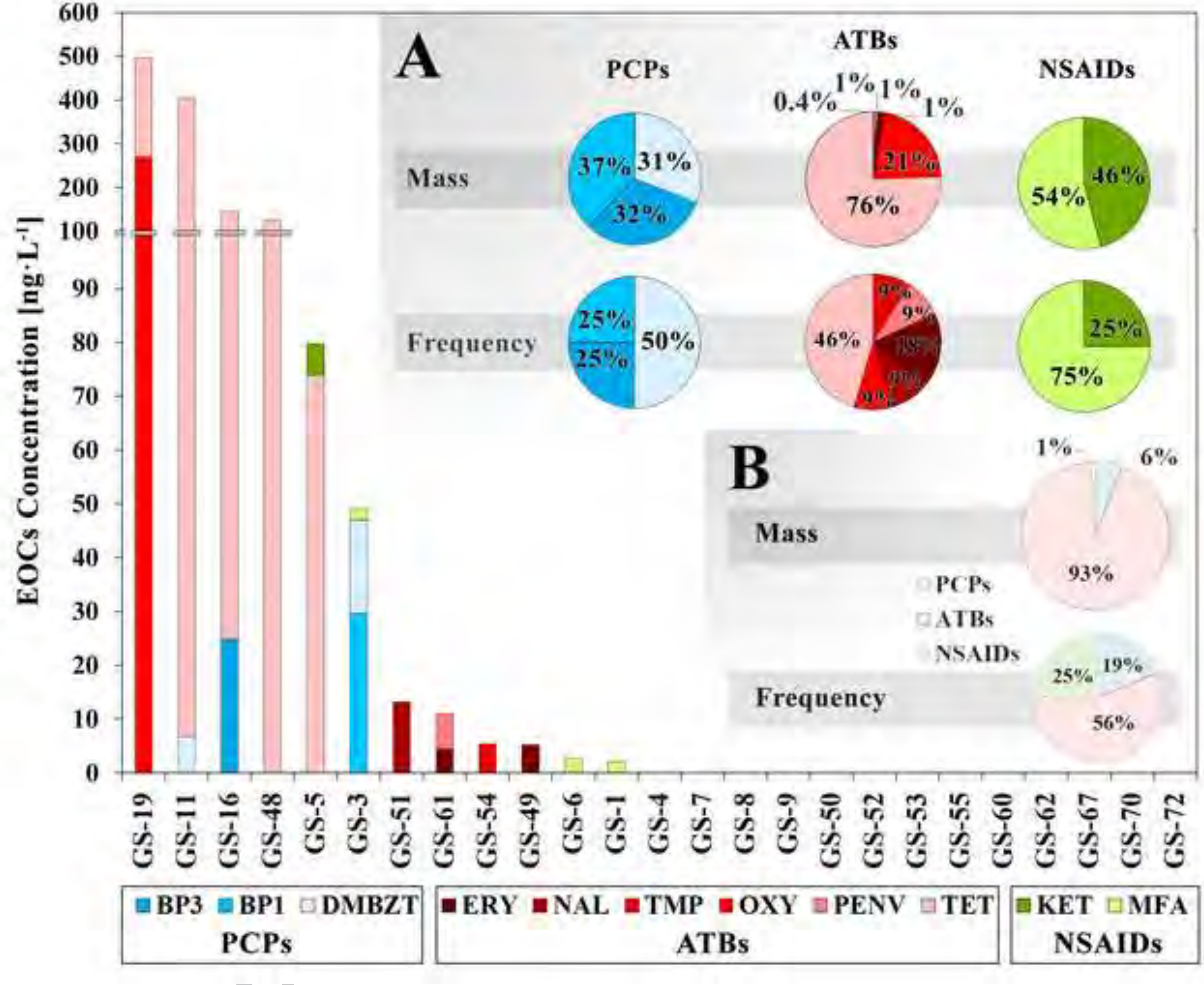
Fig. 5. Possible contaminant sourceplume scenarios for target PCPs and PhACs in the urban alluvial aquifer of Zaragoza. Contaminant plumes are tentative and represented for discussion purposes.

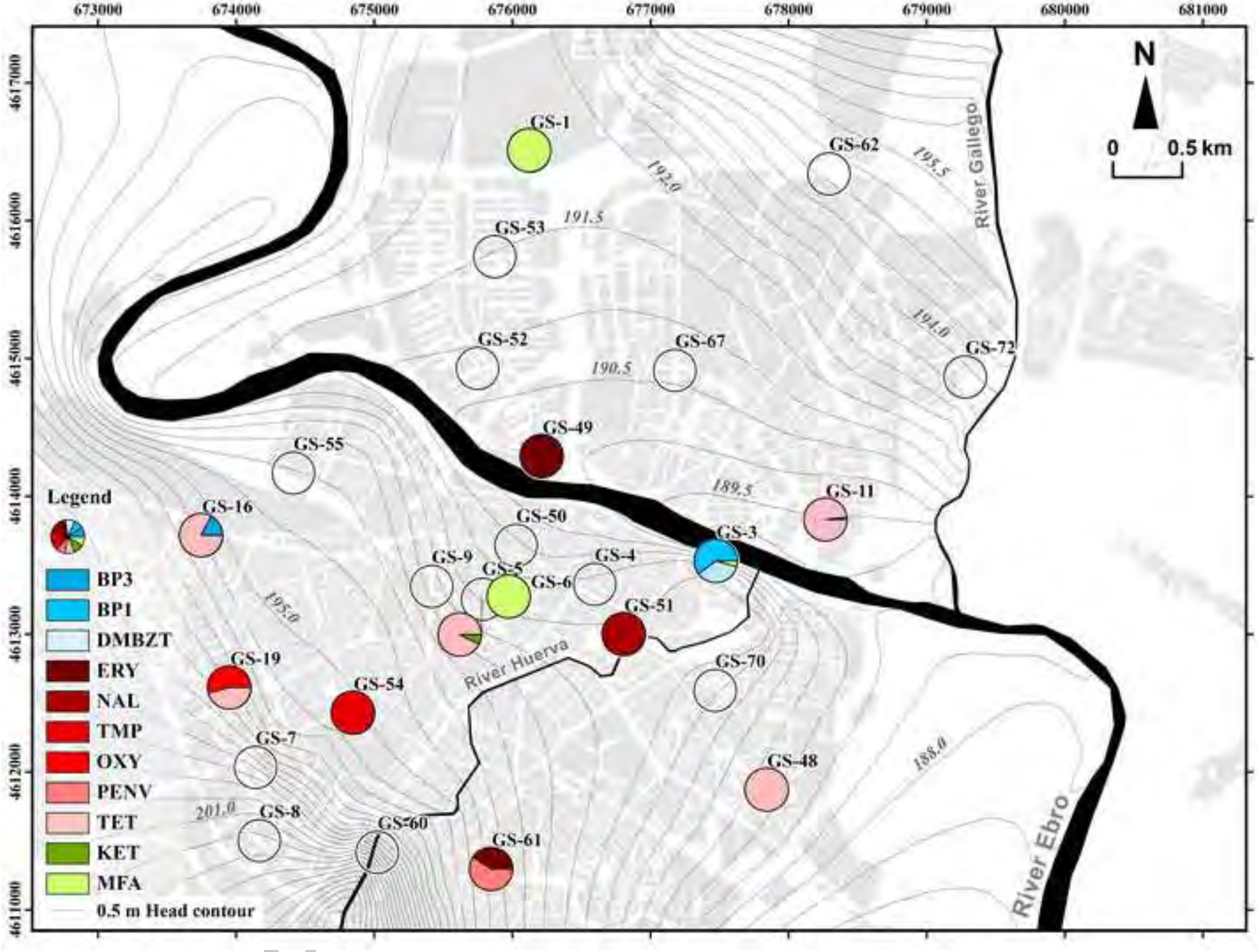
Fig. 6. Significant differences found in the presence (P) or absence (A) of total UVFs, ATBs, NSAIDs and EOCs connected with physicochemical and geochemical properties of the aquifer. Mann-Whitney U and statistical significance (p-values) are provided for each analysis.

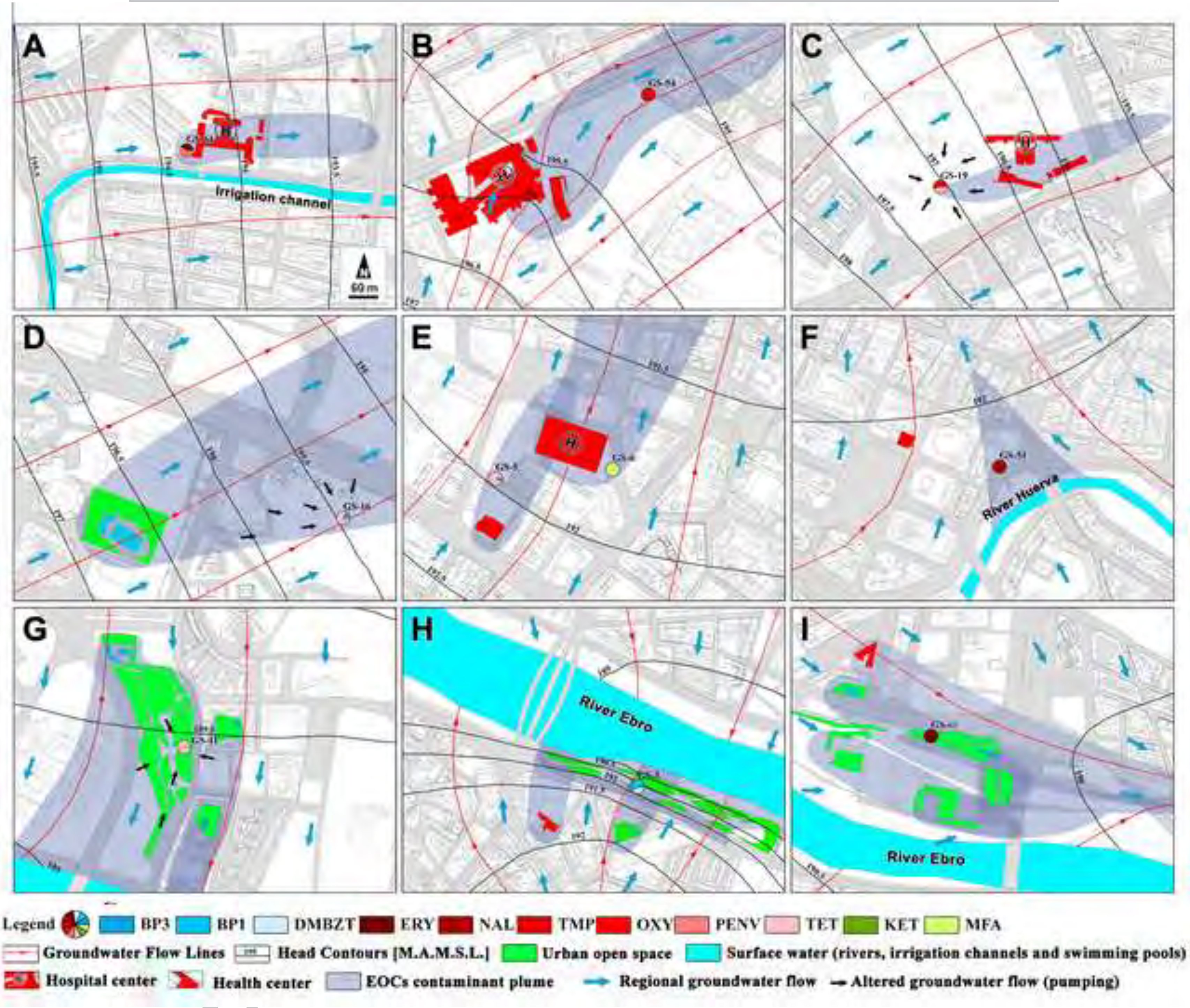
Fig. 7. Spearman's correlation of (A) ATBs with pH of groundwater sampled, (B) antibiotics (ATBs) with NO_3 contents in groundwater sampled (pH values are labeled), (C) NSAIDs correlation with temperature and (D) total EOCs correlation with Se contents in the aquifer. Best-fitting polynomial regression models are plotted to show identified data trends in samples where EOCs are detected.

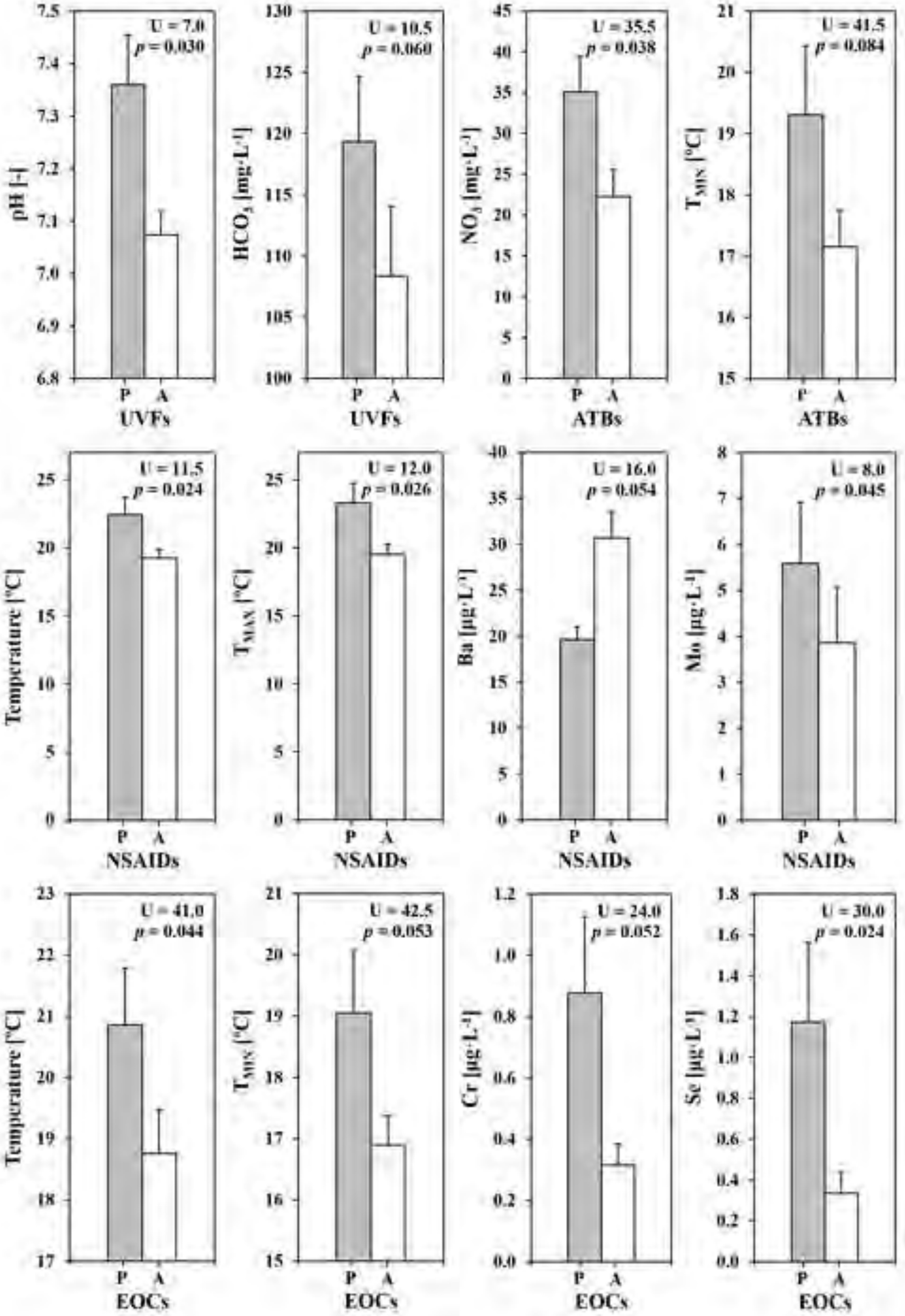

666000
674000
680000
686000
692000
4620000
4614000
4608000
N
Zaragoza City
River Ebro
0 1.5 3 6 km
Zaragoza
Spain
Alluvial quifer
Groundwater model domain
Building block
Valley bottom sediments (Holocene)
Flood plain area (Holocene)
Low river terraces (Late Pleistocene)
Glacis deposits (Middle Pleistocene)
Intermediate river terraces (Middle Pleistocene)
High river terraces (Early Pleistocene)
Nodular gypsum with marl intercalations (Middle Miocene)
Lutites with nodular gypsum (Middle Miocene)
Limestones and marls (Middle Miocene)


674000
680000
4614000
4614000
N
ZOOM
Groundwater Temperature [ºC]
32
11
GS-20
GS-63
GS-64
GS-1
GS-62
GS-53
GS-66
GS-52
GS-67
GS-72
GS-77
GS-78
GS-55
GS-76
GS-49
GS-71
GS-11
GS-16
GS-50
GS-69
GS-3
GS-68
GS-75
GS-9
GS-74
GS-5
GS-6
GS-4
GS-51
GS-56
GS-19
GS-54
GS-2
GS-70
GS-73
GS-12
GS-7
GS-48
GS-8
GS-60
GS-61
GS-65
GS-59
GS-58
GS-57
192.0
193.5
191.5
194.0
190.5
189.5
195.0
188.0
201.0
0
0.45
0.9
1.8
km
Geothermal monitoring network
Sampled point
GWHP system pumping well
GWHP system injection well
0.5 m Head contour


A
PCPs
ATBs
NSAIDs
Mass
37%
31%
32%
0.4%
1%
1%
1%
21%
76%
54%
46%
Frequency
25%
25%
50%
9%
9%
18%
9%
9%
46%
25%
75%
B
Mass
1%
6%
93%
PCPs
ATBs
NSAIDs
Frequency
25%
19%
56%
EOCs Concentration [ng·L⁻¹]
600
500
400
300
200
100
90
80
70
60
50
40
30
20
10
0
GS-19
GS-11
GS-16
GS-48
GS-5
GS-3
GS-51
GS-61
GS-54
GS-49
GS-6
GS-1
GS-4
GS-7
GS-8
GS-9
GS-50
GS-52
GS-53
GS-55
GS-60
GS-62
GS-67
GS-70
GS-72
BP3
BP1
DMBZT
PCPs
ERY
NAL
TMP
OXY
PENV
TET
ATBs
KET
MFA
NSAIDs


673000
674000
675000
676000
677000
678000
679000
680000
681000
4617000
4616000
4615000
4614000
4613000
4612000
4611000
N
0
0.5 km
GS-1
GS-62
GS-53
GS-52
GS-67
GS-72
GS-49
GS-55
GS-11
GS-16
GS-50
GS-3
GS-9
GS-5
GS-6
GS-4
GS-51
GS-19
GS-54
GS-70
GS-7
GS-48
GS-8
GS-60
GS-61
192.0
193.5
191.5
194.0
190.5
189.5
195.0
201.0
188.0
River Gallego
River Huerva
River Ebro
Legend
BP3
BP1
DMBZT
ERY
NAL
TMP
OXY
PENV
TET
KET
MFA
0.5 m Head contour


A
B
C
D
E
F
G
H
I
Irrigation channel
60 m
GS-54
GS-19
GS-16
GS-5
GS-6
GS-51
River Huerva
River Ebro
Legend
BP3
BP1
DMBZT
ERY
NAL
TMP
OXY
PENV
TET
KET
MFA
Groundwater Flow Lines
Head Contours [M.A.M.S.L.]
Urban open space
Surface water (rivers, irrigation channels and swimming pools)
Hospital center
Health center
EOCs contaminant plume
Regional groundwater flow
Altered groundwater flow (pumping)


U = 7.0
p = 0.030
pH [-]
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
P A
UVFs
U = 10.5
p = 0.060
HCO$_3$ [mg·L^{-1}]
130
125
120
115
110
105
100
P A
UVFs
U = 35.5
p = 0.038
NO$_3$ [mg·L^{-1}]
45
40
35
30
25
20
15
10
5
0
P A
ATBs
U = 41.5
p = 0.084
T$_{MIN}$ [°C]
21
20
19
18
17
16
15
P A
ATBs
U = 11.5
p = 0.024
Temperature [°C]
25
20
15
10
5
0
P A
NSAIDs
U = 12.0
p = 0.026
T$_{MAX}$ [°C]
25
20
15
10
5
0
P A
NSAIDs
U = 16.0
p = 0.054
Ba [µg·L^{-1}]
40
35
30
25
20
15
10
5
0
P A
NSAIDs
U = 8.0
p = 0.045
Mo [µg·L^{-1}]
8
7
6
5
4
3
2
1
0
P A
NSAIDs
U = 41.0
p = 0.044
Temperature [°C]
23
22
21
20
19
18
17
P A
EOCs
U = 42.5
p = 0.053
T$_{MIN}$ [°C]
21
20
19
18
17
16
15
P A
EOCs
U = 24.0
p = 0.052
Cr [µg·L^{-1}]
1.2
1.0
0.8
0.6
0.4
0.2
0.0
P A
EOCs
U = 30.0
p = 0.024
Se [µg·L^{-1}]
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
P A
EOCs

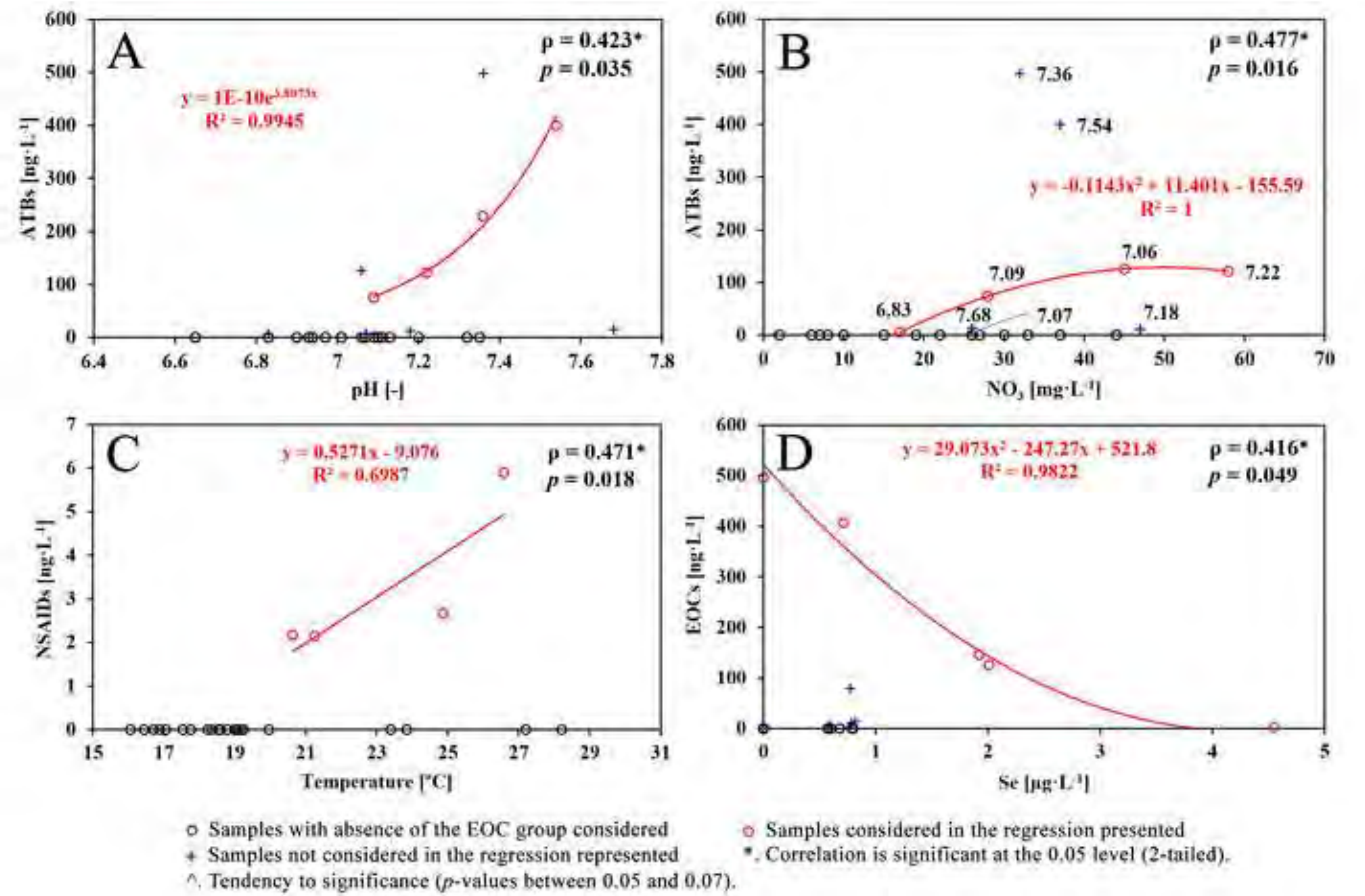

A
ρ = 0.423*
p = 0.035
y = 1E-10e^3.8073x
R² = 0.9945
ATBs [ng·L⁻¹]
pH [-]
600
500
400
300
200
100
0
6.4
6.6
6.8
7
7.2
7.4
7.6
7.8
B
ρ = 0.477*
p = 0.016
7.36
7.54
y = -0.1143x² + 11.401x - 155.59
R² = 1
7.06
7.09
7.22
6.83
7.68
7.07
7.18
ATBs [ng·L⁻¹]
NO3 [mg·L⁻¹]
0
10
20
30
40
50
60
70
C
y = 0.5271x - 9.076
R² = 0.6987
ρ = 0.471*
p = 0.018
NSAIDs [ng·L⁻¹]
Temperature [°C]
7
6
5
4
3
2
1
0
15
17
19
21
23
25
27
29
31
D
y = 29.073x² - 247.27x + 521.8
R² = 0.9822
ρ = 0.416*
p = 0.049
EOCs [ng·L⁻¹]
Se [µg·L⁻¹]
0
1
2
3
4
5
○ Samples with absence of the EOC group considered
+ Samples not considered in the regression represented
^. Tendency to significance (p-values between 0.05 and 0.07).
○ Samples considered in the regression presented
*. Correlation is significant at the 0.05 level (2-tailed).

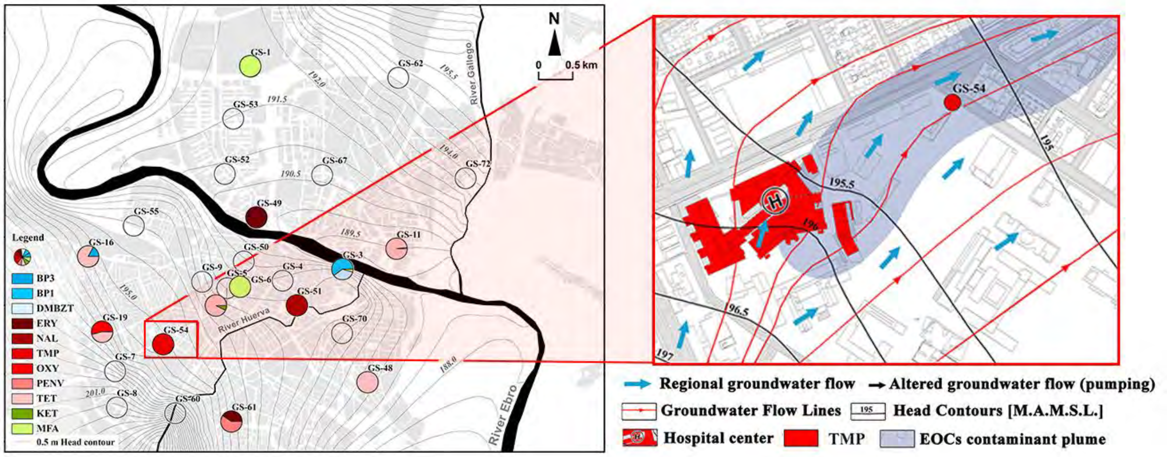
Table I. Target compounds analyzed, classified by their chemical group.

Group	Class	Target compound	Acronym	CAS Number	Elemental Formula	log K_{wo} [a]	S_w [a] [mg·L^{-1} at 25ºC]	LOD [ng·L^{-1}]	LOQ [ng·L^{-1}]	No. of detections	Site detections	Frequency [%]	Range [ng·L^{-1}]	Max. Concentration [ng·L^{-1}]
PCPs	*UVFs*	Benzophenone-3	BP3	131-57-7	$HOC_6H_3(OCH_3)COC_6H_5$	3.86	$6.90\cdot10^{1}$	0.5	1.6	1	GS-16	4	-	24.9
		Benzophenone-1*	BP1	131-56-6	$(HO)_2C_6H_3COC_6H_5$	3.24	$1.37\cdot10^{2}$	0.5	1.6	1	GS-3	4	-	29.6
		4-hydroxybenzophenone*	4HB	1137-42-4	$HOC_6H_4COC_6H_5$	2.98	$4.05\cdot10^{2}$	0.5	1.7	0	-	0	-	-
		4,4'-dihydroxybenzophenone*	4DHB	611-99-4	$(HOC_6H_4)_2CO$	2.75	$1.90\cdot10^{3}$	0.4	1.4	0	-	0	-	-
		2,2' -dihydroxy-4-methoxybenzophenone*	DHMB	131-53-3	$CH_3OC_6H_3(OH)COC_6H_4OH$	3.41	$5.20\cdot10^{1}$	0.4	1.4	0	-	0	-	-
		2-(2H-Benzotriazol-2-yl)-p-cresol	UV-P	2440-22-4	$C_{13}H_{11}N_3O$	4.31	$2.50\cdot10^{1}$	1.5	4.9	0	-	0	-	-
		5,6-Dimethyl-1H-benzotriazole	DMBZT	4184-79-6	$C_8H_9N_3{\bullet}H_2O$	2.26	$9.14\cdot10^{2}$	1.2	4.0	2	GS-3/11	8	6.72-17.4	17.4
		4-*p*-aminobenzoic acid	Et-PABA	94-09-7	$H_2NC_6H_4CO_2C_2H_5$	1.86	$1.67\cdot10^{3}$	0.5	1.6	0	-	0	-	-
Antibiotics	*Sulfonamides*	sulfadimethoxine	SDM	122-11-2	$C_{12}H_{14}N_4O_4S$	1.63	$3.43\cdot10^{2}$			0	-	0	-	-
		Sulfamethazine	SMT	57-68-1	$C_{12}H_{14}N_4O_2S$	0.89	$1.50\cdot10^{3}$	1.7	5.5	0	-	0	-	-
		sulfamethoxypyridazine	SMPZ	80-35-3	$C_{11}H_{12}N_4O_3S$	0.32	$1.47\cdot10^{2}$	0.1	0.3	0	-	0	-	-
		sulfapyridine	SPY	144-83-2	$C_{11}H_{11}N_3O_2S$	0.35	$2.68\cdot10^{2}$	0.2	0.7	0	-	0	-	-
		sulfathiazole	STZ	72-14-0	$C_9H_9N_3O_2S_2$	0.05	$3.73\cdot10^{2}$	0.1	0.2	0	-	0	-	-
		sulfacetamide	SCT	144-80-9	$C_8H_{10}N_2O_3S$	-0.96	$1.19\cdot10^{4}$			0	-	0	-	-
		sulfisomidin	SSM	515-64-0	$C_{12}H_{14}N_4O_2S$	-0.33	$3.13\cdot10^{4}$	0.2	0.6	0	-	0	-	-
		Succinyl-sulfathiazole	SYSZ	116-43-8	$C_{13}H_{13}N_3O_5S_2$	1.18	$5.60\cdot10^{2}$			0	-	0	-	-
		sulfaguanidine	SGN	57-67-0	$C_7H_{10}N_4O_2S$	-1.22	$4.06\cdot10^{5}$			0	-	0	-	-
		sulfamerazine	SMR	127-79-7	$C_{11}H_{12}N_4O_2S$	0.14	$2.02\cdot10^{2}$	1.1	3.7	0	-	0	-	-
		Sulfadoxine	SDX	2447-57-6	$C_{12}H_{14}N_4O_4S$	0.70	$2.69\cdot10^{3}$	0.6	1.9	0	-	0	-	-
		Sulfamethoxazole	SMX	723-46-6	$C_{10}H_{11}N_3O_3S$	0.89	$6.10\cdot10^{2}$			0	-	0	-	-
		Sulfaquinoxaline	SQX	59-40-5	$C_{14}H_{12}N_4O_2S$	1.68	$4.49\cdot10^{2}$	0.2	0.7	0	-	0	-	-
		Sulfabenzamide	SBM	127-71-9	$C_{13}H_{12}N_2O_3S$	1.30	$1.31\cdot10^{3}$	1.4	4.7	0	-	0	-	-
		sulfanitran	SNT	122-16-7	$C_{14}H_{13}N_3O_5S$	2.26	$3.65\cdot10^{1}$	0.3	1.0	0	-	0	-	-

		N^4-acetylsulfapyridine*	AcSPY	100-90-3	$C_{14}H_{16}N_4O_3S$	1.48	$5.06\cdot10^{2}$			0	-	0	-	-
		N^4-acetylsulfamerazine*	AcSDZ	127-73-1	$C_{13}H_{10}D_4N_4O_3S$	0.93	$1.79\cdot10^{3}$			0	-	0	-	-
	Fluoroquinolone	Ciprofloxacin	CIPRO	85721-33-1	$C_{17}H_{18}FN_3O_3$	0.28	$1.14\cdot10^{4}$			0	-	0	-	-
		Enrofloxacin	ENRO	93106-60-6	$C_{19}H_{22}FN_3O_3$	0.70	$3.39\cdot10^{3}$			0	-	0	-	-
	Quinolones	Flumequine	FLU	42835-25-6	$C_{14}H_{12}FNO_3$	1.60	$2.18\cdot10^{3}$			0	-	0	-	-
		Oxolinic acid	OXO	14698-29-4	$C_{13}H_{11}NO_5$	0.94	$8.00\cdot10^{3}$			0	-	0	-	-
		Nalidixic acid	NAL	389-08-2	$C_{12}H_{12}N_2O_3$	1.59	$3.22\cdot10^{3}$	0.4	1.2	1	GS-51	4	-	13.2
		Pipemidic acid	PPA	51940-44-4	$C_{14}H_{17}N_5O_3$	-2.15	$3.22\cdot10^{2}$			0	-	0	-	-
	Macrolides	Tylosin	TLS	1401-69-0	$C_{46}H_{77}NO_{17}$	1.63	$5.00\cdot10^{0}$	0.5	1.6	0	-	0	-	-
		Roxithromycin	ROXI	80214-83-1	$C_{41}H_{76}N_2O_{15}$	2.75	$1.88\cdot10^{-2}$	0.5	1.8	0	-	0	-	-
		Clarithromycin	CLAR	81103-11-9	$C_{38}H_{69}NO_{13}$	3.16	$3.42\cdot10^{-1}$	0.3	0.9	0	-	0	-	-
		Erythromycin	ERY	114-07-8	$C_{37}H_{67}NO_{13}$	3.06	$5.16\cdot10^{-1}$	0.5	1.8	2	GS-49/61	8	4.48-5.22	5.22
	Tetracyclines	Oxytetracycline	OXY	79-57-2	$C_{22}H_{24}N_2O_9$	-0.90	$3.13\cdot10^{2}$	0.5	1.7	1	GS-19	4	-	269
		Tetracycline	TET	60-54-8	$C_{22}H_{24}N_2O_8\cdot xH_2O$	-1.30	$2.31\cdot10^{2}$	4.0	13.4	5	GS-5/11/19/48	20	73.9-400	400
	Penicillins	Penicillin G	PENG	69-57-8	$C_{16}H_{17}N_2NaO_4S$	1.83	$2.10\cdot10^{2}$			0	-	0	-	-
		Penicillin V	PENV	132-98-9	$C_{16}H_{17}N_2O_5SK$	-2.99	$6.34\cdot10^{4}$	0.8	2.8	1	GS-61	4	-	6.56
	DHFR inhibitor	Trimethoprim	TMP	738-70-5	$C_{14}H_{18}N_4O_3$	0.91	$2.33\cdot10^{3}$	0.4	1.2	1	GS-54	4	-	5.36
NSAIDs		Ketoprofen	KET	22071-15-4	$C_{16}H_{14}O_3$	3.12	$5.10\cdot10^{1}$	0.9	3.0	1	GS-5	4	-	5.9
		Mefenamic acid	MFA	61-68-7	$C_{15}H_{15}NO_2$	5.12	$2.00\cdot10^{1}$	0.5	1.8	3	GS-1/3/6	12	2.14-2.67	2.67

***Metabolites; log K_{wo}: octanol-water partition coefficient; S_w: water solubility; LOD: method limit of detection; LOQ: method limit of quantitation; DHFR inibitor: Dihydrofolate reductase inhibitors; NSAIDs: Nonsteroidal anti-inflammatorys**

[a] S_w and log K_{ow} were calculated through the Estimation Programs Interface Suite™ for Microsoft® Windows, v 4.11 (USEPA 2012).


N
0
0.5 km
GS-1
GS-62
GS-53
GS-52
GS-67
GS-72
GS-49
GS-55
GS-16
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GS-50
GS-3
GS-9
GS-5
GS-6
GS-4
GS-51
GS-70
GS-19
GS-54
GS-7
GS-48
GS-8
GS-60
GS-61
192.0
195.5
191.5
194.0
190.5
189.5
195.0
188.0
201.0
River Gallego
River Huerva
River Ebro
Legend
BP3
BP1
DMBZT
ERY
NAL
TMP
OXY
PENV
TET
KET
MFA
0.5 m Head contour
195.5
196
195
96.5
197
Regional groundwater flow
Altered groundwater flow (pumping)
Groundwater Flow Lines
Head Contours [M.A.M.S.L.]
Hospital center
TMP
EOCs contaminant plume

Highlights

- Emerging contaminants’ reactivity induced by groundwater heat pumps is evaluated
- 42 compounds were analyzed from 31 groundwater samples at a city scale
- Heat plumes are involved in the degradation-transformation of emerging contaminants
- Geothermal activity participates indirectly in the emerging contaminants’ prevalence