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# Development and implementation of a multi-criteria aggregation operator to estimate the contributions of the natural geochemical background and anthropogenic inputs in groundwater in former mining regions: An application to arsenic and antimony in the Gardon river watershed (southern France)

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2 contributions of the natural geochemical background and anthropogenic inputs in groundwater  
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4 (Southern France)

5  
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### 9 Highlights

- 10 - The operator involves geomorphological, mine remains positioning and tectonic data
- 11 - Anthropogenic contribution to arsenic and antimony enrichment was quantified
- 12 - Mapping facilitates the identification of zones with anthropogenic As/Sb enrichment

### 13 Abstract

14 Establishing the contribution of natural enrichment of a substance and anthropogenic inputs  
15 has become a major issue for the management of groundwater systems. The issue is made  
16 more complex when the geology of the concerned territories is heterogeneous, at variable  
17 geographical scales, at a site that has experienced mining activity that has left behind mining  
18 remains. Several studies have tried to answer this problem using different approaches:  
19 statistical, geostatistical, geological, and geochemical. The limits of these studies are seen  
20 through the incomplete integration of geological and geomorphological parameters in the  
21 results. The aim of the present research is, therefore, to look deeper into an approach to  
22 estimate the respective contributions of the natural geochemical background and  
23 anthropogenic inputs, by simultaneously considering the heterogeneity of the geology, the  
24 variability of the spatial scale, and the combination of geological, geomorphological and

25 statistical factors. A multi-criteria aggregation operator was thus developed and implemented  
26 on underground water bodies delimited by the Gardon watershed in the Cevennes (a region  
27 with former mining activities – France), in order to produce quantitative and qualitative maps  
28 for discriminating between the natural geochemical background and anthropogenic inputs.  
29 176 geochemical observation points on groundwater quality were collected by sampling and  
30 through the acquisition of public data on water sources (ADES database), wells and boreholes,  
31 to reconstruct the spatial distribution of arsenic and antimony in the study site. An  
32 aggregation operator was developed, which enabled the determination of the formulae to  
33 calculate the natural geochemical background and hence deduce the anthropogenic  
34 contributions. Cartography of the quantitative and qualitative aspects of the geochemical  
35 concentrations that have been impacted by anthropogenic activity made it possible to  
36 determine remarkable focal points located on the Cevennes fault and other specific points of  
37 geochemical interest.

### 38 **Keywords**

39 mining activities, groundwater contamination, anthropogenic contribution, natural  
40 contribution, Cevennes mountains.

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## 48 1. Introduction

49

50 The past exploitation of metals in Europe left behind various mining remnants, including  
51 mining galleries, open pits, remains from processing plants, and waste piles. The  
52 management of these areas continues to be an issue today (Vic 2017). Toxic metals and  
53 metalloids from abandoned mine sites can be a source of groundwater contamination, due to  
54 intense water-solid interactions during groundwater drawdowns or exchanges between  
55 groundwater and surface water. Concentrations of metals and metalloids exceeding  
56 guidelines can jeopardise the use of freshwater resources for irrigation or drinking water  
57 supplies. This is a major issue in the context of climate change and increased pressure on  
58 water resources. From the perspective of freshwater resource management at the river basin  
59 level, it is therefore essential to identify bodies of groundwater enriched with metals linked  
60 to past mining activity. This information can be used to prioritise remediation operations and  
61 to define site-specific water quality objectives. To do this, the natural level of metals and  
62 metalloids in the groundwater bodies needs to be determined: the natural geochemical  
63 background (NGB). The difference between the measured concentration and the NGB is  
64 therefore considered to be the anthropogenic contribution to the trace metal enrichment of  
65 groundwater. The NGB of groundwater is defined as "the natural concentration of an  
66 element, compound or substance in a body of groundwater in the absence of any specific  
67 external input, such as human activity" (Directive 2006/118/EC 2006). The determination of  
68 the NGB in former mining catchment areas is hampered by the presence of mineralised rocks  
69 in the local geology, which contribute to the release of toxic trace elements into groundwater  
70 through natural water-rock interaction processes. Local hydrogeological structures and water  
71 flow paths can cause important changes in the hydrochemical composition of groundwater

72 on a seasonal basis. In this context, significant variations in NGB can occur at a localised scale.  
73 This natural enrichment can be wrongly attributed to mine-related contamination. In such  
74 cases, determination of the local NGB will be crucial in order to differentiate and quantify any  
75 mining-related contamination from naturally occurring geochemical variations.

76 Determination of the NGB is usually performed using statistical techniques, probability plots,  
77 screening methods (Preziosi et al. 2014), or a combination of these methods and tools  
78 (Parrone and al. 2019). Statistical techniques aim to identify outliers in series, based on  
79 assumptions or the characterisation of distributions. Probability diagrams express the  
80 continuity trend of values. Zones of discontinuity reveal a change in structure or a noticeable  
81 disturbance. Atypical values are then observed that deviate from the general trend and help  
82 to describe the resulting processes. Changes in the slope of the curves describing the  
83 distribution of measurements may correspond to the transition between different  
84 populations. These changes could therefore separate the natural from the anthropogenic  
85 components, but they could also be indicative of a natural variation in geochemical facies or  
86 a local geochemical anomaly. Screening methods consist of using a selection of groundwater  
87 samples that have not shown evidence of anthropogenic inputs; these samples are used to  
88 determine the NGB. In former mining catchments, where both mining remains and natural  
89 mineralisation can induce significant variations in trace element concentrations (Zaporozec  
90 1981; Bril. H et al. 2000; Tiwary, et al. 2006; Sprague et al. 2018), especially in surface  
91 aquifers, all of these methods may underestimate the NGB. As a result, trace element  
92 enrichment related to natural sources may be wrongly attributed to anthropogenic  
93 disturbances. In this situation, other factors should be considered to quantify the  
94 anthropogenic (mining) contribution to groundwater trace metal enrichment. Several factors  
95 may tip the balance in favour or against anthropogenic contribution: the geographical

96 proximity of the mine remnants, their altitude and distance from the groundwater level, the  
97 geological heterogeneity of the sampled area, and the proximity of tectonic structures of  
98 significant extension.

99 In the present study, we used a methodology based on a multi-criteria clustering operator  
100 that involved both quantitative and qualitative parameters to consider these various factors.  
101 The methodology was applied to study arsenic and antimony enrichment in groundwater in  
102 the Gardon catchment area on the south-eastern border of the French Massif Central. The  
103 area has been mined since Roman times for lead, zinc, silver, antimony and coal.  
104 Concentrations exceeding the guidelines have occasionally been observed in tap water for  
105 arsenic and antimony, two metalloids of concern in terms of their toxicity. In the area, arsenic  
106 and antimony are present in the form of sulphides, that undergo oxidative dissolution  
107 (Resongles et al. 2014). This process occurs naturally but is increased in mine tailings and  
108 waste piles compared to unmined rocks, due to the presence of a larger reactive surface area  
109 of fine particles (Nordstrom 2011; Rawle 2003). The objective is to quantify the overlay of  
110 mine-related contamination with the natural background of arsenic and antimony in the  
111 region.

## 112 2. Geological, hydrogeological and mining contexts

### 113 2.1 Geological and hydrogeological contexts

114

115 The study site in southern France (between the Gard and Lozere departments) extends over  
116 2200 km<sup>2</sup> and is characterised by two geomorphological complexes oriented in a  
117 North/Western - South/Eastern direction. The Cevennes, covering the upstream section to  
118 the north-west, covers more than three-quarters of the total surface area with locally very  
119 steep slopes (5% to 25%), creating deep valleys which cut the relief into sharp ridges. The

120 downstream part, to the south-east, is located in the Cevennes foothills, with relatively very  
121 low slopes (less than 2%). The study site is drained by the hydrographic network of the  
122 Gardon watershed, which has its sources in the high Cevennes. The Gardon flows into the  
123 Rhône after a journey of 127 km (Agence de l'Eau Rhône-Mediterranee Corse, 2021). The site  
124 is part of the Mediterranean climate domain (Smage des Gardons, 2011). The geological  
125 context consists of the three classic types of geological formations: magmatic, metamorphic  
126 and sedimentary (Figure 1(a)). The granitic Cevennes are comprised primarily of magmatic  
127 rocks. They generally consist of porphyritic granite, with large crystals of orthoclase  
128 (potassium feldspar), several centimetres in size. The establishment of this granite was  
129 probably linked to the end of the Hercynian phase during the Carboniferous period, around  
130 330 million years ago (Rolley, 2007). After are the schistose Cevennes, with mainly  
131 metamorphic rocks. The main dominant rock types are mica schists and gneisses. These mica  
132 schists generally result from the metamorphism of ancient sedimentary rocks (clay-  
133 sandstone), whereas the gneisses containing large feldspar crystals (eyed gneisses) probably  
134 come from the oriented recrystallisation of old granites (Peyroles gneiss for example). These  
135 metamorphic formations are intersected by veins of milky white quartz, sometimes  
136 mineralised, and by a few veins of magmatic rocks (Rolley, 2007). Finally, the sedimentary  
137 formations constitute the coalfields, the limestone plateaus of the Causses, and the  
138 secondary terrains of the sub-Cevennes border. The Cevennes coal basin, covering about 200  
139 km<sup>2</sup>, is shaped like a triangle around the Rouvergue gneissic massif, to the north of Ales, at  
140 the junction of two faults; the Villefort fault (N 155° East) and the Cevennes fault (N 30° East).  
141 The limestone plateaus of the Causses cover the crystalline formations (schists, granites)  
142 along the base of the Cevennes, at the limit between the Gard and Lozere departments. In  
143 the south, this series generally starts with the conglomerate sandstones of the Triassic, which

144 cover an irregular surface. The Triassic series continues with limestone, often dolomitic, and  
145 then marl. Above this, the more recent Jurassic series of marls and limestone developed. In  
146 addition, aquifers are formed through these geological formations (Figure 1(b)). The alluvial  
147 aquifer systems, formed on the one hand by recent river alluvium, and on the other hand by  
148 ancient alluvium, are of Villafranchian age and are layered into terraces more or less  
149 preserved from erosion. These aquifers are generally relatively homogeneous and  
150 continuous, with interstitial permeability. They are made up of sands, gravels and pebbles  
151 with a fine matrix that is sometimes clayey or finely sandy. In addition, sedimentary aquifers  
152 were identified which may or may not be karstic. Sedimentary karst aquifers are marked by  
153 tectonic activity and variations in the base level, responsible for the creation of more or less  
154 superimposed karst conduits. These systems are often binary and drain surface runoff  
155 through losses, in addition to directly infiltrating into the limestone. Non-karstic aquifers  
156 were identified in the Oligocene basin between Boisset Gaujac and Saint Ambroix (marlstone)  
157 via Ales, which are practically impermeable (rift valleys filled by a series of marls) (Blaise et al.  
158 2006). Next, can be distinguished the substratum aquifer systems, identified by crystalline  
159 formations (granite, gneiss, mica schists, schists), characterised at the surface by a  
160 discontinuous altered horizon resting on a substratum. The main elements that favour their  
161 permeability are the discontinuities (fractures and faults).

162

## 163 2.2 Mining context

164 The study site has a history of mining (Figure 1(a)) for coal and metals (iron, antimony,  
165 copper, lead, zinc), or the extraction of aluminium from bauxite (industrial site of Salindres).  
166 Several types of mineralised deposits were discovered and exploited in the 19<sup>th</sup> and 20<sup>th</sup>  
167 centuries. Industries linked to the processing of pyrite, baryte, quartz, and combustible rocks



168 (lignite, coal) were also developed. Since 1980, the activity has been greatly reduced due to  
169 the depletion of deposits, foreign competition, and the consequences resulting from the  
170 disruption of ecosystems and the environment.

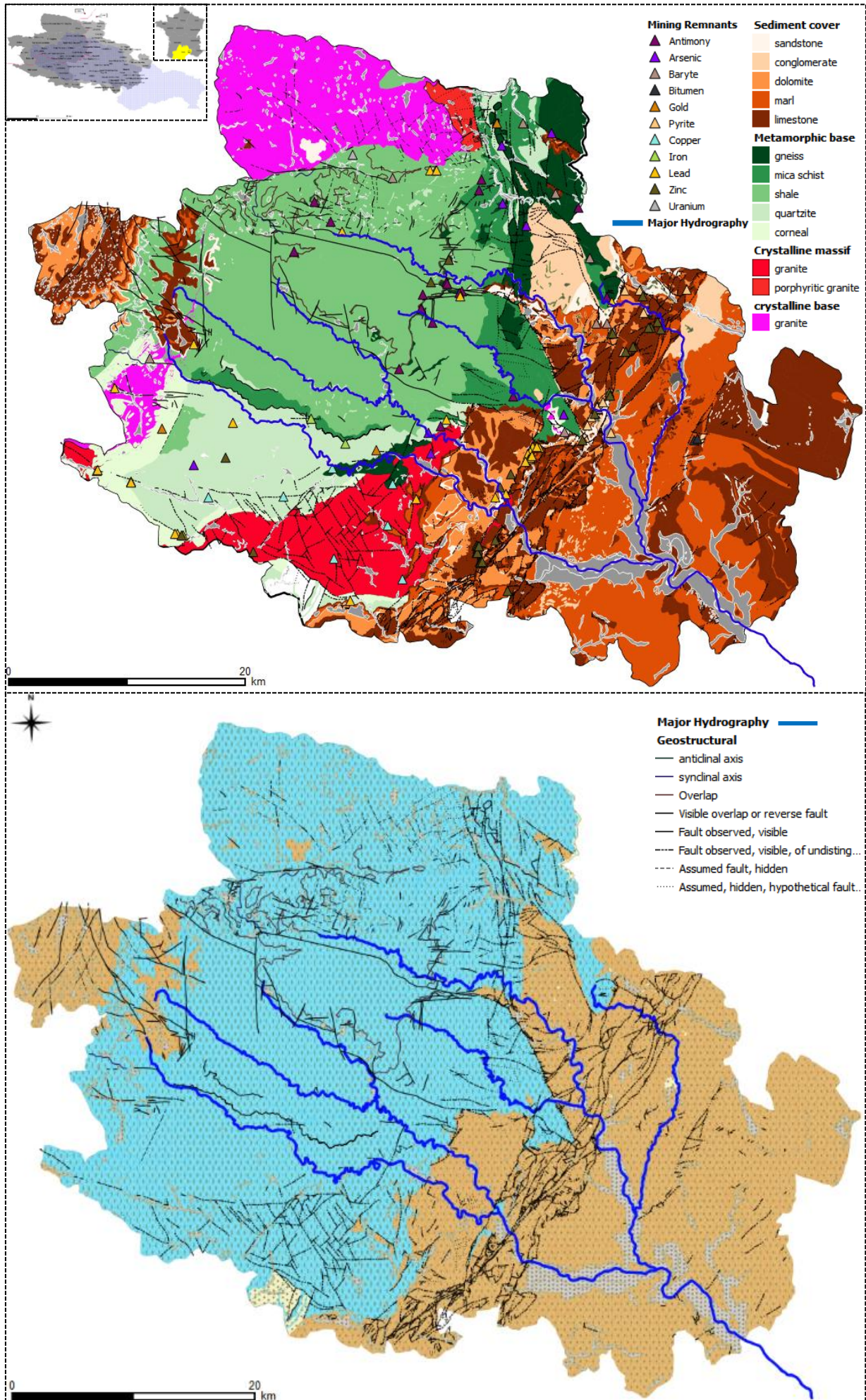


Figure 1 : (a) geological, mining and (b) hydrogeological context

## 172 3. Materials and methods

173

### 174 3.1 Data

175 Several types of data were collected during this study: geological, hydrogeological,  
176 geomorphological, mining, and water quality data. The collection of geological,  
177 hydrogeological, geomorphological and mining data was achieved mainly through the  
178 exploitation of existing maps and the synthesis of previous works (Alabouvette et al. 1988;  
179 Faure et al. 2008; Guerange-Lozes et al 1990; Elmi et al. 1989; Berger 1972; Arene et al.  
180 1978; Rolley 2007; Faure et al 1999; Vic 2017; BRGM 1994; Cochet et al. 2018; Beziat et al.  
181 1995; Coste 2003). A detailed analysis was carried out at different scales in order to obtain  
182 more specifics on the lithological and structural formations and the hydrogeological  
183 characteristics of the various aquifers. The mining data was acquired by carrying out an  
184 inventory of old and recent mining structures. The location of the mining sites, the types of  
185 mineralization exploited, their geological and geometric characteristics (quality and  
186 quantity) were recorded at different scales (BRGM 1994; Beziat et al. 1995). Additional  
187 geological field reconnaissance campaigns enabled certain information that was imprecise in  
188 the bibliography to be updated and better appreciated.

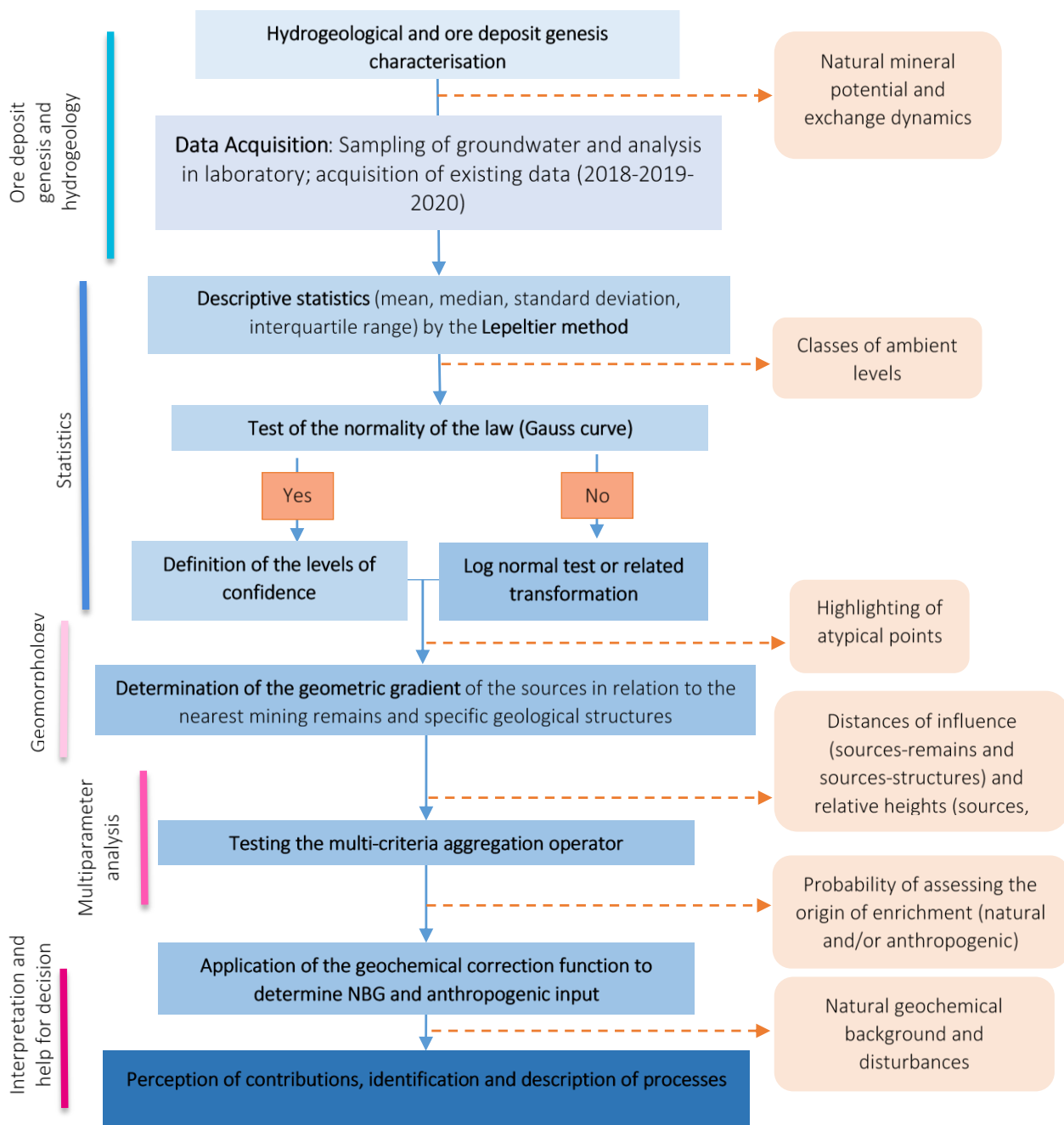
189 Data on groundwater quality were acquired by two means: exploitation of public databases,  
190 and sampling. The collection of existing data on groundwater quality was mainly carried out  
191 through the national portal of Access to Groundwater Data for Metropolitan France and the  
192 Overseas Departments (ADES). This portal gathers on a public website quantitative and  
193 qualitative data on groundwater (ADES 2021). For the data acquisition by sampling, a  
194 sampling strategy was defined, which integrated an optimised spatial layout of the sampling  
195 points. This strategy considered the geological and hydrogeological formations traversed,

196 the means of access to the available sampling, the proximity to the anthropisation indicators  
197 linked to the geochemical parameters sought, and the proximity to particular geological  
198 structures (faults, folds, shear zones, seams, lithological contacts, etc.). Springs and  
199 boreholes were the main sampling points. The springs incorporate all the chemical  
200 characteristics of the water table encased by the host aquifer. They are therefore  
201 representative of the system because their supplies have been identified with sufficient flow  
202 rates. Boreholes, in turn, allow access to deeper water and increase understanding of the  
203 vertical variability of the chemical characteristics of the water table. The samples were taken  
204 during the low-water period (summers of 2018 and 2019) to allow the most perennial  
205 sources to be sampled. In this way, it is easier to identify the source's supply. Furthermore,  
206 during these low-water periods, it can be considered that these samples of groundwater  
207 have had the longest possible transfer time, allowing chemical equilibrium with the bedrock.  
208 The choice of sampling points depended on the existence, availability and geolocation of  
209 springs and boreholes, as well as the lithological type on which the sampling is based. Each  
210 sampling point was georeferenced in the Lambert 93 coordinate system. Physical  
211 parameters (pH, electrical conductivity, and temperature) were measured in situ and water  
212 samples were collected, filtrated, preserved and analysed for major and trace element  
213 concentrations according to standardised methods used at HydroSciences laboratory, and  
214 described in previous studies (Resongles et al. 2015). Arsenic and antimony were the  
215 contaminants of interest in this study. The quantification limits were 0,01 µg/L for arsenic  
216 and 0,09 µg/L for antimony for samples collected in the present study and 0,1 µg/L and 0,01  
217 µg/L, respectively, for ADES data. In order to make the data set suitable for mapping  
218 purposes, all concentrations less than the greater of the two quantification limits were

219 modified and replaced with the greater limit of quantification values. Less than 5% of  
 220 samples were below the limit of quantification.

221 3.2 Methods

222  
 223 The general methodology integrates a combination of statistical methods and geological and  
 224 geomorphological factors (Figure 2).



225  
 226 *Figure 2: Conceptual Flow Chart of Analysis, Modelling and Data Interpretation*



227

228

229 3.2.1 Statistical methods

230

231 **Descriptive statistics and graphical methods:** groundwater As and Sb concentrations data were  
232 described for each geological formation using classical positional criteria (mean, median) and  
233 dispersion criteria (standard deviation, interquartile range, extremes). The methods of  
234 Lepeltier and Gauss were used to detect anomalies. Lepeltier proposed a method for  
235 detecting chemical anomalies in the context of mineral prospecting, based on the cumulative  
236 sum of frequencies and represented on a double-log scale graph (Lepeltier, 1969). This  
237 method assumes that trace element values follow a lognormal distribution. By accumulating  
238 the frequencies on a scale, a deviation from the lognormal distribution can be easily shown  
239 by an abrupt change in slope. This approach has been used in soil geochemical background  
240 characterisation (Matschullat and al. 2000). It was used in this work with a slight  
241 modification, as it was coupled with the occurrence probabilities to highlight the major  
242 geochemical trends that provide information on the local geochemical specificities of the  
243 area studied. It was not used here to directly determine the geochemical background, but to  
244 highlight the geochemical variability due to the variation in scale. Furthermore, several  
245 statistical tests assume that the variables describing the elements of the population follow a  
246 normal distribution.

247 **Identification of outliers:** outliers are infrequent observations that do not follow the  
248 characteristic distribution of the rest of the data. In this study, outliers represent the As and  
249 Sb concentrations data that significantly deviate from a standardised trend in regional data.  
250 Highlighting these atypical points allows initial hypotheses to be made about the likelihood

251 that the sample in question has been subject to significant anthropogenic disturbance.  
252 However, in mineralised areas, atypical points can also originate from a particular natural  
253 geological context. Thus, to better ensure the determination of these atypical points, the  
254 statistical and geological approaches have been combined in the present method. The  
255 statistical approach used the  $\pm 2\sigma$  method (Reimann and al. 2005; bridgewp2 2006; Galuszka  
256 2007). The geological approach to identifying atypical points was mainly based on the  
257 consideration of the predisposition of a sample to present high levels of a substance or not. A  
258 conditional probability of the eventualities of the sources/origins of the sample  
259 concentrations was determined, considering the geological characteristics of the aquifer, the  
260 relationship between this geology and the ore deposit genesis of the parameter sought, and  
261 the hydrogeological context (characteristics of the aquifer, permeability, water circulation  
262 lines).

263

### 264 3.2.2 Integration of geological and geomorphological factors

265 The following geological and geomorphological factors were integrated into the methodology:  
266 the lithological types, the variation in elevation between the groundwater sampling point and  
267 the lowest elevation of the mine remnant, the proximity (acceptable radius of one kilometre)  
268 between the sampling point and the mine remnant, the proximity (less than 200 metres as  
269 the crow flies) between the sampling point and particular geological structures such as  
270 lithological contacts, faults and veins, and magmatic intrusions.

271

### 272 3.2.3 Multi-criteria aggregation operator

273 The multi-criteria aggregation operator  $\phi$  is defined by the composition law  $\Lambda$  which takes as  
274 input a sample point characterised by its grade, its position within a geological formation, and

275 its position relative to nearby anthropisation (old or recent mining). Boolean characteristic  
276 variables are associated with these inputs in a standardised format. The following domains  
277 are used (i) An area subject only to the contribution of natural processes such as climate and  
278 erosion (absence of anthropisation); (ii) Area geologically enriched in substances that may  
279 imply mining (geological concentration potential due to two main factors: lithological  
280 boundaries and tectonic history); and (iii) Area that has been mined (confirmed  
281 anthropisation).

282

### 283 *3.2.3.1 Definition of variables*

284

285 **Variable “a”:** the variable "a" is defined by the event: the sample taken shows a predisposition  
286 to natural enrichment of the measured parameter. By predisposition to natural enrichment,  
287 we mean the combination of factors and processes that favour the release and mobilisation  
288 of the parameters measured in the groundwater. This predisposition includes the  
289 mineralogical composition of the host rock and the hydrogeological characteristics of the  
290 aquifer. The distribution of arsenic (Welch et al. 2000; Ungaro et al. 2008) and of antimony  
291 (Onishi 1969; Ziserman 1971) in rocks have been documented. For rocks rich in sulphides  
292 accompanying arsenic or antimony, the rock-water-oxygen contact may favour oxidative  
293 dissolution of As- and Sb-bearing sulphides, leading to the release and mobilisation of arsenic  
294 or antimony in water. If, in addition, the characteristics of the aquifer are favourable  
295 (permeability, porosity) this process can be accentuated. The variable "a" therefore integrates  
296 the proximity to geological structures (lithological contact, faults, veins, etc.), the  
297 mineralogical composition, and the hydrogeological characteristics of the aquifer containing  
298 the measured sample. Clearly, "a" expresses the probability that, in the absence of



299 anthropisation, the sample will be influenced by natural processes that involve significant  
300 rock-water interaction. This predisposition is conditioned by the ore deposit genesis and  
301 mineralization of the host rock, the geology and structures that affect it, and the dynamics of  
302 natural processes of release and mobilization of the measured substances. The event "a" is  
303 quantified by a Boolean variable defined by:

304 "a" = {1} if "a" is true: "the sample has a predisposition to natural enrichment of the measured  
305 parameters". A groundwater sample defined by the variable "a" is therefore found in domain  
306 (ii). " $\bar{a}$ " = {0} if "a" is false. A groundwater sample defined by the negation of the variable "a",  
307 i.e., " $\bar{a}$ " is therefore found in domain (i)

308 **Variable "b":** the variable "b" is defined by the event: the sample has a predisposition to  
309 anthropogenically induced enrichment of the measured parameter. Predisposition to  
310 anthropogenically induced enrichment refers to the possibility that the measured sample is  
311 influenced by anthropogenic processes and factors. In the case of this study, the notion of  
312 anthropisation is centred around past or recent mining activities. Based on the observations  
313 made in the mining inventory, the areas of mining remnants extend over a maximum radius  
314 of 1km with a maximum mining depth of 100m. Thus "b" refers to the probability that in the  
315 presence of an anthropogenic factor (mining works and structures), the sample is influenced  
316 by anthropogenic processes (drilling, milling, in situ processing) that involve significant  
317 exchanges between the anthropogenic structures and the sampled water. This predisposition  
318 is conditioned by the geomorphological gradient between the sampled point and these  
319 anthropogenic structures (mining works). The gradient is defined by the rate of  
320 geomorphological change which relates the change in elevation to the distance between the  
321 sampled point and the anthropisation point. The event "b" is quantified by a Boolean variable  
322 defined by: "b" = {1} if "b" is true: "the sample presents a predisposition to an enrichment of

323 the measured parameters induced by anthropisation". A groundwater sample defined by the  
324 variable "b" is therefore in the domain (iii). " $\bar{b}$ " = {0} if "b" is false. A groundwater sample  
325 defined by the negation of the variable "b", that is " $\bar{b}$ ", is thus in the domains (i) or (ii).

326 **Variable "c"**: the variable "c" is defined by the event: the measured concentration belongs to  
327 the main population. To determine the atypical values of a measured population proven to be  
328 anthropogenically disturbed, thresholds are calculated by the Gauss formula ( $m+1.65 \sigma$ , at  
329 95% confidence). The calculation of this threshold makes it possible to highlight two  
330 geochemical populations, a main Gaussian population and a secondary residual population.  
331 The event "c" is quantified by a Boolean variable defined by:

332 "c" = {1} if "c" is true: "the sample belongs to the Gaussian main population". The main  
333 population is grouped around a range and centred around a central characteristic (mean or  
334 median). " $\bar{c}$ " = {0} if "c" is false, and the following event is true: "the sample belongs to the  
335 residual secondary population". A groundwater sample defined by the variable "c" or by its  
336 negation " $\bar{c}$ " can be found in all domains (i), (ii) or (iii). In summary, the multi-criteria  
337 integration of variables includes: 1) parameter "a" which considers mineral composition,  
338 hydrogeological characteristics, and proximity to particular geological structures, 2)  
339 parameter "b", which considers proximity to mining remnants, elevation variation between  
340 mining remnants and sample points, and 3) parameter "c" which considers statistical  
341 considerations.

342

### 343 *3.2.3.2 Definition of the operator*

344 This multi-criteria aggregation operator is defined by the function  $\phi$  which takes as input a  
345 sampled groundwater source S and is governed by the three characteristic Boolean variables  
346 (a, b, c) (Figure 3). It combines and outputs the geochemical contributions that this sample

347 has undergone. The function returns qualitative information that will help guide the choice of  
 348 the calculation of the natural geochemical background. It is therefore expressed by a law  
 349 noted " $\wedge$ " which means "and". For example, the expression  $(S; a \wedge \bar{b} \wedge c)$  reads: the sample S  
 350 was taken in an aquifer naturally rich in the measured parameter (arsenic or antimony in the  
 351 case of this study) "and then" this aquifer has not experienced any mining activity "and then"  
 352 the content of S of the measured parameter belongs to the local trend. We can therefore  
 353 define a set of criteria K made up of the three variables according to whether the propositions  
 354 that characterise them are true or false: So  $K = \{a, b, c, \bar{a}, \bar{b}, \bar{c}\}$ . The law " $\wedge$ " is governed by a  
 355 relative chronology of events described by the variables a, b and c. Therefore " $\wedge$ " is not  
 356 commutative.

357

358 We then define  $\Phi_K(S)$  by:

		<b>Description</b>	<b>Interpretation</b>	
359		$c = a \wedge b \wedge c = abc = 111$	Predisposition for natural and anthropogenic enrichment and no noticeable impact.	The natural contribution has an expected influence and the anthropogenic contribution has no noticeable influence.
360		$\bar{c} = a \wedge b \wedge \bar{c} = ab\bar{c} = 110$	Predisposition for natural and anthropogenic enrichment and noticeable impact	Superimposition of natural and anthropogenic contributions with a noticeable influence.
361		$c = a \wedge \bar{b} \wedge c = a\bar{b}c = 101$	Predisposition for natural enrichment and no noticeable impact	Expected natural situation.
362		$\bar{c} = a \wedge \bar{b} \wedge \bar{c} = a\bar{b}\bar{c} = 100$	Predisposition for natural enrichment and noticeable impact	(Noticeable influence of natural contribution characterised by a geological process) or (noticeable influence due to an unidentified anthropogenic contribution).
363		$c = \bar{a} \wedge b \wedge c = \bar{a}bc = 011$	Predisposition for anthropogenic enrichment and no noticeable impact	Anthropogenic contribution, not associated with local geology, with no noticeable influence
364		$\bar{c} = \bar{a} \wedge b \wedge \bar{c} = \bar{a}b\bar{c} = 010$	Predisposition for anthropogenic enrichment and noticeable impact	Anthropogenic contribution, not associated with local geology, with noticeable influence
365		$c = \bar{a} \wedge \bar{b} \wedge c = \bar{a}\bar{b}c = 001$	No predisposition for both natural and anthropogenic enrichments, no noticeable impact	Expected natural situation.
366		$\bar{c} = \bar{a} \wedge \bar{b} \wedge \bar{c} = \bar{a}\bar{b}\bar{c} = 000$	No predisposition for both natural and anthropogenic enrichments, noticeable impact	Unidentified contribution (geological or anthropogenic) with noticeable influence
367				
368				
369				

370

371

372

373 *Figure 3: Definition of the multi-criteria operator from the variables: ("a"= predisposition to natural enrichment of the*  
374 *measured parameter; "b"= predisposition to anthropogenically induced enrichment of the measured parameter; "c"= the*  
375 *measured concentration belongs to the main population)*

376

377 3.2.4 Discrimination of the natural geochemical background from anthropogenic

378 contributions

379 **Definition of the natural geochemical background calculation function**

380 In order to separate the natural geochemical background from diffuse anthropogenic inputs,  
381 a function for approximating the natural geochemical background was defined. It takes as  
382 input the image of a sample by the aggregation operator and its concentration of the  
383 measured parameter to determine the upper limit of the characteristic range of the natural  
384 geochemical background. At the scale of each sample, a local geochemical background  $NGB_i$  is  
385 defined by:

$$NGB_i(S) = \begin{cases} NGB_i = "M_i", & \text{if } \varphi_k(S) = \{111; 101; 011; 001; 100\}, \text{ where } M_i \text{ is the measurement of the concentration of} \\ & \text{the sample } S \text{ of the fixed parameter.} \\ NGB_i = "med + 1.65 \sigma", & \text{if } \varphi_k(S) = \{110; 010; 000\}, \text{ where } med \text{ is the median and } \sigma \text{ the standard} \\ & \text{deviation of the main population, separate from the residual secondary population for 95\% test power} \end{cases}$$

386

387 Depending on the density of available data, the approximation confidence can be adapted to  
388 obtain a better estimate. At the scale of a territory, the geochemical background is presented  
389 as an interval of values whose upper limit is defined by:

390 upper limit = max " NGB ". Therefore,  $NGB = ]0; \max " NGB_i "[$

## 391 **Assessment of the anthropogenic contribution**

392 The contribution from anthropogenic activities was assessed by defining and implementing an  
393 anthropogenic contribution factor  $\alpha$ . It is based on the variation of the geochemical  
394 background due to anthropogenic activities that may modify it in time and space. It is defined  
395 as  $\alpha = 1 - \text{NGB}_i / M_i$ . In the absence of anthropogenic contribution,  $\text{NGB}_i$  converges towards  
396  $M_i$ , so  $\alpha$  tends towards 0. If the anthropogenic contribution is significant,  $M_i$  moves away from  
397  $\text{NGB}_i$  and so  $\alpha$  tends towards 1.

## 398 **4. Results and discussions**

### 399 **4.1 Results**

#### 400 **4.1.1 Statistical analysis**

401

402 Table 1 summarises the description of the data representative of the distribution of arsenic  
403 and antimony in the groundwater of the different aquifers of the study site. Detailed  
404 distribution and dispersion models can be found in the supporting information SI (Figures-SI  
405 1,2,3)

#### 406 **Arsenic**

407 Arsenic concentrations ranged from 0.1 $\mu\text{g/L}$  to 156  $\mu\text{g/L}$ . A significant difference (15 $\mu\text{g/L}$  for  
408 the crystalline bedrock and massif formations, and 2.5 $\mu\text{g/L}$  on average for the other  
409 geological formations) between the medians and the respective averages evidenced  
410 geochemical series shifted to the right. Some observed values are more than five standard  
411 deviations above the mean value. This implies the existence of strong perturbations to the  
412 right of the distribution. Moreover, the values of the interquartile ranges are significant  
413 (14.23 $\mu\text{g/L}$  for the crystalline bedrock and massif, and 4 $\mu\text{g/L}$  on average for the other

414 geological formations) and the standard deviations are on average five times lower than the  
415 ranges of the respective series. Thus, these series can be qualified as having a strong  
416 statistical dispersion, with a multimodal distribution, deviating from the conventional  
417 hypothesis of the existence of a local geochemical background, characterised by a  
418 monomodal distribution.

419 The distribution of arsenic concentrations allows two geochemical populations to be  
420 observed, with very similar dispersion forms for each geological support (Figure 4a; SI-2). The  
421 first densest populations are marked by steep slopes ( $80^\circ$  on average) of the cumulative  
422 frequencies and are intersected by the highest probabilities (0.4 on average). They have a  
423 relatively localised dispersion characteristic around a narrow range of values (modal class).  
424 The second populations have similar characteristics from one geological formation to  
425 another: relatively low slope, with very discrete and isolated concentrations, they tend not to  
426 cluster around a central trend. The first metamorphic basement population is concentrated  
427 around the range of 0.5 to 7.32  $\mu\text{g/L}$ . Its second population is marked by isolated  
428 concentrations such as 17.65  $\mu\text{g/L}$ , 27.48  $\mu\text{g/L}$  and 58  $\mu\text{g/L}$ . The crystalline basement and  
429 massif define their first population around the range of 0.1 to 6.98  $\mu\text{g/L}$ . The second  
430 population is marked by isolated concentrations of 18.83  $\mu\text{g/L}$ , 25.2  $\mu\text{g/L}$  and 156.81  $\mu\text{g/L}$ .  
431 The sediment cover and surface formations have essentially the same first populations,  
432 concentrated around the range of 1 to 6  $\mu\text{g/L}$  at the same frequencies. Their respective  
433 second populations are different with isolated concentrations of 11.45  $\mu\text{g/L}$ , 17.48  $\mu\text{g/L}$  and  
434 18.48  $\mu\text{g/L}$  for the sediment cover; 10.48  $\mu\text{g/L}$ , 12.57  $\mu\text{g/L}$  and 43.98  $\mu\text{g/L}$  for the superficial  
435 formations.

436 **Antimony**

437 In contrast to arsenic, the variations for antimony concentrations are relatively less important,  
438 ranging from 0.01µg/L to 8.51µg/L. The differences between the medians and averages are  
439 relatively small (2µg/L for the crystalline bedrock and massif formations, and 0.3µg/L on  
440 average for the other geological formations), showing data centred around the median.  
441 However, in general, the maximums are far from the upper limit of the modal classes (by  
442 three standard deviations for the crystalline bedrock and massif formations and six standard  
443 deviations on average for the other geological formations). The interquartile ranges are low  
444 (1.86µg/L for the superficial formations, and 0.05µg/L on average for the other geological  
445 formations) and the standard deviations are almost equivalent to the amplitude of the modal  
446 classes. It can be hypothesised that there are disturbances in the local concentrations of  
447 antimony, but they are relatively low in scattering density.

448 The pattern of distribution of antimony concentrations in groundwater is similar to that of  
449 arsenic (Figure 4b; SI-3). For all geological media, two geochemical populations are observed.  
450 The first populations on steep slopes are the densest and most localised. They are  
451 concentrated around a narrow range of values (modal class presented in the descriptive  
452 statistics), grouped around the range between 0 and 1 µg/L. The second populations are  
453 discretely distributed and isolated, with values such as 3.96 µg/L and 7.28 µg/L for the  
454 metamorphic basement, 2.54 µg/L for the crystalline basement and massif, 2.22 µg/L and  
455 5.34 µg/L for the sedimentary cover, 2.41 µg/L, 6.78 µg/L, 7.11 µg/L and 8.21 µg/L for the  
456 superficial formations.

457

458 **Modified Lepeltier distribution and Gaussian distribution:** the first populations from the  
459 modified Lepeltier distribution model constitute the main Gaussian bell curves (Figure 4b; SI-  
460 3). They have the highest probability densities for low variance bell curves. The second

461 populations constitute the secondary or residual curves. These patterns confirm the actions  
462 of two modification factors of the natural geochemical background: a regional modification  
463 factor (natural hydro and biogeochemical processes) giving rise to the main curve, and a  
464 localised or isolated modification factor (anthropic disturbance) giving rise to the residual  
465 curves.

466

467 **Determination of atypical concentrations:** To identify outlier concentrations, we determined a  
468 filter threshold value using the formula  $m+1.65 \sigma$ , with 95% confidence. The calculation was  
469 made with the median as the central value, which is recommended for a small number of  
470 data (less than 30 or 20), as it is more stable than the mean. The values of the filtering  
471 thresholds, allowing us to distinguish the main population from the atypical concentrations,  
472 are indicated in Table 1 for each geological support type.

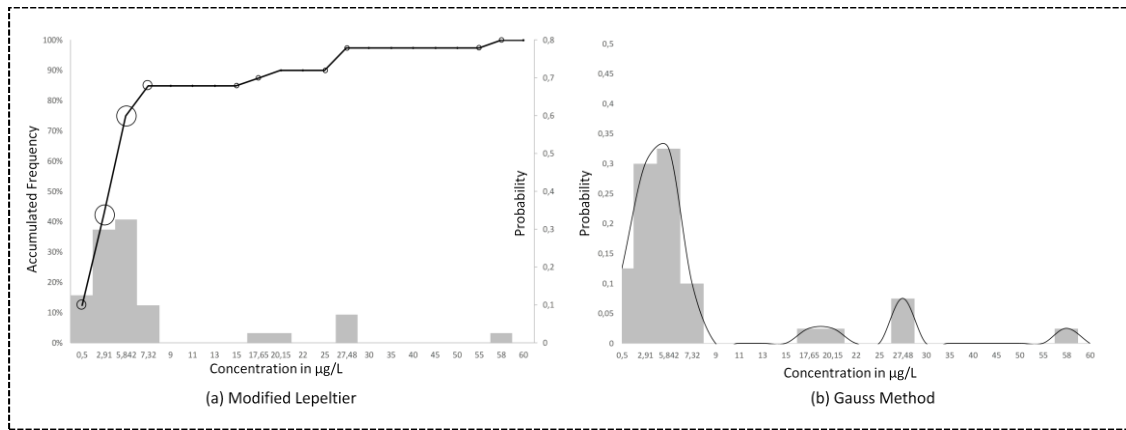
473



Parameter	Arsenic				Antimony			
	Metamorphic base	Crystalline Bedrock and Massif	Sedimentary cover	Surface formations	Metamorphic base	Crystalline Bedrock and Massif	Sedimentary cover	Surface formations
Size of population	40	15	22	20	31	15	19	13
%<LQ	2,5 %	6,67%	4,54%	0%	6,45%	0%	0%	0%
Min	0,333	0,1	0,1	0,4	0,031	0,035	0,04	0,01
Max	58,36	156,81	18,47	43,99	7,28	2,54	5,34	8,21
Scope	58,02	156,71	18,37	43,59	7 251	2 515	5,3	8,2
Standard deviation	10 865	39,43	5,74	9,48	1,43	0,57	1,17	2,97
Average	7,44	17,59	5,28	6,86	0,88	0,58	0,83	2,33
Median	5 069	2,65	2,52	4,13	0,55	0,54	0,54	0,59
C. Modal	[2;6[	[2;3[	[2;4[	[2;6[	[0;1[	[0;1[	[0;1[	[0;1[
Quartile 1	2 205	2 282	2,16	2,47	0,53	0,51	0,52	0,53
Quartile 3	5 881	16,52	5,68	6,88	0,58	0,56	0,57	2,4
Interquartile range	3 676	14,23	3,52	4,4	0,05	0,05	0,05	1,86
S(95%)=mean+1.65σ	25,37	82,66	14,75	22,5	3,24	1,53	2,67	7,24
S(95%)=median+1.65σ	22,99	67,72	11,99	19,78	2,91	1,49	2,47	5,5

474

Table 1: descriptive statistics for arsenic and antimony measurements



475

476 *Figure 4: Distribution of concentrations for one type of geological formation according to Lepeltier (left) and*  
 477 *Gauss (right) methods. Example for arsenic on metamorphic basement. The cases of arsenic and antimony on*  
 478 *the different types of geological formations are represented in Supplementary Information, (Figures SI-2 and SI-*  
 479 *3).*

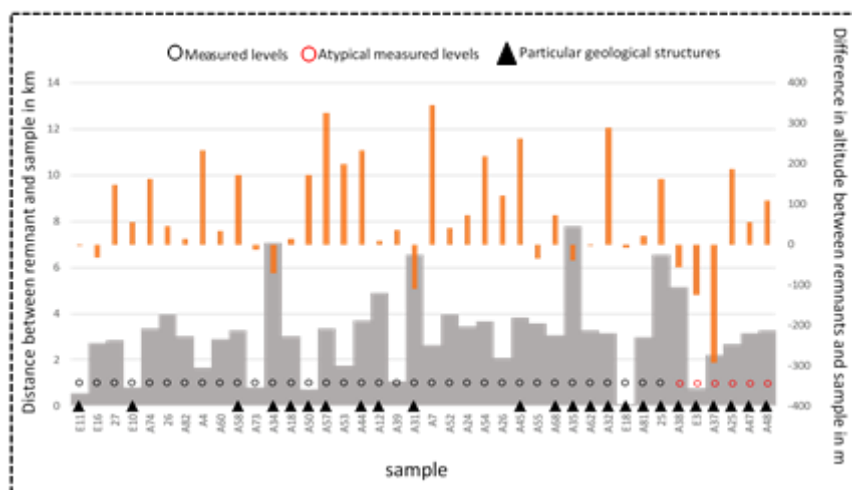
480

#### 481 4.1.2 Integration of geological and geomorphological parameters

482

483 (Figure 5) superimposes the geographical characteristics of the samples likely to play a role in  
 484 the enrichment of the water in a substance on one type of geological formation on the  
 485 measurements observed for this substance. These include the variation in elevation between  
 486 the groundwater sampling point and the bottom of the mine remnant, the proximity  
 487 (acceptable radius of one kilometre) between the sampling point and the mine remnant, and  
 488 the proximity (less than 200 metres as the crow flies) between the sampling point and specific  
 489 geological structures such as lithological contacts, faults and veins, and magmatic intrusions.  
 490 The objective of these representations is to highlight possible correlations between  
 491 concentration variation and proximity to one of these structures. In general, all of the samples  
 492 with the highest arsenic and antimony contents (secondary populations) were in the vicinity  
 493 (less than 200 metres as the crow flies) of particular structures (lithological contacts, zones of

494 intense tectonics, drop-offs, faults). These samples were located on average within a radius of  
495 4 km of a mining site. No correlation was observed due to the variation in elevation between  
496 the sampling points and these mining remains. Depending on whether or not the elevation  
497 differences were significant, and whether or not the respective piezometric levels of the  
498 sampling points were above the elevation levels of the bottoms of the mining remains, the  
499 levels of arsenic and antimony were more or less high.



500  
501 *Figure 5: Superimposition of the geographical characteristics of the samples (distance (grey bars) and difference in altitude*  
502 *(orange bars) between remnant and sample; proximity to particular geological structure (dark triangle)) on the*  
503 *measurements observed for a substance (samples belonging to the first population are represented with a black circle;*  
504 *samples belonging to the second population (above the filter threshold value) are represented with a red circle). Example of*  
505 *arsenic on metamorphic basement. The cases of arsenic and antimony on the different types of geological formations are*  
506 *represented in the Supplementary Information, Figure SI-4).*

507  
508 4.1.3 Discrimination of geochemical background from anthropogenic contributions

509  
510 The operator's calculation provided the upper limit of the geochemical background  
511 concentration range to the scale of the geological formation, together with the contribution  
512 of anthropisation to As or Sb enrichment in each sample (Table 2). It is clear that there are  
513 natural and anthropogenic contributions that may or may not be geologically identified. It is  
514 generally noted that the calculated geochemical background does not stray too far from the  
515 main population (Table 2).

516 **Arsenic:** for metamorphic base aquifers the calculated geochemical background varies in the  
517 range ]0.3; 8[  $\mu\text{g} / \text{L}$  with a mean of  $4.25 \mu\text{g} / \text{L}$  and a median of  $5.06 \mu\text{g} / \text{L}$ . For crystalline  
518 bedrock and massif aquifers the calculated geochemical background varies in the range] 0.1;  
519 5.54 [ $\mu\text{g} / \text{L}$  with a mean of  $3.46 \mu\text{g} / \text{L}$  and a median of  $2.65 \mu\text{g} / \text{L}$ . For aquifers of the  
520 sedimentary cover, the calculated geochemical background varies in the range] 0.1; 3.79 [ $\mu\text{g} /$   
521  $\text{L}$  with a mean of  $2.58 \mu\text{g} / \text{L}$  and a median of  $2.52 \mu\text{g} / \text{L}$ . Finally, for surface aquifers, the  
522 calculated geochemical background varies in the interval] 0.4; 6.52 [ $\mu\text{g} / \text{L}$  with a mean of  $4.03$   
523  $\mu\text{g} / \text{L}$  and a median of  $4.13 \mu\text{g} / \text{L}$ .

524

525 **Antimony:** for metamorphic base aquifers the calculated geochemical background varies in  
526 the range] 0.03; 0.89 [ $\mu\text{g} / \text{L}$  with a mean of  $0.5 \mu\text{g} / \text{L}$  and a median of  $0.55 \mu\text{g} / \text{L}$ . For  
527 crystalline basement and massif aquifers, the calculated geochemical background varies in  
528 the range] 0.03; 0.87 [ $\mu\text{g} / \text{L}$  with a mean of  $0.47 \mu\text{g} / \text{L}$  and a median of  $0.54 \mu\text{g} / \text{L}$ . For  
529 aquifers of the sedimentary cover, the calculated geochemical background varies in the  
530 range] 0.04; 0.81 [ $\mu\text{g} / \text{L}$  with a mean of  $0.52 \mu\text{g} / \text{L}$  and a median of  $0.54 \mu\text{g} / \text{L}$ . Finally, for  
531 surface aquifers, the calculated geochemical background varies in the interval] 0.01; 0.92 [ $\mu\text{g}$   
532  $/ \text{L}$  with an average of  $0.62 \mu\text{g} / \text{L}$  and a median of  $0.59 \mu\text{g} / \text{L}$ .

533

#### 534 **Uncertainty**

535 The error in this assessment of the natural geochemical background lies in the approximate  
536 values of the true mean and standard deviation. Since by definition the natural geochemical  
537 background is centred around a central feature (mean or median) as a rule, then this error  
538 tends towards 0 the higher the power of the test. A descriptive and comparative analysis of  
539 the dispersion characteristics of the measured concentrations, the calculated geochemical

540 background and the main population was made (Table 2; Figure SI-5). Generally speaking, the  
 541 main population showed very similar characteristics to the calculated geochemical  
 542 background. The median, mean and standard deviation were quite stable. The measured  
 543 concentrations, unlike the main population and the geochemical background, showed a  
 544 strong variation in the dispersion characteristics, in particular the mean and standard  
 545 deviation. This proves that the residual secondary population is the main factor modifying the  
 546 natural geochemical background.

Parameters	Arsenic				Antimony			
Geological support	Metamorphic Base	Crystalline Bedrock and Massif	Sedimentary Cover	Superficial Formations	Metamorphic Base	Crystalline Bedrock and Massif	Sedimentary Cover	Superficial Formations
<b>Geochemical support</b>								
Measures	]0,3 ; 58,36[	]0,1 ; 156[	]0,1 ; 18,47[	]0,4 ; 43,98[	]0,03 ; 7,28[	]0,03 ; 2,54[	]0,04 ; 5,34[	]0,01 ; 8,21[
Geochemical background	]0,3 ; 8[	]0,1 ; 5,54[	]0,1 ; 3,79[	]0,4 ; 6,52[	]0,03 ; 0,89[	]0,03 ; 0,87[	]0,04 ; 0,81[	]0,01 ; 0,92[
Contribution of anthropisation	]55% ; 90%[	]20% ; 95%[	]25% ; 80%[	]30% ; 85%[	]70% ; 90%[	]60% ; 70%[	]60% ; 85%[	]65% ; 90%[
<b>Characterisation and evaluation of geochemical media</b>								
<b>Characteristics of the measured contents</b>								
Mean	7,44	17,59	5,28	6,86	0,88	0,58	0,83	2,33
Median	5,07	2,65	2,52	4,13	0,55	0,54	0,54	0,59
Standard deviation	10,87	39,43	5,74	9,48	1,43	0,57	1,17	2,97
<b>Characteristics of the calculated geochemical background</b>								
Mean	4,25	3,46	2,58	4,03	0,5	0,47	0,52	0,62
Median	5,06	2,65	2,52	4,13	0,55	0,54	0,54	0,59
Standard deviation	2,5	1,9	1,12	2,11	0,24	0,22	0,18	0,3

547

548 *Table 2: abstract of discrimination of geochemical background from anthropogenic contributions*

#### 549 4.1.4 Cartography Summary

##### 550 *4.1.4.1 Qualitative classification of anthropic disturbances*

551

552 The application of the multi-criteria aggregation operator  $\phi$  to the study site allowed us to  
553 determine a qualitative classification of the collected geochemical data according to their  
554 degree of geochemical disturbance. From the two sources of enrichment of a sample (natural  
555 and anthropogenic), specificities were determined. The different qualitative synthesis maps  
556 for arsenic and antimony (Figure 6) illustrate the eight specific geochemical disturbance  
557 classes.

558

559 **Predisposition for natural enrichment and no noticeable impact (101) and No predisposition for**  
560 **both natural and anthropogenic enrichments, no noticeable impact (001):** In both cases the  
561 interpretations are similar, i.e. expected natural situation. 18% of the arsenic and 27% of the  
562 antimony measurement points show a natural contribution with expected influence. The  
563 influence is said to be expected because, in the absence of anthropisation, these samples  
564 have levels within the characteristic ranges of the regional trend, i.e., below 10 $\mu$ g/L for  
565 arsenic and 5 $\mu$ g/L for antimony. Two characteristic cases can be distinguished: samples with a  
566 low probability of natural enrichment (001) (alluvial aquifers) and samples with a high  
567 probability of natural enrichment (other types of aquifers). Alluvial aquifers are generally  
568 recent and do not always show a natural predisposition towards arsenic and antimony  
569 enrichment. In the case of other aquifers, the samples belong to radii that are relatively  
570 unaffected by mining remains (minimum distance from the nearest remains is 5km (for  
571 arsenic) and 3km (for antimony).

572

573 **Predisposition for natural enrichment and noticeable impact (100):** Noticeable influence of  
574 natural contribution characterised by a geological process or noticeable influence due to an  
575 unidentified anthropogenic contribution. We note a data point that behaves as an outlier to  
576 the local trend while there is no characteristic anthropogenic activity (old or recent) in the  
577 radii. 1% of samples show this characteristic for arsenic with a content of 17.6 µg/L, and it is  
578 not observable for antimony. The specific geological structures and natural processes that  
579 made this data remarkable were identified. A detailed assessment of the context allows us to  
580 identify that these samples are located in an intense fault zone with a lithological contact  
581 between schist, limestone and granitic belt, all of which are likely to be carriers of arsenic  
582 mineralization. There are no mining remains within a radius of at least 6km with an altitude  
583 variation of over 200m. No specific industry or other anthropogenic activity has been  
584 recorded in this environment. It was concluded that this feature is a result of intense water-  
585 rock exchange catalysed by tectonic structures that favour arsenic release and mobilisation  
586 processes (Smedley and Kinniburgh 2002c).

587

588 **Predisposition for natural and anthropogenic enrichment and no noticeable impact (111):** The  
589 natural contribution has an expected influence and the anthropogenic contribution has no noticeable  
590 influence. The influence of anthropisation is not perceived even though it exists. The data  
591 behaves like a sample from a non-anthropogenic environment. 54% of the arsenic and 53% of  
592 the antimony measurement points have this characteristic. It has the largest number of  
593 samples. The samples were taken from aquifers likely to contain mineralization and were  
594 relatively close to mining remains (generally less than 3km distance). Because of the dual  
595 natural and anthropogenic predisposition to arsenic and antimony enrichment, the different  
596 inputs are superimposed. Since the observed concentrations also belong to the regional

597 trend, this proves that the anthropogenic disturbance was not sufficient to raise the chemical  
598 concentrations to atypical levels. Thus, there is a high probability of anthropogenic  
599 disturbance, but with natural processes causing a greater impact.

600

601 **Predisposition for natural and anthropogenic enrichment and noticeable impact (110):**

602 Superimposition of natural and anthropogenic contributions with a noticeable influence. The  
603 influence of anthropisation was perceived to be absorbing the natural contribution, as the  
604 data behave as outliers to the local trend. 11% of the arsenic and 6% of the antimony  
605 measurement points show this characteristic. This includes the samples with the highest  
606 concentrations. As in the characteristic (111), the samples are located in aquifers likely to be  
607 mineralized and are relatively close to mine remnants (generally less than 3km distance). Due  
608 to the dual natural and anthropogenic predisposition to arsenic and antimony enrichment,  
609 the different inputs are superimposed. The concentrations are particularly atypical and depart  
610 from the regional behaviour of the support aquifer. Therefore, we note a strong effect from  
611 anthropogenic disturbance superimposed on the regional trend which represents natural  
612 modifications.

613

614 **Predisposition for anthropogenic enrichment and no noticeable impact (011):** anthropogenic

615 contribution, not associated with local geology, with no noticeable influence. 10% of the  
616 arsenic and 6% of the antimony measurement points have this characteristic. The  
617 contribution is qualified as anthropogenic and not geologically identified because the  
618 geological support which constitutes the aquifer is alluvial, which does not always present the  
619 predispositions for natural enrichment in arsenic and antimony. Specifically, in the case of  
620 alluvial aquifers, the anthropogenic contribution can go beyond 1km, due to the dynamics



621 within these aquifers. Furthermore, the influence is said to be negligible because the  
622 concentrations are part of the regional trend through characteristic ranges below 10µg/L for  
623 arsenic and 5µg/L for antimony.

624

625 **Predisposition for anthropogenic enrichment and noticeable impact (010):** anthropogenic  
626 contribution, not associated with local geology, with noticeable influence. 3% of the arsenic  
627 and 1% of the antimony concentration measurement points have this characteristic. As in  
628 case (011), the contribution is qualified as anthropogenic and not geologically identified  
629 because the geological support which constitutes the aquifer is alluvial, superficial and recent,  
630 which does not always present the predispositions for natural enrichment in arsenic and  
631 antimony.

632

633 **No predisposition for both natural and anthropogenic enrichments, noticeable impact (000):**  
634 unidentified contribution (geological or anthropogenic) with noticeable influence. No mining  
635 remnants are recorded in the sample environment, but the sample presents data that  
636 behaves as an outlier to the regional trend. 1% (1 point) of the arsenic and 1% (3 points) of  
637 the antimony measurement points show this characteristic. In the case of arsenic, the point  
638 with a content of 17 µg/L is based on a lithological contact between shale and limestone.  
639 Since the shales at the study site are the carrier of mineralization, the hypothesis of arsenic  
640 enrichment is supported by this lithological contact structure. As in case 010, it is important  
641 to note that the anthropogenic contribution can go beyond 1km due to the dynamics within  
642 these aquifers. In the case of antimony, the points are underlain by recent superficial alluvial  
643 aquifers which cannot reveal the source of production of these concentrations; hence they  
644 are termed geologically unidentified.

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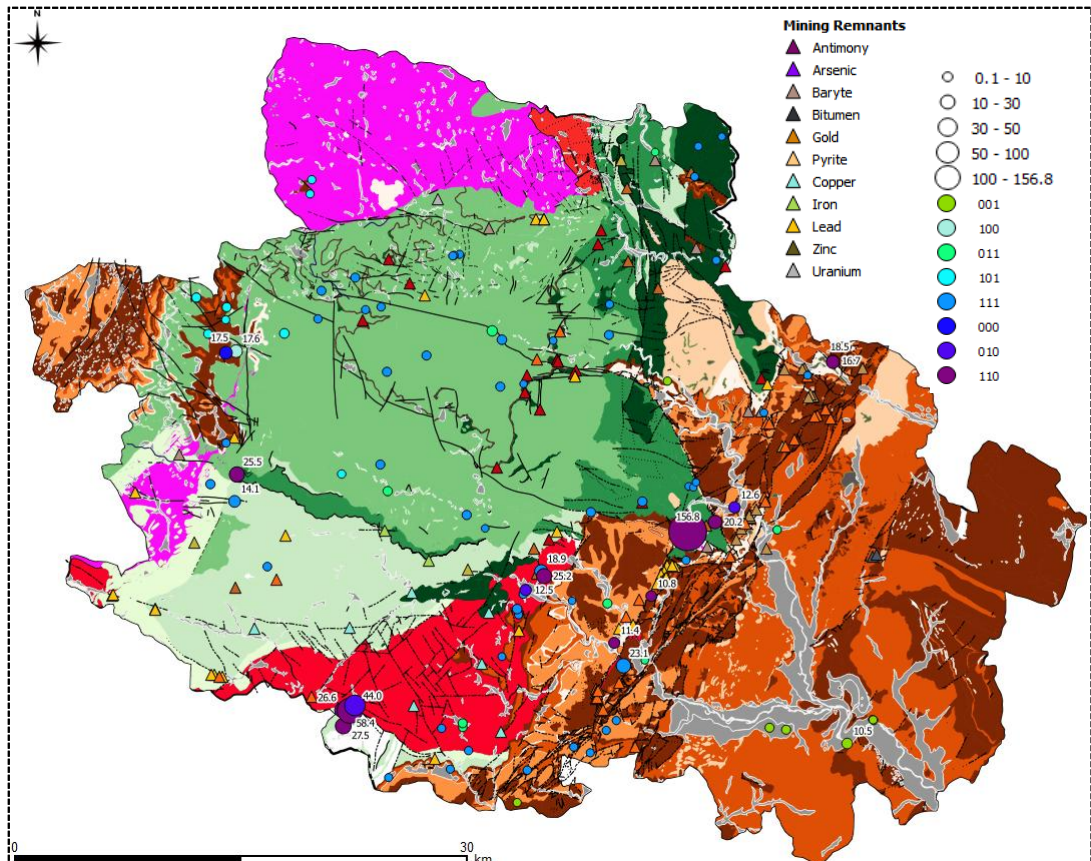
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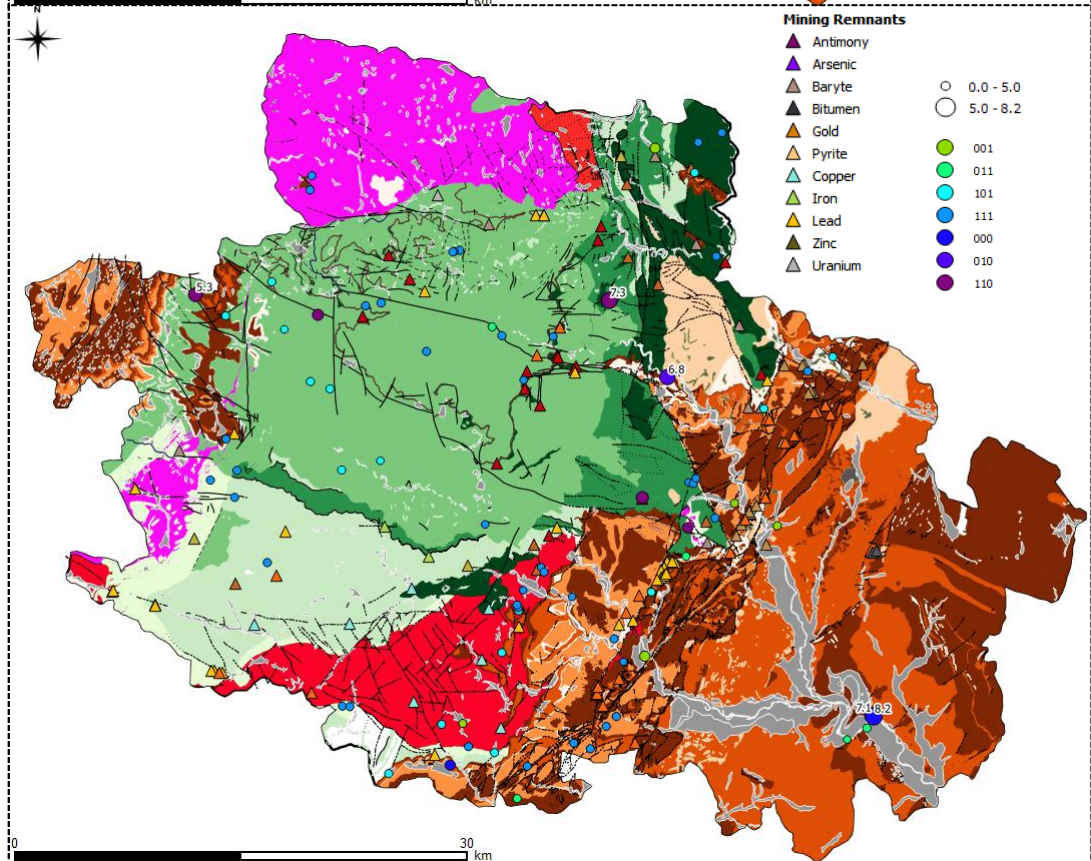


Figure 6:Qualitative classification of anthropogenic disturbances for (a) arsenic and (b) antimony

669

670

671

#### 672 *4.1.4.2 Quantitative perception*

673

674 The following maps (Figure 7) summarise and highlight the quantitative contrast between the  
675 measured concentrations of arsenic and antimony and the natural geochemical background,  
676 after extraction of anthropogenic inputs. A 3D representation allows better visualization and  
677 appreciation of this decomposition (Figure-SI 7).

#### 678 **Arsenic**

679 There are five focal points where the anthropic disturbances are most expressed. They can be  
680 classified into two main areas: the area around the Cevennes fault mining field and the area  
681 to the north-west, upstream of the catchment area in Barre-des-Cevennes, close to the  
682 mining remnants. For the domains located around the Cevennes fault, the most impactful  
683 disturbance is due to mining activity, given its proximity to mining remains and the brutal  
684 variations in concentration between the natural geochemical background and the measured  
685 concentrations. The most important anthropogenic impact linked to past mining activity is  
686 located on the trajectory of the Cevennes fault in the vicinity of the communes of Saint  
687 Sebastien d'Aigrefeuille, Cendras, Soustelle, Saint-Paul-la-Coste and Saint Jean du Pin.  
688 Concentrations measured recently of up to 156 µg/L of arsenic did not exceed 20 µg/L from  
689 the calculated geochemical background. This variation expresses an increase of about eight  
690 times in the concentrations compared to the calculated natural geochemical background. In  
691 the commune of Saint-Jean-du-Gard and the vicinity of the communes of Corbes, Anduze and  
692 Generargues, we also note a zone of significant disturbance where the concentrations are

693 twice those of the calculated natural geochemical background of about 10µg/L. In the  
694 commune of Saint-Martial and periphery, one also retains a strong disturbance which started  
695 from a natural geochemical background of 7µg/L up to observed and measured  
696 concentrations of around 58µg/L. An accentuation that multiplied the levels by 8. For the  
697 Barre-des-Cevennes area, we note very punctual variations without any correlation with the  
698 proximity of the mining remains (located at approximately 7km from the measurement  
699 points). In addition to the classification results, it can be concluded that this area has  
700 experienced mining activity that is not geologically identified. The input would therefore  
701 come from another anthropic activity rich in arsenic (mine tailings dam, other industry).

702

### 703 **Antimony**

704 As a general remark, the calculated geochemical background concentrations do not exceed 3  
705 µg/L, whereas the measured concentrations are up to 8 µg/L. Therefore, in the case of the  
706 most impactful disturbance, the concentrations were increased by 3 times compared to the  
707 calculated natural geochemical background. This is the case for the concentrations observed  
708 in the communes of Saint Cecile d'Andorge and Branoux-les-Taillades, and in the vicinity of  
709 the communes of Grand Combe and Saint Julien des Points. These significant variations are  
710 also observed in the surface formations to the southeast at the intersection of the Anduze  
711 and Ales Gardon rivers in the commune of Ners. We also note a significant variation to the  
712 northeast (in the communes of Cans-et-Cevennes in the vicinity of the communes of Barre-  
713 des-Cevennes and Cassagnas), taking the concentrations from a geochemical background  
714 estimated at around 1µg/L to measured values of up to 5 µg/L, i.e., a 5-fold increase. Two  
715 other areas present a relatively weak but remarkable variation located on the Cevennes fault  
716 in the vicinity of the communes of Anduze and Generargues on the one hand, and Cros and



717 Saint-Roman-de-Cordieres on the other hand. The variations ranged from a calculated natural  
718 geochemical background around 1µg/L to measured concentrations of up to 2 µg/L.

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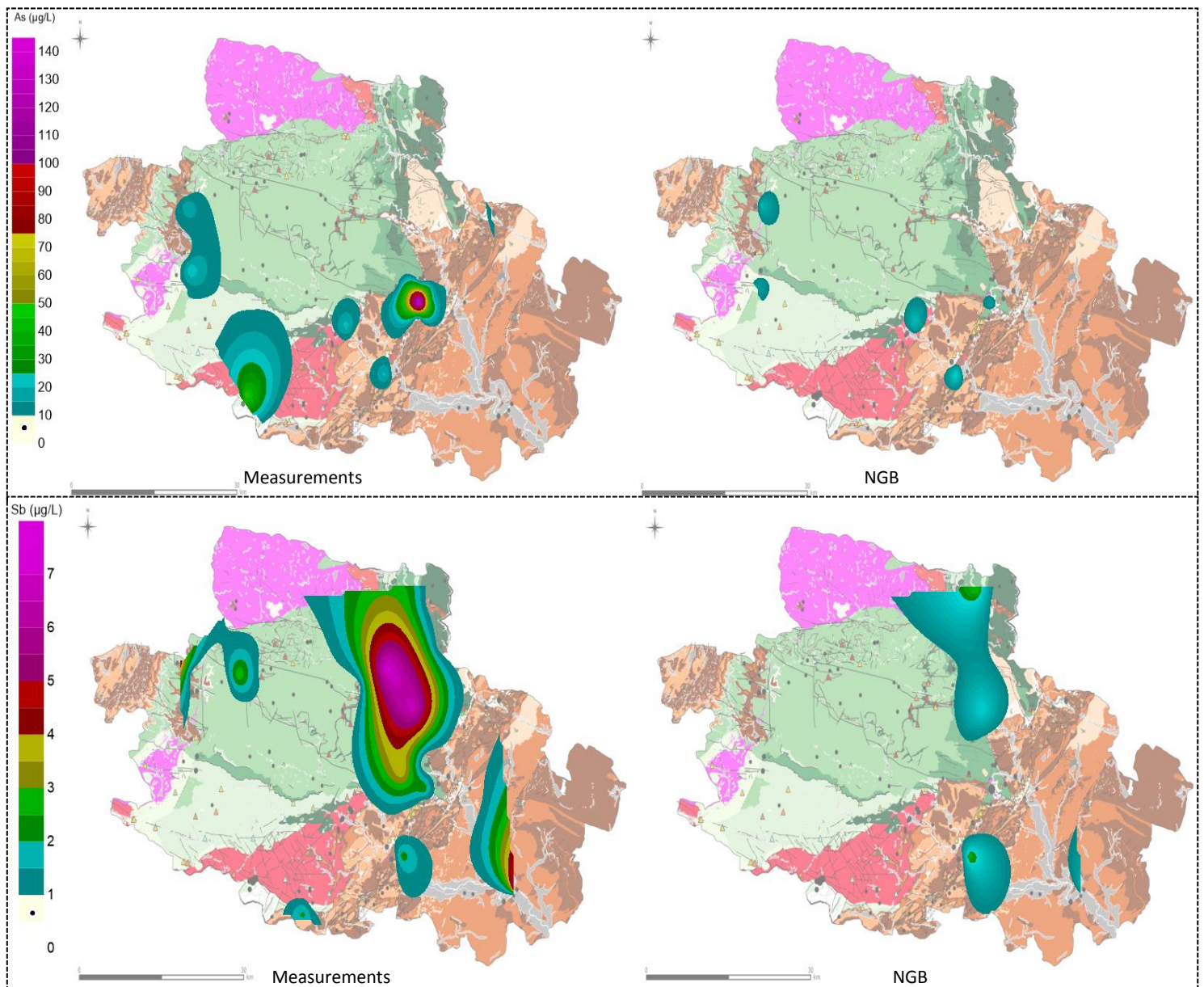
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Figure 7: Map representing measured isoconcentration curves (left side) and estimated Natural Geochemical Background (right side) for arsenic (up) and antimony (down)

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744 [4.2 Discussion](#)

745

746 **Anthropogenic versus natural origin of arsenic and antimony enrichment in the studied area:**

747 The proposed methodology allowed the mapping of natural and anthropogenic contributions to  
748 arsenic and antimony concentrations in a former mining catchment. The results showed one area  
749 for antimony and five areas for arsenic with a significant anthropogenic contribution; this induced  
750 an increase in concentrations up to a factor of five for antimony and eight for arsenic compared to  
751 the natural geochemical background values. It was associated with the proximity of former mining  
752 sites. The impact of these remnants on the quality of surface water had been demonstrated in  
753 several studies (Casiot et al., 2009; Resongles et al., 2015) but this is the first time that the  
754 anthropogenic contribution related to past mining activity has been quantified in the studied area.  
755 The results also showed that in the arsenic-enriched areas, the contribution of the natural  
756 geochemical background exceeded the European standard of 10 µg/L for water intended for human  
757 consumption. This was not the case for antimony, whose calculated natural geochemical  
758 background contribution remained below the standard of 5 µg/L. This has implications for the  
759 management of groundwater resources in the studied area. Groundwater quality would likely  
760 benefit from the remediation of ancient mines in the catchment; however, arsenic concentrations  
761 would likely continue to exceed 10 µg/L locally.

762 **Relevance of the methodology for the determination of the natural geochemical background:**

763 There is no universal approach to determine the natural geochemical background with absolute  
764 certainty (Galuszka 2007). The statistical approach considers the distribution of data as a

765 superposition of two populations corresponding respectively to the geochemical contributions of  
766 natural and anthropogenic origin. The method assumes that different sources generate different  
767 populations that can be separated by statistical procedures. However, the large discrepancy  
768 between different concentrations of sampled elements and analyses may not be related to an  
769 anthropogenic contribution (Galuszka 2007). This is especially true in mineralized areas with high  
770 geological and geomorphological heterogeneity, as in our case study. Different lithologies will  
771 produce different geochemical patterns. Thus, data treatment should consider the spatial  
772 distribution of the samples, in relation to geology, geomorphology, and location of anthropogenic  
773 sources. Until now, none of the approaches used for natural geochemical background  
774 determination allowed the integration of geological heterogeneity criteria at a large scale,  
775 considering local geochemical and environmental realities. In a region that experienced a mining  
776 history, the consideration of geological structures and geomorphology in the determination of the  
777 natural geochemical background is of prime importance (Müller et al. 2006; Griffioen and al.2008;  
778 Marandi and al. 2008; Hinsby and al. 2008; Wendland et al. 2008; Coetsiers et al. 2009; Preziosi and  
779 al.2010a; Molinari et al. 2019; Rotiroti et al. 2015; Zabala et al. 2016). In the present case study,  
780 sulphide-rich rocks, which are rich in arsenic and antimony mineralisations, were found in the  
781 metamorphic base and crystalline base. Intense tectonics were also present, marked by shear  
782 zones, faults and fractures (sometimes filled by the crystallisation of hydrothermal fluids) and  
783 lithological contacts. These structural elements are sometimes indicative of geochemical activity  
784 and oxygen supply using the fracture network. Oxidation reactions are favourable and exchanges  
785 between rock and water are accentuated. In the sedimentary basement, there are several  
786 lithological contact zones due to sedimentation processes and tectonic zones. shows The  
787 sedimentary basement formations are not very rich in arsenic, and this correlated, in our case, the  
788 spatial distribution of the mining remains. For the samples from the surface formations, the

789 predominant structures are lithological contacts. Since these formations are recent and are  
790 regularly being reworked, these lithological contacts serve as exchanges between surface water and  
791 groundwater. Their sources of As enrichment are mostly from surface water, as these formations  
792 do not carry arsenic-rich mineralization.

793

#### 794 **Is the methodology generalizable?**

795 The proposed geochemical multi-criteria aggregation operator was built with a view to generalise  
796 the tool to all types of chemical elements, and to any variation in spatial and geological scale. The  
797 geological and hydrogeological natures of the aquifers were considered, with the geomorphological  
798 parameters favouring the exchanges between rock and water. This makes it possible to extend the  
799 application of this tool to any type of chemical element that enters the mineral composition of the  
800 aquifer host rocks. In addition, the description of the operator's components and the method of  
801 calculating the geochemical background integrates the lithological types on the one hand, and the  
802 density of sampled data on the other hand, in order to appreciate the relevant geochemical  
803 information associated with the geological support. The example of the study site presents an  
804 heterogeneous catchment made up of the three main rock families (magmatic, crystalline and  
805 sedimentary). Thus, by considering the variations of geographical scales and the variation of  
806 geological supports, this aggregation operator responds to the cases of regions with highly  
807 heterogeneous geology. This is where one of the original points of this method lies, through the  
808 integration of geological heterogeneity at a given scale. Arsenic concentrations have been observed  
809 that do not belong to the regional trend but are of natural origin. Purely statistical approaches  
810 would have classified this as an anthropogenic disturbance (Portier 2001; Reimann et al. 2005;  
811 Preziosi et al. 2014).

#### 812 **Which limitations?**



813 More detailed studies on the characteristics of each geological formation are needed to improve  
814 the integration of mineralogical parameters in this operator. For alluvial aquifers, the area of  
815 contribution of mining remains should be considered with caution due to river water exchanges. If  
816 this approach is applied to another type of anthropogenic activity than mining, it will be necessary  
817 to reconstruct the variable "a", a variable that considers the characteristics of the anthropogenic  
818 activity.

## 819 5. Conclusion

820

821 The methodology proposed in this study provided the development and implementation of a multi-  
822 criteria geochemical aggregation operator able to determine both the element concentrations  
823 inherited from the natural geochemical background and those induced by anthropogenic activities  
824 related to the mining history of the territory. An application to the Gardon catchment area  
825 highlighted zones where the water bodies were most impacted by anthropogenic inputs. The  
826 developed methodology incorporates qualitative data (geology, hydrogeology, geomorphology,  
827 anthropogenic activities) characterising the measurement points, making it possible to identify  
828 predisposition to enrichment of natural or anthropogenic origin, with statistical analyses, for the  
829 determination of threshold values between the main population and outliers in each geological  
830 formation. Qualitative classification maps of anthropogenic disturbances and quantitative  
831 concentration maps of the natural geochemical background facilitate the perception of the origin  
832 (natural or anthropogenic) of contamination. It may help to share information between scientists,  
833 the public and water management stakeholders, to optimize the management of water resources  
834 at the scale of a territory.

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843 **Author contributions**

844 The manuscript was written through the contributions of all authors. All authors have approved the  
845 final version of the manuscript.

846

847

848 **Declaration of Interest statement**

849

850 Declarations of interest: none

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852

853

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