

1 **GROUNDWATER QUALITY CHANGES IN PERI-URBAN AREAS OF THE WALLOON**

2 **REGION OF BELGIUM**

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11 **0. ABSTRACT**

12 An extensive survey of groundwater quality was performed at the regional scale in peri-urban
13 and industrial contexts of the Walloon Region (Belgium). To this end, 243 sampling locations
14 from 8 areas located in different geological contexts and different peri-urban areas of the
15 region were sampled outside pollution hotspots related to contaminated sites. Each
16 groundwater sample was analyzed for 19 inorganic trace elements, 59 organic micro-
17 pollutants and 8 major and minor elements. Five physico-chemical parameters were
18 measured in the field, at the time of sampling to determine the environmental conditions
19 prevailing in groundwater. Existing groundwater chemical data available outside such peri-
20 urban and industrial areas were also compiled from existing groundwater quality databases
21 for comparison. Most of the organic and inorganic pollutants are detected and their levels of
22 occurrence are described statistically. Cumulative distribution function plots allow comparing
23 the distributions of inorganic trace elements in and outside the urbanized and industrialized
24 areas and among the different prevailing geological contexts. Two indicators are introduced,
25 one quantifying the impact on inorganic trace elements of diffuse pollution in urban and
26 industrial areas, the other reflecting the influence of lithology on concentrations in
27 groundwater. Results show that the composition of groundwater is altered in peri-urban and
28 industrial areas with increased concentrations for several organic pollutants and for most
29 inorganic trace elements. However, the results clearly indicate that for the inorganic trace
30 elements, anthropogenic influence is not limited to increased discharge of pollutants in the
31 urban and industrial areas but also to significant changes in environmental conditions, with
32 more reducing and acidic conditions observed in groundwater. The influence of lithology is
33 also marked in the data set. From a more pragmatic point of view, the data set has been also
34 used to derive upper limits of pollutant background concentrations to be used in decision-
35 making related to the management of contaminated groundwater in urban and industrial
36 environments in the Walloon Region.

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38 Keywords: Groundwater quality, background concentration levels, organic pollutants,
39 inorganic trace elements, diffuse urban and industrial pollution

40 1. INTRODUCTION

41 High population growth and industrial development has increased the demand for freshwater
42 resources during last years and they are expected to become increasingly scarce in the
43 future, partly due to climate change (Aslam et al., 2018). Urban aquifers are more and more
44 considered as a valuable resource for water supply but also for industrial purposes in many
45 countries such as Belgium (SPW-DGO3, 2016), Switzerland (Minnig et al., 2017), Germany (;
46 Hellauer et al. 2018) or Italy (Colombo et al., 2020; Pollicino et al., 2021), among others.
47 Thus, conservation and protection of groundwater are key issues in the management of
48 water resources.

49 Groundwater pollution is a serious issue because in many aquifers, groundwater quality is
50 deteriorated, and thus, identifying the factors of its deterioration is of paramount importance.
51 In particular, it is important to determine if the chemical substances of concern are really
52 associated to exogenous anthropogenic pollution sources or if they have any geogenic origin
53 and to determine the hydrogeochemical conditions that contribute to their occurrence in
54 groundwater. On the one hand, many aquifers are impacted by several anthropogenic
55 activities (Schirmer et al., 2013). In urban and industrial areas, pollution sources are of
56 various types such as: atmospheric deposition, urban runoff, industrial or domestic
57 wastewater discharges, industrial solid or liquid wastes, gas stations, landfill leakage, septic
58 systems and road de-icing salts, among others (Zhang et al., 2004; Vázquez-Suñé et al.,
59 2010). The addition of point sources close to each other, diffuse pollution and multiple source
60 pollution can also induce widespread contamination of groundwater resources (Rivett et al.,
61 1990, Jamin et al. 2012; Sorichetta et al., 2012; Colombo et al., 2020; Pollicino et al., 2021).
62 As a result, a wide array of organic (chlorinated volatile organic compounds (VOCs), non-
63 chlorinated chlorinated VOCs and contaminants of emerging concern, among others), and
64 inorganic pollutants (e.g., heavy metals) may enter aquifers leading to the deterioration of
65 groundwater quality (Navarro and Carbonell, 2007; Rivett et al., 2012; Shepherd et al., 2006;
66 Taylor et al., 2006; Serra-Roig et al., 2016; Pollicino et al., 2021).

67 On the other hand, groundwater quality can also be deteriorated by geogenic inorganic
68 contaminants. In this case, their occurrence in groundwater may be due to geochemical
69 changes in aquifer materials (e.g., high concentrations of the contaminants in the rock matrix
70 dissolving during water-rock interactions) or related to changes towards more reducing
71 conditions in the aquifer that facilitate the mobilization of contaminants in groundwater (Gosh,
72 2017). Uranium, arsenic (As), radon and fluoride were found to be the most hazardous
73 geogenic contaminants in terms of human health impacts (Grützmacher et al., 2013).
74 Geogenic As contamination is a menace in the alluvial aquifers of the Ganges delta (India)
75 and it is believed to be released from As-rich iron oxyhydroxides when dissolved oxygen is
76 depleted from groundwater (Meharg et al., 2006).

77 As a result of both anthropogenic and geogenic factors, the value of the groundwater
78 resource can be completely or partially lost when this freshwater resource is contaminated
79 (Shanahan, 2009) and thereby limits its utility (Howard, 2002). Hence, to define the potential
80 uses of groundwater, it is of paramount importance to assess its quality. For example, higher
81 quality standards are expected if it is intended for drinking water purposes but groundwater
82 also plays other key roles like delivering base flow to surface watercourses or in relation with
83 aquatic and terrestrial groundwater-dependent ecosystems (EC, 2011, 2015).

84 The limit for a given chemical substance is set up by a number of organizations that have
85 formulated guidelines of which the World Health Organization drinking water guidelines
86 (WHO, 2017) or the European Groundwater Directive 2006/118/EC (EC, 2006) which also
87 considers other quality objectives. Thus, the identification of the contaminants in the aquifers
88 is the first step to assess its quality. This step is particularly important in regions where
89 groundwater is the main source of water supply such as the Walloon Region (southern part
90 of Belgium) where groundwater abstraction represents 381.3 million m³ (2014 data) and
91 78.1% is devoted to drinking water purposes (SPW-DGO3, 2016). In rural areas of the
92 Walloon Region, the impacts of diffuse groundwater pollution from agriculture have already
93 been already studied concerning nitrate (Orban et al., 2010), pesticides (Hakoun et al., 2017)

94 and greenhouse gases (Jurado et al., 2018; Nikolenko et al., 2019). However, there is a lack
95 of data on the state of groundwater pollution in urban and industrial areas sites, and
96 particularly in the sub-urban areas that are located around the most urbanized areas.
97 Because of that, the suitability of groundwater for different uses in such transition zones
98 between urban and rural areas remains uncertain.

99 In this context, the general objective of the present research is to assess the groundwater
100 contamination level in urban and industrial contexts for the Walloon region of Belgium at the
101 regional scale. More specifically, the objectives are to identify the most detected
102 contaminants in groundwater, to describe statistically their levels of occurrence, and to
103 discuss about mechanisms that can explain their occurrence in groundwater. The chemical
104 compounds considered are inorganic trace elements and organic pollutants. From a more
105 pragmatic point of view, this data set has been also used to derive an upper limit of
106 background concentration levels to be used in decision-making related to the management of
107 contaminated groundwater in urban and industrial environments. To this end, an extensive
108 survey of groundwater contaminants was undertaken outside pollution hotspots specifically
109 associated with polluted sites. Presented results are based on 243 samples collected in both
110 shallow and deep aquifers from 8 areas located in different geological contexts and different
111 urban and industrial contexts in Belgium and are compared to data collected outside urban
112 and industrial contexts.

113 **2. DESCRIPTION OF THE WALLOON REGION URBAN AND INDUSTRIAL CONTEXTS**

114 Major cities and industrial areas of Wallonia (southern Belgium) are located along a West-
115 East alignment formed by the Haine, Sambre, Meuse and Vesdre rivers (Figure 1). The main
116 industrial cities are Charleroi and Liège, whose urban agglomeration had 291,000 and
117 501,000 inhabitants, respectively, in 2020 (<https://www.citypopulation.de/en/belgium/agglo/>).
118 The extreme South of Belgium, on the border of France and Luxembourg, is also an old
119 industrial area.

120 The Walloon industry developed significantly during the 19th century. It was dominated by
121 metallurgy (steelworks and zinc and lead extraction) and coal (extraction and blast furnaces).
122 Other minor industrial areas included, among others, quarries, glass and textile industry. The
123 decline of these industries was initiated early in the 20th century. Currently, the industry is
124 more diversified and specialized. The main industries always concern metallurgy but also
125 chemical, pharmaceutical, power generation industrial activities (Boveroux et al., 2004). Coal
126 is no longer extracted but many big coal heaps impact the landscape and the old mining
127 galleries are embedded in the upper Carboniferous geological layers.

128 From a geological point of view, three main contexts are distinguished: 1) Sambre, Meuse
129 and Vesdre basins, 2) Haine basin and 3) southern Belgium. In Figure 2, geological units are
130 grouped into main aquifers, per age and lithology. More information on the main
131 hydrogeological contexts of the region can be found in Dassargues & Walraevens (2014)

132 The Sambre, Meuse and Vesdre rivers are located along a major European set of aligned
133 faults. The bedrock is composed of a succession of limestone, sandstone and shale, dated
134 from Devonian to Carboniferous ages, the main one being the Upper-Carboniferous shale
135 and sandstone formation containing coal and pyrite. Floodplains can reach a width of 3.5
136 kilometers. The general groundwater flows occur along the direction of the floodplains, the
137 alluvial aquifers being generally drained by the rivers. Devonian detrital formations and
138 Upper Carboniferous shale and sandstone formations form aquitards. In these contexts,
139 groundwater is located in the upper fringe of the altered rocks and the direction of
140 groundwater flow is mainly governed by topography. Along the Meuse River, old terraces are
141 locally confounded with local deposits of Eocene and Oligocene sands that overlie the
142 bedrock. Sand deposits and old terraces generally contain superficial aquifers (Dassargues
143 et al., 2014; Ruthy et al., 2014).

144 In the valley of the Haine River, to the west, the bedrock is overlain by Meso-Cenozoic
145 formations. Marl and chalk of upper Cretaceous and clays and sands of Paleocene and
146 Eocene form a sedimentary basin, whose thickness can reach 150 meters. Pleistocene and

147 Holocene colluvium and alluvial sediments are in the valley bottoms. Pleistocene wind
148 deposits, consisting of silt, locally cover the top of the slopes. Groundwater flows are directed
149 to the Haine River (Rorive and Goderniaux, 2014).

150 In southern Belgium, the geological structure is typical of the Paris Basin (Triassic to
151 Pliocene ages), consisting of a succession of monoclinical geological layers with south
152 dipping. Sedimentary aquifer and aquiclude layers alternate, consisting of sandstone, marl
153 and limestone. The thickness of each hydrogeological unit exceeds thirty meters.
154 Groundwater flows are directed to the south along the layers inclination, but surface water
155 locally drains groundwater to south-west or to south-east (Debbaut and Bouezmarni, 2014).

156 **3. MATERIALS AND METHODS**

157 **Preliminary analysis of the data set**

158 Existing groundwater analyses available for the whole region, to the exclusion of urban and
159 industrial areas, were compiled from several databases, for comparison with new data
160 collected in the urban and industrial areas. The selection and aggregation criteria for these
161 chemical data were based on the most recent recommendations, particularly the proposals of
162 the European project FP6 « BRIDGE » (Müller, 2006). Values smaller than detection limits
163 were replaced by half the detection limit, as recommended in the BRIDGE project.

164 The dataset contains 70870 records of inorganic trace elements analyzed on 7418 samples
165 that come from 1965 sampling points located in all aquifers of the Region. The 1965
166 available sampling locations were grouped into 1432 sites. A site is here defined as a group
167 of sampling points intercepting the same main aquifer in a same hydrogeological context and
168 located within a distance of 600 meters from each other. A single groundwater composition is
169 attributed to each site: the median value is calculated per element and per site from all the
170 analyses, even when multiple analyses were performed at the same point at different times.

171 **Sampling network and analysis procedure**

172 Eight areas representative of the different urban and industrial contexts of the Walloon region
173 of Belgium were selected (Figure 2), with two areas located in the Haine valley, one in the
174 Sambre valley, two in the Meuse valley, two in the Vesdre valley and one in the South of
175 Belgium.

176 Sampling locations include existing wells (79), piezometers (40) and springs (9), but also
177 new shallow (74) and deep piezometers (41) specifically drilled for the project in areas where
178 existing sampling points were not available. Several criteria were considered for the selection
179 of existing wells, piezometers and springs: (1) every hydrogeological unit was sampled; (2)
180 groundwater samples were collected from the first encountered aquifer, usually at shallow
181 depth; (3) using information and databases on polluted sites in the investigated areas, local
182 pollutions were avoided. The main aquifers sampled in the urban and industrial areas are
183 alluvial gravels (46 sampling locations), sands (27 sampling locations), Cretaceous chalk and
184 marl (27 sampling locations), Jurassic sandstone and shale (26 sampling locations), Upper
185 Carboniferous shale and sandstone (48 sampling locations), Carboniferous and Devonian
186 limestone (23 sampling locations) and Devonian to Cambrian shale and sandstone (46
187 sampling locations).

188 The sampling campaign was performed from June 2010 to August 2011. Each groundwater
189 sample was analyzed for 19 inorganic trace elements (Ag, Al, As, B, Ba, Be, Cd, Co, Cr, Cu,
190 Fe, Hg, Mn, Mo, Ni, Pb, Sb, Se and Zn), 59 organic micro-pollutants (16 polycyclic aromatic
191 hydrocarbons, 8 monocyclic aromatic hydrocarbons, 18 halogenated volatile organic
192 compound, 4 fractions of petroleum hydrocarbons and 13 chlorobenzenes, detailed list in
193 Supplementary Material Nb 1) and 8 major and minor elements (Ca^{2+} , Mg^{2+} , HCO_3^- , NO_3^- ,
194 SO_4^{2-} , Cl^- , K^+ and Na^+). Samples for inorganic trace elements were filtered at 0.45 μm . Five
195 physico-chemical parameters (pH, temperature, electrical conductivity, redox potential and
196 dissolved oxygen) were measured in the field, in a flow-cell, at the time of sampling to
197 determine the environmental conditions prevailing in groundwater.

198 Temperature, pH, redox potential and dissolved oxygen were determined in situ by
199 potentiometry. The electrical conductivity was measured in situ by a conductivity meter.
200 Calcium concentrations and alkalinity were obtained by potentiometric titration in the
201 laboratory. Concentrations of major elements (Mg^{2+} , Na^+ , K^+ , Cl^- , SO_4^{2-} , and NO_3^-) were
202 obtained by capillary electrophoresis. Most inorganic trace elements were analyzed by
203 inductively coupled plasma mass spectrometry (ICP-MS). Mercury concentrations were
204 determined by atomic absorption spectrometry with cold vapor (CV-AAS). Total chromium
205 concentrations were obtained by inductively coupled plasma atomic emission spectroscopy
206 (ICP-AES). Iron and manganese concentrations were obtained by atomic absorption
207 spectrometry. BTEX, styrene and HVOC concentrations were obtained by gas
208 chromatography coupled to mass spectrometry with static headspace (HS-GCMS). Non-
209 halogenated polycyclic aromatic hydrocarbons (PAH) concentrations were determined by
210 high-performance liquid chromatography (HPLC). Petroleum hydrocarbons were analyzed by
211 gas chromatography coupled with a flame ionization detector (GC-FID). Chlorobenzene
212 concentrations were obtained by gas chromatography coupled to mass spectrometry with
213 static headspace (HS-GCMS) or coupled to an electron-capture detector (GC-ECD)
214 according to the compound.

215 **Statistical description and graphical representation of the data**

216 Data are first described by main statistical values: mean, median and different percentiles.
217 Distribution function plots are one of the most informative graphical displays of geochemical
218 distributions (Reimann et al., 2005a, 2005b). The shape of the curve may reflect the
219 presence of various geochemical processes influencing the concentrations in water, such as
220 redox reactions, adsorption - desorption reactions and mineral solubility – precipitation
221 (Shand et al., 2007). Inflections or break points indicate the presence of multiple populations
222 and outliers (Sinclair, 1974). Cumulative distribution functions are used here to plot the
223 distribution because they have the advantage of not compressing the central part of the data
224 range. The y-axis shows the cumulative probability of the distribution function between 0 and

225 1. The x-axis shows values of concentration on a log-scale, because of right skewed
226 distributions.

227 Cumulative distribution function plots (CDFPs) allow comparing the distributions of inorganic
228 trace elements in urban and industrial areas (UIS) to those obtained in the entire Wallonia
229 outside these areas (W). Because it is difficult to objectively compare different pollutants with
230 different natural background and concentration levels in groundwater, we suggest to
231 compute an indicator reflecting as much as possible the impact of inorganic trace elements
232 of diffuse pollution in urban and industrial areas (Indicator of the Impact of Urban and
233 industrial areas – I²U). The distribution curves are sometimes disturbed by the detection
234 limits achieved. Therefore, the indicator is based on the comparison of medians (sometimes
235 influenced by the detection limits) and on the comparison of 90th percentiles (not influenced
236 by the detection limits for the elements considered). The indicator used to classify the
237 elements from most affected to least affected is calculated according to the Equation (1). The
238 greater the coefficient, the greater the impact of urban and industrial contamination on
239 inorganic trace elements concentrations. CDFPs are also used to plot the distribution of
240 major elements, of physico-chemical parameters and to compare the distribution of inorganic
241 trace elements in the different lithologies, in urban and industrial contexts. An indicator
242 equivalent to I²U is calculated to quantify the influence of lithology on concentrations in
243 groundwater. This indicator, named I²L (Indicator of the Influence of Lithology), is calculated
244 according to the Equation (2). The indicator is based on the comparison of medians
245 calculated by lithology and on the comparison of 90th percentiles calculated by lithology.

$$246 \quad I^2U = \left[\left(\frac{med_{UIS} - med_W}{med_{UIS}} \right) + \left(\frac{P90_{UIS} - P90_W}{P90_{UIS}} \right) \right] / 2 \quad (1)$$

$$247 \quad I^2L = \left[\left(\frac{med_{max} - med_{min}}{med_{max}} \right) + \left(\frac{P90_{max} - P90_{min}}{P90_{max}} \right) \right] / 2 \quad (2)$$

248 Moreover, correlation coefficients were calculated for each pair of inorganic trace elements.
249 Correlation coefficients were also calculated between inorganic trace elements and major
250 ions or physico-chemical parameters measured during sampling operations. Correlation

251 coefficients are determined to highlight chemical compounds with a similar behavior and the
252 physico-chemical parameters affecting element mobility. The Kendall-tau method (Kendall
253 1938) is used because data distributions of most parameters are skewed. Correlations are
254 considered as non-significant when the p-value is greater than 0.001.

255 **Determination of background concentrations for inorganic trace elements per** 256 **main aquifer**

257 Background concentrations have been determined in urban and industrial areas, taking into
258 consideration the hydrogeological context. The 90th percentile of the concentration
259 distribution is selected as the background value, as advised by European guidelines (Müller,
260 2006).

261 **4. RESULTS AND DISCUSSION**

262 **3.1 Hydrochemical characterization of the investigated areas**

263 The general environmental conditions prevailing in groundwater can be described using the
264 physico-chemical parameters measured in the field (Figure 3). In urban and industrial areas,
265 pH values are symmetrically distributed and close to neutrality (median: 7.02). The median of
266 electrical conductivity values is 761 $\mu\text{S}/\text{cm}$ (at 25 °C). Half of the values range between
267 519 $\mu\text{S}/\text{cm}$ (1st quartile) and 1032 $\mu\text{S}/\text{cm}$ (3rd quartile). Measured redox potentials range
268 between -128 mV (highly reducing conditions) and 585 mV (strongly oxidizing conditions).
269 Half of the values are between 237 mV (1st quartile) and 398 mV (3rd quartile). Half of the
270 dissolved oxygen concentrations are between 0.40 mg/L (1st quartile) and 5.72 mg/L (3rd
271 quartile). Water temperature is generally around 12 °C, the usual temperature of
272 groundwater in Belgium. The environmental conditions are more acidic and more reductive in
273 urban and industrial areas than in natural areas and the electrical conductivity is higher in
274 urban and industrial areas.

275 As expected in the Piper diagram (Piper, 1944), the dominant cationic form is calcium and
276 the dominant anionic form is bicarbonate (Supplementary Material Nb 2). However, several
277 groundwater samples show significant proportions of sulfate. Few samples also show large
278 proportions of Cl^- or NO_3^- , indicative of anthropogenic influence on groundwater composition.

279 Cumulative distribution function plots (CDFPs) are plotted for major elements to show the
280 range of concentrations and to compare the distributions between the different chemical
281 compounds (Figure 3). The concentrations in major elements are generally higher in urban
282 and industrial areas (blue line) than in natural areas (dashed green line), particularly for
283 sulfate, sodium and potassium. CDFPs for sodium, potassium, chloride and sulfate show a
284 large range of concentrations, over two orders of magnitude. Impact of pollution on their
285 concentrations is evident (Shand et al., 2007). CDFPs for nitrate shows a strong negative
286 skew, particularly in urban and industrial areas. This is probably the consequence of
287 denitrification related to more reducing subsurface environments. CDFPs for calcium,
288 magnesium and bicarbonate also show a slight negative skew. In these cases, the low
289 concentrations can be associated with lower carbonate contents of the rock, short residence
290 time or CO_2 degassing in the shallow part of the aquifer (Shand et al., 2007).

291 **4.2 Occurrence of contaminants affecting groundwater in urban and** 292 **industrial areas**

293 This section summarizes the occurrence of organic and inorganic contaminants in the
294 groundwater of selected urban and industrial sections of the Walloon Region. Concentrations
295 of these compounds are compared with the regulations for drinking water set by WHO
296 regulation (WHO, 2017).

297 ***Concentrations of organic contaminants***

298 Organic contaminants have been rarely detected in the investigated areas and CDFPs were
299 meaningless for these compounds. As an alternative, Figure 4 shows the percentages of
300 detection of the most often detected organic compounds. Supplementary Material Nb 1

301 provides a list of all the organic compounds analyzed and the respective percentages of
302 detection. The concentrations at which organic contaminants were detected are below their
303 solubility in groundwater. Naphthalene and phenanthrene are the most often detected PAHs
304 in the dataset with 90th percentile of 0.1 µg/l and 0.03 µg/l, respectively. Because of their
305 molecular properties, they are more soluble and less adsorbed than other PAHs.
306 Surprisingly, the heavier fraction of petroleum hydrocarbons is observed more frequently
307 than the lighter fraction in the data set. The explanation is most probably related to the fact
308 that lighter compounds are more bioavailable and readily degraded than heavier compounds.
309 Toluene is the most found monocyclic aromatic halogenated hydrocarbons (MAHs) at 90th
310 percentile of 0.61 µg/l. Finally, dichloromethane is the most often detected halogenated
311 volatile organic compound (HVOC) at 90th percentile of 0.26 µg/l.

312 When considering the 90th percentile of concentrations of these organic compounds, none of
313 them exceeded the WHO drinking water guidelines (WHO, 2017).

314 ***Concentrations of inorganic trace elements***

315 Figure 5 shows the percentages of detection for inorganic trace elements. The most detected
316 elements are iron, barium, arsenic, manganese and boron (more than 90% of detection rate)
317 at median concentrations of 62, 40, 1.20, 48 and 56 µg/L, respectively. Chromium, copper,
318 selenium, aluminum, nickel and zinc are often detected (more than 60% of detection rate) at
319 median concentration lower than 12 µg/L. Antimony, lead, cobalt, cadmium and molybdenum
320 show values below the detection limit for more than half of the analyses (respectively less
321 than 40%, 39%, 38%, 36% and 33% of detection rate). Beryllium and mercury are rarely
322 detected (less than 4% of detection rate). Silver is never detected. Consequently, beryllium,
323 mercury and silver will not be considered further in the descriptions and interpretations.
324 Among these metals, only the 75th and 90th percentile of concentrations for iron and
325 manganese exceed the threshold values considered in Wallonia for the implementation of
326 the EU groundwater directive or the limits established by the WHO for drinking water
327 (Supplementary Material Nb 1).

328 Figure 6 shows the CDFPs for the studied inorganic trace elements in the industrial and
329 urban areas (blue line) compared to data outside these areas (dashed green line). Despite
330 the large differences in the detection range, the different inorganic trace elements show very
331 contrasted ranges of concentrations, with narrow distributions for elements such as arsenic,
332 boron, chromium, selenium or nickel (concentrations ranging over less than 2 orders of
333 magnitude) and large distributions for iron, barium, manganese, aluminum, zinc or antimony
334 (concentrations ranging over more than 3 orders of magnitude). The main statistical values
335 (mean, median, 25th, 75th and 90th percentile) can be deduced from these graphs and are
336 compiled in Supplementary Material Nb 3.

337 Compared to the rest of the Walloon region, urban and industrial areas show strongly higher
338 concentrations for manganese, arsenic, iron, boron and chromium ($I^2U = 0.90$ to 0.53).
339 Nickel, aluminum, barium and selenium concentrations show slightly higher concentrations in
340 urban and industrial areas ($I^2U = 0.28$ to 0.10). Copper and zinc show moderately lower
341 concentrations in urban and industrial areas ($I^2U = -0.5$ to -0.6). For antimony, lead, cobalt,
342 cadmium and molybdenum, more than half of the values in urban and industrial areas are
343 below the detection limit and the I^2U indicator is not calculated. For these elements, the
344 comparison can be based on the 90th percentile. This indicates that cadmium, molybdenum
345 and antimony show similar concentrations within and outside the urban and industrial areas.
346 Lead concentrations appear lower in the urban and industrial areas while cobalt
347 concentrations are higher.

348
349 Figure 7 allows comparing the CDFPs drawn per main aquifer for the studied inorganic trace
350 elements. Most elements show contrasted concentrations depending on lithology. This is
351 particularly the case for selenium ($I^2L = 0.98$), but also for aluminum and copper ($I^2L = 0.94$
352 and 0.90). Other elements show more similar concentration distributions regardless of the
353 geological context. This is particularly the case for arsenic ($I^2L = 0.44$).

354 In addition, results obtained in the investigated urban and industrial areas were used to
355 calculate background concentrations per inorganic trace elements and per main aquifer
356 (Table 1) based on 90th percentile.

357 **3.3 Discussion on factors controlling the occurrence of inorganic trace** 358 **elements in groundwater**

359 Inorganic trace elements are natural constituents of soil, rocks and groundwater. In addition,
360 in urban and industrial areas, the amount of emitted pollutants is potentially high. This is
361 especially true for inorganic trace elements in areas subject for many years to metallurgy and
362 exploitation of metals deposits. Nevertheless, the mobility and dissolution of such elements
363 remains dependent on environmental conditions such as redox conditions and pH.
364 Therefore, the presence of inorganic trace elements in groundwater can be influenced by 3
365 factors: (F1) their emissions in the environment caused by industrial or urban activities, (F2)
366 the geological context and (F3) environmental conditions prevailing in groundwater
367 (especially pH and Eh) that are dependent on hydrogeochemical conditions in the
368 environment, but can potentially be affected by urban and industrial activities. These factors
369 may occur simultaneously and explain the occurrence of inorganic trace elements in
370 groundwater.

371 The potential influence of anthropogenic emissions (F1) can be examined first by comparing
372 concentrations within and outside urban and industrial areas (Figure 6). The influence of
373 geology (F2) can be examined by comparing concentration distributions between different
374 geological contexts (Figure 7). And finally, the influence of environmental conditions
375 prevailing in groundwater (F3) can be examined based on correlation coefficients between
376 chemical compounds (Table 2).

377 Manganese, arsenic and iron are the elements for which the effect of urban and industrial
378 areas on concentrations is most pronounced (F1). These elements are well correlated. They
379 are highly negatively correlated with the oxidation-reduction potential Eh and dissolved

380 oxygen content (O_{2diss}). In addition, manganese is inversely correlated with pH, with the
381 highest concentrations being found where the conditions are most acidic. Consequently, the
382 environmental conditions (F3) play a decisive role in the presence of these metals in
383 dissolved form, the highest concentrations being found in the presence of reducing or even
384 acidic conditions. Indeed, in oxidizing conditions, iron and manganese form complexes with
385 oxides and hydroxides and with organic matter, and precipitate. Arsenic is then adsorbed or
386 co-precipitated with iron or manganese oxides and oxi-hydroxides (Dzomback and Morel,
387 1990). Correlation between arsenic and sulfate also suggests that arsenic originates from the
388 oxidation of sulfide minerals (e.g. pyrite and arsenopyrite) by oxygen or nitrate. As has
389 already been shown in other contexts (e.g. Pauwels et al. 2010; Lazareva et al. 2015), the
390 presence of arsenic in solution is linked to a succession of several processes: oxidation of
391 sulfide minerals, adsorption on manganese and iron oxy-hydroxides subsequently dissolved
392 in a more reducing environment. In the data set, arsenic concentrations are similar
393 regardless of lithology (F2), arsenic having the lowest I²L value of all inorganic trace
394 elements.

395 The effect of urban and industrial areas is also marked on boron levels (F1), probably caused
396 by high boron concentrations in urban effluents, boron being used as a bleaching agent
397 (Barth, 1998). Boron concentrations are also significantly correlated with the electrical
398 conductivity measured in-situ and with the concentrations of most major elements. These
399 correlations, coupled with a strong variation in concentrations according to the lithology,
400 indicate that boron must also have a geogenic origin (F2).

401 Zinc, copper and lead are significantly correlated. Contrarily to most of the other inorganic
402 trace elements, although copper, lead and zinc are generally emitted in greater quantities in
403 industrial contexts, they show lower concentrations in urban and industrial areas than outside
404 (F1). Copper shows significant correlation with the redox potential and the three elements
405 are positively correlated with nitrate (F3). Sulfide oxidation coupled with nitrate reduction is
406 probably one of the main processes responsible for high concentrations of these elements.

407 The link between high nitrate concentrations and the presence of zinc has already been
408 observed (Pauwels et al., 2010). The concentrations in the different lithologies are very
409 different for copper, lead and zinc (F2).

410 Nickel, cobalt and aluminum are well correlated with the inverse of pH. Occurrence of slightly
411 more acidic conditions appears to be the main factor favoring higher concentrations for these
412 inorganic trace elements (F3). Nickel and cobalt are easily incorporated into or sorbed on Mn
413 and Fe oxides and oxi-hydroxides and their presence in dissolved form in groundwater is
414 partly related to the dissolution of these oxyhydroxides (Dzomback and Morel, 1990).
415 Moreover, aluminum is amphoteric, soluble under acidic conditions ($\text{pH} < 5$) in the form of
416 Al(III) , but also in very alkaline conditions ($\text{pH} > 8.5$ rarely encountered in groundwater)
417 (Hem, 1991). In the dataset, aluminum and nickel show high indicators (I^2L) of the influence
418 of lithology on concentrations in groundwater (F2).

419 Selenium shows very contrasted concentrations depending on lithology (F2), with a
420 significant correlation with in-situ electrical conductivity and with the concentrations of most
421 major elements, mainly nitrate. These correlations, coupled with the large variation in
422 concentrations per lithology, indicate that selenium has a geogenic origin. The strong
423 correlation of selenium with nitrate and, to a lesser extent, with sulfate suggests that
424 selenium is mainly dissolved in relation with the sulfide oxidation coupled to autotroph nitrate
425 reduction (F3). The occurrence in groundwater of selenium under slightly reducing
426 conditions, as well as the role of nitrate on selenium oxidation and dissolution have been
427 reported already in other contexts (Bailey et al., 2012; Cary et al., 2014; Mast et al., 2014;
428 Wright, 1999).

429 The effect of diffuse urban and industrial contamination on barium (F1) levels is not
430 significant and barium does not seem sensitive to environmental conditions (F3). The
431 geological context only has an impact on barium concentrations (F2).

432 The effect of urban and industrial areas is also marked on (total) chromium levels (F1),
433 probably caused by dissolution of Mn and Fe oxy-hydroxides containing co-precipitated

434 chromium. Chromium concentrations are also very significantly different according to
435 geological contexts (F2). However, no correlation is evident between chromium and other
436 parameters.

437 **5. CONCLUSIONS AND PERSPECTIVES**

438 The composition of groundwater is altered in urban and industrial areas with increased levels
439 of most organic contaminants and inorganic trace elements. Some organic contaminants are
440 often detected in urban and industrial areas. The most frequently detected organic
441 compounds are naphthalene, toluene, phenanthrene, the heavier fraction (21-35) of
442 petroleum hydrocarbons, fluoranthene, chrysene, dichloromethane, pyrene, and fluorene.

443 Anthropogenic influence is not limited to inputs of inorganic pollutants. It also causes
444 changes in environmental conditions prevailing in groundwater with, in general, significantly
445 more reducing and slightly acidic conditions. This results in changes in the precipitation -
446 dissolution of mineral phases (such as iron and manganese oxi-hydroxides or sulfide
447 minerals) and to sorption – desorption and immobilization - mobilization of inorganic
448 pollutants in groundwater. This seems to be the main factor responsible for high
449 concentrations of manganese, arsenic and iron (mainly associated with more reducing
450 conditions), and of nickel, aluminum and cobalt (mainly associated with slightly more acidic
451 conditions). In contrast, copper, lead and zinc show lower concentrations in urban and
452 industrial areas because the redox conditions are more reducing in these areas. Copper,
453 lead and zinc are indeed more often observed in groundwater in slightly reducing (anaerobic)
454 redox conditions, in association with the oxidation of sulfide and coupled to the reduction of
455 nitrate. Selenium is also more often observed in groundwater under the same environmental
456 conditions. An indicator, I²U, allow quantifying the impact on organic trace elements of diffuse
457 pollution in urban and industrial areas. The influence of lithology is also marked in the data
458 set. Most elements have contrasted concentrations depending on lithology, particularly
459 selenium and aluminum, but not arsenic which is present in equivalent concentrations

460 whatever the lithology. Another indicator, I²L, allow quantifying the influence of lithology on
461 concentrations in groundwater.

462 As a general conclusion, the results show that, regardless of any additional intake of
463 inorganic pollutants related to industrial and urban activities, environmental conditions
464 prevailing in groundwater have a determinant effect on the occurrence at higher (or lower)
465 concentrations of many inorganic compounds in groundwater. However, such changes in
466 environmental conditions may be the indirect consequence of the industrial and urban
467 activities which are more prone to contaminate groundwater with organic compounds which
468 biodegradation contributes to modifications in Eh and pH. Geological contexts and lithologies
469 may also partially influence environmental conditions prevailing in groundwater. Therefore,
470 the influence of environmental conditions is fundamental and the influence of the additional
471 anthropogenic inputs is less pronounced.

472 Finally, background concentrations calculated per inorganic trace elements and per main
473 aquifer, in the urban and industrial areas, allow considering the “ambient background” in site
474 remediation decision procedures. In general, remediation objectives are established from
475 threshold concentrations based on health and ecotoxicological standards and associated
476 risks. In areas where regional background concentrations exceed those thresholds, there is
477 no evidence that soil or groundwater degradation is the responsibility of the site owner and
478 remediation objectives can be adapted to this regional context. Following this study, decision
479 makers have useful data for determining remediation objectives adapted to the current
480 context.

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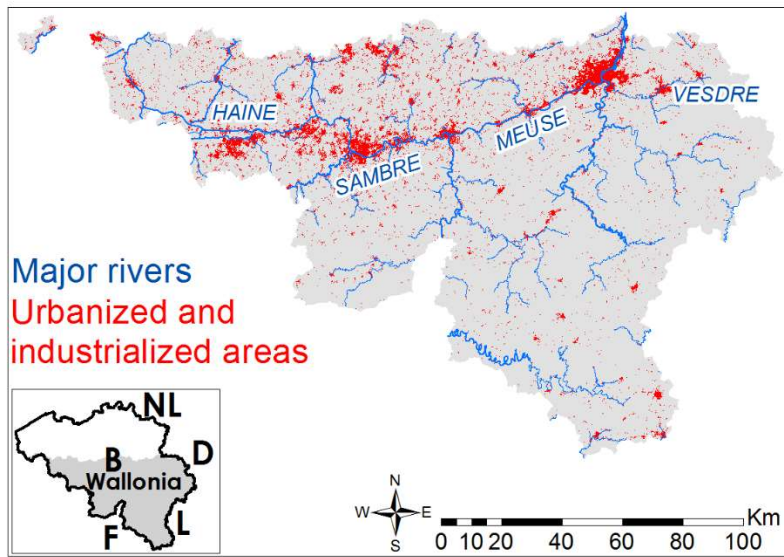
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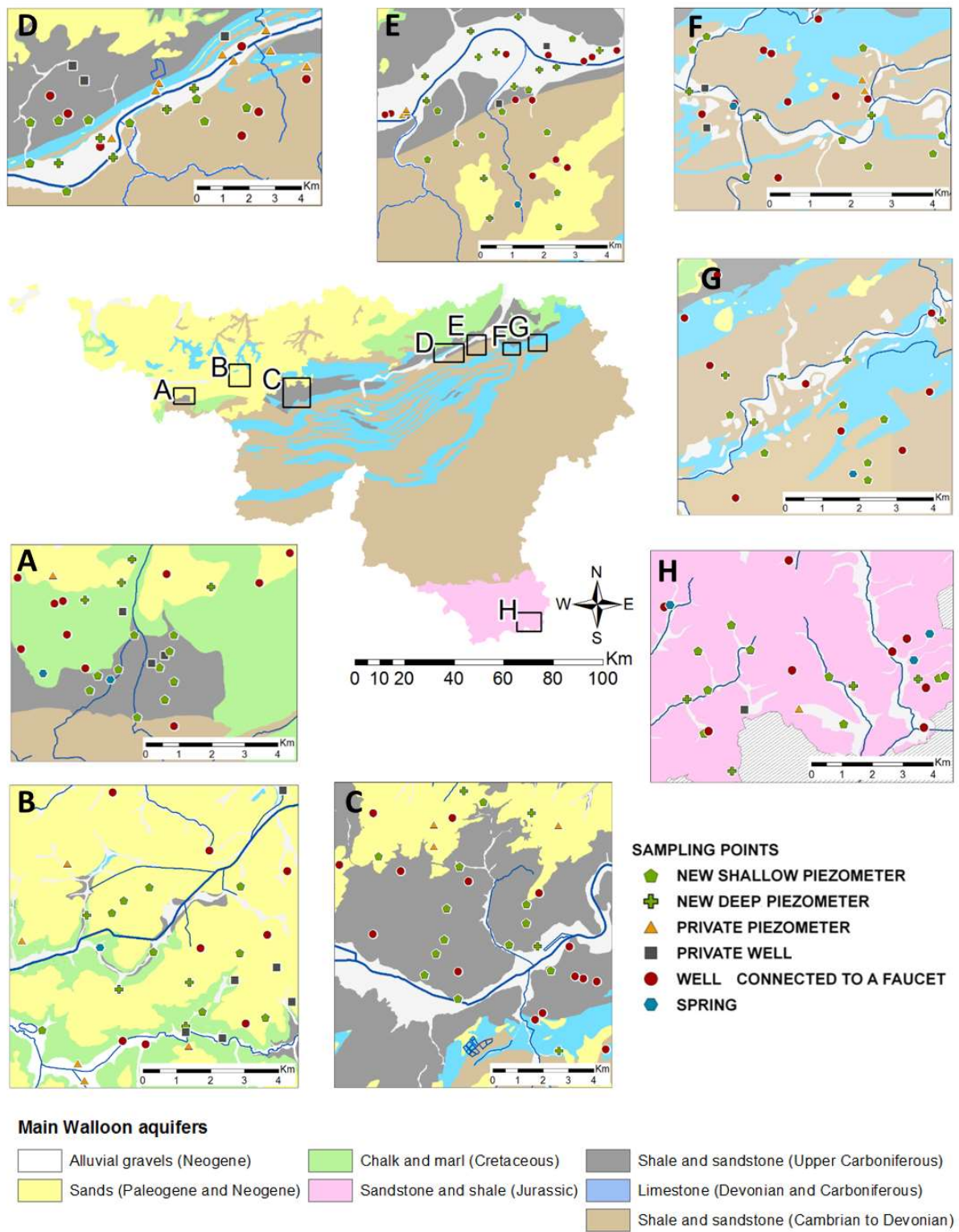
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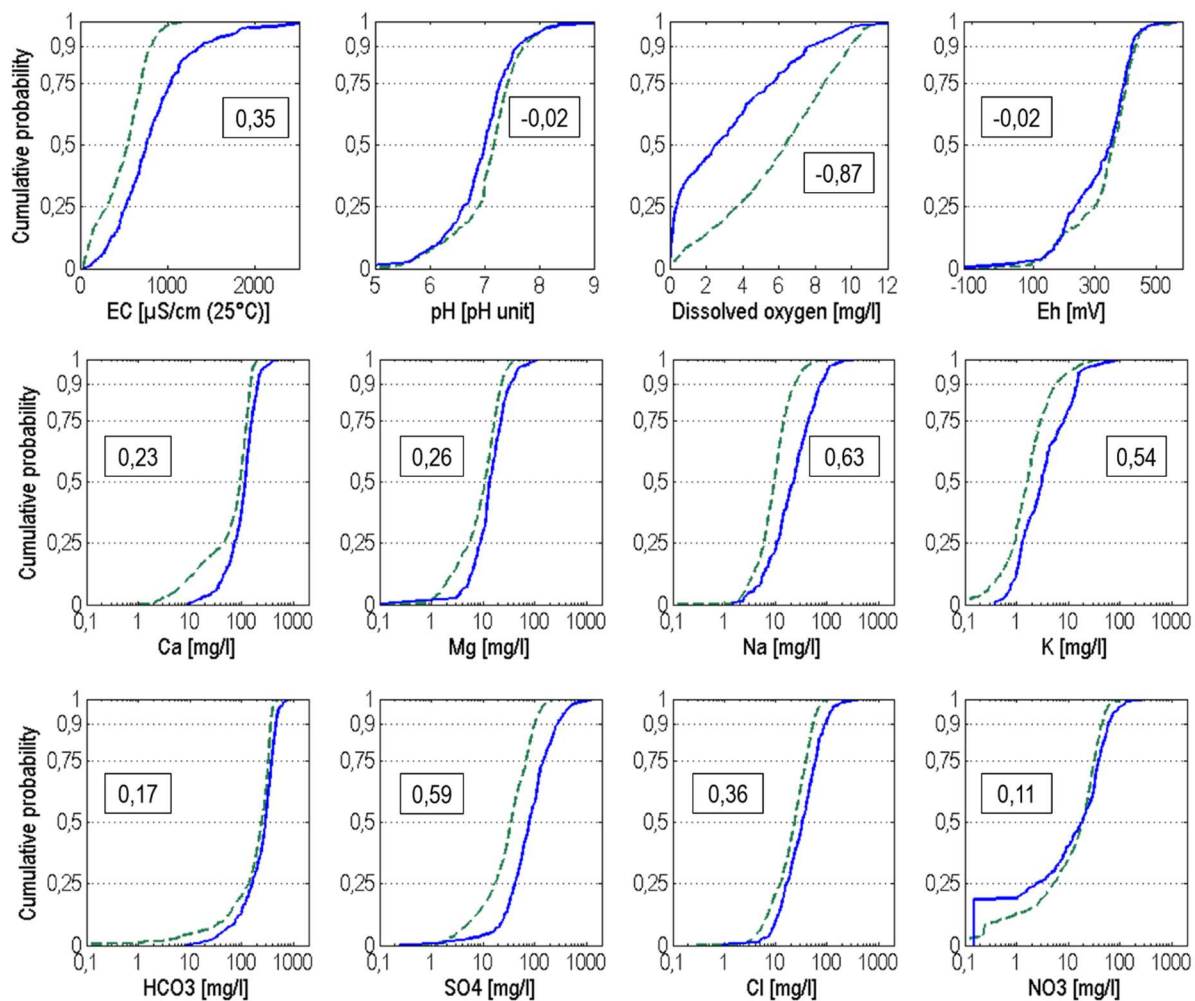
650 **Figure 1 : Major rivers and urban and industrial areas of Wallonia (southern Belgium) (B: Belgium, F:**

651 **France, L: Luxembourg, NL: Netherlands, D: Germany) (Modified from SPW - DGO3 - DGARNE 2015b)**



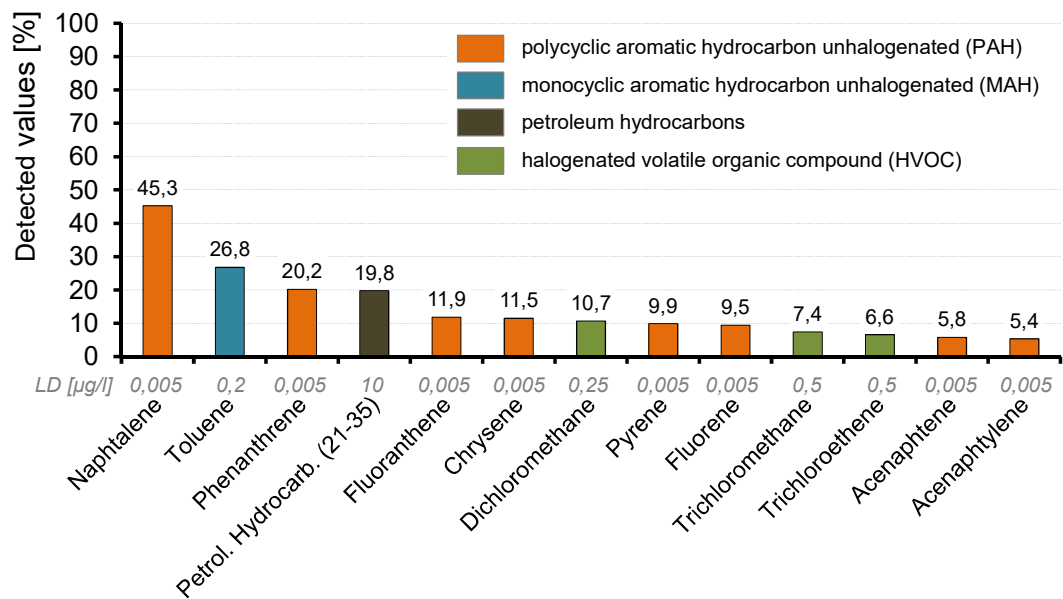
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653 **Figure 2 : Main Walloon aquifers, zoom on the 8 areas (A-G) of investigation in urban and industrial**
 654 **context and sampling points types and location (from SPW - DGO3 - DGARNE 2015a; SPW - DGO3 2014,**
 655 **modified).**



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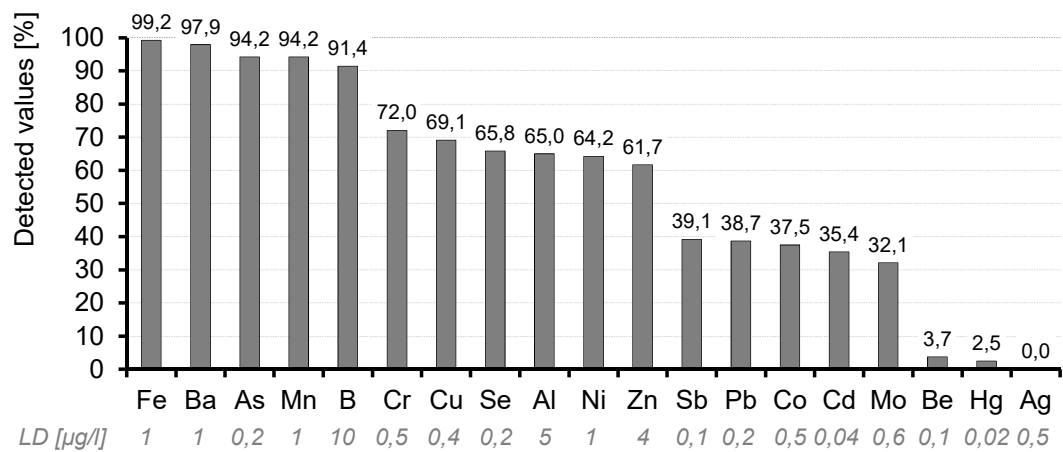
657 **Figure 3 : Comparison of the distribution (CDFPs) of physico-chemical parameters and major inorganic**
 658 **elements in the urban and the industrial areas (blue line) and in the entire Wallonia outside these areas**
 659 **(dashed green line). The calculated indicator of impact (I²U) is noted in the box.**



660

661 **Figure 4 : Frequency of detection (%) and limits of detection (LD) for the organic compounds. Only**
 662 **compounds detected in at least in 5% of the collected groundwater samples are represented.**

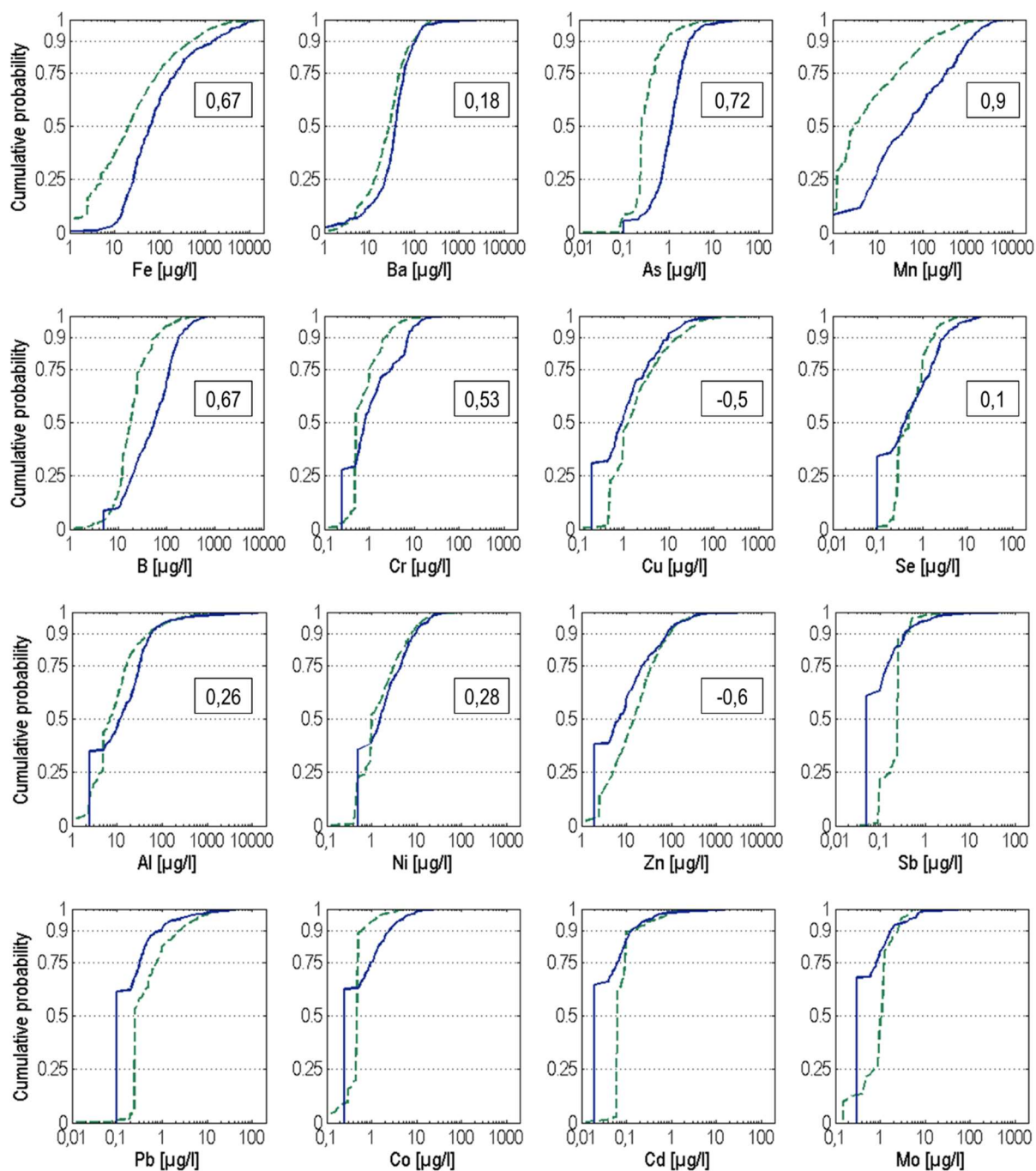
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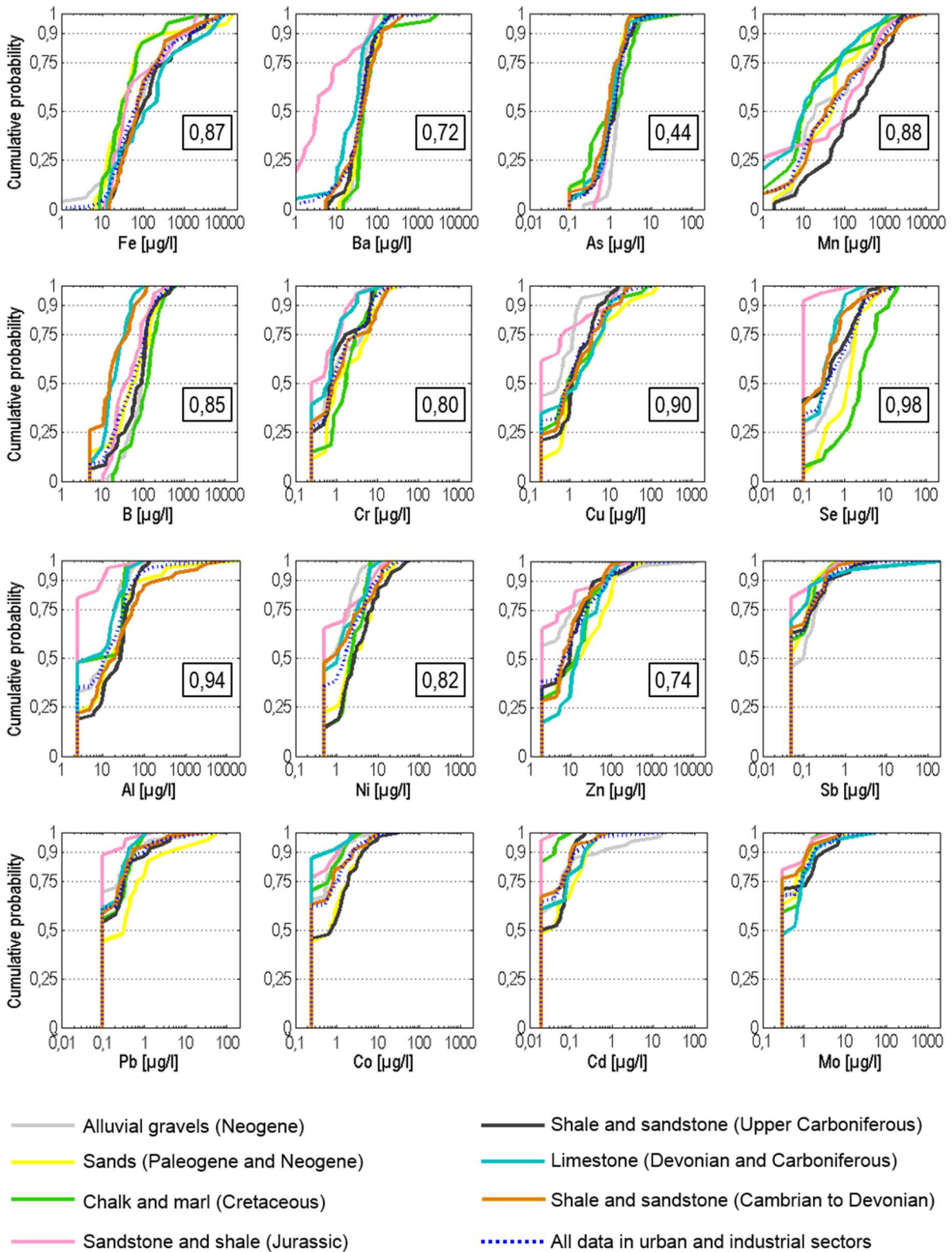
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Figure 5 : Frequency of detection (%) and limits of detection (LD) for inorganic trace elements.



666

667 **Figure 6: Comparison of the distribution (CDFPs) of inorganic trace elements in the urban and industrial**
 668 **areas (blue line) and in the entire Wallonia outside these areas (dashed green line). The calculated**
 669 **indicator of impact (I²U) is indicated in the box (calculation of I²U for Sb, Pb, Co, Cd and Mo was not**
 670 **possible because of their low detection level). Inorganic elements are ranked from largest to smallest**
 671 **percentage of detection in urban and industrial areas.**



672

673 **Figure 7 : Comparison of the distribution (CDFPs) of inorganic trace elements in the urban and industrial**
 674 **areas per main aquifer and for all data. The calculated indicator of the influence of lithology on**
 675 **concentrations in groundwater (I^2L) is indicated in the box (calculation of I^2L for Sb, Pb, Co, Cd and Mo**

676 was not possible because of their low detection level). Inorganic elements are ranked from largest to
677 smallest percentage of detection in urban and industrial areas.

678

679

680

	<i>Fe</i>	<i>Ba</i>	<i>As</i>	<i>Mn</i>	<i>B</i>	<i>Cr</i>	<i>Cu</i>	<i>Se</i>	<i>Al</i>	<i>Ni</i>	<i>Zn</i>	<i>Sb</i>	<i>Pb</i>	<i>Co</i>	<i>Cd</i>	<i>Mo</i>
Alluvial gravels (Neogene)	1124	66,0	2,57	807	185	6,80	1,70	2,50	37,5	3,25	70,4	0,43	0,43	1,25	0,09	1,68
Sands (Paleogene and Neogene)	112	118	2,30	460	262	11,08	25,6	4,16	53,5	15,2	114	0,20	1,07	4,32	0,25	1,68
Chalk and marl (Cretaceous)	313	111	3,75	591	290	7,32	10,0	12,4	34,0	5,62	70,2	0,24	0,59	1,48	0,04	1,32
Sandstone and shale (Jurassic)	1306	67,5	2,95	875	180	2,20	9,70	0,20	10,0	8,70	72,5	0,26	0,21	1,15	0,04	1,25
Shale and sandstone (Upper Carboniferous)	1774	91,4	2,88	1710	206	7,20	5,75	2,86	64,3	19,0	47,6	0,35	0,46	3,90	0,12	3,25
Limestone (Devonian and Carboniferous)	4325	85,6	2,40	744	50,8	3,20	9,68	1,07	34,8	6,00	80,0	0,28	0,41	0,79	0,29	1,60
Shale and sandstone (Cambrian to Devonian)	886	118	2,40	1670	66,5	12,0	13,9	1,75	87,8	11,5	61,5	0,35	0,47	2,50	0,11	1,30

681

682 **Table 1 : Background concentration (µg/l) for each inorganic trace element, calculated from new data in**
683 **the urban and industrial areas, per main aquifer. Values in bold green correspond to the detection limit.**

Fe	Fe														
Ba		Ba													
As	0,24		As												
Mn	0,33		0,29	Mn											
B			0,27		B										
Cr						Cr									
Cu						0,16	Cu								
Se	-0,17	0,16		-0,17	0,21	0,16		Se							
Al		0,17							Al						
Ni				0,22			0,18			Ni					
Zn							0,45			0,19	Zn				
Sb			0,31		0,16			0,24		0,17		Sb			
Pb			-0,17			0,18	0,44						Pb		
Co	0,27	0,17							0,27	0,44		0,18		Co	
Cd							0,21			0,34	0,36	0,21		0,21	Cd
Mo			0,29												Mo
O ₂ diss	-0,25		-0,20	-0,40										-0,21	
EC			0,29		0,37			0,21							
Eh	-0,26		-0,19	-0,27			0,19								
pH				-0,19					-0,23	-0,24				-0,20	-0,17
Ca			0,31		0,31			0,21							
Mg			0,19		0,24		-0,16								
Na		0,21	0,15		0,39			0,30	0,17	0,15				0,16	
K		0,16	0,24		0,45			0,24		0,16	0,16	0,27			0,28
NH ₄															
Cl					0,23			0,16							
SO ₄			0,30	0,16				0,26		0,18				0,18	
NO ₃	-0,34			-0,36			0,23	0,45		0,16		0,18	-0,16		
HCO ₃			0,17		0,32										-0,20
SiO ₂			0,19						0,17						

684

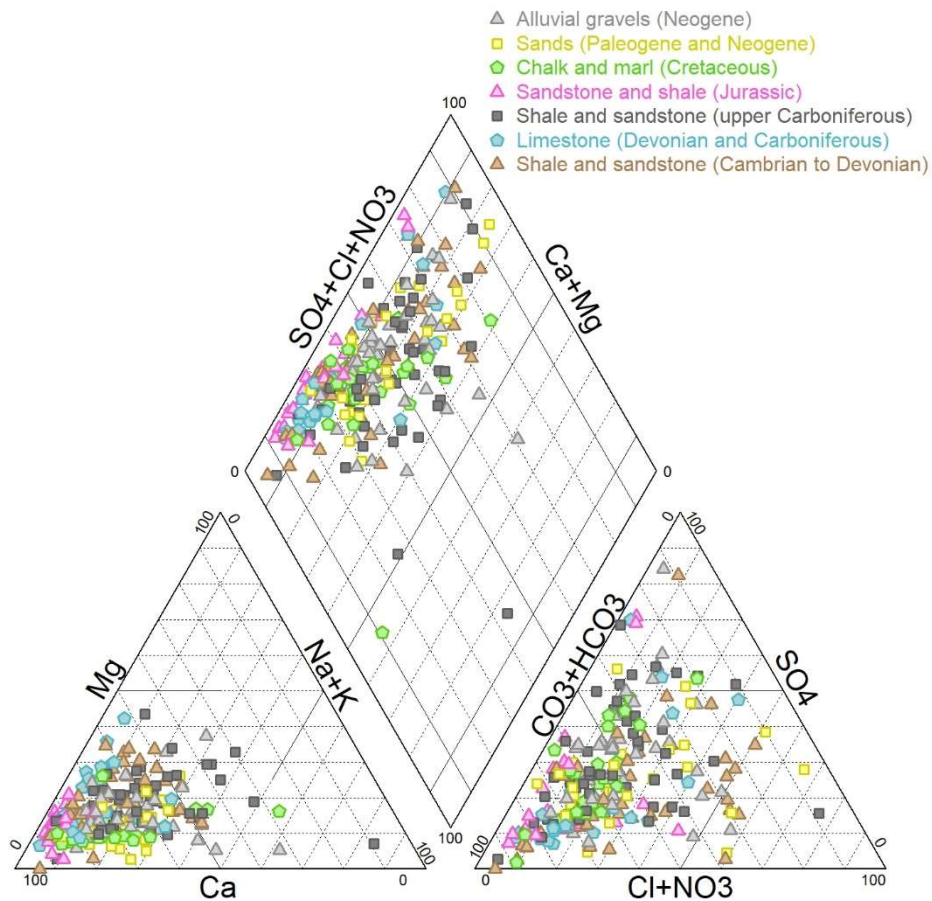
685 **Table 2 : Correlation coefficients for the pairs of inorganic trace elements. Correlation coefficients for**
686 **inorganic trace elements with physico-chemical parameters and with major elements. Only significant**
687 **correlations are displayed (p-value < 0.001). The higher the correlation, the darker the frame. EC =**
688 **electrical conductivity. Inorganic elements are ranked from largest to smallest percentage of detected**
689 **values.**

9. SUPPLEMENTARY MATERIAL

Organic compound	LD (µg/l)	> LD (%)	Organic compound	LD (µg/l)	> LD (%)
monocyclic aromatic hydrocarbon unhalogenated			polycyclic aromatic hydrocarbon unhalogenated		
Toluene	0,2	26,8	Naphtalene	0,005	45,3
o- xylene (or 1,2-dimethylbenzene)	0,08	3,3	Phenanthrene	0,005	20,2
Xylenes	0,23	3,3	Fluoranthene	0,005	11,9
Benzene	0,2	2,9	Chrysene	0,005	11,5
Styrene	0,2	2,9	Pyrene	0,005	9,9
Ethylbenzene	0,2	2,5	Fluorene	0,005	9,5
m- + p- xylenes	0,2	0,8	Acenaphtene	0,005	5,8
Isopropylbenzene (cumene)	0,25	0,0	Acenaphtylene	0,005	5,4
halogenated volatile organic compound			Benzo(b)fluoranthene	0,005	4,5
Dichloromethane	0,25	10,7	Benzo(a)anthracene	0,005	3,3
Trichloromethane	0,5	7,4	Benzo(a)pyrene	0,005	3,3
Trichloroethene (TCE)	0,5	6,6	Benzo(ghi)perylene	0,005	3,3
Tetrachloroethene (PCE)	0,5	4,5	Benzo(k)fluoranthene	0,005	2,9
1,2 dichloroethene (cis-)	0,5	4,1	Indeno(1,2,3-cd)pyrene	0,005	2,9
1,1,1-trichloroethane	0,5	3,7	Anthracene	0,005	2,5
1,2-dichloroethene (cis + trans)	0,5	3,3	Dibenz(a,h)anthracene	0,005	0,4
1,1-dichloroethane	0,5	2,1	chlorobenzenes		
1,1-dichloroethene	0,5	1,2	1,4-Dichlorobenzene (= p-dichlorobenzene)	0,5	0,8
Tetrachloromethane	0,5	0,4	1,2-Dichlorobenzene (= o-dichlorobenzene)	0,5	0,4
Chloroethane	0,5	0,4	1,3-Dichlorobenzene (= m-dichlorobenzene)	0,5	0,4
Chloroethene	0,25	0,4	1,2,3-Trichlorobenzene	0,5	0,4
1,2-dichloroethane	0,5	0,4	1,2,3,4-Tetrachlorobenzene	0,005	0,4
1,2-dichloroethene (trans-)	0,5	0,4	Monochlorobenzene (=chlorobenzene)	0,5	0,0
1,1,2-trichloroethane	0,5	0,4	1,2,4-Trichlorobenzene	0,5	0,0
Bromodichloromethane	0,5	0,0	1,3,5-Trichlorobenzene	0,5	0,0
Dibromochloromethane	0,5	0,0	Tetrachlorobenzenes (mixture of isomers)	0,03	0,0
Tri bromomethane	0,5	0,0	1,2,3,5-Tetrachlorobenzene	0,005	0,0
petroleum hydrocarbons			1,2,4,5-Tetrachlorobenzene	0,005	0,0
Fraction EC 21-35	10	19,8	Pentachlorobenzene	0,003	0,0
Fraction EC 12-16	10	3,7	Hexachlorobenzene	0,003	0,0
Fraction EC 10-12	10	2,9			
Fraction EC 16-21	10	2,9			

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692 **Supplementary Material Nb 1 : Limit of detection (LD) and percentage of analysis for which the value is**693 **greater than the detection limit (>LD), per organic compound.**



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695 **Supplementary material Nb 2: Piper diagram showing the hydrochemical facies of groundwater sampled**
 696 **in the urban and industrial areas, per main aquifer.**

	Fe	Ba	As	Mn	B	Cr	Cu	Se	Al	Ni	Zn	Sb	Pb	Co	Cd	Mo
LD	1	1	0,2	1	10	0,5	0,4	0,2	5	1	4	0,1	0,2	0,5	0,04	0,6
mean	683	72,4	1,94	399	88,7	2,84	4,69	1,43	177,2	3,9	90,7	1,92	0,96	1,19	0,218	1,35
P25	27	23,5	0,69	9	20,5	< 0,5	< 0,4	< 0,2	< 5	< 1	< 4	< 0,1	< 0,1	< 0,5	< 0,04	< 0,6
median	62	40,0	1,20	48	56,0	0,79	0,91	0,41	12,0	1,6	6,9	< 0,1	< 0,1	< 0,5	< 0,04	< 0,6
P75	232	60,5	1,90	345	120,0	3,15	3,20	1,60	31,5	4,6	23,5	0,15	0,33	0,98	0,066	0,85
P90	1570	110,0	2,88	1038	180,0	7,46	9,78	3,08	59,0	9,8	81,8	0,36	0,99	2,48	0,138	1,80
GWD - Wallonia	200*	--	10	50*	1000	50	2000	10	200	20	200	5	10	--	5	--
WHO	300	1300	10	100	2400	50	2000	40	100	70	3000	20	10	-	3	70

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699 **Supplementary Material Nb 3 : limit of detection (LD), main statistical values (mean, median, 25th, 75th**
 700 **and 90th percentile), threshold values adopted by the Wallon region from the EC Groundwater Directive**
 701 **and limits established by the WHO for drinking water, per inorganic trace element (µg/l). Values with a ***
 702 **are indicative values given for the corresponding parameters.**