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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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Highlights

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

Abstract

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

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

Keywords

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

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

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

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

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

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

2. Geological, hydrogeological and mining contexts

2.1 Geological and hydrogeological contexts

The study site in southern France (between the Gard and Lozere departments) extends over 2200 km² and is characterised by two geomorphological complexes oriented in a North/Western - South/Eastern direction. The Cevennes, covering the upstream section to the north-west, covers more than three-quarters of the total surface area with locally very 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 km², is shaped like a triangle around the Rouvergüe 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

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

2.2 Mining context

The study site has a history of mining (Figure 1(a)) for coal and metals (iron, antimony, copper, lead, zinc), or the extraction of aluminium from bauxite (industrial site of Salindres). Several types of mineralised deposits were discovered and exploited in the 19th and 20th 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.

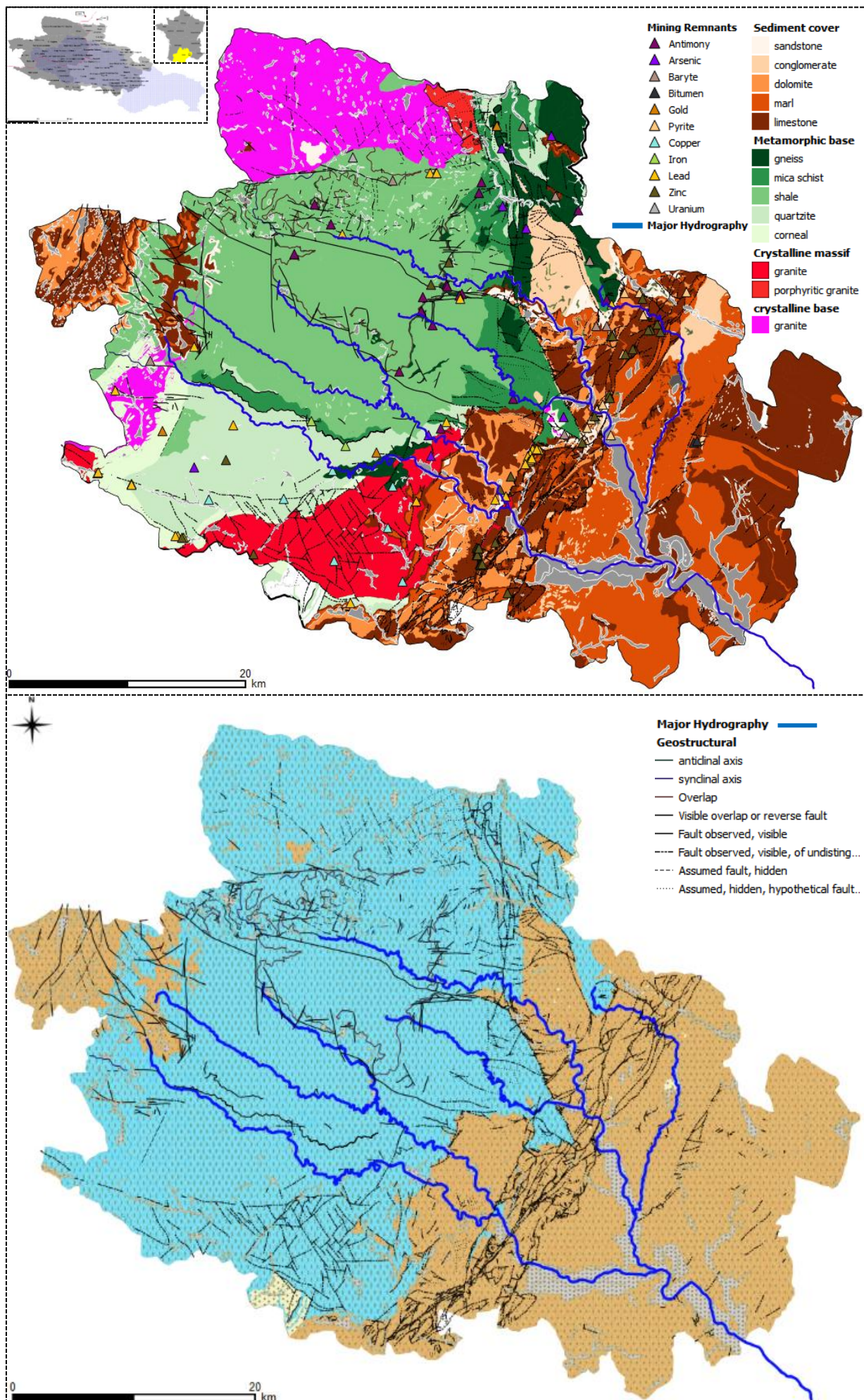


Figure 1 : (a) geological, mining and (b) hydrogeological context

3. Materials and methods

3.1 Data

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

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

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

3.2 Methods

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

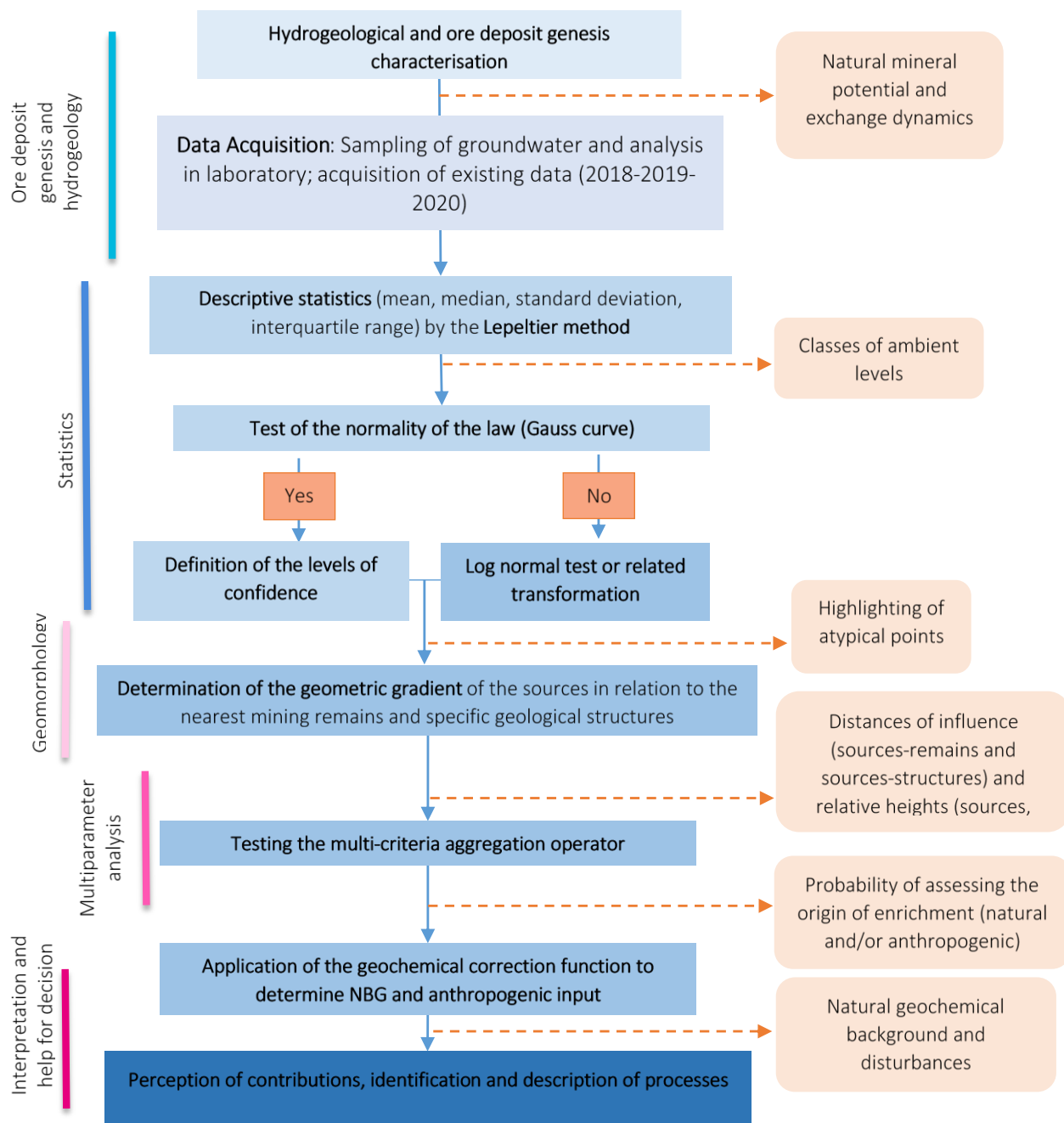


Figure 2: Conceptual Flow Chart of Analysis, Modelling and Data Interpretation

3.2.1 Statistical methods

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

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

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

3.2.2 Integration of geological and geomorphological factors

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

3.2.3 Multi-criteria aggregation operator

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

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

3.2.3.1 Definition of variables

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

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

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

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

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

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

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

3.2.3.2 Definition of the operator

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

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

We then define $\varphi_K(S)$ by:

		Description	Interpretation	
a	b	$c = a \wedge b \wedge c = abc = 111$	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.
		$\bar{c} = a \wedge b \wedge \bar{c} = ab\bar{c} = 110$	Predisposition for natural and anthropogenic enrichment and noticeable impact	Superimposition of natural and anthropogenic contributions with a noticeable influence.
	\bar{b}	$c = a \wedge \bar{b} \wedge c = a\bar{b}c = 101$	Predisposition for natural enrichment and no noticeable impact	Expected natural situation.
		$\bar{c} = a \wedge \bar{b} \wedge \bar{c} = a\bar{b}\bar{c} = 100$	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).
\bar{a}	b	$c = \bar{a} \wedge b \wedge c = \bar{a}bc = 011$	Predisposition for anthropogenic enrichment and no noticeable impact	Anthropogenic contribution, not associated with local geology, with no noticeable influence
		$\bar{c} = \bar{a} \wedge b \wedge \bar{c} = \bar{a}b\bar{c} = 010$	Predisposition for anthropogenic enrichment and noticeable impact	Anthropogenic contribution, not associated with local geology, with noticeable influence
	\bar{b}	$c = \bar{a} \wedge \bar{b} \wedge c = \bar{a}\bar{b}c = 001$	No predisposition for both natural and anthropogenic enrichments, no noticeable impact	Expected natural situation.
		$\bar{c} = \bar{a} \wedge \bar{b} \wedge \bar{c} = \bar{a}\bar{b}\bar{c} = 000$	No predisposition for both natural and anthropogenic enrichments, noticeable impact	Unidentified contribution (geological or anthropogenic) with noticeable influence

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

3.2.4 Discrimination of the natural geochemical background from anthropogenic contributions

Definition of the natural geochemical background calculation function

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

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

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

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

391 **Assessment of the anthropogenic contribution**

392 The contribution from anthropogenic activities was assessed by defining and implementing an
393 anthropogenic contribution factor α . 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, NGB_i converges towards
396 M_i , so α tends towards 0. If the anthropogenic contribution is significant, M_i moves away from
397 NGB_i and so α 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

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

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

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 model
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

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

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

Parameter	Arsenic				Antimony			
Geological support	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

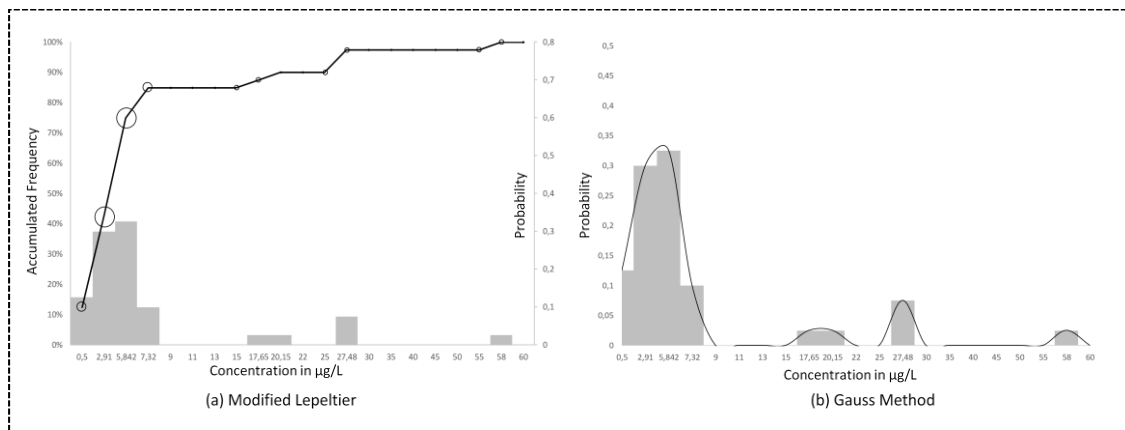


Figure 4: Distribution of concentrations for one type of geological formation according to Lepeltier (left) and Gauss (right) methods. Example for arsenic on metamorphic basement. The cases of arsenic and antimony on the different types of geological formations are represented in Supplementary Information,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

4.1.2 Integration of geological and geomorphological parameters

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

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

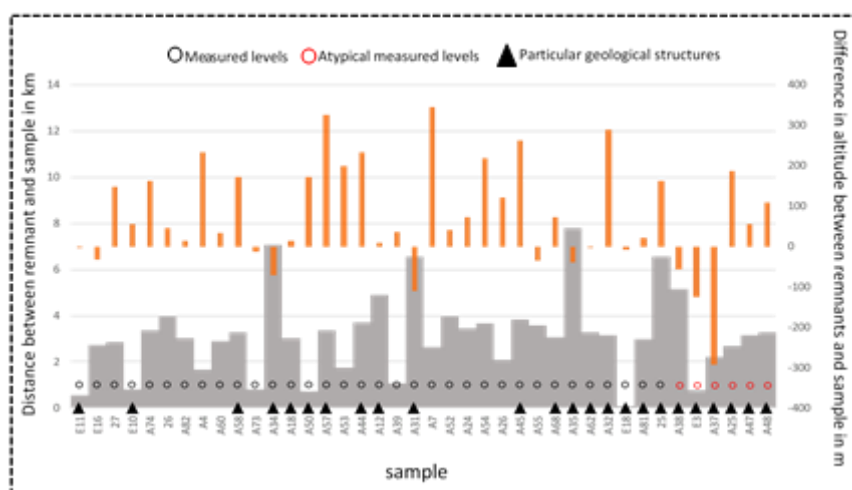


Figure 5: Superimposition of the geographical characteristics of the samples (distance (grey bars) and difference in altitude (orange bars) between remnant and sample; proximity to particular geological structure (dark triangle)) on the measurements observed for a substance (samples belonging to the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

4.1.3 Discrimination of geochemical background from anthropogenic contributions

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

Arsenic: for metamorphic base aquifers the calculated geochemical background varies in the 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 bedrock and massif aquifers the calculated geochemical background varies in the range] 0.1; 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 sedimentary cover, the calculated geochemical background varies in the range] 0.1; 3.79 [$\mu\text{g} / \text{L}$ 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 calculated geochemical background varies in the interval] 0.4; 6.52 [$\mu\text{g} / \text{L}$ with a mean of 4.03 $\mu\text{g} / \text{L}$ and a median of 4.13 $\mu\text{g} / \text{L}$.

Antimony: for metamorphic base aquifers the calculated geochemical background varies in 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 crystalline basement and massif aquifers, the calculated geochemical background varies in 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 aquifers of the sedimentary cover, the calculated geochemical background varies in the 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 surface aquifers, the calculated geochemical background varies in the interval] 0.01; 0.92 [$\mu\text{g} / \text{L}$ with an average of 0.62 $\mu\text{g} / \text{L}$ and a median of 0.59 $\mu\text{g} / \text{L}$.

Uncertainty

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

background and the main population was made (Table 2; Figure SI-5). Generally speaking, the main population showed very similar characteristics to the calculated geochemical background. The median, mean and standard deviation were quite stable. The measured concentrations, unlike the main population and the geochemical background, showed a strong variation in the dispersion characteristics, in particular the mean and standard deviation. This proves that the residual secondary population is the main factor modifying the 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
Geochemical support								
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%[
Characterisation and evaluation of geochemical media								
Characteristics of the measured contents								
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
Characteristics of the calculated geochemical background								
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

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

4.1.4 Cartography Summary

4.1.4.1 Qualitative classification of anthropic disturbances

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

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

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

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

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

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

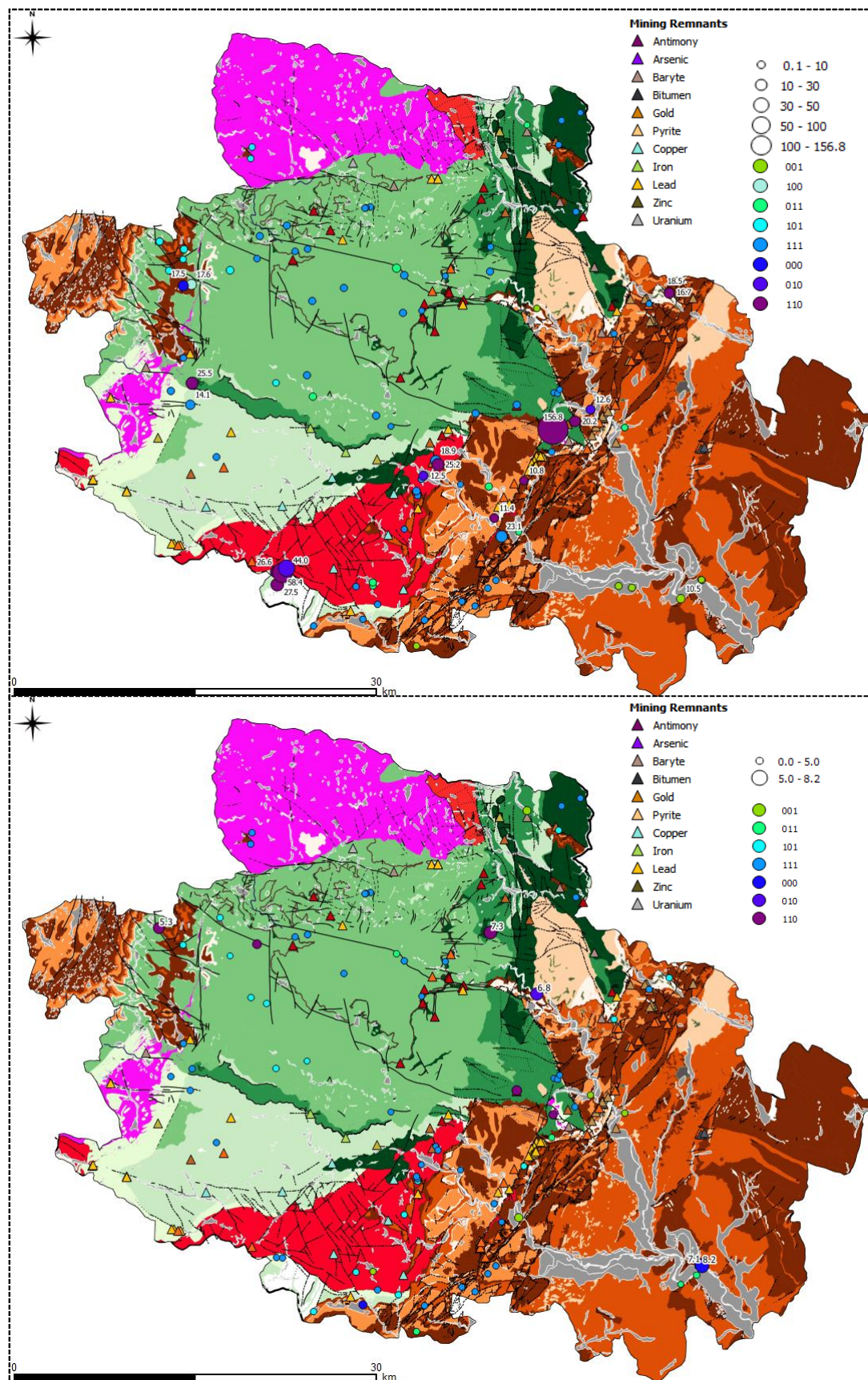


Figure 6:Qualitative classification of anthropogenic disturbances for (a) arsenic and (b) antimony

4.1.4.2 Quantitative perception

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

Arsenic

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

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

Antimony

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

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

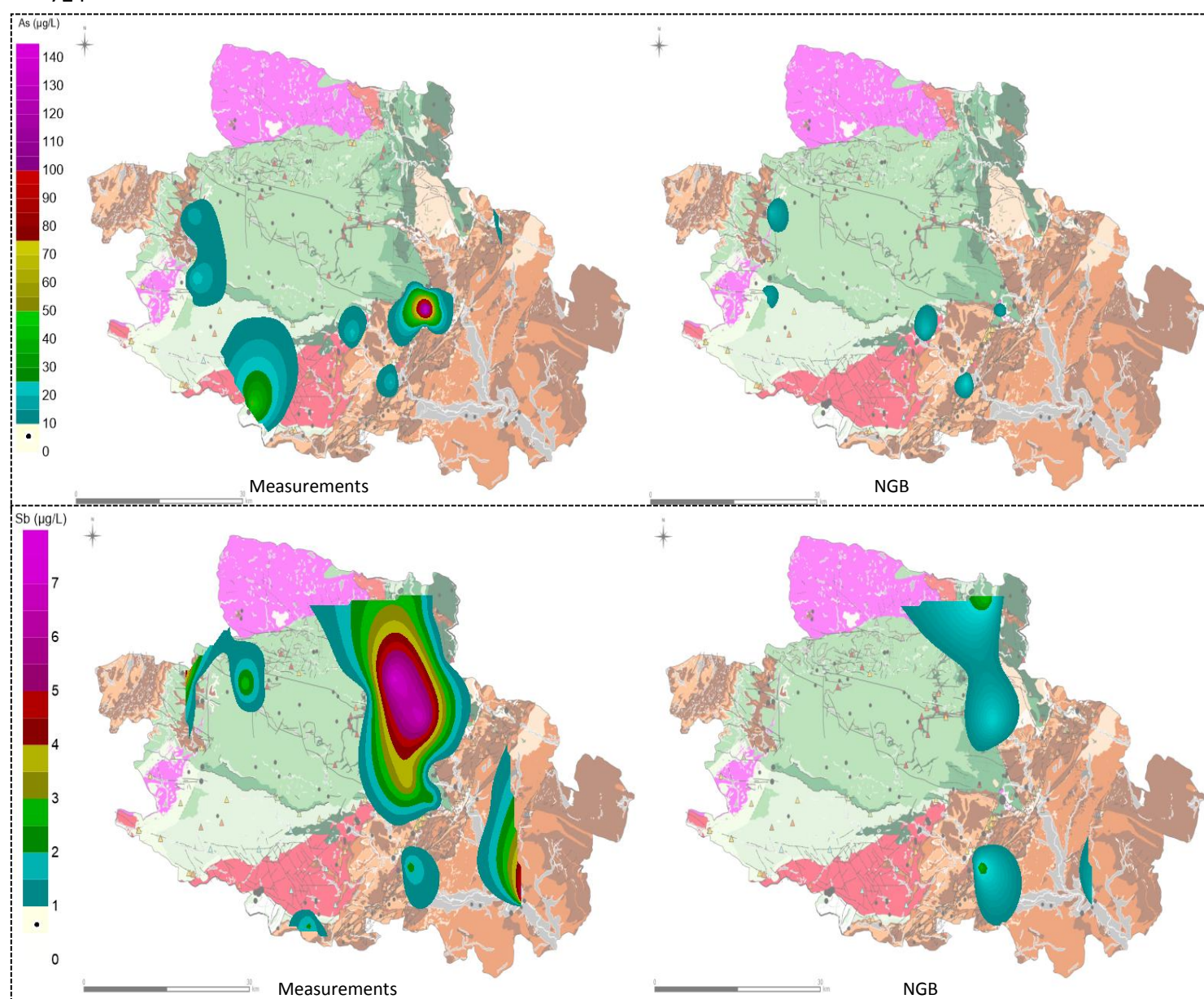


Figure 7: Map representing measured isoconcentration curves (left side) and estimated Natural Geochemical Background (right side) for arsenic (up) and antimony (down)

4.2 Discussion

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

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

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

There is no universal approach to determine the natural geochemical background with absolute 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

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

Is the methodology generalizable?

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

Which limitations?

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

5. Conclusion

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

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847

848 **Declaration of Interest statement**

849

850 Declarations of interest: none

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