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1 **On inorganic tracers of wastewater treatment plant discharges along the Marque River**
2 **(Northern France)**

3

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11

12 **Abstract**

13 Increase of water quality in aquatic systems has become a hot button issue in recent decades.
14 However, with the aim to implement an effective remediation strategy, the first step is to
15 identify the sources of diffuse and point-source pollutions using several tracers. In urban
16 areas, B isotopes, Gd enrichment, Cl⁻ or carbamazepine concentrations can be used as
17 wastewater treatment plant tracers.

18 In this study, a focus was made on the quantification of a wide variety of inorganic
19 compounds (elements, ions, isotopic ratios) all along the Marque River, a small stream
20 located in Northern France receiving effluents coming from seven wastewater treatment
21 plants (WWTPs). The objectives were (i) to determine the importance of the WWTPs
22 discharge during low water events, (ii) to assess the efficiency of conventional tracers in
23 quantifying the contribution of the WWTPs and (iii) to investigate new potential tracers less
24 commonly used.

25 The results have shown, through statistical analyses ANOVA (Analysis Of Variance) tests,
26 PCA (Principal Component Analysis) and contribution calculations, that the WWTPs
27 discharges strongly impact the water composition of all the watercourse and particularly
28 during the first six kilometres. However, due to high discharges of wastewaters not always
29 well treated, some classical indicators (*e.g.* B, Rb/Sr) have shown limitations when used
30 alone. The use of a set of relevant tracers including alkali metals could therefore be one
31 solution for overcoming such a problem. Finally, other indicators like Rb/B or Gd/Pt ratios
32 may also be a way to tackle this issue; they are indeed promising to discriminate the source of
33 wastewaters.

34

35 **Keywords:** anthropogenic impact, inorganic tracers, river, WWTP discharge

36

37 **Highlights**

38 The Marque River is highly impacted by WWTPs especially in its first six kilometres.

39 The contribution of WWTPs could be skewed using classical tracers

40

41 Concentrations of Ca, K, Na, Rb were found suitable to determine WWTPs contribution.

42 Gd/Pt ratio could be a good indicator of the impact of WWTP discharges into the river.

43 **Graphical abstract**

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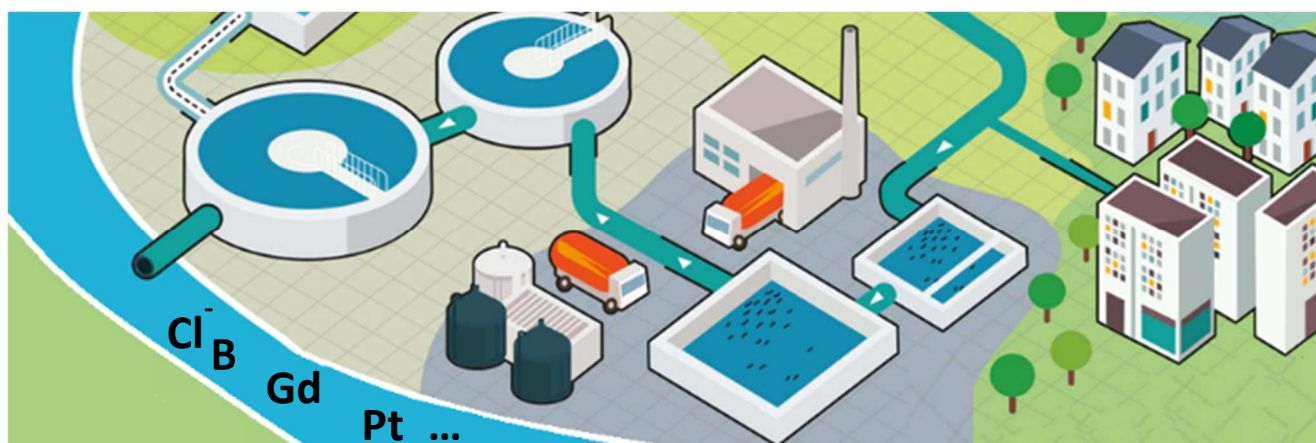
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52 **I. Introduction**

53 Anthropogenic activities have intensified over the last decades at an unprecedented pace
54 resulting in burdening pressures on all the environmental compartments (*i.e.* air, water or soil)
55 (Vareda et al., 2019; Vystavna et al., 2013; Gworek et al., 2014; Moldovan, 2007; Da Silveira
56 et al. 2011; Leterme et al., 2014; Douay et al., 2007; Donoso et al., 2015). Concerning more
57 specifically water resources and aquatic ecosystems, the impacts observed originate from
58 various sources including urban, agricultural or industrial activities (Müller et al., 2020).
59 Regardless of the geographical location, type or nature of the water bodies, the omnipresence
60 of anthropogenic contamination is often linked to various processes, including infiltrations,
61 atmospheric fallouts, industrial or urban discharges, runoff (Moldovan, 2007; Lapworth et al.,
62 2012; Müller et al., 2020). Therefore, the ability to determine the origin of the contamination
63 is of primary importance from the environmental regulation and mitigation perspectives. This
64 ability is supported by studying (geo)chemical tracers, such as pharmaceutical compounds for
65 urban pollution (Collado et al., 2014; Lacey et al., 2012, Currell et al., 2022), isotopes
66 (Adebowale et al., 2019) or groups of pollutants/elements associated with specific industrial
67 contamination, *e.g.* metals for smelters (Prygiel et al., 2015; Saha *et al.*, 2017; Kerfoot et al.,
68 2018), La and Sm for fluid catalytic cracking (Kulaksiz and Bau, 2006). However, as some
69 tracers are not specific to a unique anthropogenic source, it is therefore important to use a
70 panel of tracers to determine accurately the origin of the contamination (Rabiet, 2005; Gasser
71 et al., 2014, McCance et al., 2020).

72 For surface freshwater such as rivers, one of the most important anthropogenic inputs come
73 from wastewater treatment plants (WWTPs). Numerous tracers can be used to determine the
74 impacts of these facilities on their surrounding environment (Rabiet et al., 2005; Gasser et al.,
75 2010; Williams et al., 2013; Lockmiller et al., 2019). For instance, boron isotopes are known

76 to be good tracers of household water inputs associated with the use of boron in detergents
77 and cleaning products (Barber et al., 2006; Guinoiseau et al., 2018). Carbamazepine (an anti-
78 epileptic drug) (Clara et al., 2004; Dickenson et al., 2011), sucralose (sweetener) (Van
79 Stempvoort et al., 2013; Stefania et al., 2019), caffeine (Buerge et al., 2003; Warner et al.,
80 2019) and other contaminants of emerging concerns such as pharmaceuticals or
81 polyfluoroalkyl substances (Tian et al., 2020) can also be relevant tracers of domestic
82 wastewaters. Chloride and nitrate ions have also been reported but their concentrations could
83 be naturally high in some specific environments (Gasser et al., 2014; Khazaei and Milne-
84 Home, 2017). However, they can be used successfully as co-tracers (Gasser et al., 2014;
85 McCance et al., 2018). Because of the utilization of Gd as a contrast agent in Magnetic
86 Resonance Imaging (MRI), this metal is found routinely in WWTPs and can efficiently
87 highlight wastewater inputs (Bau and Dulski, 1996; Hatje et al., 2016). Its high stability in the
88 environment has been demonstrated so that Gd has become an excellent indicator of WWTPs
89 discharges (Holzbecher et al., 2005; Lawrence and Bariel, 2010).

90 The Marque River in Northern France is classified as a river with a high anthropogenic
91 impact and is declassified as “bad status” for both ecological status (because of nutrients and
92 oxygen) and chemical status (because of polycyclic aromatic hydrocarbons, some pesticides
93 and industrial substances) according to the European Water Framework Directive (WFD)
94 (data available on <https://www.eau-artois-picardie.fr/>). Understanding the anthropogenic
95 pressures exerted on the Marque River through a study along the river course is also of
96 interest to improve the management of this watercourse, given that a non-negligible
97 contribution of WWTPs is suspected. It is particularly crucial during dry periods. A sampling
98 campaign along the Marque River was therefore performed in July 2019 with the aim to
99 determine the chemical compositions (major, trace and ultra-trace elements) as well as stable
100 water isotopes during a low water period. This campaign was specifically performed during a

101 dry event with the aim to emphasize the impact of the discharge of WWTPs on the Marque
102 River.

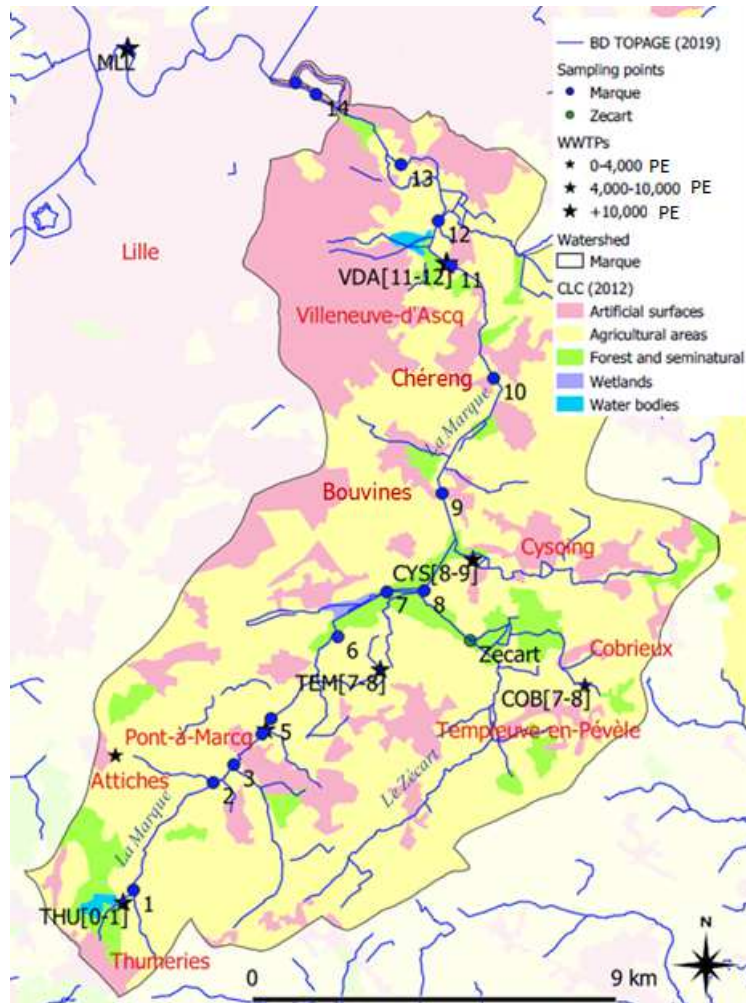
103 Several problematic are raised along the study: (i) how the WWTPs modify the
104 concentrations of substances chosen and are these modifications significant?; (ii) is PCA
105 allowed to demonstrate the WWTPs impact on the river and to discriminate anti-correlated
106 and correlated substances to the WWTPs?; (iii) are several well-known conservative
107 substances and/or WWTPs conventional tracers efficient in the case of a river highly impacted
108 by WWTP; (iv) are some new substances (and/or ratio of substances) could be used as
109 alternative tracers of WWTPs discharges?

110

111 **II. Material and Methods**

112 II.1. Study site and water sampling

113 The Marque River is located in Northern France and is 32-kilometer-long (Figure 1). It has its
114 source at Mons-en-Pévèle and flows into the Roubaix Canal at Wasquehal, before joining the
115 Deûle River. The chemical composition of the Marque River has been already monitored at
116 high frequency through various physico-chemical parameters, nutrients (Ivanovsky et al.,
117 2016) and Mn (Superville et al., 2018). However, these studies were limited to specific
118 sampling points located in the vicinity of the WWTP of Villeneuve d'Ascq. Here, water
119 samples were collected along the river course from Mons-en-Pévèle to Wasquehal at 23
120 sampling points in July 16 and 17, 2019. Seven out of the 23 sampling points were sampled
121 directly in the discharges of WWTPs whose characteristics are reported in Table S1. The
122 other sampling points are located along the watercourse except for one sampling site
123 corresponding to a tributary of the Marque River: the Zécart stream (Figure 1).



124

125 **Figure 1: The Marque River watershed and the sampling points.** WWTPs are labelled as
 126 AAA[X-Y], with AAA an abbreviation for the facility's name, X and Y referring to the two
 127 most adjacent sampling points with X the one upstream and Y the downstream sampling
 128 points. BD TOPAGE is the French hydrographic reference system representing the streams
 129 (blue line), PE stands for population equivalent, MLL stands for Marquette-Lez-Lille, CLC
 130 stands for Corine Land Cover, a European biophysical land cover database.

131

132 Annual average flow rate of Marque River is monitored by the Regional Direction of the
 133 Environment, Development and Housing (DREAL) at sampling points 5 (Pont-à-Marcq) and
 134 9 (Bouvines). In 2019, the annual flow averages were respectively 14,200 and 29,250 m³ d⁻¹
 135 in Pont-à-Marcq and Bouvines (<http://www.hydro.eaufrance.fr/>) and the WWTPs average

136 contributions over the total water flow were respectively 20% and 22% (See Table S1 in
137 Supporting Information for the WWTP inflows values). The Marque River receives the
138 discharge of several WWTPs representing around 144,000 population equivalent (PE), of
139 which the Villeneuve d'Ascq WWTP representing the major part with 118,000 population
140 equivalent.

141 Water samples were collected on July 16 & 17, 2019 during a dry event; no precipitation was
142 recorded since June 20, 2019. Consequently, contributions from runoff originating from
143 impermeable surfaces or agricultural fields were considered insignificant and allow only the
144 wastewater treatment plant influence on the watercourse to be estimated. It was also likely
145 that major anthropogenic pressures on the Marque River were mainly associated with
146 WWTPs discharges, and to a lesser extent with untreated sewage discharges. The daily
147 average flows of the river during the sampling campaign were around 900 m³ d⁻¹ (sampling
148 point 5 - Pont-à-Marcq) and 8,200 m³ d⁻¹ (sampling point 9 - Bouvines)
149 (<http://www.hydro.eaufrance.fr/>). Water at sampling point 5 received the discharges from the
150 3 small WWTPs [Thumeries (THU[0-1]), Attiches (ATT[1-2]) and Pont-à-Marcq (PAM[3-
151 5])], while the river water at sampling point 9 was subject to the three previously cited
152 WWTPs plus three additional WWTPs: Templeuve (TEM[7-8]), Cobrieux (COB[7-8]) and
153 Cysoing (CYS[8-9]). Based on the discharges of WWTPs given by the sewer operator system
154 (Noreade) in Table S1, WWTPs discharges contribution was estimated. At Pont-à-Marcq, the
155 flow of the Marque River was almost equal to the sum of the WWTP discharges. Between
156 Pont-à-Marcq and Bouvines, several referenced streams or wetlands contribute to dilute the
157 effluents of the WWTPs and represent 30% of the total flow. Moreover, exchanges between
158 groundwater and the Marque River cannot be excluded as previously demonstrated (Crastes
159 de Paulet and Dufrenoy, 2012). Overall, it is likely that the contribution of WWTPs is
160 important at least until Pont-à-Marque (the first six kilometres) during dry period.

161 II.2. Chemicals

162 All solutions were prepared using ultrapure water (Milli-Q gradient, Millipore, electrical
163 resistivity of 18.2 M Ω cm). Mono-elemental standard solutions were purchased either from
164 SCP Science (Courtaboeuf, France) or from Courtage Analyses Services (Mont-Saint-Aignan,
165 France). The multistandard solutions of platinum group elements (PGEs) (Astasol, 100 mg L⁻¹
166 in 20% HCl, v/v) and of rare earth elements (REEs) (100 mg L⁻¹ in 5% HNO₃, v/v) used for
167 calibration were obtained from SCP Science. Nitric acid (67-69%, Optima and trace metal
168 grade) was purchased from Fisher Scientific (Illkirch, France). Trace metal grade
169 hydrochloric acid (35-38%) and thiourea (>98%) were acquired from Merck (Darmstadt,
170 Germany). Certified reference material SLRS-6 (river water) was purchased from the
171 Canadian National Research Council (NRC-CNRC, Ottawa, Canada). Acetate cellulose filters
172 (0.45 μ m), polyethersulfone filters (0.45 μ m) and glass fiber filters (0.70 μ m) were purchased
173 from Sartorius.

174

175 II.3. Sampling strategy

176 For each site, two precleaned high density polyethylene (HDPE) bottles (500 mL) were used
177 for the sampling. One was dedicated to physicochemical parameters measurements on site
178 (*i.e.* pH, O₂, temperature, conductivity) immediately after sampling. These parameters were
179 measured using a portable multimeter instrument (WTW, Weilheim, Germany) previously
180 calibrated in the laboratory. The other bottle was used to collect water for further chemical
181 composition determination. Upon various targeted parameters, several protocols were applied
182 for the storage and the treatment of the samples.

183 For anions, water was filtered through acetate cellulose filter (0.45 μ m) and stored in HDPE
184 scintillation vials at 4°C until analysis. For PGEs the protocol was similar to that used for
185 anions with an additional acidification and stabilization step after filtration (acidification up

186 2% v/v using concentrated HCl and addition of solid thiourea to reach a concentration around
187 10 mmol L⁻¹) (Rodushkin et al., 2018). Concerning major, trace and rare earth elements,
188 filtrated water samples were immediately acidified (up to 2% v/v HNO₃) and stored in
189 polypropylene vials instead of HDPE. For the determination of organic carbon, waters were
190 filtered through glass fiber filters (0.70 μm) and stored at 4°C in previously calcinated glass
191 vials.

192 For stable water isotopes, HDPE vials were filled to the brim with filtered water
193 (polyethersulfone filters, 0.45 μm) to prevent evaporation or condensation which could lead to
194 water isotope fractionation. Samples were sent to Trent University (Canada) for isotopic
195 analyses.

196 For all parameters studied, blank samples were analysed to ensure no contamination occurred.
197 These samples were made with the same acids and materials used on the field. Finally, no
198 correction was performed during this study because blank levels represented less than 1% of
199 the total concentrations.

200

201 II.4. Instrumentation

202 Major elements (B, Ca, K, Mg, Na, Sr) were quantified using an inductively coupled plasma -
203 optical emission spectrometer (ICP-OES 5110 VDV, Agilent Technologies) calibrated using
204 standard solutions. Concentrations of REEs (except Sc), PGEs and trace metal elements were
205 determined using an inductively coupled plasma - single quadrupole mass spectrometer (ICP-
206 MS 7900, Agilent Technologies) using He as collision gas and Kinetic Energy Discrimination
207 (KED) to eliminate spectral interferences (Trommetter et al., 2020; Trommetter et al., 2021).
208 To correct possible matrix effects and signal drift, ⁷⁴Ge, ¹¹⁵In, ¹⁸⁵Re and ²⁰⁵Tl were used as
209 internal standards (ISTDs) whose selection for each element was done according to the best
210 fit with SLRS-6 certified concentrations. The recoveries of the measured concentrations were

211 in the range of 76% (Lu) to 117% (Ca) with the exception of Cs (54%). For rare earth
212 elements, which concentrations varied from hundreds pg.L^{-1} to few $\mu\text{g.L}^{-1}$, limits of
213 quantification were comprised from 41 pg L^{-1} (Tm) to 537 pg L^{-1} (Y) (Trommetter et al.,
214 2020).

215 Total Organic Carbon (TOC) concentrations were measured using a TOC-V_{CSH} device
216 (Shimadzu). Analyses were performed using the Non-Purgeable Organic Carbon method.
217 Anions (Cl^- , F^- , SO_4^{2-} , PO_4^{3-}) were quantified using an ion chromatography Dionex ICS-
218 5000+ EG device (Thermo Fisher) equipped with an AS18 column ($\text{Ø} = 4 \text{ mm}$, length = 250
219 mm) and an AG18 guard column ($\text{Ø} = 4 \text{ mm}$, length = 50 mm) using KOH (30 mmol L^{-1}) as
220 isocratic eluent.

221 Water Isotopes ($\delta^{18}\text{O}$ and δD , Deuterium) were measured using a liquid water isotope
222 analyzer (LWIA-24d, Los Gatos Research) at the Water Quality Center (Trent University,
223 Ontario, Canada). The delta notation was calculated relative to the V-SMOW (Vienna-
224 Standard Mean Ocean Water) standard (Equations 1 and 2) (Dang et al., 2021).

$$225 \quad \delta^{18}\text{O} = \left(\frac{\left(\frac{^{18}\text{O}}{^{16}\text{O}} \right)_{\text{sample}}}{\left(\frac{^{18}\text{O}}{^{16}\text{O}} \right)_{\text{V-SMOW}}} - 1 \right) \times 1,000 \quad (\text{Eqn. 1})$$

226

$$227 \quad \delta\text{D} = \left(\frac{\left(\frac{\text{D}}{^1\text{H}} \right)_{\text{sample}}}{\left(\frac{\text{D}}{^1\text{H}} \right)_{\text{V-SMOW}}} - 1 \right) \times 1000 \quad (\text{Eqn. 2})$$

228 Analytical recovery was assessed by using three isotopic natural water reference materials
229 (CRMs, Elemental Microanalysis, UK), which cover a broad range of values found in natural
230 waters (See Table S2 in Supporting Information). Averages and standard deviations of each
231 measurement (standards and samples) were calculated based on eight injections (*i.e.* $n = 8$,
232 750 nL each). We also used ultra-high purity water (18.2 $\text{M}\Omega\cdot\text{cm}$) as an in-house standard,

233 which was used together with official CRMs to bracket every two samples to monitor
234 analytical drift. However, no correction was necessary.

235

236 II.5. Data treatment, statistical treatment and principal component analysis

237 (PCA)

238 ANOVA tests were performed to highlight significant differences between concentrations
239 observed in WWTPs discharges ($n = 7$) and in the watercourse ($n = 14$). A p-value of 0.001
240 was chosen for significance due to the low number of sampling points with the aim to ensure
241 the robustness of the statistical analysis. These results were obtained by using R software with
242 the R Commander interface. The R Commander interface was conceptualized by Fox (2005).
243 A hierarchical classification was also carried out for an overall overview of the sampling
244 points and to highlight outlier points. In addition, FactoMineR package was used to perform
245 PCA analysis. The description of this package and its use are available in the literature (Lê *et*
246 *al.*, 2008). Prior to these multivariate analyses, data were standardized to give similar weight
247 to all the parameters. With the exception of Gd, as REEs showed similar behaviour in the
248 watercourse, it was decided to use only the concentrations of one element (Ce) to enhance
249 readability of the figures. The normalization of the rare earth elements profiles showed no
250 cerium anomalies in the samples. Three typical normalized profiles are represented in Figure
251 S1 (Supporting information).

252

253 **III. Results and discussion**

254 III-1. Overview on the data

255 The averaged concentrations and ANOVA tests for all the parameters are available in Table
256 S3 (see Supporting Information).

257 *III.1.1. Evolution of physical-chemical parameters along the Marque River*

258 Among the physicochemical parameters recorded (pH, O₂, temperature, conductivity and
259 TOC), conductivity appears to be the most suitable tracer of WWTPs discharges (Figure 2a).
260 Indeed, conductivity values were significantly different from those determined in the Marque
261 River according to ANOVA test with p-values < 0.001. Generally, it could be noticed that the
262 conductivity in the Marque River water was generally above 1,000 μS cm⁻¹. These high
263 values can be explained by the presence of chalk in groundwater as reported by previous field
264 campaigns (Cary et al., 2014). However, the human consumption of salt, either as a cooking
265 ingredient or as water softener, can explain the higher conductivity found in WWTPs (up to
266 1,500 μS cm⁻¹) (Yotova et al., 2019; Langhammer and Rödlová, 2013). Conductivity profile
267 (Figure 2a) clearly demonstrates the impact of some WWTPs and the dilution of the WWTPs
268 effluent by several tributaries. Increase of conductivity due to WWTPs (*e.g.* PAM[3-5] or
269 VDA[11-12]) or decrease due to tributaries input and dilution (*e.g.* between sampling points 5
270 and 7 or between sampling points 9 and 11) could indeed be observed. The impact of WWTPs
271 on the physicochemical parameters were mainly observable when the discharges of the
272 WWTPs were directly connected to the Marque River (THU[0-1], PAM[3-5] and VDA[11-
273 12]). Note that the term “impact” is here used to describe the modification of the
274 concentration of a parameter/element in the Marque River caused by the input of WWTPs
275 discharges.

276 On the other hand, higher temperatures in WWTPs discharges than river water were also
277 noticed. However, pH, TOC and O₂ were not significantly different between WWTPs
278 discharges and the Marque River water according to the ANOVA tests. Such observations
279 have been previously noticed in the literature (García-Armisen et al., 2014).

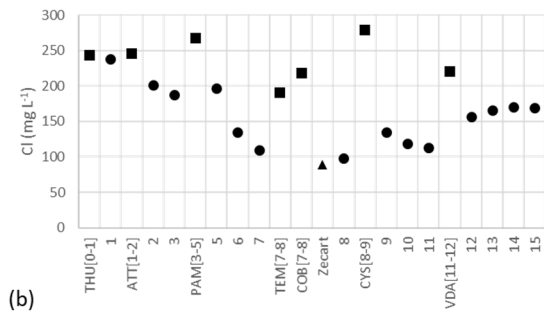
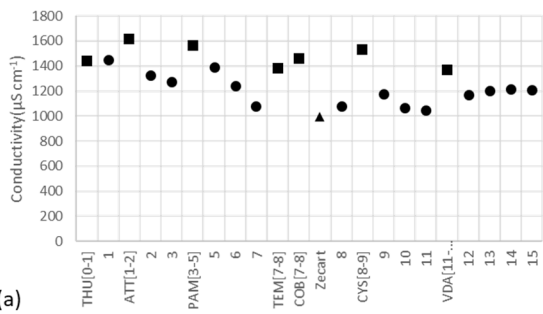
280 *III.1.2. Evolution of elemental concentrations along the Marque River*

281 **Anions** – The concentrations of chloride ions were generally higher in WWTPs than in the
282 Marque River (Figure 2b). Along the river watercourse, concentrations of chloride ions were
283 quite variable in comparison with other anions like fluorides ($0.34 \pm 0.04 \text{ mg L}^{-1}$). Concerning
284 sulphate ions, their concentrations were relatively constant in WWTPs ($111 \pm 12 \text{ mg L}^{-1}$)
285 while their concentration in Marque samples was more variable ($126 \pm 41 \text{ mg L}^{-1}$). Finally,
286 phosphate ions did not exhibit any particular trend. Indeed, 3 WWTPs had really high
287 concentrations while the 4 others removed efficiently phosphate ions during the wastewater
288 treatment process.

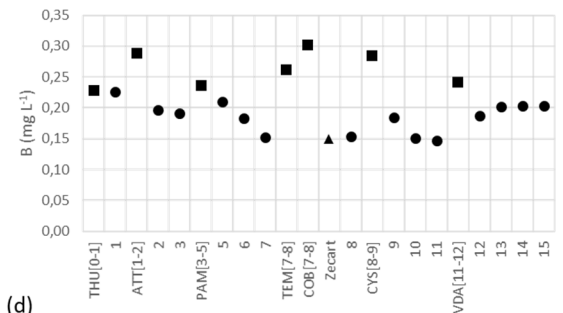
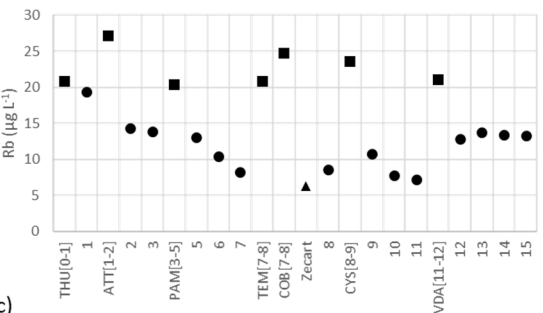
289 **Alkali and alkaline earth metals** – Concentrations of Ca and Mg were quite constant
290 (respectively 140 ± 8 and $20 \pm 3 \text{ mg L}^{-1}$) along the river and were close to the concentration
291 in WWTPs discharges (respectively 133 ± 7 and $23 \pm 1 \text{ mg L}^{-1}$). For the other elements,
292 standard deviations ranged from 17% (Sr) to 72% (Cs). ANOVA tests were also performed to
293 evaluate the differences between WWTPs discharges and Marque River samples (p-values set
294 at 0.001). Cs (semi-quantitative), K, Na, Rb had concentrations significantly higher in
295 WWTPs than in the Marque River. Their average concentrations were respectively $0.076 \pm$
296 $0.023 \text{ } \mu\text{g L}^{-1}$, $39 \pm 6 \text{ mg L}^{-1}$, $165 \pm 20 \text{ mg L}^{-1}$, $23 \pm 3 \text{ } \mu\text{g L}^{-1}$ in WWTPs discharges while in
297 the Marque River their average concentrations were $0.014 \pm 0.010 \text{ } \mu\text{g L}^{-1}$, $23 \pm 6 \text{ mg L}^{-1}$, 100
298 $\pm 27 \text{ mg L}^{-1}$, $12 \pm 4 \text{ } \mu\text{g L}^{-1}$. Their profiles of concentrations along the river were close to the
299 profile obtained for conductivity (e.g. profile of concentration for Rb depicted Figure 2c).
300 Concentrations of Ba in wastewaters were found to vary significantly from one plant to
301 another and no pattern/model for the evolution of barium along the river watercourse could be
302 established ($25 \pm 18 \text{ } \mu\text{g L}^{-1}$ in WWTP discharges and $34 \pm 9 \text{ } \mu\text{g L}^{-1}$ in the Marque sampling
303 points). Various parameters used usually in irrigation (sodium adsorption ratio, magnesium
304 adsorption ratio, sodium percentage, sodium soluble percentage and Kelly's ratio) were

305 calculated. The definition of these parameters, their calculations and the p-value from the
306 analysis of variance (Gaussian distribution for all the parameters) between WWTP and natural
307 averages are compiled in the Supporting Information (see Table S4). The results obtained
308 from these parameters tend to confirm the trends observed with the comparison of elemental
309 concentrations between WWTP discharge samples and natural ones. Parameters based on
310 alkali concentrations tend to have a lower p-value than those based on alkaline earth metals
311 and could therefore be of interest for tracing WWTP discharges.

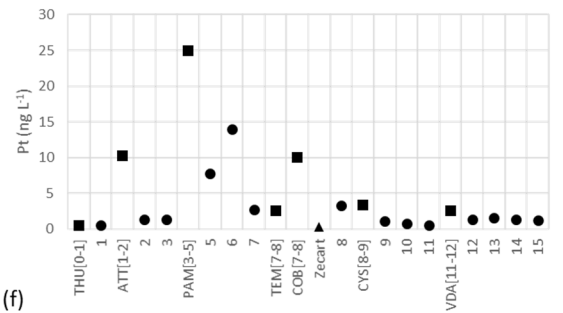
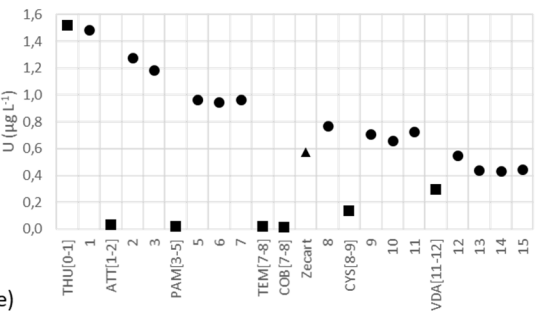
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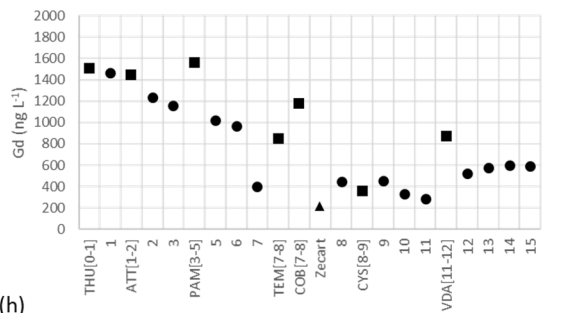
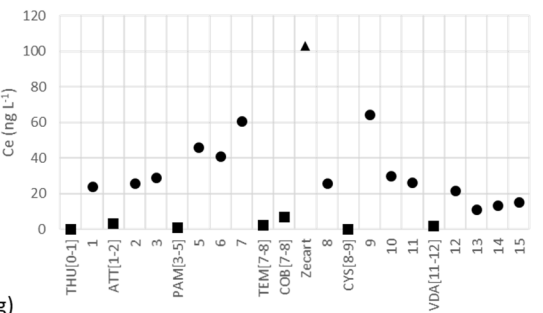
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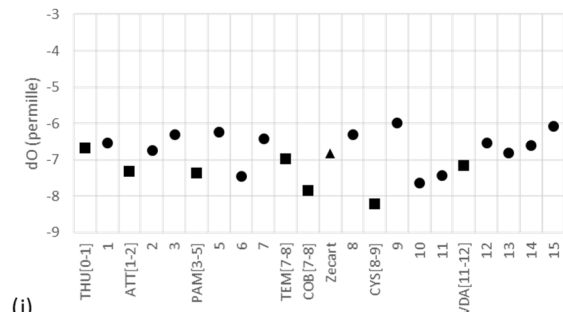
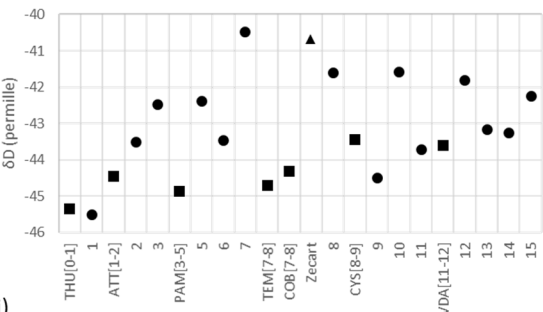
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316



317 **Figure 2:** Evolution of (a) EC, (b) Cl, (c) Rb, (d) B, (e) U, (f) Pt, (g) Ce, (h) Gd, (i) δD and (j)
318 δO along the different sampling points (squares: WWTPs, dots: Marque River, triangle:
319 Zécart)

320

321 **Trace elements** – This section includes a wide variety of elements. Some of them showed
322 very variable concentrations into WWTPs without any particular trend along the Marque
323 River (*i.e.* Fe, Mn, Mo, Ni, Co, Al, W, Zr, Pb, Sb and Ti). It appeared that occasionally, one
324 of the sampling sites was found to exhibit an unusual concentration (at least twice higher than
325 the average in the watercourse samples) without any particular explanation. These “hot spots”
326 were also not necessarily the same depending on the elements studied. Other elements
327 exhibited only slightly different concentrations in WWTPs compared with the values recorded
328 in the Marque River, according to their p-value between 0.001 and 0.01 (*i.e.* Zn [rooftops,
329 pipelines, industries, etc. (Müller et al., 2020)], Bi [cosmetics and plastics (Fuerhacker et al.,
330 2003; Amneklev and Sörme, 2015)], V and Ni [geological background (Campbell et al., 2015;
331 Moskalyk and Alfantazi, 2003)]). In contrast, Cr, Sn and As showed significantly different
332 concentrations between the WWTPs discharges and the Marque River samples. Chromium
333 (Kanagaraj et al., 2008; Baral et al., 2006) and tin (Fent, 1996; Chahinian et al., 2013;
334 Pougnet et al., 2014) are used in various industries, which may explain their higher
335 concentrations observed in the WWTPs. The low levels of As in WWTPs are likely due to its
336 low concentration in the chalk aquifer [As is below $2 \mu\text{g L}^{-1}$ in drinking water according to
337 the regional health agency (ARS) data] and to an efficient removal of residual As through
338 flocculation processes and the removal of orthophosphates by ferric chloride addition
339 (Ociński et al., 2016).

340 A particular focus was set on boron and uranium (Figures 2d and 2e respectively) as boron
341 concentration is sometimes used as WWTP tracer and U exhibits a particular decrease in

342 concentration along the Marque River watercourse. Boron, and particularly its isotopic
343 signature, has already been reported as a good tracer for domestic water due to its use in
344 laundry products inducing high concentrations of this element in WWTPs discharges
345 (Guinoiseau et al., 2018). ANOVA test (p -value < 0.001) and the profile obtained during this
346 study (see Figure 2d) confirmed its potential to highlight the impact of WWTPs on the
347 watercourse. The profile of boron concentration followed a similar trend than those of other
348 tracers such as EC ($R= 0.92$) (see Table S5 in supporting information). U concentrations
349 varied from hundreds of ng L^{-1} to few $\mu\text{g L}^{-1}$. The lowest concentrations were observed in the
350 WWTPs discharges (see Figure 2e), excepted for THU[0-1] where the highest concentration
351 of uranium ($1.5 \mu\text{g L}^{-1}$) was recorded. In northern France, water used for domestic and
352 industrial activities mainly comes from aquifers and this water ends up in WWTPs. In this
353 study, Thumeries water inputs come from another sources mixture than the other cities of the
354 studied watershed, which can explain higher natural concentration of U than in other WWTPs
355 and subsequent dilution along the Marque. However, these concentrations remain low as the
356 average concentration of tap water in France is $3.08 \mu\text{g L}^{-1}$ and the threshold value proposed
357 by the World Health Organization is $[U] = 15 \mu\text{g L}^{-1}$ (Caamano et al., 2011).

358 ***Platinum group and rare earth elements*** – The highest Pt concentrations were found in the
359 WWTPs (from 0.53 up to 25 ng L^{-1}) (Figure 2f). This result suggests a medical origin for Pt,
360 which can be employed as anticancer drug. While automotive catalytic converters could be
361 also a major source of Pt, medical Pt is in this case more likely the major source as we did not
362 observe high concentrations of other PGEs (in particular Rh and Pd) which are more specific
363 for catalytic converters (Omrani et al., 2020). Indeed, no peak of palladium and rhodium
364 concentrations were observed during this study. Ir and Ru were below the limits of
365 quantification which were respectively 0.1 ng L^{-1} and 0.2 ng L^{-1} .

366 In this study, all rare earth elements were quantified. In the river, REEs concentrations ranged
367 from hundreds of pg L^{-1} to dozens of ng L^{-1} and lower concentrations were observed in
368 WWTP discharges than in the Marque samples. The highest concentrations were observed in
369 the tributary of the Marque River, the Zécart stream (a 7-km long tributary less impacted by
370 anthropogenic activities), while the lowest concentrations were observed in the WWTP
371 discharges. By contrast with some other trace elements (see additional elements), WWTPs did
372 not seem to impact significantly the evolution of the REEs. Conductivity and REEs profiles
373 were totally different (*e.g.* increase of the concentration of REEs between sampling points 1
374 and 3 *vs* a decrease for conductivity). As a representative example, Ce evolution along the
375 Marque River watercourse is shown Figure 2g.

376 Among the REEs, one exception should be highlighted: Gd. It is now well established that
377 gadolinium can be a relevant tracer for WWTPs inputs due to the high stability of the Gd-
378 based contrast agents used for MRI, its specific used in medical field and its high
379 concentrations in WWTP discharges (Holzbecher et al., 2005). Unlike the other REEs
380 elements, its maximal levels were generally recorded in WWTPs discharges with
381 concentrations ranging from 360 to 1,560 ng L^{-1} (Figure 2h). Thus, the evolution of the
382 concentration of Gd was found to be totally different from that observed for the other rare
383 earth elements. Moreover, its concentrations were much higher than the other REEs, ranging
384 from hundreds of ng L^{-1} to several $\mu\text{g L}^{-1}$. Contrary to the other REEs, the concentration of
385 Gd was lower in the Zécart stream than in the Marque River. The evolution of Gd
386 concentrations was almost the same than the one depicted for the conductivity ($R = 0.80$) (see
387 Table S5 in supporting information). Two major differences could however be observed:
388 PAM[3-5] strangely did not seem to impact the point 5 and CYS[8-9] did not induce an
389 increase of the concentration of Gd. If the second observation can be explained by the similar
390 concentrations of Gd of the WWTP discharge and the upstream sampling points for the point

391 8 and CYS[8-9], the first observation is more difficult to justify. The lack of information due
392 to contamination of the point 4 (see “outliers, PCA and correlation” section thereafter) is
393 damaging in this case.

394

395 *III.1.3. Stable water isotopes*

396 δD and $\delta^{18}O$ were quantified during this study (Figures 2i and 2j). Their average values in
397 WWTP discharges were $-44.4 \pm 0.7\text{‰}$ and $-7.4 \pm 0.5\text{‰}$ respectively for δD and $\delta^{18}O$. In
398 Marque samples, the values were $-42.8 \pm 1.3\text{‰}$ and $-6.6 \pm 0.5\text{‰}$. Concerning the evolution of
399 these parameters along the Marque River we could observe that $\delta^{18}O$ was quite constant
400 between the sampling points 1 and 9 ($-6,7$ to $-6,0\text{‰}$) with an exception at the sampling point 6
401 where $\delta^{18}O$ fell down to -7.5‰ . At sampling point 10 the $\delta^{18}O$ value fell down once again ($-$
402 7.5‰) before increasing between sampling points 11 to 15 for reaching $-6,1\text{‰}$. For δD , the
403 evolution was more difficult to synthesize. An increase of δD values was observable from the
404 sampling point 1, corresponding to the lowest value (-45.5‰), to sampling point 3. Then, a
405 decrease was observed for sampling points 5 and 6 before a huge increase for reaching the
406 maximal value at sampling point 7 (-40.5‰). A decrease was once again observed from
407 sampling points 7 to 9. After sampling point 9, δD values alternated between increase and
408 decrease with the exception of sampling points 13 and 14 with similar values.

409

410 *III.2. Data treatment and calculations*

411 *III.2.1. Outliers, PCA and correlations between the parameters of interest*

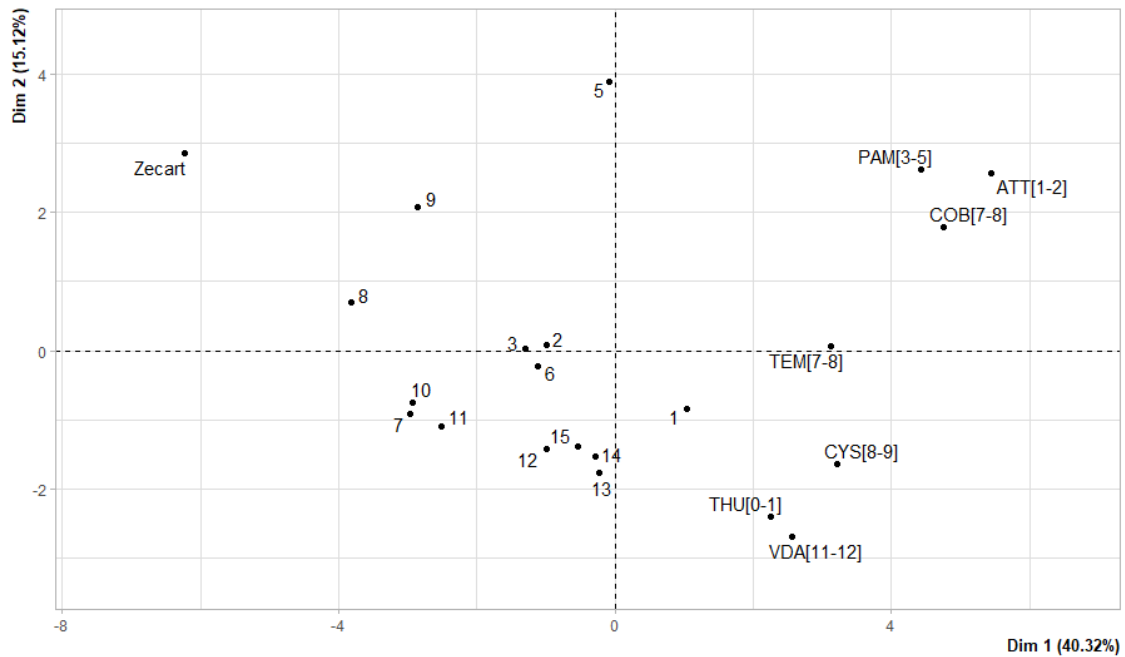
412 Before analysing the data thoroughly, a hierarchical classification was carried out to
413 determine potential outliers (See Figure S2 in Supporting Information). The sample
414 corresponding to the upstream of Pont-à-Marcq WWTP (sampling point 4) was found to be
415 significantly different from the others. Indeed, this point was characterized by very high

416 concentrations of Gd ($3.6 \mu\text{g L}^{-1}$), Pt (71 ng L^{-1}), Al ($18 \mu\text{g L}^{-1}$), Ti ($12 \mu\text{g L}^{-1}$), Cu ($4 \mu\text{g L}^{-1}$),
417 TOC (35 mg L^{-1}). These concentrations were 4 to 20 times above the average calculated with
418 the other Marque River samples and a low percentage of dissolved oxygen was also observed
419 (14% vs 60% on average). Explanations were given by the sewer system operator (Noréade)
420 on an accidental raw wastewater input just upstream this location during the campaign. This
421 short incident was confirmed by an additional sampling performed one week later and
422 showing no more unusual concentrations. Such kind of input are punctual but not exceptional
423 in the Marque River.

424 PCA allows having a better understanding and visualization of the distribution of the
425 sampling points and elements influencing the most the Marque River. It was decided to keep
426 22 parameters of interest. As one of the aims of the study was to find new potential inorganic
427 tracers for assessing the origin of contaminated waters, the selection of the most suitable
428 parameters was done by selecting: (i) parameters already known for being good tracers of
429 WWTPs effluents (*i.e.* B, Cl⁻, EC, Gd and temperature); (ii) elements or parameters often
430 studied in literature in case of punctual contaminations (*i.e.* As, Cu, Fe, Mn, Ni, Pb, pH and
431 Zn); and (iii) other elements belonging to technology critical elements or showing interesting
432 behaviour in the global PCA (*i.e.* Rb, Ba, Pt, Ce, Sr, SO₄²⁻, U, δD and TOC).

433 The results of the PCA based on the 22 selected parameters are shown through PCA score
434 plot (Figure 3) and PCA loading plot (Figure 4).

435



436

437 **Figure 3:** PCA score plot of the first two principal components.

438 The first dimension is strongly linked to the WWTPs discharges. It is also possible to
 439 determine which elements might be more abundant in WWTP discharges than in the river
 440 (Rb, EC, Gd, Cl⁻ or B). As expected, the Zécart stream is the most anti-correlated sampling
 441 point with respect to the WWTPs. Figure 3 also confirms the first sampling point in the
 442 upstream of the Marque River is strongly influenced by THU[0-1] before being diluted by
 443 river water. It is interesting that from point 10 to point 13 the behaviour of the sites is more
 444 and more similar to that of the VDA[11-12] sampling point and then seem to slightly shift
 445 toward natural river water (Zécart point) for sampling points 14 and 15. For other WWTPs
 446 (with the exception of THU WWTP but no upstream points are available), their impact looks
 447 less important than the VDA WWTP may be due to low discharge compared with the river
 448 flow or discharge far from the downstream point associated.

449

450

463 S5 in SI) (Bacquart et al., 2015; Gorny et al., 2015). To confirm the trends observed with
464 PCA, correlation coefficients values for the selected elements and the studied sites are
465 presented Table S5 and agree with the PCA results.

466 Concerning the second and third dimensions, they appeared to be much more complex to
467 interpret and only hypotheses can be formulated. The second dimension could be related to
468 the variability of speciation of the elements according to the water evolution (*e.g.*
469 precipitation, redox conditions, etc.). Indeed, EC, B, Cl⁻ or δD are normally considered as
470 conservative parameters and it can be observed that they are hardly impacted by the second
471 dimension. Gd is conservative as a complex but not conservative naturally (Kulaksiz and Bau,
472 2007). In the Marque River, the percentages of natural Gd have been calculated (see Figure
473 S3 in Supporting Information and Eqn. 3) and found to be mainly anthropogenic (>98%
474 except for Zécart).

$$475 \quad \%Gd_{Nat} = \frac{(0.4 * Nd_N + 0.6 * Dy_N)}{Gd_N} * 100 \quad (\text{Eqn. 3})$$

476 With Gd_N, Nd_N, and Dy_N, the concentrations of Gd, Nd and Dy normalized with the
477 concentrations of European shale (Bau et al., 2018).

478 On the third dimension, Co, U, V and in a lesser extent Ni were correlated. One hypothesis
479 could be the drinking water source that finally ends up in WWTPs. In THU[0-1], the origin is
480 known to be partly different and thus could influence the evolution of these elements along
481 the Marque River.

482

483 *III.2.2 Determination of the WWTPs impact using inorganic tracers*

484 *III.2.2.1. Conventional tracers used for WWTPs discharges advantages and*
485 *drawbacks*

486 ***Concentrations of chloride, conductivity and boron*** – The Marque River was found to be
487 strongly impacted from its source by WWTPs discharges. The results of the Section III.2.1

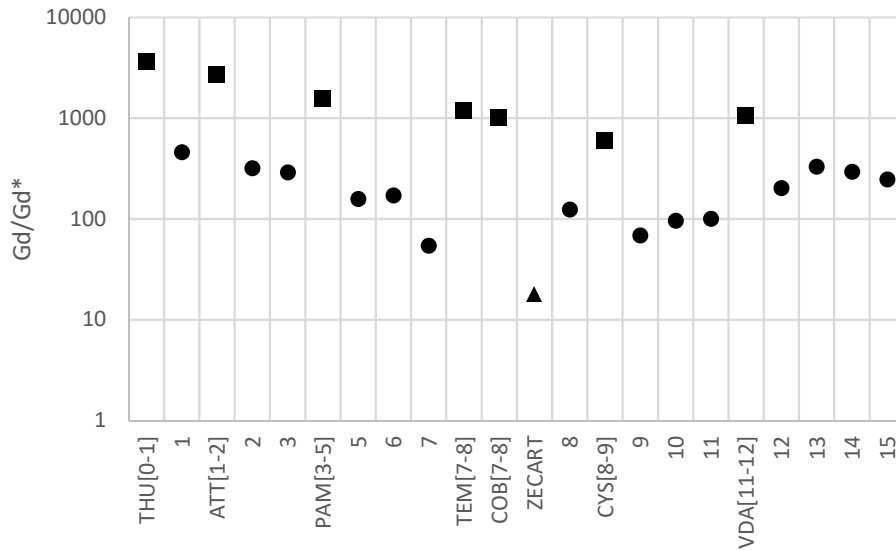
488 showed significant differences between concentrations of chloride ions in WWTPs and those
489 found in the Marque River. Conductivity, Cl⁻ and boron were among the physicochemical
490 parameters significantly different between WWTPs and natural samples according to
491 ANOVA. These parameters still appeared interesting for assessing the contribution of
492 WWTPs. However, the high concentrations found at the beginning of the Marque River due
493 to high WWTPs inputs limited the observed enrichment especially for both chloride and
494 conductivity (Figures 2a and 2b). Boron is often used as tracer due to its isotopic signature.
495 However, the boron isotopes ratios were not determined in this study.

496
497 ***Rb/Sr ratios and concentrations of rubidium*** – Rb/Sr ratio is used to determine the influence
498 of WWTPs because rubidium is more concentrated than Sr in WWTPs discharges (Nirel and
499 Revaclier, 1999; Rabiet, 2006). An increase of the Rb/Sr values is thus expected for each
500 sampling point immediately downstream a WWTP. However, in the case of the Marque River
501 strongly impacted by WWTPs, this ratio does not seem of interest. Indeed, in some samples of
502 the river, the ratio Rb/Sr was found to be higher than in WWTPs discharges. Nevertheless, the
503 concentration of Rb alone could be a good indicator to discriminate WWTPs and Marque
504 samples (Nirel and Revaclier, 1999; Rabiet, 2006) (see Figure 2c). In our case study, despite
505 the high values recorded in the WWTPs effluents, an increase of the concentration of Rb was
506 not necessarily observed downstream (as for as Gd, EC and B). Moreover, this ratio is not
507 adequate for tracing WWTP discharges at long scale.

508 ***Gd anomaly*** – Gd anomaly (Gd/Gd*) is calculated using Equation 4 (Hissler et al., 2015;
509 Louis et al., 2020):

510
$$Gd/Gd^* = \frac{Gd_N}{0.4 * Nd_N + 0.6 Dy_N} \quad (\text{Eqn. 4})$$

511 With Gd_N , Nd_N , and Dy_N the concentrations of Gd, Nd and Dy normalized with the
 512 concentrations of European shale (Bau et al., 2018). The Figure 5 represents the evolution of
 513 the Gd anomaly along the Marque River.



514
 515 **Figure 5:** Evolution of Gd/Gd* (logarithmic scale) along the Marque River. (squares =
 516 WWTPs, dots = Marque River and triangle = Zécart sampling point)

517
 518 According to Figure 5, the highest Gd anomalies were observed for the WWTPs while the
 519 lowest one was observed in the Zécart stream. This sampling point was only impacted by
 520 COB[7-8] (and eventually by some septic tanks). The natural Gd anomaly for the Marque
 521 River could not be calculated as the source of the Marque River was almost dry. In literature,
 522 when Gd/Gd* is above 1.4-1.8, an anthropogenic effect could be suspected (Rabiet, 2006;
 523 Louis et al., 2020). This chart clearly demonstrates a high impact of WWTPs and possibly the
 524 impact of septic tanks discharges and exceptional (such as the outlier point 4) or recurrent
 525 direct untreated sewage discharges onto the Marque River.

526

527 *III.2.2.2. Selection of other tracers of WWTP discharges.*

528 Data used were based on the results obtained around Villeneuve d'Ascq. Indeed, for this
529 point, VDA WWTP discharges directly in the Marque River and this WWTP was found as the
530 most impactful WWTP during this study. Assuming only the river flow upstream and WWTP
531 discharge contribute to the river flow downstream the WWTP, the mixing equation is defined
532 by Equation 5:

$$533 \quad Q_{WWTP} = Q_{downstream} * \frac{[A]_{downstream} - [A]_{upstream}}{[A]_{WWTP} - [A]_{upstream}} \quad (\text{Eqn. 5})$$

534 With [A] representing the concentration of the studied tracer, $Q_{downstream}$ the discharge
535 downstream the WWTP, Q_{WWTP} the discharge of the WWTP. By modifying (Eqn. 5) we
536 could calculate the contribution of the WWTP discharge onto the downstream flow (Eqn. 6):

$$537 \quad \text{Contribution (\%)} = \frac{Q_{WWTP}}{Q_{Downstream}} * 100 = \frac{[A]_{downstream} - [A]_{upstream}}{[A]_{WWTP} - [A]_{upstream}} * 100 \quad (\text{Eqn. 6})$$

539 This contribution calculation requires that the element studied has a conservative behaviour.
540 The expected contribution was calculated based on parameters Gd, Cl⁻, EC and B known for
541 being conservative. Here these tracers could be used as the differences between upstream
542 concentrations (point [11]) and VDA[11-12] concentrations are significant to allow
543 calculation. Four downstream sampling points (12, 13, 14 and 15) were used to evaluate the
544 evolution of the contribution and the potential conservative behaviour of the studied
545 parameters. Gd, Cl⁻ and EC showed contributions between 39-41% for the closest
546 downstream sampling point [12] and 48-54% for the sampling points 13 to 15. The gap
547 between the contributions of the WWTP calculated for the points 12 and 13 could be
548 explained by another discharge of untreated water (not evidenced during this monitoring).
549 Such difference could also be explained by daily variations of the WWTP treatment plant
550 discharges or the uncertainty of the measurements. All the parameters studied were

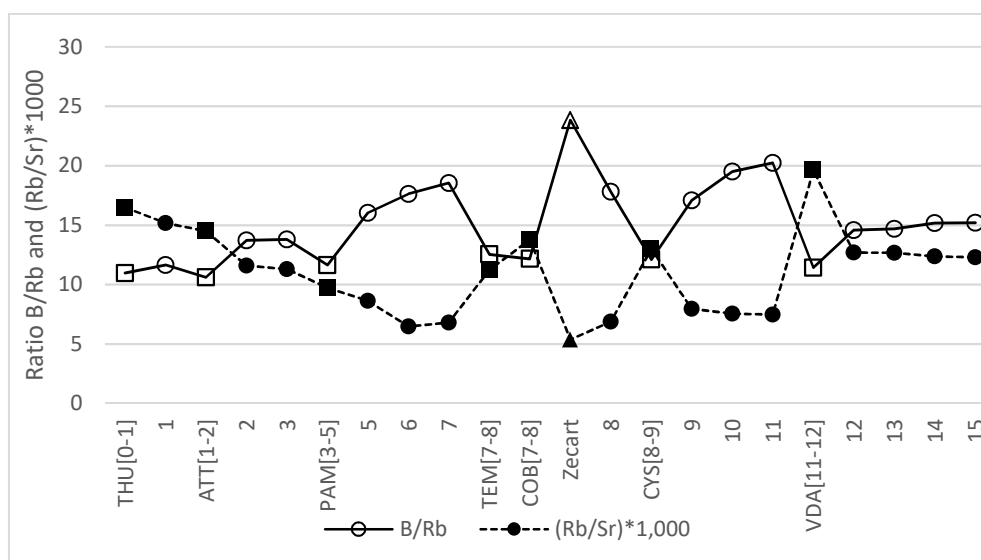
551 considered suitable for the contribution calculation when the calculated values were around
 552 $\pm 5\%$ the values obtained with these three reference parameters (*i.e.* Gd, Cl⁻ and EC). For each
 553 sampling point, only the elements which were determined suitable as tracing elements were
 554 considered in Table 1.

555 **Table 1:** Assessment of the conservative behaviour of several elements in comparison with
 556 Cl⁻, Gd and EC.

Point 12 (1.4 km)	Point 13 (4 km)	Point 14 (6.9 km)	Point 15 (7.7 km)
B, F ⁻ , SO ₄ ²⁻ , NO ₃ ⁻ , PO ₄ ³⁻ , Ca, K, Mg, Na, Sr, Ni, As, Rb, Mo, Sb, Cs, Ba, U, Pt, O ₂ , TOC	F ⁻ , NO ₃ ⁻ , Ca, K, Na, Ni, Rb, Ba, Pt, Mo, Sb	NO ₃ ⁻ , Ca, K, Na, Ni, Rb	NO ₃ ⁻ , Ca, K, Na, Rb

557
 558 From this table, we can notice that really few parameters can be used for calculating the
 559 contribution of WWTPs at long distance. Indeed, additionally to the classical tracers selected
 560 in this study (Cl⁻, Gd and EC), only 4 major elements (Na, Ca, K and Rb) were found suitable.
 561 Alkali metals appear to be conservative and could be good and easily measurable indicators in
 562 case of high natural Cl⁻ concentration or higher boron contribution due to potential other
 563 sources (Hasenmueller and Criss, 2013). A slight overestimation was observed for B over the
 564 point 12 (60% vs 50% for the other classical tracers). Such overestimation can be explained
 565 by other sources of boron. Boron isotopic analyses could help to understand the origin of this
 566 element. For calculating contribution at short distance F⁻, Ni, Ba, Sb, Mo and Pt could be
 567 added to the list of selected elements. The conservative behaviour of Pt at short scale was
 568 confirmed by additional experiments (section thereafter) considering the concentrations of Gd
 569 and Pt. This set of elements could be interesting for calculating in short range direct
 570 contribution of WWTP on a river and understanding potential transformation occurring
 571 thereafter in the river.

572 Inter-elements ratios were also investigated to better discriminate between WWTPs
 573 discharges and natural samples. By contrast with the ratio Rb/Sr, the ratio B/Rb ratio was
 574 found to be quite constant in the 7 WWTPs varying from 10.6 to 12.5 (vs 9.7 to 19.6 for
 575 Rb/Sr). The higher the ratio, the less impacted the river by WWTPs inputs (Figure 6). Thus,
 576 this B/Rb ratio allows discriminating efficiently the WWTPs from the natural samples in this
 577 aquatic system.



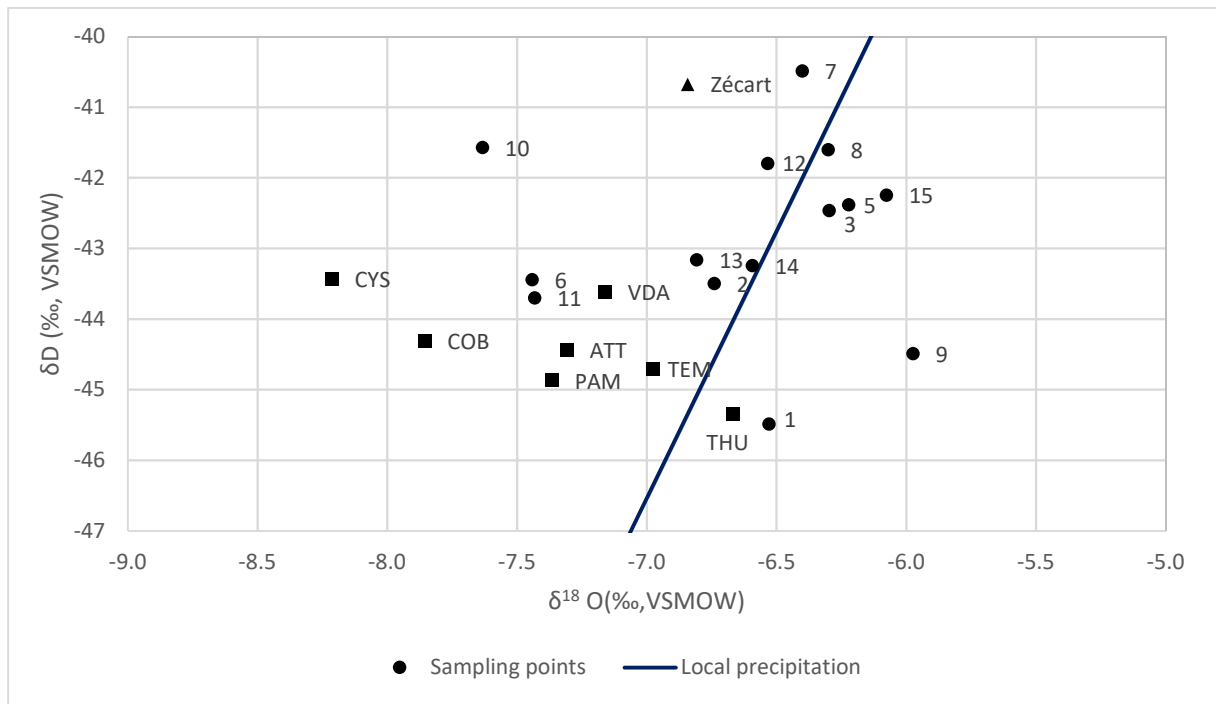
578
 579 **Figure 6:** Evolution of B/Rb and Rb/Sr ratios along the Marque River (square = WWTPs, dots =
 580 Marque River, triangle = Zécart).

581
 582 Water isotopes were also analysed. Correlations were performed with all elements and no
 583 correlation was found for $\delta^{18}\text{O}$. On the contrary, as depicted in Table S5 and Figure 3, δD
 584 showed a significant anticorrelation with Cl^- , Gd and EC which are the usual tracers of
 585 WWTPs discharges. The evolution of δD is shown in Figure 2i.

586 δD could therefore be of interest in determining WWTP discharges. Moreover, we could
 587 observe that the value of δD for point 13 was close to that of VDA[11-12] while for point 12,
 588 the value was close to the least contaminated sampling site (characterized by the lowest
 589 values of EC and Gd). This change of δD value could indicate an additional input coming
 590 from WWTP or non-treated discharge. Looking at the profiles of Gd, Cl^- , EC and B (Figure

591 2a, 2b, 2h and 2d), a slight difference between points 12 and 13 has already been observed,
 592 but not as significant as the variation of δD . However, point 11 also had a similar δD as the
 593 VDA treatment plant, but in this case no other parameters showed the presence of discharge
 594 from the treatment plant. This parameter could be interesting for tracing WWTP discharge but
 595 a better understanding of its variation is needed.

596 The representation of δD as a function of $\delta^{18}O$ can also be studied and is shown in Figure 7.



597
 598 **Figure 7:** Representation of water isotopes for the samples and the global precipitation. The
 599 average isotopic composition of local precipitation is calculated using monthly data found on
 600 waterisotopes.org a website designed by Gabriel Bowen for Villeneuve d'Ascq city (squares=
 601 WWTPs, dots= Marque River, triangle= Zécart).
 602

603 The same pattern was generally observed for WWTPs samples with lower $\delta^{18}O$ values than
 604 expected for precipitation. Only THU[0-1] had a different behaviour. This difference further
 605 strengthens the hypothesis of different water origin for this sampling point (as already
 606 evidenced with U). Three watercourse samples (6, 10 and 11) had a behaviour close to that
 607 observed for the treatment plants. For points 10 and 11 the explanation was probably the
 608 same. A significant decrease in values was observed for a large number of parameters

609 between points 9 and 10 showing that dilution occurred. Two hypotheses can be proposed.
610 Dilution may come from (i) the two surface tributaries shown in Figure 1 and/or (ii) an
611 exchange with groundwater. Exchange with groundwater is not expected to occur between
612 point 11 and 15 according to the calculation of the contribution of the VDA[11-12] WWTP.
613 The increase of the concentrations of calcium, the decrease of temperatures, the decrease of
614 the concentrations of REE possibly due to their low concentrations in groundwater
615 (Munemoto et al., 2015; Johannesson et al., 1997) and the decrease of the values for $\delta^{18}\text{O}$ may
616 validate the hypothesis of groundwater input from hyporheic zone possibly coupled with an
617 infiltration upstream of this zone. However, δD which is often used as a tracer for
618 groundwater input (Johannesson et al., 1997) did not seem to confirm this hypothesis with a
619 value different from those observed in wastewater treatment plants. Point 6 also behaved
620 similarly to WWTPs. High values for some elements (Ni, Pt, SO_4^{2-} , etc.) were observed but
621 no explanation could be given for these inputs.

622 *III.2.2.3. Does a relationship exist between Pt and Gd elements?*

623 A particular focus was performed on Pt and Gd. Both are described as Technology Critical
624 Elements which are necessary for the development of new technologies and could be
625 potentially subject to supply shortages (Cobelo-García et al., 2015). In addition, these
626 elements can have a common medical source due to their utilization as contrast agents for
627 MRI (Gd) and anticancer drugs (Pt) (Kümmerer and Helmers, 1997; Lenz et al., 2005). It
628 should then be interesting to find a relation between these elements even if their
629 concentrations were found to be highly variable in wastewaters. Ratios of Gd to Pt were then
630 calculated in the different WWTPs ranging from 60 (PAM[3-5]) to 2,800 (WWTP THU[0-
631 1]). Various hypothesis can be put forward to explain such differences: (i) differences in the
632 processes applied for wastewater treatment allowing a higher removal of Pt (as Gd being
633 considered as conservative); and (ii) a locally different proportion of people treated for cancer

634 diseases with platinum-based drugs and for people undergoing MRI. Even if no hospitals are
635 present in the vicinity of the WWTP (no direct discharges), patients coming back home after a
636 cancer treatment or a MRI analysis are a source of Gd and Pt as an important percentage of
637 the excretion (70-80%) takes place outside hospitals or medical centers. For the first
638 hypothesis, sampling of the inflow and discharge of the different WWTPs could be of interest.
639 In the literature, some publications have shown a decrease of the concentration of platinum
640 between the discharge and inflow (Monteiro et al., 2017; Isidori et al., 2016) while others
641 have pointed out no differences (Goullé et al., 2011). The ratio found in the studied WWTP
642 did not seem to be impacted by the punctuality of the sampling. Indeed, grab sampling was
643 performed ($n = 5$) for VDA[11-12] over 3 weeks in July 2019 and the Gd/Pt ratio was found
644 to vary from 270 to 340. In this WWTP, concentrations of Gd and Pt were also quite constant
645 (varying from 830 to 980 ng L⁻¹ and from 2.6 to 3.2 ng L⁻¹ for Gd and Pt respectively).
646 Additional grab samplings were performed ($n = 5$ from June 25 to July 9, 2019) in the same
647 period in another WWTP in Marquette-lez-Lille, the biggest WWTP in the Hauts-de-France
648 region. In this WWTP, concentrations of Gd and Pt were much variable ranging from 870 to
649 1,670 ng L⁻¹ and from 7.7 to 15.2 ng L⁻¹ respectively. The ratios obtained were thus different
650 from those obtained in VDA[11-12] but remained quite constant over time, varying from 100
651 to 130 over the 3 weeks. Additionally, stability tests for short distances were also conducted
652 for these two WWTPs by sampling one point upstream, the WWTP effluent and four points
653 downstream (the furthest one is at least than 2 kilometres). The differences observed between
654 the direct discharge and the 3 others downstream sampling points were less than 10%
655 showing a conservative behaviour of Pt at short scale. The stability of platinum-based drugs
656 in the natural flow of rivers is not yet well documented in the literature (Curtis et al., 2010;
657 Turner and Mascorda, 2015; Lenz et al., 2007) but it is well known that degradations of
658 anticancer Pt-drugs occur in body and during WWTPs processes (Di Pasqua et al., 2012;

659 Hann et al., 2005). The short-term stability added with the non-conservative behaviour of Pt
660 at longer scale should indicate an adsorption process of Pt on particulate organic matter
661 (Wood et al., 1990; Cobelo-García et al., 2007).

662 Gd/Pt ratios could also be a relevant parameter to determine the sources of a pollution as well
663 as the change of speciation that could occur after the mixing of WWTP discharge in the river
664 flow. The common source of Gd and Pt is really interesting and the fact that Pt can also come
665 from catalytic converters abrasion can be a way to discriminate between WWTPs effluent and
666 rainwater intakes. In this study, Gd and Pt are two elements easily quantifiable by ICP-MS
667 because their interferences are not really concentrated. Here, the ratios were quite constant over
668 time (for each WWTP separately), in dry conditions. Further experiments like high frequency
669 sampling should be performed to see in what extent rainwater falls can modify (i) the ratio in
670 WWTP; (ii) the conservative behaviour of Pt on short scale; and (iii) the ratio in the Marque
671 River. Based on previous studies obtained from WWTPs, the concentrations of Pt are
672 expected to increase, during the first rains due to the intake from soil erosion containing Pt
673 particles coming from automotive catalytic converters (Monteiro et al., 2017; Laschka and
674 Nachtwey, 1997). Such studies have been performed only on WWTPs but assessing the
675 change of platinum behaviour between dry and rainy weather along a riverbed could be of
676 interest for understanding the sources of the pollution by this element.

677

678 **IV. Conclusion**

679 Through statistical analyses and the use of several tracers (mostly EC, Rb, Cl⁻, Gd, As, B, Cr,
680 Cs, Ho, K, Na, Rb, Sn, Sr, Y and to a lesser extent Pt), the large impact of WWTPs onto the
681 Marque River elemental composition has been demonstrated. This conclusion was also
682 confirmed based on flow calculation thanks to the data obtained from the WWTPs owners and
683 the flows recorded by two monitoring stations along the river watercourse. The evolution of

684 various parameters was monitored and PCA analysis showed that the first dimension, related
685 to WWTPs discharges, represented around 40% of the total variability. The PCA treatment
686 also allowed determining which elements are positively or negatively correlated with the
687 presence of WWTPs confirming results already obtained in the literature with the strong
688 correlation between WWTPs discharges and the presence of elements such as Gd and B. Note
689 that to go further on B behaviour, an isotopic study should be undertaken in the future.

690 During this study, some classical tracers were sometimes difficult to validate due to the high
691 input of WWTP discharges upstream of the Marque River (high concentrations/values at the
692 river source for EC, Rb/Sr and Cl^- , no reference value for Gd/Gd^*). Based on the calculation
693 of the contribution of the biggest WWTP on the river (VDA[11-12]) and the results obtained
694 with PCA, we evaluated if some other elements, preferably conservative, could be better
695 tracers than the conventional ones in our system. The calculated contributions found with all
696 the parameters collected were compared with those of the known conservative tracers (*i.e.* Gd,
697 Cl^- and EC). The contribution of the VDA WWTP on the global flow of the Marque River
698 was estimated to be 50%. Numerous elements were found to be reliable for the calculation of
699 the WWTP contribution on short scale (less than 2km). For long scale studies, few elements
700 were found really interesting mainly belonging to the alkali metals group (*i.e.* Rb, Cs, Na and
701 K). Other ratios (such as B/Rb) or parameters (*e.g.* δD) values were also investigated to obtain
702 a better discrimination of WWTPs discharges and natural samples. B/Rb seems more relevant
703 than Sr/Rb ratio due to its constant values for WWTP discharge in comparison with Sr/Rb in
704 this study while further study on δD , including groundwater sampling, should be performed to
705 determine if this indicator can give information on the source of the water entering in WWTP
706 or on potential exchange of the Marque River with groundwater in hyporheic zone.

707 Finally, even if Pt was found to be non-conservative at long scale, a focus on this element has
708 been made. Indeed, this element may allow, in conjunction with the monitoring of Gd, to

709 determine the origin of WWTP effluents because of its dual potential origin (medical field vs.
710 automotive catalytic convertors). The Gd/Pt ratios were calculated and investigated as a new
711 tracer for WWTPs discharge. It was found that although these ratios vary from one plant to
712 another, they appear to remain relatively constant within the same WWTP over time in dry
713 periods. Further investigations have to be performed to assess the influence of rainfalls on the
714 stability of Pt and on the ratios of Gd/Pt. Following Gd/Pt ratios at long scale could also
715 potentially allow to understand adsorption process which can occur as Pt-based drugs are
716 known to be more sensitive to degradation processes than Gd-based contrast agents.

717

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