



# Survey of 218 organic contaminants in groundwater derived from the world's largest untreated wastewater irrigation system: Mezquital Valley, Mexico

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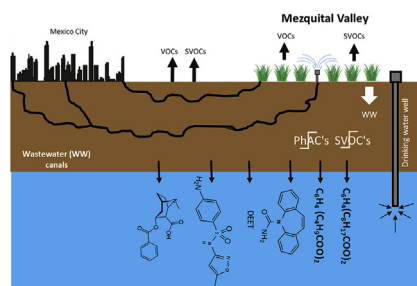
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## HIGHLIGHTS

- 218 organic contaminants were analyzed in springs, groundwater and wastewaters.
- Organic contaminants are volatilized or degraded during wastewater transport/storage.
- Two SVOCs and 23 PhACs were detected in spring and groundwater sources.
- Bis-2-(ethylhexyl) phthalate levels in water may pose adverse effects to human health.
- Sulfamethoxazole, DEET and carbamazepine were frequently detected in groundwater.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The Mezquital Valley system is the world's oldest and largest example with regard to use of untreated wastewater for agricultural irrigation. Because of the artificial high recharge associated with the Mezquital Valley aquifers, groundwater is extracted for human consumption, and there are plans to use this groundwater as a water resource for Mexico City. Thus, this study analyzed 218 organic micro-contaminants in wastewater, springs, and groundwater from Mezquital Valley. Five volatile organic compounds (VOCs) and nine semi-volatile organic compounds (SVOCs) were detected in the wastewater used for irrigation. Only two SVOCs [bis-2-(ethylhexyl) phthalate and dibutyl phthalate] were detected in all the wastewater canals and groundwater sources, whereas no VOCs were detected in groundwater and springs. Of the 118 pharmaceutically active compounds (PhACs) and 7 reproductive hormones measured, 65 PhACs and 3 hormones were detected in the wastewater. Of these, metformin, caffeine, and acetaminophen account for almost sixty percent of the total PhACs in wastewater. Nevertheless, 23 PhACs were detected in groundwater sources, where the majority of these compounds have low detection frequencies. The PhACs sulfamethoxazole, N,N-diethyl-meta-toluamide, carbamazepine, and

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benzoylecgonine (primary cocaine metabolite) were frequently detected in groundwater, suggesting that although the soils act as a filter adsorbing and degrading the majority of the organic pollutant content in wastewater, these PhACs still reach the aquifer. Therefore, the presence of these PhACs, together with the high levels of the endocrine disruptor bis-2-(ethylhexyl) phthalate, indicate that water sources derived from the recharge of the studied aquifers may pose a risk to consumer health.

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## 1. Introduction

Recently, the release of pharmaceuticals, personal care products, and other emerging organic contaminants into the environment has received increased attention due to their adverse effects on public health and biota (Muñoz et al., 2009; Pal et al., 2010; Niemuth and Klaper, 2015; Kong et al., 2016). Among these contaminants, the occurrence of pharmaceutically active compounds (PhACs) and endocrine disrupting compounds (EDCs) in the environment has been highlighted because of their intrinsic biological activity and their human health risk implications (Ma et al., 2017; Wee and Aris, 2017). PhACs include a wide group of antibiotics, fungicides, antimicrobials, anti-inflammatories, analgesics, and other therapeutic drugs, whereas EDCs can be natural and synthetic hormones, steroids, industrial chemicals and any compound that, at certain doses, could interfere with the endocrine system. The production of PhACs and EDCs increases rapidly as the human population grows, and high concentrations of known and new prescription drugs are discharged into terrestrial and aquatic environments through treated/untreated wastewater and sewage systems (Masters et al., 2004; López-Doval et al., 2017). Moreover, given that conventional wastewater treatment plants are not designed to remove emerging pollutants (Díaz-Garduño et al., 2017), most of them can persist in the environment, eventually reaching groundwater and superficial water bodies (Lapworth et al., 2012; López-Doval et al., 2017).

On the other hand, the occurrence of both volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs) in water resources has become a matter of public concern because they can contaminate rivers, reservoirs, lakes, and groundwater surrounding urban and/or industrial areas (Liu et al., 2016; Yu et al., 2017). SVOCs include phthalates and phenols, and they are contained in products such as plastics, cleaning agents, and personal care products. SVOCs also comprise polycyclic aromatic hydrocarbons (PAHs), a group of carcinogenic compounds originating from the incomplete combustion of gasoline, oil, and other fuels (Weschler and Nazaroff, 2008). Unlike SVOCs, VOCs have a higher tendency to volatilize. They are the major constituents of scents and deodorants, and are also present in coatings, paints, gasoline, and organic solvents. Although several SVOCs and VOCs can be derived from nature, the principal source of these compounds stems from the usage of products containing them and industrial activities. However, non-point sources, such as urban air, filling stations, parking lots, urban sewage, highways, and other roads influence their presence in surface waters and groundwater, since stormwater runoff acts as a carrier for them (Lopes and Dionne, 1998). Therefore, stormwater and untreated wastewater from large cities with huge industrial complexes can contain considerable concentrations of the aforementioned organic micro-pollutants (Chen et al., 2014; Postigo and Barceló, 2015; Yu et al., 2017).

Mexico City Metropolitan Area (MCMA), with more than 21 million inhabitants, is one of the most populated urban agglomerations in the world. More than 70% (60 m<sup>3</sup>/s) of the wastewater generated by this megacity is discharged without conventional

treatment into Mezquital Valley in order to provide crops with nutrients and increase soil fertility in this semi-arid region. The remaining (approximately 30%) of wastewater is discharged into the Pánuco River, which flows to the Gulf of Mexico (Fonseca-Salazar et al., 2016). Wastewater irrigation, which has been performed for more than a century, makes Mezquital Valley the oldest and largest example worldwide of urban wastewater reuse for agricultural irrigation (Jiménez and Chávez, 2002). However, long-term wastewater irrigation has contributed to the salinization and accumulation of heavy metals, pharmaceuticals, bacteria, PAHs, and other contaminants in soils (Huerta et al., 2002; Ramirez-Fuentes et al., 2002; Reyes-Solis et al., 2009; Gibson et al., 2010; Broszat et al., 2014; Dalkmann et al., 2014; Guédron et al., 2014), as well as the chemical and bacteriological contamination of groundwater in this area (Lesser-Carrillo et al., 2011; Guédron et al., 2014).

Several studies have assessed the occurrence and fate of SVOCs, PhACs, and other emerging contaminants in Mezquital Valley. However, most of them are focused on their accumulation and dissipation, or their sorption/desorption from soils (Gibson et al., 2010; Dalkmann et al., 2014; Carrillo et al., 2016a, 2016b). Conversely, only few works have evaluated the content of these organic contaminants in wastewaters and groundwater of this area, and even so, they measured a few compounds only (Siemens et al., 2008; Chávez et al., 2011; Durán-Álvarez et al., 2015). Therefore, as the groundwater of Mezquital Valley has been considered as a potential water resource for the MCMA (Jiménez and Chávez, 2004), the current study assesses the occurrence and distribution of a larger number of potential organic micro-pollutants (SVOCs, VOCs, and PhACs) in both the wastewater used for irrigation and groundwater in Mezquital Valley, Mexico.

## 2. Study area

The Mezquital Valley is located 80 km north from the MCMA. It constitutes a Paleogene-age alternation of lacustrine sediments with lava and pyroclastic deposits (Tarango Formation), which are covered with a thin layer of Quaternary alluvium. This valley is bordered by hills and mountains composed by volcanic and calcareous sedimentary rocks, and the altitude varies from 2100 masl (meters above sea level) in the south to 1700 masl in the north. The dominant soils in the valley are Phaeozems associated either with Leptosols or Vertisols. The climate is semiarid, with a mean annual temperature that varies from 16 to 18 °C, and rainfall ranging from 400 to 700 mm. The rainy season occurs between May and October, whereas the dry season extends from November to April. The potential evapotranspiration (about 1700 mm per year) exceeds the mean annual precipitation three times over.

Over 80,000 ha of Mezquital Valley are currently irrigated with wastewater through a complex system of 9 dams (3 freshwater and 6 wastewater reservoirs) and 850 km of open canals. This agricultural area is important for the production of crops such as alfalfa, corn, bean, tomato, onion, green pepper, lettuce, radish, and beet. Wastewater from the MCMA is transported to Mezquital Valley via three principal canals (Emisor Profundo, Emisor Poniente, and Gran

Canal). The southern zone of Mezquital Valley is irrigated with wastewater that has not been stored in reservoirs, whereas wastewater used for irrigation in the northern region has been stored in the Requena and Endhó Dams, where it receives only a sedimentation treatment. Fig. 1 shows a map of the wastewater irrigation system in Mezquital Valley.

Hydrogeological and piezometric studies have defined three aquifer horizons in different parts of the valley: i) a shallow aquifer with a static level between 7 and 8 m, which is formed by alluvial and clastic Quaternary material, ii) a deeper aquifer formed by Quaternary volcanic rocks and several layers of altered basalt of the Tarango formation that wedge with detritus units to a depth of about 150 m, and iii) a third aquifer with a thickness of about 200 m located in the Cretaceous limestones (Cervantes-Medel and Armienta, 2004; Lesser-Carrillo et al., 2011). The direction of the groundwater flow is southeast-northwest at the south, while at the center of the valley groundwater flows from southwest to northeast and discharges into the Tula River, or flows into the northern Ixmiquilpan Aquifer (Cervantes-Medel and Armienta, 2004; Lesser-Carrillo et al., 2011).

Eighty-one percent of the main canals, and the 52% of the secondary ones used for wastewater irrigation are not covered. Thus, wastewater infiltration along large and small uncovered canals, and through agricultural plots by excess of irrigation, has promoted the artificial recharge of the three aquifers ( $25 \text{ m}^3/\text{s}$ ), which is equivalent to 13.3 times the natural recharge (Jiménez and Chávez, 2004). The increased groundwater recharge has led to the region's development, because the new superficial and groundwater sources supply water to the industrial park and 500,000 inhabitants. Similarly, the appearance of new springs as a consequence of the water table rise has increased the Tula River flow (the main river in the valley) from 1.6 to  $12.7 \text{ m}^3/\text{s}$  (Jiménez and Chávez, 2004).

### 3. Materials and methods

#### 3.1. Sampling

Fieldwork consisted of sampling of both groundwater and spring waters of the valley, and sampling of wastewater in several irrigation canals (Fig. 1). Overall, 17 groundwater wells, 4 springs

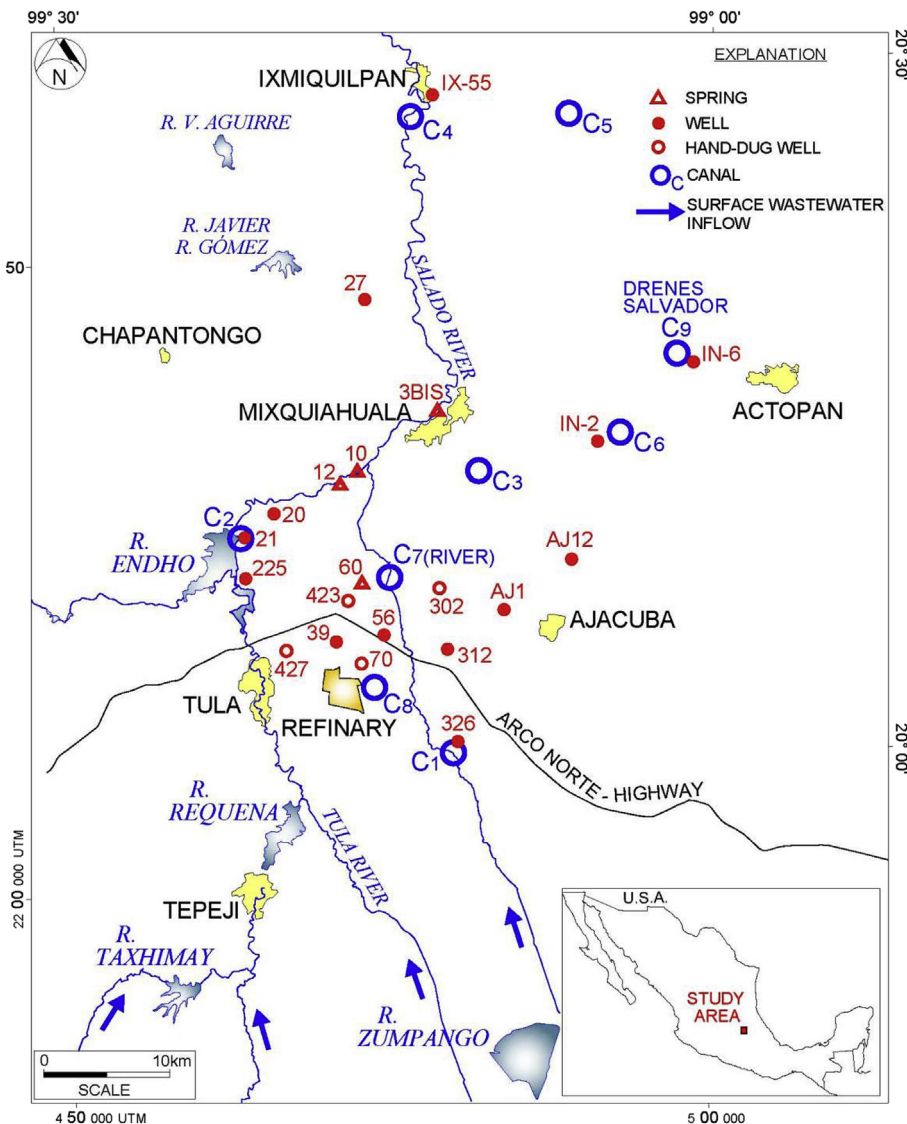


Fig. 1. Map of the study area showing the inflow of surface wastewater into the Mezquital Valley and the sampling locations of wells, springs and wastewater canals used for irrigation.

and 9 irrigation canals were sampled during the dry season (last week of February 2013) in a single sampling campaign. Indeed, it is expected that the level of organic contaminants is the highest during this period due to the lack of dilution by rainwater. The selection of the sampled wells and springs was performed on the basis of locations that had shown positive pollution in two previous monitoring campaigns that assessed physicochemical and bacteriological parameters (major ions, total and fecal coliforms, etc.). The sampled springs were located toward the northern part of the valley according to the groundwater flow path. The sampled wells were distributed all over the study area. The majority of these wells have pumping rates ranging from 3 to 35 L/s, and are mainly used for domestic use, including drinking. Several studied wells were shallow (7–8 m deep), whereas others were up to 260 m in depth. Nevertheless, some deep wells have been equipped with slotted pipes, capturing the groundwater that flows within the two or three aquifer horizons. Further details of the sampling sites are included in [Supplementary Information Table S1](#).

Three grab water samples were taken at each above-mentioned sampling site in pre-washed amber glass bottles: one 2000-mL bottle for SVOCs analyses, one 50-mL bottle for VOCs analyses and one 3000-mL bottle (1000-mL for wastewater of the irrigation canals) for PhACs and human reproductive hormone analysis. During the sampling process, the bottles were rinsed three times and then filled completely, capped tightly, and immediately stored at 4 °C until processing. The maximum storage time before analysis was 7 days.

### 3.2. Analysis

Water samples for the measurement of SVOCs and VOCs were analyzed in the laboratories of ABC Química, Investigación y Análisis S.A. de C.V., Mexico City. In general, 54 SVOCs and 39 VOCs were determined by gas chromatography coupled to mass spectrometry (GC/MS) using the EPA methods 8270D-1998 (for SVOCs) and 8260B-1996 (for VOCs). The analyzed compounds are shown together with their method detection limits in [Table S2](#). Concisely, for the analysis of VOCs, 5 mL of water samples were injected directly into the chromatographic system by the purge-and-trap method. A purge-and-trap concentrator with a trap packed with tenax, silica gel, and activated carbon of 0.125 and 0.105 in of external and internal diameter respectively, was used during the analysis. Internal standards and surrogates (toluene-d<sub>8</sub>) were employed to perform a quality control during analysis. For SVOCs analysis, 1000 mL of each water sample was treated with methylene chloride, which was used as the extractant (Separatory funnel liquid-liquid extraction, EPA method 3510C). First, 20 μL of a mixture of combined surrogates containing 2-fluorophenol, nitrobenzene-d<sub>5</sub>, *p*-terphenyl-d<sub>14</sub> and 2,4,6-tribromophenol was added to each sample. Then, the pH was adjusted to 2 with H<sub>2</sub>SO<sub>4</sub> (1:1), and the samples were transferred to separatory funnels, where the SVOCs were extracted three times with 30 mL of methylene chloride. The aqueous phases were then subjected to a basic extraction with methylene chloride, adjusting pH to 12 with a solution of KOH 10 M. The acid and basic extracts were mixed and dried with anhydrous sodium sulfate. After the extraction procedure, these extracts were allowed to concentrate to 1 mL in a Kudema-Danish concentrator placed in a water bath to 65 °C. Finally, an internal standard mixture (dichlorobenzene-d<sub>4</sub>, naphthalene-d<sub>8</sub>, acenaphthene-d<sub>10</sub>, phenanthrene-d<sub>10</sub>, chrysene-d<sub>12</sub>, and perylene-d<sub>12</sub>) was added. These extracts were injected in the GC/MS equipment. The concentrations of VOCs and SVOCs in laboratory blanks analyzed for each sample batch were below the detection limits. Instrumental operational conditions for the

**Table 1**  
Concentrations of SVOCs and VOCs detected in springs, groundwater and wastewaters of the Mezquital Valley (μg/L). ND (not detected). Bold values indicate detected concentrations.

Compounds	3	BIS	10	12	20	21	27	39	56	60	70	427	225	302	312	326	423	IX-55	IN 2	IN 6	AJ/1	AJ/12	C1	C2	C3	C4	C5	C6	C7	C8	C9	
<b>Semivolatile Organic Compounds (SVOCs)</b>																																
Phenol	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	24.9	23.8	8.12	ND	ND	0.85	14.6	27.9	ND	
M,P-Cresol	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	177	155	36	ND	ND	2.17	63.7	190	ND	
Isophorone	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.75	3.26	1.75	ND	ND	0.86	2.8	2.84	ND	
Naphthalene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.28	0.3	0.28	ND	ND	0.04	0.32	0.33	ND	
Pyridine	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.52	ND	ND	ND	ND	ND	0.45	ND	ND	
Bis-2-(Ethylhexyl) Phthalate	0.32	0.49	0.17	0.6	0.26	0.12	0.25	0.24	0.17	0.28	0.17	0.28	0.66	0.19	0.18	0.15	0.49	1.83	0.17	0.13	0.17	0.13	36	51.3	51.8	0.66	6.77	54.7	62.3	3.92		
Diethyl Phthalate	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	14	15.2	13.8	ND	ND	0.32	4.06	15.6	14.9	2.34
Dimethyl Phthalate	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.77	3	1.14	ND	ND	0.42	2.73	12.6	0.26	
Dibutylphthalate	0.22	0.42	0.21	0.23	0.17	0.22	0.17	0.18	0.24	0.25	0.35	0.36	0.29	0.22	0.3	0.25	0.35	0.24	0.18	0.22	0.17	0.23	3.7	8.7	6.1	0.31	0.29	2.22	71.6	9.49	0.95	
<b>Volatile Organic Compounds (VOCs)</b>																																
Toluene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	3.89	7.15	2.31	ND	ND	ND	4.39	8.19	ND	
M,P-Xylene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.83	0.43	0.42	ND	ND	ND	0.39	0.89	ND	
O-Xylene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.63	ND	ND	ND	ND	ND	0.43	1.48	ND	
Chloroform	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.74	ND	ND	ND	ND	ND	0.76	1.4	ND	
1,2-Dichloroethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	20.4	ND	ND	ND	ND	ND	ND	ND	ND	
Tetrachloroethylene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.47	0.65	ND	

analyses of VOCs and SVOCs are described in Tables S3 and S4, respectively.

Water samples for PhACs and human reproductive hormone analyses were sent to laboratories of SGS AXYS Analytical Services Ltd., Canada. A total of 118 PhACs and 7 hormones were determined in these water samples by liquid chromatography electrospray ionization tandem mass spectrometry (LC/ESI-MS/MS) using the USEPA method 1694 (U.S. EPA, 2007). All the analyzed compounds are shown in Table S5, together with their method detection limits. This information classifies the studied compounds into five lists, according to the extraction pH, the electrospray ionization mode (ESI-positive or -negative) and practical considerations that allow an optimal performance of the compounds content in each list (in the case of lists 1 and 5) during the measurements. Also, this information includes the analyzed hormones, which were measured in the ESI negative mode. Briefly, water samples were filtered (1.6  $\mu\text{m}$ ), adjusted to pH 2 by adding HCl (for analysis of hormones and compounds of the lists 1, 2, 3, and 5), or to pH 10 by adding  $\text{NH}_4\text{OH}$  (for analysis of the compounds of list 4), and spiked with surrogate standards. Each acidic aqueous portion was treated with  $\text{Na}_4\text{EDTA}$  prior to solid phase extraction (SPE). Each sample was extracted with aqueous buffered acetonitrile, or pure acetonitrile on an HLB Oasis SPE cartridge. Ionization and quantification of analytes were performed on a triple quadrupole mass spectrometer running in MRM (Multiple Reaction Monitoring) mode. The quantification was carried out by recording the peak areas of the applicable parent ion/daughter ion transitions. Analytes of the lists 1, 2, 4, and 5 were measured in the ESI positive mode, whereas human reproductive hormones and compounds of list 3 were measured in the ESI negative mode. Procedural blanks that were analyzed for each batch of twenty samples showed values lower than the detection limits. Chromatography and instrument operational conditions used in the SGS AXYS laboratories for these compounds in water samples have been described in detail elsewhere (Klosterhaus et al., 2013; Ferrey et al., 2015).

#### 4. Results

The concentrations of VOCs and SVOCs found in wastewaters, springs, and groundwater wells are summarized in Table 1. Regarding the wastewater canals used for irrigation, five VOCs and nine SVOCs were detected, and at least two SVOCs [bis-2-(ethylhexyl) phthalate and dibutyl phthalate] were detected in all the canals. The maximum concentrations and the detection frequencies (%) of these 14 compounds in the wastewater canals are depicted in Fig. 2. Naphthalene was the only PAH detected in wastewaters. Overall, the major number of compounds were detected in the canals C1, C2, C3, C7, and C8, where 13, 9, 9, 13, and 13 compounds were respectively detected. These canals are located in the southern Mezquital Valley (Fig. 1), and are closer to the main canals (Emisor Profundo, Emisor Poniente and Gran Canal) and the Endhó Reservoir. With regard to spring water and groundwater, the only SVOCs detected were bis-2-(ethylhexyl) phthalate and dibutyl phthalate. However, these phthalate esters were detected in all the monitored wells and springs. No VOCs were detected in groundwater or springs.

The measured concentrations of PhACs and reproductive hormones detected in springs, groundwater, and wastewaters are summarized in Table 2. Of the 118 PhACs measured, 70 were detected, whereas three endocrine disruptor hormones ( $17\alpha$ -estradiol,  $17\beta$ -estradiol, and estrone) were found, specifically in wastewaters. Among those detected PhACs, 17 compounds [caffeine, carbamazepine, clarithromycin, erythromycin- $\text{H}_2\text{O}$ , lincomycin, trimethoprim, gemfibrozil, naproxen, triclocarban, atenolol, cotinine, enalapril, metformin, benzoylcegonine, N,N-diethyl-meta-toluamide (DEET), metoprolol, and valsartan] were detected in all the wastewater canals. Fig. 3 depicts the quantity of PhACs and hormones detected in each wastewater canal sampled during the monitoring campaign, and the sum of their concentrations. Similar to VOCs and SVOCs, the highest concentrations, and the highest number of PhACs and hormones were detected in the southern canals (C1, C2, C3, C7, and C8), which are closer to the

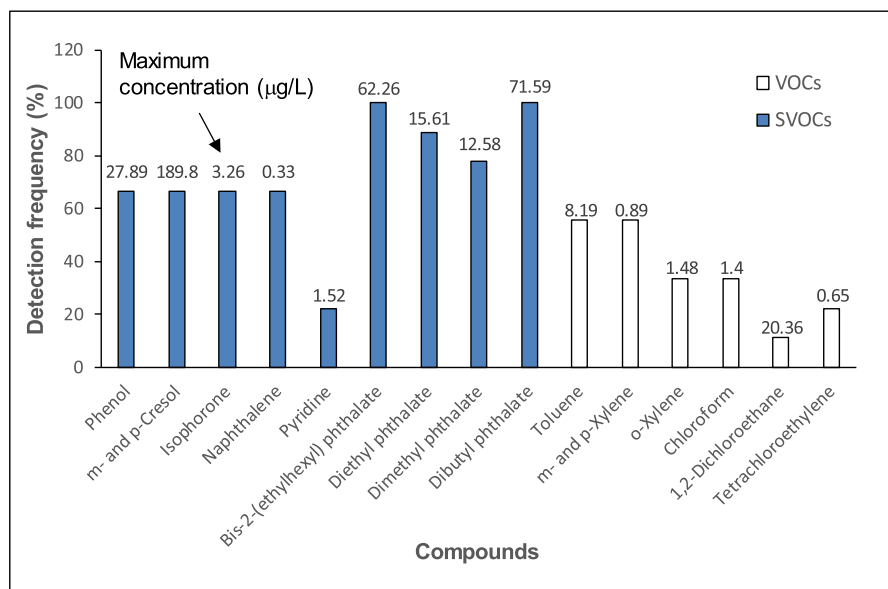


Fig. 2. Detection frequency and maximum concentration values of the SVOCs and VOCs found in wastewater canals used for irrigation purposes.





property of high volatility (Huang et al., 2014).

Fig. 2 indicates that the most-detected SVOCs in the wastewater canals were bis-2-(ethylhexyl) phthalate, diethyl phthalate, dimethyl phthalate, and dibutyl phthalate. These phthalate esters are widely used as plasticizers and as common additives in cosmetics, pesticides, adhesives, lubricants, and paints. Their abundant production and intensive use in a variety of industrial processes makes them the most frequently detected persistent organic pollutants in the environment (Gao and Wen, 2016). Other SVOCs – such as phenol, cresol, isophorone, and naphthalene – were also detected in the wastewater canals, although with lower frequencies and concentrations (in the case of isophorone and naphthalene) than those shown by phthalate esters. These compounds (phenol, cresol, isophorone, and naphthalene) commonly appear in many different industrial effluents because they are useful in the textile, petrochemical, and paper industry (Dzikowitzky and Schwarzbauer, 2014).

As expected, with the exception of Cresol, two of the SVOCs with the largest detection frequencies [bis-2-(ethylhexyl) phthalate and dibutyl phthalate] showed the highest concentrations in wastewaters, while the other SVOCs with lower detection frequencies showed lower concentration values. Indeed, this is related with the volatilization and/or degradation during transport, because SVOCs with lower concentrations are volatilized and/or degraded during the wastewater transport and storage, reaching non-detectable values in several more distant canals. In fact, in the most remote monitored canals, namely C4, C5, and C9, only two, three, and four SVOCs were detected (respectively), whereas none of the VOCs were detected, clearly indicating biodegradation and/or volatilization. Moreover, it is important to mention that the southern canals transport raw sewage, whereas the more remote canals, located toward the north of the valley, transport wastewaters that have received a primary sedimentation treatment in wastewater reservoirs, which promotes the volatilization, degradation, and dissipation of VOCs and SVOCs.

Only the most concentrated and frequently detected SVOCs in wastewater [bis-2-(ethylhexyl) phthalate and dibutyl phthalate] were also detected in spring water and groundwater. These two highly hydrophobic compounds (octanol-water partition coefficient  $\log K_{ow}$  of 7.60 and 4.50, respectively), which have been considered EDCs (Fisher, 2004; Williams et al., 2016), were found in the waters of all the 17 wells and 4 springs sampled during this study, suggesting that these 2 phthalate esters have a higher environmental persistence than the other ones. Hence, this condition could be related with the fact that phthalate esters with high

molecular weights are less biodegraded than those with a low molecular weight (Gao and Wen, 2016). Concerning water quality standards, the concentrations of dibutyl phthalate in all the spring and groundwater sampled were lower than the guideline value (20  $\mu\text{g/L}$ ) for safe water consumption proposed by the U.S. National Recommended Water Quality Criteria-2015 (USNRWQC-2015) (U.S. EPA, 2015). However, the concentrations of bis-2-(ethylhexyl) phthalate in waters of four wells and two springs were the same or higher than the guideline value of 0.32  $\mu\text{g/L}$  proposed by USNRWQC-2015, indicating that waters of these springs and wells can pose adverse effects to human health.

## 5.2. PhACs and human reproductive hormones in wastewater, surface water, and groundwater

Due to the wide use of PhACs and human reproductive hormones in large quantities by modern society (Lapworth et al., 2012), it is expected that untreated wastewaters coming from highly populated areas will have elevated concentrations of these organic pollutants. Fig. 3 shows the high concentrations and the large number of pharmaceutical compounds in the wastewater coming from MCMA. This figure also shows that the concentrations and the number of compounds decrease significantly toward the wastewater canals located to the north of Mezquital Valley, which indicates degradation and dissipation of PhACs during transport and storage. Fig. 4 shows the mean weight percentage (% w/w) of the ten more-abundant pharmaceuticals in the wastewater canals, with regard to the total concentration of PhACs and reproductive hormones. On average, these ten compounds account for more than ninety percent of the total concentration of PhACs in wastewaters. Also, four of these compounds (metformin, caffeine, naproxen, and lincomycin) were detected in all the sampled canals.

Metformin, the most used antidiabetic drug in the world, is considered an EDC because of its ecotoxicological effects in the environment, such as the reduction of fecundity and the intersex in fish (Niemuth and Klaper, 2015; Briones et al., 2016). Metformin was detected in all the canals at very elevated concentrations (between 1310 and 107,000  $\text{ng/L}$ ). However, it was detected in only two wells at very low levels (<30  $\text{ng/L}$ ), suggesting little persistence on its path through the soil column. Although metformin is expected to be present in water sources once released in the

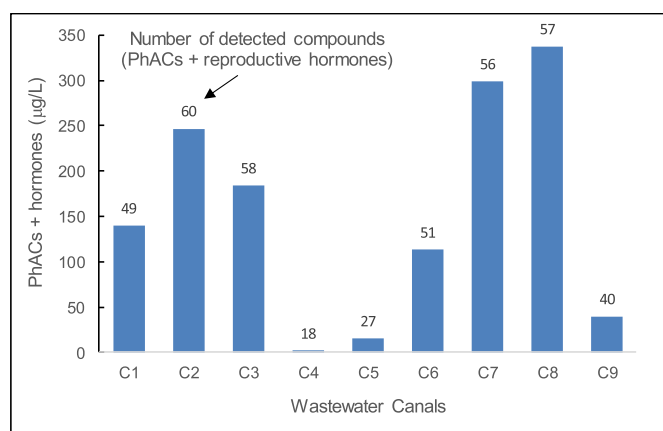


Fig. 3. Quantity and total concentration of PhACs and human reproductive hormones detected in the wastewater canals used for irrigation purposes.

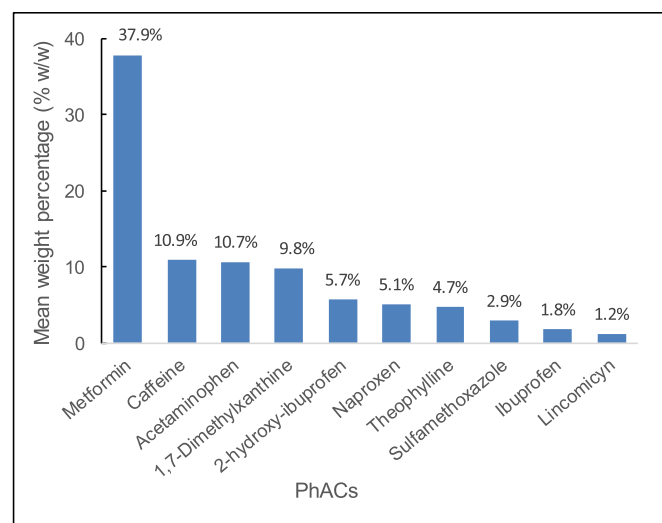


Fig. 4. Mean weight percentage of the ten more abundant pharmaceuticals in wastewater canals with respect to total concentration of PhACs and human reproductive hormones.



environment, due to its hydrophilic properties ( $\log K_{ow} -1.1$ ) and low soil-sorption capacity (solid-water partition coefficient  $K_d$  of 8 L/kg based on clayey loam) (Briones et al., 2016), recent studies have determined that metformin is the most rapidly degraded antidiabetic drug in soils, with a half-life that ranges between 1 and 5 days under aerobic conditions (Mroziak and Stefańska, 2014). Moreover, soils column tests (which simulate recharge conditions) have indicated that metformin does not persist in the outflow after the passage of wastewater through a soil column (Cordy et al., 2004). Thus, the low detection frequency of this pollutant in groundwater is related to the fact that metformin can be subject to degradation (biotic and/or abiotic) during travel through soil horizons in Mezquital Valley. However, although the transformation product of metformin (guanilyurea) was not measured, this compound is highly persistent in waters and not easily biodegradable (Briones et al., 2016), and would surely be detected in Mezquital Valley groundwater.

Other PhACs detected in elevated concentrations in wastewater, but not detected or little detected in spring and groundwater, were acetaminophen, caffeine, and its primary metabolite (1,7-dimethylxanthine), ibuprofen, naproxen, theophylline, and lincomycin. Caffeine is a hydrophilic pharmaceutical ( $\log K_{ow} -0.07$ ) and one of the most widely detected compounds in wastewater due to the high consumption of foods, beverages, and pharmaceuticals containing this substance (Díaz-Garduño et al., 2017). However, caffeine has been poorly detected in groundwater sources, probably due to this stimulant being strongly removed during transport through substrates containing high levels of organic matter (Drewes et al., 2003; Cordy et al., 2004; Hebig et al., 2017), an intrinsic characteristic of the wastewater-irrigated Mezquital Valley soils (Ramírez-Fuentes et al., 2002). Similarly, unsaturated column and serial batch-type experiments have shown a strong attenuation of caffeine and acetaminophen during soil contact, mainly because both substances are firstly absorbed by soils ( $K_d$  of 17.86 and 0.50 L/kg respectively for caffeine and acetaminophen in natural sediments and  $K_d$  of 3.7 L/kg for acetaminophen in tropical soils), and this fact gives way to biodegradation afterwards (Foolad et al., 2016; Martínez-Hernández et al., 2014, 2016; 2017). Like caffeine, its primary metabolite (1,7-dimethylxanthine or paraxanthine) is a hydrophilic stimulant ( $\log K_{ow} < 0$ ) that has been proven to be highly degraded and adsorbed during soil column experiments (Cordy et al., 2004), which can explain its absence in the groundwater of Mezquital Valley. Indeed, there is a highly significant relationship between the concentrations of both stimulants in wastewater ( $r^2 = 0.92$ ;  $p < 0.001$ ), which suggests that the major proportion of paraxanthine is derived from caffeine degradation, and that both compounds have the same behavior. Regarding ibuprofen and naproxen, earlier studies carried out in Mezquital Valley have detected those nonsteroidal anti-inflammatories at low levels ( $< 10$  ng/L) in several springs and wells (Chávez et al., 2011). However, despite both compounds having shown low  $K_d$  values (1.86 L/kg for naproxen and 1.30 and 0.42 L/kg for ibuprofen at pH 4 and 8, respectively) in comparison with caffeine and metformin (Martínez-Hernández et al., 2014; Hiller and Šebesta, 2017), in our study ibuprofen was not detected in infiltrated waters, whereas naproxen was only detected at low levels ( $< 12$  ng/L) in two wells and one spring. In spite of that, both Chávez et al. (2011) and our study indicate that wastewaters are highly concentrated in both PhACs, and there is a strong attenuation in their concentrations when the wastewater infiltrates through the soil profile. This fact could be due to their strong hydrophobic behavior ( $\log K_{ow}$  3.97 and 3.18 for ibuprofen and naproxen, respectively), which promotes their sorption onto organic matter contained in soils. Indeed, this is in agreement with other works, which showed high or complete removal of ibuprofen and naproxen during groundwater recharge

(Drewes et al., 2003; Opiel et al., 2004).

Similar to acetaminophen and ibuprofen, lincomycin was not detected in groundwater, whereas theophylline was only detected in one spring. Studies regarding the occurrence, transport, and fate of theophylline or 1,3-dimethylxanthine in aquatic environments are very scarce. Therefore, the elevated concentrations of this hydrophilic compound ( $\log K_{ow} -0.02$ ) found in wastewaters from Mexico City (which ranged from 817 to 15,700 ng/L) can lead to a greater incentive for studying its environmental fate, mainly in groundwater sources. In fact, only a recent work performed by Hajj-Mohamad et al. (2017) in the suspended and settled sediments of sewer systems describes that the organic carbon normalized sorption coefficient of this compound ( $\log K_{oc,app}$  of 1.3) is higher than that of acetaminophen (0.8), but lower than that of caffeine (1.9). Thus, its relatively high sorption coefficient and the low detection frequency shown in karst aquifers (Hillebrand et al., 2012) and groundwater sources of Mezquital Valley (this study) may suggest that theophylline is highly retained by sorption onto organic matter contained in soils and/or biodegraded during the infiltration process. In the same way, although lincomycin ( $\log K_{ow}$  0.56) has been reported to be recalcitrant to degradation in the environment, this veterinary antibiotic tends to be strongly retained by clay mineral surfaces ( $K_d$  values range from 485 to 3145 L/kg for a range of pH between 3.2 and 8.7) (Wang et al., 2009), reaching minimum concentrations in groundwater (Kuchta et al., 2009). Other PhACs that were detected in lower concentrations in all the wastewater canals but were not detected in springs or groundwater sources were the antibiotics clarithromycin, erythromycin, and trimethoprim; the anti-hypertensives atenolol, enalapril, and metoprolol; the hypolipidemic agent gemfibrozil; and the predominant metabolite of nicotine (cotinine). The anti-bacterial triclocarban was also found in all canals, but it was only detected in one well. Indeed, it is expected that the low or non-detection frequency of these PhACs in groundwater of Mezquital Valley is associated to the sorption/degradation process in soils during infiltration.

Conversely, although the compounds carbamazepine and DEET were found in relatively low concentrations in wastewater, they showed, together with sulfamethoxazole, the highest detection frequencies in groundwater. Even though the insect repellent DEET is a moderate hydrophobic compound ( $\log K_{ow}$  2.02), it is one of the most frequently detected organic contaminants in water. Households are the major sources, since DEET is removed from skin when bathing after dermal application, reaching the sewage system. In our study, the wastewaters contain between 37 and 2500 ng/L of DEET, which is in agreement with the values reported for raw wastewater worldwide. Similarly, groundwater and springs showed DEET concentrations between  $< 0.4$  and 99.9 ng/L, which agrees with values reported for groundwater in U.S., Asia, and Europe (Merel and Snyder, 2016). However, one spring (sample 10) showed double of the maximum concentration of DEET found in wastewater. This inconsistency has also been noted in other studies, which suggest that there is a lack of obvious spatio-temporal concentration patterns of DEET in waters (Merel and Snyder, 2016). A recent study performed by Merel et al. (2015) has indicated discrepancies between the DEET concentrations using different analytical methods (LC-MS/MS versus GC-MS). In addition, although quantification of DEET can be overestimated in complex aqueous matrices by potentially co-occurring compounds, the DEET concentration may be strongly underestimated in samples with complex matrices without adding a surrogate such as DEET-d6, which allows correcting for a more accurate quantification (Merel et al., 2015). Overall, although the surrogate DEET-d7 was added to water samples before the analysis, the uncertainties resulting for the measurements of DEET in wastewater can be high

because its complex matrix (Merel et al., 2015; Merel and Snyder, 2016). Thus, the quantitative DEET values reported here should be considered carefully.

The prescription drugs carbamazepine and sulfamethoxazole have been shown to be the PhACs most recalcitrant to biodegradation in soils and waters (Dalkmann et al., 2014; Durán-Alvarez et al., 2015), whereas sulfamethoxazole ( $\log K_{ow}$  0.89), together with DEET, have been the most frequent organic wastewater contaminants detected in groundwater across 18 states in U.S. (Barnes et al., 2008). Additionally, soil column experiments have demonstrated that DEET, carbamazepine, and sulfamethoxazole are poorly adsorbed by soils, and thus they have the potential to reach groundwater under recharge conditions in semiarid climates (Cordy et al., 2004). Carbamazepine and DEET have shown low affinity for sorption to tropical soils ( $K_d$  of 1.3 L/kg for both compounds), whereas carbamazepine showed the lowest sorption capacity to natural sediments ( $K_d$  0.40 L/kg) of the six PhACs evaluated (Martínez-Hernández et al., 2014; Foolad et al., 2016). Overall, the low soil sorption capacity and the high persistence in the environment of these PhACs explains their high detection frequencies in groundwater of Mezquital Valley. In fact, although carbamazepine is a moderate hydrophobic compound ( $\log K_{ow}$  2.45), its higher persistence among the measured compounds in groundwater of the valley is due to the stability of its heterocyclic structure, showing a dissipation half-life between 355 and 1624 days in Mezquital Valley soils (Dalkmann et al., 2014). The highly environmentally persistent carbamazepine has been previously detected in the groundwater of Mezquital Valley in concentrations up to 193 ng/L (Chávez et al., 2011), which is in agreement with the maximum value of 99.7 ng/L found during our monitoring campaign. In general, despite the frequency at which DEET, carbamazepine, and sulfamethoxazole were found in groundwater, their concentrations were much lower than the guideline values (2.5 mg/L, 100 µg/L, and 35 µg/L, respectively) reported by the Australian Guidelines for Water Recycling (EPHC–NHMRC–NRMCC, 2008), which refers to the use of recycled water to supplement drinking water supplies. However, transformation products of sulfamethoxazole and carbamazepine (not measured in this study) such as N4-acetylsulfamethoxazole and epoxy carbamazepine (respectively), can reach the aquifers (Martínez-Hernández et al., 2017), which could pose a threat for human health. Conversely, drinking water quality standards for these compounds and their transformation products have not been yet included in international drinking water guidelines.

Another compound that was frequently detected in groundwater was benzoylecgonine, the primary metabolite of the drug cocaine. This hydrophilic metabolite ( $\log K_{ow} < 0$ ) was present in 5 of the 21 sampled wells and springs, whereas cocaine ( $\log K_{ow}$  2.30) was detected only in two sampling sites. Both cocaine and benzoylecgonine concentrations in wastewater were within the range specified for worldwide wastewater influents (from 0.7 to 4700 ng/L and from 5 to 7500 ng/L, respectively) as reported by Yadav et al. (2017), and their presence in groundwater can be explained by the low sorption coefficients onto solid particles shown by both compounds (Huerta-Fontela et al., 2008). The low cocaine/benzoylecgonine (COC/BE) ratios found in wastewater (between 0.01 and 0.21) were much lower than those reported in wastewater from Belgium (0.18–0.69), which can be the result of further degradation of cocaine in a warm climate (Van Nuijs et al., 2009). In fact, the lowest COC/BE ratios and cocaine concentrations were found in the canals C4, C5, C6 and C9 (located far from wastewater outlets), indicating cocaine degradation during the transport/storage processes.

Beyond the groundwater survey, several PhACs measured here could also be bioaccumulated in plants and crops due to the high

concentrations in the wastewater used for irrigation. Metformin, the most concentrated PhAC in wastewater, has shown high uptake and accumulation in rapeseeds, although cereals, beans, and tomatoes show much lower bioaccumulation factors (between 15 and 70 times) than rapeseeds (Briones et al., 2016). Similarly, cucumbers can take up and bioaccumulate carbamazepine from irrigation waters with typical effluent concentrations (Shenker et al., 2011), whereas sulfamethoxazole and carbamazepine were the two PhACs that presented the highest bioaccumulation factors (17.8 and 142, respectively) in lettuces cultivated under hydroponic conditions and irrigated with water containing 50 µg/L of both compounds (Zheng et al., 2014). Thus, the untreated wastewater irrigation practice in Mezquital Valley can not only affect the health of the valley inhabitants through drinking water, but the frequent consumption of vegetables and beans cultivated in Mezquital Valley could also pose a health risk for populations.

As an additional comment, it is important to mention that the Atotonilco treatment plant will begin operating soon. With an operational capacity of 35 m<sup>3</sup>/s, this huge plant will treat about 60% of the wastewater coming from Mexico City before it can reach the crops of Mezquital Valley (Carrillo et al., 2016a), through a conventional treatment including sand filtration, flocculation, sedimentation, aeration and disinfection processes. However, as mentioned above, the conventional treatments are not designed to perform a complete removal of PhACs and other organic pollutants from wastewaters (Díaz-Garduño et al., 2017). Similarly, the use of treated wastewater for irrigation might cause desorption of PhACs from soils that have been exposed to untreated wastewater for long time periods, and these compounds and their transformation products might be released and reach the aquifer (Carrillo et al., 2016a). Therefore, we do not know for sure what will be the consequences on aquifer groundwater quality of the changes in wastewater irrigation in Mezquital Valley soils. Without a doubt, this topic will be a matter of future research.

## 6. Conclusions

The data reported herein highlight the environmental fate of 218 volatile, semivolatile, and emerging organic contaminants in waters of the world's largest untreated wastewater irrigation system, located in Mezquital Valley of Central Mexico. VOCs and SVOCs are mainly volatilized and chemically, or biologically, degraded during storage, transport, and infiltration processes. Of these compounds, only two highly persistent phthalate esters [bis-2-(ethylhexyl) phthalate and dibutyl phthalate] were detected in springs and groundwater. However, the high levels of bis-2-(ethylhexyl) phthalate found in several wells and springs can pose adverse effects to human health according to U.S. guidelines.

A total of 65 PhACs and 3 human reproductive hormones were detected in wastewater of the irrigation system. Nevertheless, the concentration and number of compounds decrease during the storage and transport of wastewaters. The most abundant PhACs in wastewater were metformin, caffeine, and acetaminophen, which account for almost sixty percent of the concentration of PhACs in wastewater. Even though 23 PhACs were detected in spring water and groundwater, only DEET, benzoylecgonine and 2 PhACs highly recalcitrant to biodegradation (carbamazepine and sulfamethoxazole) were frequently detected in those water sources.

Overall, in spite of the occurrence of some hard-to-degrade compounds in groundwater of Mezquital Valley aquifers, the soil layers seem to act as a filter, removing most of the organic contaminants during wastewater infiltration and avoiding a higher contamination in the aquifer systems. Because many areas of Mezquital Valley have been irrigated with MCMA wastewater for more than 50 years (some areas have been irrigated for more than

100 years), it is unlikely that the appearance of non-detected compounds in groundwater might occur later. The organic pollutants are mainly removed by sorption to clay mineral surfaces and/or organic matter, and then subjected to chemical or biological degradation afterwards. However, the degradation products of the analyzed compounds (which were not measured in this study) could reach the aquifer (as is the case for guanilyurea, N4-acetylsulfamethoxazole, and epoxy carbamazepine, as well as others). Therefore, it is advisable to perform an extensive study, taking into account degradation products, before making decisions about the use of Mezquital Valley groundwater sources.

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## Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.chemosphere.2018.01.154>.

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