

1 **MONITORING PHARMACEUTICALS AND PERSONAL CARE PRODUCTS IN RESERVOIR**  
2 **WATER USED FOR DRINKING WATER SUPPLY**

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24 **Abstract**

25 In this work, the presence of selected emerging contaminants has been investigated in two reservoirs, La  
26 Fe (LF) and Riogrande (RG), which supply water to two drinking water treatment plants (DWTPs) of  
27 Medellin, one of the most populated cities of Colombia. An analytical method based on solid phase  
28 extraction (SPE) of the sample followed by measurement by liquid chromatography coupled to tandem  
29 mass spectrometry (LC-MS/MS) was developed and validated for this purpose. Five monitoring  
30 campaigns were performed in each reservoir, collecting samples from 7 sites (LF) and 10 sites (RG) at  
31 three different depths of the water column. In addition, water samples entering in the DWTPs and treated  
32 water samples from these plans were also analyzed for the selected compounds. Data from this work  
33 showed that parabens, UV filters and the pharmaceutical ibuprofen were commonly present in most of the  
34 reservoir samples. Thus, methyl paraben was detected in around 90% of the samples collected, while  
35 ibuprofen was found in around 60% of the samples. Water samples feeding the DWTPs also contained  
36 these two compounds, as well as benzophenone at low concentrations, which was in general agreement  
37 with the results from the reservoir samples. After treatment in the DWTPs these three compounds were  
38 still present in the samples although at low concentrations (<40ng/L), which evidenced that they were not  
39 completely removed after the conventional treatment applied. The potential effects of the presence of  
40 these compounds at the ppt levels in drinking water are still unknown. Further research is needed to  
41 evaluate the effect of chronic exposure to these compounds via consumption of drinking water.

42

43 **Keywords:** emerging contaminants, personal care products, pharmaceuticals, UHPLC/MS/MS, drinking  
44 water, reservoir water

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## 52 1. Introduction

53 Reservoirs are artificial lakes formed by the accumulation of water from rivers, creeks, streams and other  
54 natural sources, which are subject to the influence of its tributaries and associated watersheds. Storage in  
55 a reservoir increases the availability of water for various purposes, such as the generation of electric  
56 power, irrigation of crops, industrial use and supply of drinking water for human consumption, among  
57 others (Martinez-Zapata, 2011). Specifically, the quality of drinking water is conditioned by the water of  
58 the reservoirs that feed the treatment plants producing drinking water. These systems are exposed to  
59 numerous natural and anthropogenic factors (Uhlmann et al., 2011). The impact of human activities on  
60 the aquatic environment has increased due to the growth in population and industrialization, which has  
61 intensified discharges from domestic, industrial and agricultural wastewater, the main sources of  
62 pollution.

63 Nowadays, there is a general concern on the presence of emerging contaminants in the water  
64 environment. Pharmaceuticals and personal care products (PPCPs) are of particular concern due to their  
65 wide use and their occurrence in treated wastewater and surface waters (Gracia-Lor et al., 2012a, 2012b).  
66 These compounds are not regulated yet in water legislation and can be harmful for the aquatic ecosystem,  
67 and become a hazard for human public health (Barceló and Petrovic, 2007; Daughton, 2004; Farré et al.,  
68 2008). These compounds are present in urban wastewater, but are not efficiently removed in the  
69 wastewater treatment plants (WWTP) that apply conventional treatments (Gracia-Lor et al., 2012b; Gros  
70 et al., 2010; Jelic et al., 2011; Lacey et al., 2008). In addition to the inefficient removal in WWTPs, some  
71 of them are also persistent and can be bioaccumulated in living organisms (Daughton and Ternes, 1999;  
72 Yang et al., 2014; Zeng, 2015). Within the group of PPCPs, many different families of compounds can be  
73 included, as those used in medicine, veterinary or agriculture, cosmetics, UV filters, fragrances, and even  
74 additives in food (Farré et al., 2008; Martinez Bueno et al., 2016). Oppositely to most priority pollutants  
75 included in the current legislation, which have high toxicity and/or persistence in the environment, PPCPs  
76 do not commonly have these characteristics, but are continuously released in the aquatic ecosystems (via  
77 urban wastewater), where non short-term detectable effects may occur (Muñoz et al., 2008), although  
78 long-term effects are still unknown. The fact that many PPCPs are not efficiently removed in the WWTPs  
79 means that these compounds can easily reach surface water (Dai et al., 2015; Kasprzyk-Hordern et al.,  
80 2008; Liu et al., 2015; Matamoros et al., 2012) and even drinking water (Boyd et al., 2003; Carmona et  
81 al., 2014; Kumar and Xagorarakis, 2010; Sodr  et al., 2010; Vulliet et al., 2011).

82 Colombia has many aquatic ecosystems providing water for human and industrial consumption.  
83 Specifically, Antioquia province is very rich in hydric resources, which are used for energy and drinking  
84 water production. This is the case of the reservoirs La Fe (LF) and Riogrande (RG), which are the source  
85 of water supply of the two drinking water treatments plants (DWTPs) of Medellin: La Ayur  (LA) and  
86 Manantiales (MA). Although these reservoirs are located in low population areas, they can receive the  
87 impact of wastewater, both from urban and agricultural origin (Martinez and Pe uela, 2013). Therefore, it  
88 becomes necessary to investigate the occurrence of emerging contaminants to have a better knowledge on  
89 the presence of these compounds in the reservoirs, and eventually in drinking water.

90 The objective of this work was to investigate the presence of selected PPCPs in water samples from these  
91 two reservoirs, and in samples entering in two DWTPs that use water from these reservoirs, as well as in  
92 treated drinking water samples. To this aim, an analytical method based on the use of liquid  
93 chromatography coupled to tandem mass spectrometry (LC-MS/MS) was developed and validated for the  
94 determination of ibuprofen (IBU), diclofenac (DIC), clofibric acid (ACF), carbamazepin (CBZ),  
95 benzophenone (BZP), benzophenone-3 (BZP-3), methylparaben (MePB), ethylparaben (EtPB) and  
96 buthylparaben (BuPB) in surface water. A solid phase extraction (SPE) was applied to water samples,  
97 which allowed to obtain a pre-concentration factor of 200. Five monitoring campaigns were performed in  
98 each reservoir, collecting waters from seven sites (LF reservoir) and 10 sites (RG reservoir) at three  
99 different water column depths: sub-surface, photic zone limit, and bottom. In addition, samples from the  
100 entrance and the exit of the DWTPs were also analysed for these compounds. Considering the general  
101 lack of data on PPCPs in Colombian surface waters, particularly in the Medellin area, this paper was  
102 conceived as a preliminary study to investigate the presence of some of the most consumed/used  
103 compounds in the area under study. Further studies will be required, including more PPCPs and  
104 metabolites/transformation products (TPs), to have a better knowledge of the issue treated, and to suggest  
105 subsequent actions to protect the aquatic environment, if needed.

106

## 107 **2. Experimental**

### 108 ***2.1 Regents and chemicals***

109 Reference standards of ibuprofen (99%), diclofenac (99%), clofibric acid (99.5%), and carbamazepin  
110 (99.5%) were from Dr. Ehrenstorfer (Germany); benzophenone (99.4%), methylparaben (99.5%),  
111 ethylparaben (99.5%) and buthylparaben (99.5%) from Chemservice (West Chester, USA); and  
112 benzophenone-3 (100%) from Accustandard (New Haven, USA). Isotope-labelled internal standards  
113 (ILIS) of ibuprofen-d<sub>3</sub> (IBU-d<sub>3</sub>) was from Toronto Research Chemicals TRC (Toronto-Ontario, Canada),  
114 and ethylparaben-d<sub>4</sub> (EtPB-d<sub>4</sub>) from CDN Isotopes (Quebec, Canada). LC-MS grade methanol was from  
115 Merck (New Jersey, USA) and acetonitrile from Honeywell, B. & J. Brand (USA). HPLC-grade water  
116 was obtained by purifying demineralized water in a Milli-Q Gradient A10 (Millipore, Bedford, MA,  
117 USA). Formic acid 98-100% was from Merck (New Jersey, USA).

118 Individual stock solutions of 1000 mg/L of both, reference standards and ILIS, were prepared by  
119 dissolving 10 mg in 10ml MeOH. From these individual solutions, a mix solution of 100 mg/L containing  
120 the PPCPs was prepared by dilution in MeOH. Working mix solutions of 10, 1 and 0.1 mg/L PPCPs were  
121 prepared in MeOH from the 100 mg/L mix solution. A mix solution of ILIS of 2 mg/L IBU-d<sub>3</sub> and 10  
122 mg/L EtPB-d<sub>4</sub> was also prepared in MEOH from a 100 mg/L solution.

123 Sample extraction was made by solid phase extraction (SPE) using Oasis HLB cartridges (60 mg) from  
124 Waters Corp. (Milford, MA, USA).

125

### 126 ***2.2 Liquid chromatography***

127 An Acquity UPLC system (Waters Corp., Milford, MA, USA) was used, equipped with a quaternary  
128 solvent manager and a sample manager. Chromatographic separation was performed using an Acquity  
129 UPLC BEH C18 column,, 2.1 x 50 mm, 1.7  $\mu$ m, (Waters) at a flow rate of 0.3mL/min. The column was  
130 kept at 40°C and the sample manager was maintained at 5°C. The mobile phase consisted of water with a  
131 0.01% HCOOH/methanol gradient. The methanol percentage was changed linearly as follows: 0 min,  
132 10%; 9 min, 90%; 9.5 min, 90%; 10.5 min, 100%; 10.6 min, 100%; 11.7 min, 10%. Analysis run time  
133 was 12.7 min. The sample extract injection was 20  $\mu$ L.

134

### 135 *2.3 Mass Spectrometry*

136 An Acquity UPLC system was coupled to a TQD (triple quadrupole) mass spectrometer with an ortho-  
137 gonal Z-spray-electrospray (ESI) (Waters Corp., Milford, MA, USA). Both the drying gas and the  
138 nebulising gas was nitrogen generated from pressurized air in a N<sub>2</sub> LC-MS nitrogen generator (Peak  
139 Scientific, EE. UU). The cone gas and the desolvation gas flows were set at 80 and 800L/h, respectively.  
140 For operation in MS/MS mode, the collision gas was Argon 99.995% at  $2 \times 10^{-3}$  mbar in a T-Wave  
141 collision cell. Capillary voltages of -2.8 kV (negative ionization mode) and 3.0 kV (positive ionization  
142 mode) were applied. The interface temperature was set to 450 °C and the source temperature to 150 °C.  
143 Dwell times of 0.1 s were selected. Masslynx 4.1 (Micromass, Manchester, UK) software was used to  
144 process the quantitative data.

145 The studied compounds were measured in ESI positive and/or ESI negative mode during the same  
146 injection acquiring two MS/MS transitions per compound. The acquisition of two transitions, of which  
147 the most sensitive was used for quantification (Q) and the other was used for confirmation (q), ensured  
148 the appropriate identification of the analytes in the samples. Only one transition was available for IBU  
149 205>161 (Q) due to the poor fragmentation of this compound under the conditions applied. The  
150 transitions selected, and the optimized conditions of cone voltage and collision energy are shown in  
151 **Table 1.**

152

### 153 *2.4 Sample procedure*

154 Water samples were firstly centrifuged (Boeco Centrifuge U-320R, Germany) for 10 min at 4500 rpm to  
155 separate particulate matter (filtration was discarded to avoid potential losses in the filter). Then, SPE was  
156 applied within 48h after samples collection. When this was not possible, the centrifuged samples were  
157 stored in the freezer at - 20°C (Revco-Thermo Scientific). Conditioning of the SPE cartridges was made  
158 with 3 mL MeOH and 3 mL ultrapure water. After conditioning, 200 mL of the water sample (adding 50  
159  $\mu$ L of the mix ILIS solution (2 mg/L IBU-d3, 10 mg/L EtPB-d4)) were loaded into the SPE cartridge at a  
160 flow of 1-2 mL/min. The cartridges were air dried, and analytes were eluted with 5 mL MeOH. The eluate  
161 was evaporated under a gentle nitrogen stream and the residue was reconstituted 1 mL MeOH-H<sub>2</sub>O  
162 (10:90, v/v). Finally, 20  $\mu$ L of the extract was injected into the UHPLC-MS/MS system under conditions  
163 indicated in **Table 1.**

164 Quantification was made with standards prepared in solvent, using relative responses analyte/ILIS, or  
165 absolute responses, depending on whether ILIS was used for correction or not. All compounds measured  
166 in negative mode were quantified using ILIS for matrix effects correction. Thus, parabens (MePB, EtPB  
167 and BuPB) were quantified using EtPB-d<sub>4</sub>, while IBU was quantified using IBU-d<sub>3</sub>. After a previous  
168 study on the best ILIS to be used for matrix effects correction, EtPB-d<sub>4</sub> was selected for quantification of  
169 DIC and ACF. The three compounds measured in positive mode (CBZ, BZP, BZP-3) were quantified by  
170 external calibration using standards in solvent without ILIS due to the unavailability of appropriate ILIS  
171 in our laboratory. In any case, our data did not show relevant matrix effects for these compounds in the  
172 samples tested.

173

### 174 **2.5 Study Area and samples collection**

175 The present study was carried out in two reservoirs (RG and LF) that are used for drinking water supply  
176 to the city of Medellin after the water being treated in two DWTPs. Samples were taken from three  
177 depths: the subsurface, photic zone limit and reservoir bottom in order to evaluate the presence of  
178 pollutants along the overall water column. Ten sampling locations were selected in reservoir RG (**Fig 1**)  
179 and seven locations in reservoir LF (**Fig 2**). Additionally, water samples were also collected in each  
180 tributary at locations before the entry to the each reservoir (Figure 1, numbers 12, 15, 17 and 19; Figure 2,  
181 numbers 8, 9, 10 and 11). The samples were collected using a Schindler bottle. An aliquot of 200 mL of  
182 each sample was transferred to amber glass bottles that were previously cleaned and heated to 450 °C for  
183 8 h to remove any presence of organic matter. Then, they were transported to the laboratory under cooled  
184 conditions (4°C).

185 Influent and effluent samples from the two DWTPs (Manantiales (MA), fed with water from reservoir  
186 RG; and La Ayurá (LA) fed with water from reservoir LF) consisted on 24-h composite samples. The  
187 effluent samples (i.e. drinking water supplied to Medellin) were amended with sodium thiosulfate  
188 immediately after collection to eliminate residual chlorine (Martinez and Peñuela, 2013).

189 The monitoring plan for reservoirs, tributary rivers and DWTPs is summarised in **Table 1SI**  
190 (**Supplementary Information**).

191

## 192 **3. Results and discussion**

193 The selection of the compounds under study was made based on the main human activities in the area and  
194 on previous data reported in a preliminary study performed on the presence of PPCPs (Gracia-Lor et al.,  
195 2012a). The area around reservoir LF and their tributaries has experimented an increased urbanization  
196 process and recreational events, including the touristic park Los Salados. Reservoir RG is more affected  
197 by agricultural activities, and several farms (mainly cattle and pigs) are located in the nearby areas.  
198 Despite the presumably presence of pesticides, because of the agricultural activities, we focused our study  
199 on pharmaceuticals. Thus, four compounds were selected such as ibuprofen and diclofenac, which are  
200 analgesic/anti-inflammatory drugs commonly consumed around the world (Mendez-Arriaga et al., 2010;  
201 Scheurell et al., 2009) and specifically in Colombia; they are easily accessible for consumers and are

202 included in the Colombian national strategy for Human Health. Carbamazepine is used for epilepsy  
203 treatment and is frequently found in natural and waste waters (Bade et al., 2015; Hernández et al., 2015;  
204 Sun et al., 2013); and clofibrac acid, which is used to decrease cholesterol and triglycerids levels in blood  
205 (Saravanan et al., 2011).

206 A preliminary study made by our own group in collaboration with the University Jaume I of Castellon  
207 (Gracia-Lor et al., 2012a) revealed the presence of several personal care products in waters from these  
208 two reservoirs, specifically benzophenones, commonly used in UV filters and other products of wide use.  
209 Benzophenone and benzophenone-3 were identified in several of the samples. Parabens, used as  
210 preservatives in cosmetics and even as additives in food, were also found in the water samples (methyl  
211 paraben, ethyl paraben, and buthyl paraben).

212 Altogether, 9 PPCPs were selected for this study, 4 of them being drugs of wide consumption and/or  
213 frequent detection in waters, and 5 being personal care products.

214

### 215 *3.1 Analytical Methodology*

216 The method linearity was studied in the range 1–100 µg/L. Calibration curves showed satisfactory  
217 correlation coefficients (greater than 0.99) and residuals were lower than 30%. The method accuracy was  
218 evaluated in surface water spiked (n=5) at three concentration levels (0.05, 0.25 and 0.45 µg/L). The  
219 results were satisfactory in terms of precision, expressed as relative standard deviation (RSD) (lower than  
220 20%) and accuracy, expressed as percentage recovery (between 70 and 120%) for the analysis of PPCPs  
221 under study (**Table 2**).

222 Limits of detection (LOD) were calculated as a function of the standard deviation for a 99% confidence  
223 level (Brown and Berthouex, 2002; Martinez-Zapata, 2011), (n=7) in a sample spiked at 0.25µg/L. Limits  
224 of quantification (LOQ) were taken as 3.3 x LOD (**Table 2**).

225 Confirmation of positive findings was carried out by calculating the peak area ratios between the  
226 quantification (Q) and confirmation (q) transition. The finding was considered as true positive when the  
227 experimental ion-ratio was within the tolerance range (Gracia-Lor et al., 2012b), and the retention time in  
228 the sample within ±2.5% when compared with a reference standard (see Table 1 for Q/q ratios empirically  
229 obtained for reference standards).

230 A problem occurred in the determination of BZP, which seemed to be related to a contamination of the  
231 LC-MS/MS system used for analyses. For this reason, data were available only for samples collected until  
232 October 2012. From then on, although a peak clearly differentiated from the blank was observed for  
233 several of the samples (suggesting that the sample was positive for this compound), we could not  
234 accurately quantified this analyte.

235

### 236 *3.2 Reservoir samples*

237 The validated method was applied to water samples collected from reservoirs and the drinking water  
238 treatment plants. In every sequence of analysis (around 20 samples), a calibration curve was injected.

239 Quality control (QC) samples (i.e blank samples fortified at 0.25 µg/L with the selected PPCPs) were also  
240 analyzed in every sequence in order to test the robustness and applicability of the method to the samples  
241 under study. Confirmation of positive findings was based on the agreement of Q/q ratios and  
242 chromatographic retention times between samples and reference standards (see Analytical Methodology).

243

### 244 **3.2.1 Reservoir Rio Grande (RG)**

245

246 The highest percentage of positive samples corresponded to BZP, MePB and IBU, which were detected in  
247 many of the samples analysed (**Table 3**). In relation to DIC, it was only found in the samples from April  
248 (11% positives) and November (3% positives), always at levels below LOQ. BZP-3 was only detected in  
249 samples from April with an average concentration of 238 ng/L, and EtPB was scarcely found, with only  
250 4% of positives in the monitoring of April (all < LOQ). BuPB, CFA and CBZ were not detected in any of  
251 the samples from this reservoir. In general, not a clear trend was observed in the concentrations of these  
compounds as a function of the sampling date.

252 Concentrations of MePB, and mainly IBU, seemed to slightly increase along the depth of the water  
253 column in most of sampling stations (**Fig 1SI**), which would imply that these compounds are sorbed onto  
254 the sediments (IBU, Log  $K_{ow}$  3,97; MePB, Log  $K_{ow}$  4,5) (Fatta-Kassinos et al., 2013; Vergili, 2013). In  
255 addition, humic material tends to accumulate into the bottom, which might facilitate the complexation  
256 with the contaminants (Hincapie - Upegui., 2014) that would be associated to the sediments and/or to the  
257 bottom of the water column.

258

259 We did not observe a clear trend in the spatial distribution of MePB in the different stations monitored in  
260 this reservoir, although a notable increase in concentration in the bottom samples was found in stations 7  
261 and 8 in October 2012 (**Fig 1SI**), a fact that could not be easily explainable. For IBU, the trend of the  
262 concentrations was more uniform in sub-surface, photic limit zone and bottom samples. In general,  
263 concentrations in station 1, which was near the tributary Rio Chico (number 12) were a bit higher, and  
264 then decreased along stations 2 and 3 (see map shown in Figure 1). However, the possible influence of the  
other tributaries was not so evident in those stations that might be more affected, i.e. stations 6, 4 and 10.

265

266 Additionally to samples from reservoir RG, water samples were also collected in each tributary at  
267 locations just before the entry to the reservoir (**Fig 1**) in order to evaluate whether they were the main  
268 source of pollution of the reservoir. Concentration data found in tributaries 12, 15, 17 and 19, in the two  
monitoring campaigns, are shown in **Table 4**.

269 In the tributaries, similarly to the reservoir samples, the predominant compounds were BZP, MePB and  
270 IBU, although BZP-3 was also found at notable concentrations in samples collected in April. The  
271 presence of IBU in tributary 12 (Rio Chico) in both monitoring campaigns may explain the presence of  
272 this compound in reservoir samples of station 1, located near the entry of this tributary. From sampling  
273 station 1 onwards, IBU concentrations slightly decreased along the distance (stations 2 and 3).

274 BZP and MePB were present in all tributaries, which might explain the presence of these compounds in  
275 the reservoir. Similarly to the results found in the reservoir, BZP-3 was only found in the samples  
276 collected in April 2012. Although no relevant differences were observed in general between the



277 tributaries in terms of analyte concentrations, the tributary<sup>15</sup> was the only one where the three parabens  
278 included in this study, BuPB, EtPB and MePB, were found, with the latter being present at relatively high  
279 concentrations (242 ng/L).

280

### 281 **3.2.2 Reservoir La Fe (LF)**

282 In general, the behaviour and concentrations found in this reservoir were similar to those found in  
283 reservoir RG. The higher concentrations were commonly observed in the first monitoring, June 2012,  
284 although no significant variations were observed along the different periods of the year.

285 The compounds most detected in this reservoir were again BZP, MePB and IBU, although other parabens  
286 (BuPB, EtPB) were also found in several of the samples at detectable concentrations (mostly below 60  
287 ng/L) (**Table 5**).

288 Additionally, the most important tributaries (numbers 8, 9, 10, 11; see map in Figure 2) were also  
289 monitored in October and December 2012, and February 2013 (**Table 6**). The PPCPs concentrations in  
290 these tributaries were lower than tributaries from the other reservoir (see Table 4), as only IBU and MePB  
291 were found at detectable concentrations (no data available for BZP). In all positives, concentrations were  
292 below 80 ng/L. This fact illustrates that, at least for the compounds selected in this study, the tributaries  
293 seemed not be an important source of pollution in the reservoir.

294 No clear trends were observed in the spatial distribution of the compounds in this reservoir (**Fig 2SI**) and,  
295 as stated above, the influence of the tributaries was not perceived.

296 The presence of PPCPs in urban wastewater has been widely reported in the scientific literature, at  
297 concentrations that are sometimes well above 1000 ng/L. High levels can be found even in effluent  
298 wastewater, as many of these compounds are not efficiently removed in WWTPs (Alidina et al., 2014;  
299 Anumol and Snyder, 2015; Carmona et al., 2014; Gracia-Lor et al., 2012b; Gros et al., 2010; Jelic et al.,  
300 2011; Lacey et al., 2008; Liu and Wong, 2013). This fact explains that a notable number of PPCPs are  
301 present in surface water, including the compounds studied in this work.

302 Specifically, MePB has been found in wide concentrations ranges, with average values near those  
303 reported in our work for reservoir samples (around 100 ng/L) (Carmona et al., 2014; Kasprzyk-Hordern et  
304 al., 2008; Peng et al., 2008). Ibuprofen is one of the compounds more frequently detected in surface water  
305 around the world (Fernández et al., 2010; Kasprzyk-Hordern et al., 2008; Lindholm-Lehto et al., 2016;  
306 Liu et al., 2015; Liu and Wong, 2013; Matamoros et al., 2012; Peng et al., 2008; Tran et al., 2014; Wang  
307 et al., 2010). Concentrations reported are commonly higher than those found in reservoirs RG and LF.  
308 Thus, values up to 2,700 and 1,800 ng/L have been reported for IBU in Spain and Vietnam, respectively  
309 (Fernández et al., 2010; Tran et al., 2014), which are clearly higher than in our work ( $\leq 60$  ng/L).

310 Less data exist on BZP levels in surface water, and most studies are focused on BZP-3 (Kim and Choi,  
311 2014). The presence of BZP has been reported in surface water from California, with maximum  
312 concentrations of 5.1 ng/L (Alvarez et al., 2014). Although not detected in our study, BZP-3 is commonly  
313 found in surface water, at levels up to 125 ng/L (Kim and Choi, 2014).

314 In the present work, several compounds selected (DIC, CBZ, CFA, EtPB, BuPB) were not detected in the  
315 reservoir samples. However, their presence in surface water has been reported in several previous studies.  
316 For example, CBZ has been found at low concentrations in Finland (1.2 ng/L) (Lindholm-Lehto et al.,  
317 2016), and at much higher concentrations in Vietnam (5,110 ng/L) (Tran et al., 2014). DIC is commonly  
318 reported in surface water, at concentrations from 10 ng/L, in Switzerland, to 700 or 800 ng/L, in China or  
319 Spain (Fernández et al., 2010; Wang et al., 2010). Parabens (Carmona et al., 2014; Esteban et al., 2014;  
320 Kasprzyk-Hordern et al., 2008) and CFA are usually present at low levels in fresh waters (around or  
321 below 50 ng/L) (Gros et al., 2006; Hernando et al., 2006; Kasprzyk-Hordern et al., 2008; Öllers et al.,  
322 2001; Wang et al., 2010).

323 Data from above show that the compounds selected in our study are commonly present in fresh water  
324 from many countries around the world. In general, the levels reported in our work for reservoir water and  
325 tributaries samples are lower than reported in the majority of studies performed in other countries.  
326 However, more data and extensive monitoring programs would be necessary to confirm this fact.

327

### 328 *3.3. Drinking water treatment plant samples*

329 Four monitoring campaigns were carried out in two DWTPs: Los Manatiales (MA) and La Ayurá (**Table**  
330 **1SI**). The DWTP of MA receives water from the reservoir RG, and the catchment is located at station 4  
331 (**Fig 1**), while DWTP of LA receives water from reservoir LF, with the catchment being located at station  
332 3 (**Fig 2**).

333 The results obtained for analyses of influent water (water from the reservoir collected in the catchment  
334 station) and in effluent water (treated water already used for drinking water supply) are shown in **Table 7**.  
335 The compounds IBU, MePB and BZP were the most frequently detected, similarly to the reservoir and  
336 tributary samples. These were present in both influent and treated water of the two drinking water  
337 treatment plants. The concentrations found in the influents were in general consistent with those of the  
338 reservoir samples, specifically from stations 4 (RG) and 3 (LF), where the catchments are located. This  
339 supports the observation that these compounds are present in the reservoir water and enter in the DWTP.

340 In addition to the three major contaminants, BZP-3, DIC and BuPB were occasionally detected in the  
341 influent of MA, although at concentrations < 30 ng/L. The first two compounds were also occasionally  
342 found in the RG reservoir samples in some monitoring campaigns, but BuPB was never found in the  
343 reservoir; a fact that needs further research for confirmation. A similar situation was observed in influent  
344 samples from LA, where in addition to the three major compounds, BZP-3 and DIC were occasionally  
345 detected although at low concentrations (< 30 ng/L), while they were not detected in the LF reservoir  
346 samples.

347 The comparison of data from influent and effluent samples from DWTPs showed that PPCPs present in  
348 the catchment were not completely removed in the conventional treatment applied. For example, the  
349 removal efficiency for BZP, MePB and IBU was found to be between 30-60% (BZP), 20-60% (MePB),  
350 and 0-50% (IBU) in MA DWTP, while it was much lower in the LA DWTP (**Table 7**). These results are  
351 in agreement with previous data reported on drinking water treatment (de Jesus Gaffney et al., 2014;

352 Padhye et al., 2014). Both DWTPs apply conventional treatments, based on coagulation, flocculation,  
353 sedimentation and filtration, which would be expected to efficiently remove hydrophobic compounds of  
354 high molecular weight, less soluble in water, but not necessarily emerging contaminants that are more  
355 polar in nature. For this reason, polar emerging compounds, as the majority of PPCPs, when present in  
356 water at low concentrations, would remain in the aqueous phase and would not be removed along the  
357 coagulation-flocculation process, leading to low removal efficiencies in the treatment plant (Rodríguez-  
358 Paniagua, 2015).

359 In addition, both DWTPs also apply chlorination, a process that allow to eliminate the great majority of  
360 organic compounds, although not all of them. It has been reported that the use of oxidizing agents is  
361 appropriate for removal of emerging contaminants in drinking water treatment (Huber et al., 2005),  
362 however, the kinetic of the process can be slow and other by-products (in some occasions of unknown  
363 effects on human health) can be formed (Rodríguez-Paniagua, 2015). According to our data, it seems that  
364 the low chlorine doses used in the DWTPs were not sufficient to completely remove some PPCPs.  
365 Therefore, it would be necessary to improve the treatment in order to remove trace levels of PPCPs in  
366 drinking water, for example, using higher doses of chlorine or implementing tertiary treatments, such as  
367 advanced oxidation systems, that are more efficient to this aim.

368 In any case, the levels found in drinking water (effluent already treated and used for drinking water  
369 supply) were always below 50 ng/L, with the only exception of MePB in the sample collected in MA in  
370 September 2012 (80 ng/L) (**Table 7**). Although concentrations were below 0.1 µg/L (the reference value  
371 used by default for pesticide residues in drinking water), no sufficient data exist to assess the potential  
372 harmful effects on human health. Therefore, more research is required in the near future on this issue.

373 Confirmation of positive findings was based on the agreement of Q/q ratios and chromatographic  
374 retention times between samples and reference standards (see Analytical Methodology). Similarly to the  
375 reservoir and tributary samples, QCs (drinking water samples fortified at 0.25 µg/L with the selected  
376 PPCPs) were analyzed in every sequence in order to test the robustness and applicability of the method.

377 As illustrative example, **Fig 3** shows the LC-MS/MS chromatograms for an effluent sample from  
378 Manantiales DWTP, where BZP and MePB were found and their identity confirmed by Rt and ion/ratio  
379 agreement with the reference standard.

380 Our findings are in the line of previous data reported on occurrence of PPCPs in drinking water around  
381 the world. It is not rare to find some of these compounds in drinking water at the few ng/L level.  
382 Specifically, the compounds selected in our work have been found in drinking waters, as summarized in a  
383 recent review (Bialk-Bielinska et al., 2016), where maximal concentrations reported for diclofenac,  
384 carbamazepine and ibuprofen are given. Thus, IBU was frequently reported in DW from USA, Japan,  
385 China, Portugal and Spain, typically at concentrations between 10-30 ng/L. DIC was also reported in DW  
386 from Japan and China at maximal concentrations of 16 and 10 ng/L, respectively; and also in Spain, at  
387 average concentrations of 18 ng/L (Bialk-Bielinska et al., 2016; Carmona et al., 2014). However, it seems  
388 that this compound was not present in finished water, after disinfection (Cai et al., 2014). Contrarily to  
389 our work, where CBZ was not detected in DW, this compound was frequently found, at maximal  
390 concentrations between 2 and 5.6 ng/L, in DW from Canada, Spain and USA, and between 14 and 35

391 ng/L in Portugal, Japan and China. CBZ was also found in finished water subjected to disinfection in all  
392 the five sample analysed from Beijing, China, at concentrations between 0.4 and 1.2 ng/L (Cai et al.,  
393 2014).

394 There are very few data on the presence of parabens in drinking water (Haman et al., 2015). In the United  
395 States, MePB was never detected in a study on drinking water sources and treated drinking water (Loraine  
396 and Pettigrove, 2006). However, in Spain MePB (17 and 40 ng/L) was quantified in tap water (Blanco et  
397 al., 2009; Casas Ferreira et al., 2011). These two studies did not observe any EtPB, PrPB or BuPB.  
398 Another recent Spanish study (Carmona et al., 2014) demonstrated the presence of MePB (12 ng/L), PrPB  
399 (9 ng/L) and BuPB (28 ng/L), but not EtPB. In our work, MePB was also found at concentrations  
400 between 21 and 80 ng/L, while EtPB was not detected, and BuPB was only once at 7 ng/L.

401 Although the presence of the UV filters benzophenones in effluent wastewater and surface water has been  
402 reported, there are very little studies on drinking water. BZP-4 was found in DW from Galicia, Spain, at  
403 maximum concentrations of 62 ng/L (Rodil et al., 2012) , close to the levels reported in our work (around  
404 40 ng/L). Benzophenone was also reported in an early study made in the United States in drinking water  
405 at concentrations above 100 ng/L (Loraine and Pettigrove, 2006).

406 The regulations on PPCPs in drinking water are still insufficient around the world, and no maximum  
407 levels have been established in most countries yet. Taking as a reference the maximum level allowed for  
408 pesticides in drinking water according to the European Directive (European Union, 1998) (0.1 µg/L), the  
409 concentrations found for the PPCPs under study were lower than this value. However, it is not possible to  
410 fully evaluate the potential hazard of PPCPs at these low levels for public health due to the lack of long-  
411 term exposition risk data for these compounds. However, the application of the precautionary principle  
412 seems necessary, and measurements should be taken to efficiently remove PPCPs in the DWTPs.

413 The research presented in this paper can be considered as a preliminary study that reveals the occurrence  
414 of selected PPCPs in reservoirs of Medellin, and their potential presence in drinking water produced from  
415 these reservoirs. Subsequent actions will be needed in the near future, including ambitious monitoring  
416 programs where the number of compounds should be notably increased. In addition, selected  
417 metabolites/TPs should be also included in the monitoring, because most pharmaceuticals are excreted as  
418 metabolites more than as the parent compound, and can also suffer degradation/transformation processes  
419 in the aquatic environment. Therefore, the occurrence of TPs can be more frequent than that of the parent  
420 compounds (Boix et al., 2016; Ibáñez et al., 2016).

421

#### 422 **4. Conclusions**

423 In this work, several PPCPs have been monitored in two important reservoirs near Medellin, as well as in  
424 the main tributaries of these reservoirs. Our data showed that some preservatives (parabens, mainly  
425 MePB), UV-filters, as BZPs and BZP-3, and the pharmaceutical IBU were present in most of the samples  
426 analysed. The presence of these compounds in the tributaries may explain their detection in the reservoir  
427 water samples, although other sources of pollution should not be discarded.

428 As reservoir water is used for catchment of drinking water treatment plants, these compounds (mainly  
429 MePB, IBU and BZP) were also present in the influent of the DWTPs. Analysis of treated water showed  
430 that these compounds were not completely removed after the conventional treatments applied for drink  
431 water supply (coagulation, flocculation, sedimentation, filtration, and subsequent disinfection by  
432 chlorination). This reveals that conventional treatments, which had been designed to remove the great  
433 majority of organic matter, are not efficient enough to remove polar contaminants present at low  
434 concentrations in the influent water, as occurs for most of emerging contaminants.

435 The PPCPs concentrations found in drinking water were all below 80 ng/L (e.g. below 0.1 µg/L, which is  
436 the maximum concentration allowed for pesticides –a group of contaminants subjected to strict regulation  
437 in drinking water). Insufficient information exists to assess the potential harmful effects of these low  
438 levels on human health. It seems necessary the application of the precautionary principle until more data  
439 are available to properly evaluate the risks for the population. More research is required in the near future  
440 considering a higher number of PPCPs, including the most consumed by population, because synergic  
441 effects have to be taken into account. The presence of metabolites and transformation products is another  
442 issue of concern, as many pharmaceuticals are hardly excreted as parent compound; therefore, the  
443 presence of some parent pharmaceuticals may only be the visible part of the iceberg of this complex and  
444 of current concern issue.

445

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452

## 453 **SUPPLEMENTARY MATERIAL**

454 In this section, two figures are included, showing the distribution of IBU and MePB in reservoir RG  
455 (Figure 1SI) and in reservoir LF (Figure 2SI) water collected at three depths for different sampling  
456 stations and monitoring dates. Also three tables, 1SI: Monitoring plan for reservoirs, tributary rivers and  
457 DWTPs, 2SI: Concentrations (ng/L) found for BZP, MePB and IBU in samples from reservoir RG, 3SI:  
458 Concentrations (ng/L) found for BZP, MePB and IBU in samples from reservoir LF, are included to  
459 support the information given in the manuscript.

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- 633

634 **Table 1. MS conditions for the LC-MS/MS measurement of the compounds under study.**

<b>Compound</b>	<b>ESI mode</b>	<b>Quantification transition (Q)</b>	<b>Cone Voltage (V)</b>	<b>Confirmation transition (q)</b>	<b>Collision Energy (ev)</b>	<b>Q/q<sub>1</sub> *</b>
<b>Benzophenone (BZP)</b>	+	182.9>104.9	34	182.9>76.9	14	3.39 (3.5)
<b>Benzophenone-3 (BZP-3)</b>	+	228.9>150.9	42	228.9>104.9	18	1.18 (5.1)
<b>Butylparaben (BuPB)</b>	-	193.1>92.0	42	192.9 >136.1	24	2.15 (3.6)
<b>Carbamazepine (CBZ)</b>	+	237.1>194.1	25	237.1>165.2	20	42.6 (4.2)
<b>Clofibric Acid (CFA)</b>	-	215.2>129.0	20	213.7>127.0	15	5.03 (7.0)
<b>Diclofenac (DIC)</b>	-	294.1>250.0	20	295.8>252.0	10	1.33 (3.2)
<b>Ethylparaben (EtPB)</b>	-	165.1>92.0	36	164.8>136.7	20	1.78 (9.5)
<b>Ibuprofen (IBU)</b>	-	205.1>161.1	20	-	5	-
<b>Methylparaben (MePB)</b>	-	151.0>92.0	34	150.8>135.9	20	1.67 (4.3)
<b>Ibuprofen-D3</b>	-	208.1>164.0	20	-	10	-
<b>Ethylparaben-D4</b>	-	169.2>96.1	30	-	25	-

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637 \* Average ion intensity ratios for calibration standards (7 calibration points), and relative standard  
638 deviation in brackets

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**Table 2. Analytical characteristics of the method: average recovery (%) and precision (expressed as % RSD, in brackets) for three fortification levels (five replicates each). Limits of quantification of the method (LOQ)**

Compound	t <sub>R</sub>	LOQ (ng/L)	<i>Reservoir LF</i>			<i>Reservoir RG</i>			<i>Ultra Pure water</i>		
			0.05 µg/L	0.25 µg/L	0.45 µg/L	0.05 µg/L	0.25 µg/L	0.45 µg/L	0.05 µg/L	0.25 µg/L	0.45 µg/L
<b>BZP</b>	7.47	2.8	96 (1)	76 (9)	75 (7)	88 (4)	71 (10)	73 (8)	69 (6)	75 (17)	80(11)
<b>BZP-3</b>	8.24	2.3	115 (17)	78 (10)	90 (7)	97 (12)	85 (8)	88 (10)	90 (2)	78 (5)	76(2)
<b>BuPB</b>	7.54	7.8	97 (8)	79 (4)	85 (2)	84 (5)	88 (3)	82 (10)	103 (5)	95 (4)	106 (4)
<b>CBZ</b>	6.22	4.6	98 (9)	84 (4)	89 (1)	91 (8)	89 (2)	85 (8)	78 (26)	89 (5)	84 (2)
<b>CFA</b>	7.22	10.3	91 (14)	80 (7)	81 (2)	65 (9)	69 (5)	59 (8)	82 (8)	97 (8)	90 (5)
<b>DIC</b>	8.57	9.6	90 (8)	83 (5)	89 (3)	86 (7)	87 (2)	84 (10)	104 (9)	93 (6)	104 (4)
<b>EtPB</b>	5.64	7.6	87 (10)	71 (10)	79 (2)	82 (6)	82 (3)	78 (8)	99 (3)	95 (7)	106 84)
<b>IBU</b>	8.77	6.8	100 (15)	84 (11)	99 (6)	87 (17)	88 (6)	89 (10)	90 (19)	108 (16)	108 (7)
<b>MePB</b>	4.46	4.2	91 (10)	89 (4)	87 (2)	87 (9)	90 (3)	85 (10)	117 (7)	104 (9)	107 (3)

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Table 3. Results of the monitoring in reservoir RG (data correspond to all samples collected at the different sites and at three depths).

	04/2012		09/2012		10/2012		11/2012		02/2013	
	%Positives	Conc ng/L <sup>(1)</sup>	%Positives	Conc ng/L	%Positives	Conc ng/L	%Positives	Conc ng/L	%Positives	Conc ng/L
<b>BZP</b>	100	9-100 (62)	62	8-243 (110)	53	84-385 (253) <sup>(2)</sup>	n.a. <sup>(3)</sup>	n.a	n.a.	n.a
<b>BZP-3</b>	96	30-502 (238)	0		0		0		0	
<b>BuPB</b>	0		0		0		0		0	
<b>CBZ</b>	0		0		0		0		0	
<b>CFA</b>	0		0		0		0		0	
<b>DIC</b>	11	<LOQ <sup>(4)</sup>	0		0		3	<LOQ	0	
<b>EtPB</b>	4	<LOQ	0		0		0		0	
<b>IBU</b>	89	7-19 (11)	63	5-34 (10)	57	10-25(15)	100	7-62 (17)	100	7-58 (16)
<b>MePB</b>	100	0-122 (38)	87	5-46 (22)	97	5-425(63)	87	6-39 (32)	100	22-265 (81)

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(1) Range of concentrations and average (in brackets) for the positive samples

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(2) Data only available for 6 out of 10 sampling stations included in the monitoring. The percentage of positives and average value correspond to the samples of those 6 sampling stations (Table 2SI for more detailed information)

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(3) n.a: data not available

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(4) &lt; LOQ: detected, concentration lower than the LOQ.

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Table 4. Concentrations (ng/L) of selected compounds in tributaries of reservoir RG

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	April 2012					November 2012				
	E12	E15	E17	E19	QC <sup>(1)</sup> Rec (%)	E12	E15	E17	E19	QC Rec (%)
<b>BZP</b>	13	48	54	25	<b>105</b>	n.a. <sup>(2)</sup>	n.a.	n.a.	n.a.	<b>n.a.</b>
<b>BZP-3</b>	98	66	162	-	<b>81</b>	-	-	-	-	<b>90</b>
<b>BuPB</b>	- <sup>(3)</sup>	<LOQ <sup>(4)</sup>	-	-	<b>94</b>	-	-	-	-	<b>78</b>
<b>CBZ</b>	-	-	-	-	<b>90</b>	-	-	-	-	<b>71</b>
<b>CFA</b>	-	-	-	-	<b>87</b>	-	-	-	-	<b>87</b>
<b>DIC</b>	-	-	-	-	<b>108</b>	-	-	-	-	<b>97</b>
<b>EtPB</b>	-	29	-	<LOQ	<b>98</b>	-	-	-	-	<b>91</b>
<b>IBU</b>	32	-	<LOQ	<LOQ	<b>94</b>	9	-	<LOQ	12	<b>94</b>
<b>MePB</b>	<LOQ	242	10	17	<b>99</b>	29	23	14	58	<b>95</b>

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678 (1) QC: Quality control. Rec (%): % recovery

679 (2) n.a.: data not available

680 (3) -: not detected

681 (4) &lt;LOQ: detected, concentration lower than the LOQ

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700 **Table 5. Results of the monitoring in reservoir LF (data correspond to all samples collected at the different sites and at three depths)**

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	<b>06/2012</b>		<b>09/2012</b>		<b>10/2012</b>		<b>12/2012</b>		<b>02/2013</b>	
	%Positives	Conc ng/L <sup>(1)</sup>	%Positives	Conc ng/L	%Positives	Conc ng/L	%Positives	Conc ng/L	%Positives	Conc ng/L
<b>BZP</b>	55	5-143(57)	80	9-102 (40)	20	16-54 (34)	n.a. <sup>(2)</sup>	n.a.	n.a.	n.a
<b>BZP-3</b>	0		0		0		0		0	
<b>BuPB</b>	10	8-16(12)	5	11	0		5	<LOQ <sup>(3)</sup>	10	18
<b>CBZ</b>	0		0		0		0		0	
<b>CFA</b>	0		0		0		0		0	
<b>DIC</b>	0		0		0		0		0	
<b>EtPB</b>	55	8-50 (30)	0		5	8	5	59	10	18
<b>IBU</b>	100	7-39 (12)	95	7-15 (11)	85	8-16 (11)	90	7-10 (8)	100	7-25 (12)
<b>MePB</b>	100	21-276 (84)	15	11 (11)	100	3-57 (16)	40	6-49 (19)	100	8-113 (29)

702

703 (1) Range of concentrations and average (in brackets) for the positive samples (Table 3SI for more detailed information)

704 (2) n.a: data not available

705 (3) &lt; LOQ: detected, concentration lower than the LOQ.

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Table 6. Concentrations (ng/L) of selected compounds in tributaries of reservoir LF

	October 2012					December 2012					February 2013				
	E8	E9	E10	E11	QC <sup>(1)</sup> Rec %	E8	E9	E10	E11	QC Rec %	E8	E9	E10	E11	QC Rec %
<b>BZP</b>	71	- <sup>(3)</sup>	67	-	<b>78</b>	n.a. <sup>(2)</sup>	n.a	n.a	n.a	<b>n.a.</b>	n.a.	n.a	n.a	n.a	<b>n.a.</b>
<b>BZP-3</b>	-	-	-	-	<b>85</b>	-	-	-	-	<b>75</b>	-	-	-	-	<b>88</b>
<b>BuPB</b>	-	-	-	-	<b>114</b>	-	-	-	-	<b>88</b>	-	-	-	-	<b>79</b>
<b>CBZ</b>	-	-	-	-	<b>102</b>	-	-	-	-	<b>77</b>	-	-	-	-	<b>91</b>
<b>CFA</b>	-	-	-	-	<b>112</b>	-	-	-	-	<b>94</b>	-	-	-	-	<b>109</b>
<b>DIC</b>	-	-	-	-	<b>84</b>	-	-	-	-	<b>114</b>	-	-	-	-	<b>94</b>
<b>EtPB</b>	-	-	-	-	<b>87</b>	-	-	-	-	<b>81</b>	-	<LOQ	-	-	<b>79</b>
<b>IBU</b>	10	-	<LOQ <sup>(4)</sup>	<LOQ	<b>92</b>	<LOQ	-	<LOQ	<LOQ	<b>94</b>	20	-	-	8	<b>84</b>
<b>MePB</b>	5	6	6	-	<b>104</b>	10	14	17	13	<b>112</b>	24	57	25	34	<b>110</b>

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(1) QC: Quality control. Rec (%): % recovery

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(2) n.a.: data not available

717

(3) -: not detected

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(4) &lt;LOQ: detected, concentration lower than the LOQ

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Table 7. Concentrations of PPCPs (ng/L) in drinking water treatment plants

Manantiales (MA)										
		BZP	BZP3	BuPB	CBZ	CFA	DIC	EtPB	IBU	MePB
September/12	Influent	101	30	12	-( <sup>1</sup> )	-	-	-	16	140
	Effluent	46	29	7	-	-	-	-	<LOQ( <sup>2</sup> )	80
QC (%Rec) ( <sup>3</sup> )		<b>114</b>	<b>80</b>	<b>80</b>	<b>91</b>	<b>97</b>	<b>103</b>	<b>99</b>	<b>115</b>	<b>106</b>
October/12	Influent	103	11	-	-	-	-	-	14	27
	Effluent	33	7	-	-	-	-	-	14	21
QC (%Rec)		<b>73</b>	<b>108</b>	<b>67</b>	<b>74</b>	<b>119</b>	<b>90</b>	<b>120</b>	<b>110</b>	<b>127</b>
November/12	Influent	n.a( <sup>4</sup> )	-	-	-	-	-	-	15	69
	Effluent	n.a.	-	-	-	-	-	-	8	29
QC (%Rec)		<b>n.a.</b>	<b>n.a.</b>	<b>87</b>	<b>94</b>	<b>124</b>	<b>122</b>	<b>119</b>	<b>110</b>	<b>114</b>
February/13	Influent	n.a.	-	-	-	-	23	-	26	27
	Effluent	n.a.	-	-	-	-	22	-	21	27
QC (%Rec)		<b>n.a.</b>	<b>n.a.</b>	<b>70</b>	<b>97</b>	<b>115</b>	<b>102</b>	<b>87</b>	<b>123</b>	<b>95</b>

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La Ayurá (LA)										
		BZP	BZP3	BuPB	CBZ	CFA	DIC	EtPB	IBU	MePB
September/12	Influent	32	30	-	-	-	16	-	14	32
	Effluent	30	24	-	-	-	<LOQ	-	14	33
QC (%Rec)		<b>114</b>	<b>80</b>	<b>80</b>	<b>91</b>	<b>97</b>	<b>103</b>	<b>99</b>	<b>115</b>	<b>106</b>
October/12	Influent	41	14	-	-	-	12	-	15	44
	Effluent	40	7	-	-	-	-	-	12	35
QC (%Rec)		<b>73</b>	<b>108</b>	<b>67</b>	<b>74</b>	<b>119</b>	<b>90</b>	<b>120</b>	<b>110</b>	<b>127</b>
December/12	Influent	n.a.	-	-	-	-	-	-	11	34
	Effluent	n.a.	-	-	-	-	-	-	12	34
QC (%Rec)		<b>n.a.</b>	<b>n.a.</b>	<b>87</b>	<b>94</b>	<b>124</b>	<b>122</b>	<b>119</b>	<b>110</b>	<b>114</b>
February/13	Influent	n.a.	-	-	-	-	-	-	22	26
	Effluent	n.a.	-	-	-	-	-	-	24	26
QC (%Rec)		<b>n.a.</b>	<b>n.a.</b>	<b>70</b>	<b>97</b>	<b>115</b>	<b>102</b>	<b>87</b>	<b>123</b>	<b>95</b>

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729

(1) -: not detected

730

(2) &lt;LOQ: detected, concentration lower than the LOQ

731

(3) QC: Quality control. Rec: % recovery

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(4) n.a.: data not available

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738 **Figure captions**

739 **Fig 1.** Sampling sites at the reservoir RG. Numbers 12, 15, 17 and 19 correspond to tributaries

740 **Fig 2.** Sampling sites at the reservoir LF. Numbers 8, 9, 10 and 11 correspond to tributaries

741 **Fig 3.** LC-MS/MS chromatograms for the effluent water sample of the DWTP of Manantiales, collected in  
742 September 2012, showing positive findings of BZP (A) and MePB (B). Q/q ratios and deviations with  
743 respect to the reference standard are shown.

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