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# **Spatial distribution of trace elements in the soils of south-western France and identification of natural and anthropogenic sources**

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Abstract:

The contamination of soils by trace elements is a major concern for soil quality. This study is based on the analysis of 356 samples from the RMQS soil-monitoring network to establish the spatial distribution and origin of six trace elements (As, Cd, Cu, Cr, Ni, Pb) in soils of south-western region of France (area of 90,293 km<sup>2</sup>). An exploratory and multivariate statistical analysis, and geostatistics combined with a geographic information system (GIS) were used to identify and characterize any concentration anomalies in trace elements. For all the trace elements studied, the exploratory analysis shows that there are more anomalies in this region than in the rest of the country. Analysis of the semivariograms shows that the six elements are spatially auto correlated. The spatial structure of As highlights anisotropic behaviour with a direction that corresponds to the gold deposit and mining activities of the region. This indicates a dual origin anthropogenic and geogenic for As. The correlation between Cd and inherent features of calcareous soil (pH, CaCO<sub>3</sub> and cation exchange capacity) suggest a mainly geogenic origin for this element; Cd origin is confirmed by its spatial distribution associated with the Jurassic limestone bedrock. The correlations between Cr, Ni and clays highlight a geogenic origin for these elements, as weathered parent material rich in clays is also rich in Cr and Ni. The high Cu concentrations are of anthropogenic origin, linked to viticulture and the spreading of Bordeaux mixture as a fungicide. Locally high Pb concentrations are associated with mining activities and automobile emissions in large cities in the region.

## 33 **1. Introduction**

34 The contamination of soils by trace elements (TE) are of major concern with regard to  
35 potential plant growth and food health issues due to high concentrations of metals and/or  
36 metalloids in soils (McLaughlin et al., 1999). TEs are naturally present in soils. Their natural  
37 concentrations depend not only on the physical and chemical weathering of the parent rock  
38 and on pedogenesis, but also on the transport of materials of colluvial, fluvial and even wind  
39 origin; they also depend on their mobility, which is different from one element to another  
40 depending on the physico-chemical parameters (e.g. pH, Eh,...). TE concentrations in soils  
41 can be modified significantly by anthropogenic pressures of urban, industrial, mining and  
42 agricultural origin (Belon et al., 2012). Thus, anthropogenic inputs can exceed inputs from  
43 natural cycles and the assimilative capacity of soils. Due to natural variability and widespread  
44 and diffuse anthropogenic inputs, it is common for the spatial distribution of TE  
45 concentrations in soils to be not random. That is, observations that are close to each other tend  
46 to resemble each other more than those that are further away. It is therefore common for TE  
47 concentrations in soil topsoil to be spatially correlated. In this case, geostatistical  
48 spatialisation methods may prove useful in assessing spatial variability and sources of trace  
49 elements in soils (Atteia et al., 1994; Facchinelli et al., 2001). The combined use of  
50 Geographic Information System (GIS) and tools such as multivariate analysis and exploratory  
51 data analysis can help determine the origin of trace elements (Facchinelli et al., 2001; Hou et  
52 al., 2017; Saby et al., 2009).

53 The spatial distribution of trace elements over large national or continental areas has been  
54 studied for a long time in order to establish geochemical baseline (Chen et al., 1991; McGrath  
55 and Loveland, 1992; Salminen, 2005; Shacklette and Boerngen, 1984). More recently,  
56 national and continental soil monitoring networks have been set up in Europe to determine  
57 soil qualities (including TE content) and monitor their temporal and spatial changes in TE

58 levels (Morvan et al., 2008). In Europe, the LUCAS survey was launched to build a consistent  
59 spatial database of the soil cover over the EU (Orgiazzi et al., 2018). In France, the national  
60 monitoring network (Réseau de Mesures de la Qualité des Sols, RMQS), was designed to  
61 assess the concentration of 11 TE (As, Cd, Cr, Cu, Hg, Mo, Ni, Pb, Tl, Zn), among other  
62 objectives (Arrouays et al., 2003). This network has enabled the spatial distribution of trace  
63 elements in soils to be established at a national scale (Marchant et al., 2017, 2010; Saby et al.,  
64 2011). We propose to use this network at a regional scale, over the southwestern region of  
65 France (SWF), which covers a surface of 90,293 km<sup>2</sup> similar to European countries such as  
66 Belgium, Austria or mainland Portugal.

67 The main objective of this study was to determine the spatial distribution and origin of TE in  
68 the soils of SWF; this in order to produce knowledge that can be used to support regional  
69 territorial decisions. Indeed, in this region the agricultural productions are numerous and  
70 varied, and they are subject to many risks of contamination by TE, either of geogenic origin  
71 or of anthropogenic origin. To achieve this objective, we (i) used the national RMQS  
72 program, (ii) determined the reference concentrations of selected TE in the SWF soils, (iii)  
73 determined their spatial variability in the region using geostatistics, and then, (iv) highlighted  
74 anomalies and their origins using statistical and geostatistical tools and the crossing of  
75 geographic databases with spatial distributions. The trace elements were selected according to  
76 the risk of contamination for the production of food biomass. Therefore, the following  
77 elements were considered:

78 - As, ubiquitous metalloid, the use of which as a pesticide and the presence in mineral  
79 fertilizers have led to severe pollution of soil and water, causing accumulations in the food  
80 chain. This element presents a high health risk because it is toxic in all its inorganic forms  
81 (Mandal, 2002).

82 - Cd, found in phosphate fertilizers and manure spread on soils (Belon et al., 2012). This  
83 element presents a high health risk as a carcinogen (IARC, 1993).

84 - Cu, widely used in vineyard areas and present in the manure spread. This element affects  
85 the microbial life of the soil due to its biocidal action (Ranjard et al., 2008).

86 - Cr, resulting from industrial activities (e.g. effluents from tanneries) and which can be  
87 found in soils due to irrigation. It is also brought into the soil by manure spreading. This  
88 element presents a health risk because it is carcinogenic in its hexavalent form.

89 - Ni, brought into the soil by manure spreading, due to mining activities or as a by-product  
90 associated with other types of pollutants such as PAHs (Barcan and Kovnatsky, 1998;  
91 Belon et al., 2012; Zehetner et al., 2009). This element is not very phytotoxic and presents  
92 less health risk than the elements above. However, anthropogenic contributions to soils can  
93 be significant (Rooney et al., 2007).

94 - Pb, from mining, industrial and road traffic emissions. Its accumulation in the food chain  
95 induces a significant health risk (lead poisoning).

96 Complementarily, Fe, Mn and Al were also considered to be major elements involved in  
97 different types of pedogenesis. Their concentrations were compared with the  
98 concentrations of the selected trace elements to highlight correlations and deduce the  
99 origin of these trace elements.

## 100 **2. Materials and methods**

### 101 *2.1 Study area*

102 The area includes the Nouvelle Aquitaine region, which is the largest agricultural region in  
103 France (39,000 km<sup>2</sup> of usable agricultural area) and the department of Gers. The agricultural  
104 production of this area is varied (field crops, livestock farming, viticulture and arboriculture).

105 The area also includes large forest areas (28,000 km<sup>2</sup>) with particularly the Landes de  
106 Gascognes massif, the largest forest surface of Western Europe, located to the south-west of  
107 the region (Figure 1A). The study area is inhabited by 6.1 million people, including  
108 1.2 million within the urban area of Bordeaux (Figure 1A).

109 The soils of this region are described by three major soil systems depending on the nature of  
110 the parent material and the climate (Figure 1B): (i) the soils derived from materials of  
111 sedimentary origin among which there are calcareous alkaline soils (Cambisol, Rendzina),  
112 acidic black sandy soils of the Landes (Podzol), and soils resulting from recent alluvial  
113 deposits (Fluvisol, Histosol, Gleysol) (Figure 1B); (ii) the Cambisols of the north-western part  
114 of the region are soils derived from materials of granite or metamorphic origin (Figure 1C),  
115 and (iii) in the south of the region, near the Pyrenees mountain range, the soils resulting from  
116 folded geological formations on which limestone Cambisols and Lithosols have formed.

## 117 2.2 *Sampling plan*

118 The RMQS network grid in SWF corresponds to 356 sampling sites, sampled between 2000  
119 and 2009. The locations of the sites were chosen if possible at the centre of each 16x16 km  
120 cell (Figure S1), or otherwise in a radius of 1 km around (Jolivet et al., 2006). The types of  
121 land use are also listed as well as the crop management technique used on each plot concerned  
122 by the sampling. On each site, soil samples were collected according to the protocol of the  
123 RMQS network manual (Jolivet et al., 2006): 25 individual cores in the topsoil (0-30 cm to  
124 +/- 5 cm depending on the thickness of the first organo-mineral horizon) using a stratified  
125 random sampling plan in an area of 20 × 20 m (see Figure S1). For each site, the cores were  
126 mixed to obtain composite soil samples. The organic horizon was discarded from composite  
127 soil samples. A pit was dug near (5 m) and to the south of the sampling area in order to  
128 describe the soil profile and to perform specific measurements (bulk density, coarse elements,

129 etc.). This protocol was used for all studies based on the RMQS (Marchant et al., 2017; Saby  
130 et al., 2011, 2006, 2009).

### 131 2.3 *Physico-chemical analyses*

132 Soil samples were air dried and sieved at 2 mm before analysis (AFNOR, 1994a). The  
133 granulometry (clays, coarse and fine silts, coarse and fine sands) was determined without  
134 decarbonation by Robinson pipette (AFNOR, 2003). The pH was measured after mixing the  
135 soil with deionised water (soil /water ratio 1/5, v/v) (AFNOR, 1994b). The cation exchange  
136 capacity (CEC) was determined by extracting cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ) with  
137 cobaltihexamine chloride (AFNOR, 1999).  $\text{CaCO}_3$  content was determined by treatment with  
138 HCl (12%), then the volume of carbon dioxide produced is measured with a Scheibler  
139 apparatus (AFNOR, 1995a). The total organic carbon and total nitrogen contents were  
140 determined by dry combustion after decarbonation (AFNOR, 1995b). The total concentrations  
141 of trace (As, Cd, Cr, Cu, Ni and Pb) and major elements (Al, Fe, Mn) were determined, after  
142 digestion of samples with a mixture of HF (49 %) /  $\text{HClO}_4$  (69 %) (5 / 1.5 mL), by inductively  
143 coupled plasma mass spectrometry for trace elements, and by inductively coupled plasma  
144 atomic emission spectrometry for major elements (AFNOR, 2001). These analyses were  
145 carried out by the Soils Analysis Laboratory of INRA in Arras (France), accredited by the  
146 French authorities for the analysis of soils and sludges.

### 147 2.4 *Statistical analyses*

148 The exploratory data analysis technique (Tukey, 1977) was used to obtain the reference total  
149 concentrations (median, minimum, maximum) of the studied TE. This method is based on  
150 nonparametric statistics (i.e. which do not depend on a probability law) and enables robust  
151 indicators (medians, quartiles) of the data set to be obtained (Reimann et al., 2005). The limit  
152 values, called lower whisker and upper whisker, are calculated with the following formulas:

153 (1) Lower whisker =  $Q1 - 1.5 \times IQR$

154 (2) Upper whisker =  $Q3 + 1.5 \times IQR$

155 where Q1 is the first quartile, Q3 the third quartile and IQR the interquartile range (Q3–Q1).  
156 Extreme values are defined as being outside the limit values. For the statistical analyses of  
157 this study, the concentration values below the limit of quantification were replaced  
158 numerically by half of the value of the limit of quantification (Farnham et al., 2002).  
159 Cartograms of the study area were generated to illustrate the distribution of concentrations of  
160 studied trace elements relating to each sampling site with a classification by quartiles.

161 Principal component analysis (PCA) enables the correlations (or their absence) between  
162 selected variables to be highlighted. When PCA was applied to TE concentrations in soils, it  
163 provided answers regarding their sources (Facchinelli et al., 2001). A PCA was therefore  
164 carried out by taking as variables the concentrations of the 6 selected trace elements (As, Cd,  
165 Cr, Cu Ni, Pb) and pedologic variables: the concentrations of the major elements (Fe, Mn and  
166 Al), granulometry (5 fractions), pH, organic carbon and total nitrogen. The data analysis was  
167 carried out with R software version 3.5.1 (R Core Team, 2019) and for the calculation of the  
168 PCA the FactoMineR library was used (Lê et al., 2008).

### 169 2.5 *Spatial and geostatistical analysis*

170 The geostatistical treatments were carried out from the study of semivariograms.  
171 Semivariograms are used to describe the structure (organization and regularity of the variable  
172 in the space considered) and the spatial variability of the data. They estimate the semivariance  
173  $\gamma(h)$  of a variable measured at two points distant from  $h$ , and thus estimate the importance of  
174 the link (i.e. the degree of continuity) between these points for this variable (autocorrelation).  
175 Semivariograms show how the information between two measurement points of this variable  
176 degrades as the distance increases. The evolution of information is therefore represented by an



177 increasing function up to a sill defined by the maximum interpolation distance. This distance  
 178 also corresponds to the distance from which two consecutive values are independent. The  
 179 equation of the semivariogram is:

$$180 \quad (3) \quad \gamma(h) = \frac{1}{2N(h)} \sum_{i=1}^{N(h)} \left\{ [Z(x_i + h) - Z(x_i)]^2 \right\}$$

181 where  $\gamma(h)$  is the semivariance,  $N(h)$  the number of point pairs,  $h$  the distance between 2  
 182 points,  $Z(x_i)$  is the concentration of the element at location  $x_i$ . The experimental  
 183 semivariograms of the various variables considered were calculated for an interpoint distance  
 184 of 16 km (which corresponds to the size of the cell of the RMQS grid). They were then  
 185 empirically fitted by a mathematical function comprising a sill. The fitting enabled  
 186 information on the spatial structure of the variable to be obtained thanks to the following  
 187 parameters: the nugget (value of the y-intercept; represents the part of variability lower than  
 188 the sampling interval), the sill, and the range (distance from which the sill is reached and  
 189 beyond which there is no longer any autocorrelation). The fitting of the semivariogram by an  
 190 experimental empirical mathematical model was performed by iterative least squares  
 191 weighting, minimizing the following expression:

$$192 \quad (4) \quad \sum_{j=1}^n N(h) (\hat{\gamma}(\bar{h}_j) - \gamma(\bar{h}_j))^2$$

193 Where  $\gamma(\bar{h}_j)$  is the experimental value of the semivariance, and  $\hat{\gamma}(\bar{h}_j)$  is the modeled value  
 194 of the semivariance. The geostatistical calculations were carried out with the gstat library and  
 195 the R software (Pebesma, 2004). The ratio between the nugget and the total variance  
 196 (hereinafter called nugget/variance ratio) was calculated in order to have a relative assessment  
 197 of the nugget effect (expressed in %), which is more explicit than the absolute value and  
 198 enables comparisons. The anisotropy was studied from a semivariance map with two direction  
 199 axes for each trace element considered. This map enables a possible preferential direction in

200 the variation of the semivariance to be highlighted. Directional semivariograms were modeled  
201 with an angle tolerance of 45° to obtain a sufficient number of point pairs.

202 From the semivariogram modeling parameters (nugget, sill, range), ordinary kriging was  
203 applied to produce spatial distribution maps of TE concentrations. The maps were generated  
204 using ArcGIS version 10.1 software (Esri, 2012). Several databases were used to determine  
205 the origin of the trace elements: SIG Mines France for the location of old mines and ore  
206 deposits (BRGM, 2007), and BD-CHARM geological maps (scale 1/50000) for parent  
207 material (BRGM, 2005). Soil occupation was described directly from the RMQS sites. All  
208 these data were crossed with the distribution maps of the trace elements in order to highlight  
209 the possible sources of contamination and the modes of transfer of these elements to the soil.

210

### 211 **3. Results and discussion**

#### 212 *3.1 Descriptive statistics*

213 The preliminary observation of the statistical variables enables any particularities of the  
214 studied dataset to be identified, and thus a better guided statistical analysis strategy to be  
215 carried out.

216 Table 1 presents the statistical characteristics of the concentrations of the trace elements  
217 studied. The regional and national median values are close, which seems to show the  
218 homogeneity of the concentrations in SWF compared to the whole of France. In more detail,  
219 Figure 2 shows the maps of TE concentrations. The distribution of concentrations does not  
220 appear to be regular. In particular, on the one hand, the Landes massif (around 15 % of the  
221 soil samples) shows very low concentrations of the trace elements studied. On the other hand,  
222 by defining the whiskers as anomaly thresholds, there are more sites with anomalous TE  
223 concentrations (As, Cu, Pb) in the SWF according to the national threshold than according to

224 the regional threshold (Table 1). Therefore, there would be geogenic anomalies and/or  
225 regional contaminations for As, Cu, and Pb while anomalies would be less substantial for Cd,  
226 Cr and Ni. All of these observations highlight the interest of carrying out a more in-depth  
227 spatial study in order in particular to locate these anomalies and identify their origin. In  
228 addition, Table 2 presents the statistical characteristics of the soil variables considered in this  
229 study. For all these variables, large amplitude of values is observed for the 356 soils sampled.  
230 This is particularly the case for the concentrations of clay, pH, CaCO<sub>3</sub>, organic matter, Fe and  
231 Al. Special attention was therefore granted to these variables, known to drive the TE  
232 variability.

### 233 *3.2 Multivariate analysis: first approach to the origin of the trace elements*

234 In order to complete the previous observations by considering all the information points of the  
235 datasets, a multivariate analysis was carried out by PCA. Figure 3 presents, by decreasing  
236 contributions, the 6 components (or dimensions) that explain 79% of the total variance. The  
237 main contributions of the variables to the components are as follows (Table S1). The  
238 concentrations of clay, coarse sand, Al, Fe, Cr, Ni, Cd and CEC for the principal component 1  
239 (PC1); organic carbon, total nitrogen, pH and CaCO<sub>3</sub> for principal component 2 (PC2); coarse  
240 silt, CaCO<sub>3</sub>, CEC, pH and Cd for PC3; As, silt, carbon and nitrogen for PC4; fine sand, Pb  
241 and Cu concentration for PC5; fine sand and Cu for PC6. The negative correlation between  
242 coarse sands and TE concentrations suggests that soils with a high percentage of coarse sand  
243 are rather poor in trace elements. This is confirmed by the lowest TE concentrations that are  
244 located in the Landes forest, with mainly sandy soils of recent geological formation (<1 Ma),  
245 and with an acidic pH which causes the solubilisation of the elements (Righi and Wilbert,  
246 1984). In addition, sand has a lower specific surface, which does not promote the adsorption  
247 of elements (Daskalakis and O'Connor, 1995; Schiff and Weisberg, 1999).

248 It can be also observed:

249 - In Figure 3A, the concentrations of Cr, Fe, Ni and the clay content correlate positively.

250 This suggests a rather geogenic origin of Cr and Ni. Indeed, the materials resulting from  
251 the degradation of rocks rich in Cr and Ni are also rich in clays. Thus Cr, Ni and clays  
252 would remain bound after the weathering of these rocks and transfer to the soil (Cheng et  
253 al., 2011; Kierczak et al., 2007). This was observed in a previous study (ASPITET) on  
254 trace elements in soils in France (Baize, 1997).

255 - In Figure 3B, Cd concentrations,  $\text{CaCO}_3$ , pH and CEC also correlate positively. In the  
256 study region, soils with high  $\text{CaCO}_3$  content, pH, and CEC are limestone soils. The  
257 association between Cd and certain carbonate minerals could therefore explain this  
258 correlation, as it was already observed in natural environments (Chada et al., 2005; Martin-  
259 Garin et al., 2002). This association is the result of the carbonate dissolution reaction,  
260 where  $\text{Cd}^{2+}$  would replace  $\text{Ca}^{2+}$  to form  $\text{CaCO}_3\text{-CdCO}_3$  or  $\text{CdCO}_3$  (Papadopoulos and  
261 Rowell, 1988). The introduction of Cd into soils by amendments based on calcium  
262 carbonates and phosphate fertilizers is also a possible source of Cd in soils (Senesil et al.,  
263 1999).

264 - In Figure 3C and 3D, no correlation could be noted for the concentrations of As, Cu and Pb  
265 with the other variables in PCs that explain a low amount of the total variance. This  
266 suggests rather a predominantly anthropogenic origin of these elements.

### 267 3.3 *Spatial and geostatistical analysis: factors influencing spatial distribution*

268 In order to bring a spatial dimension to the analysis of TE concentrations, their  
269 semivariograms were calculated and are shown in Figure 4. These semivariograms were  
270 obtained using equation (3) and are given with their associated parameters (especially nugget  
271 effect, range and nugget/variance ratio; shown in the column to the right of each

272 semivariogram). To complete, Figure 5 presents the thematic maps of the TE concentrations  
273 predicted by ordinary kriging (using the parameters of the semivariograms of each trace  
274 element). Geographical information on land use, mining activities, parent material and  
275 mineral deposits are overlaid on concentration maps. Thus, all of the information obtained and  
276 used can be viewed together.

277 All semivariograms (Figure 4) are bounded. This means that the spatial structures of the TE  
278 concentrations are included in the regional study area. In other words, the concentrations of a  
279 given trace element spatially depend on the range scale, which varies from 86 to 154 km  
280 depending on the element considered. For all variograms, the nugget/variance ratios are  
281 between 40 and 80 %. These values are partly induced by the size of the sampling grid  
282 (16x16 km). This indicates that it was not possible to detect significant local variations.

283 The directional analysis of the semivariograms revealed an anisotropy for As only, as  
284 illustrated in Figure 6. The spatial structure of this element differs according to the direction  
285 considered (as illustrated in the Figure S2 drawn in orthogonal directions north–south and  
286 east–west). In particular, in the north–south direction (0°) the semivariogram is circular,  
287 without nugget effect and with a very short range (24 km). In the northeast–east direction  
288 (60°) the semivariogram is spherical, with a strong nugget effect and a range close to that of  
289 the omnidirectional semivariogram (115 km). The direction of the directional semivariogram  
290 of As (60°) points to the gold mining zones located to the north and northeast of the region. In  
291 this area, the deposits consist of quartz veins containing native As and Au-As-S minerals  
292 resulting from hydrothermal processes in granitic and metamorphic rocks (gneiss).  
293 Consequently, As can be considered as a geochemical tracer of Au in this area (Bossy, 2010;  
294 de Gramont and Braux, 1990). In addition, gold mining from the Gallic period until the end of  
295 the 1960s led to the contamination of the Isle watershed by mining residues and therefore in  
296 particular by As (Cauet, 1991; Courtin-Nomade et al., 2002; Grosbois et al., 2007).

297 Cd does not exhibit a particularly high nugget/variance ratio (60 %) but has a greater range  
298 compared to the majority of trace elements studied (> 135 km). This suggests a distribution of  
299 Cd due to a single and extended source. In fact, and given that Cd is positively correlated with  
300 pH and CEC, the presence of Cd would correspond to the presence of limestone substrates  
301 (parent material and/or coarse fragments), therefore to a mainly geogenic origin. This is in  
302 agreement with the work by Atteia et al. (1995) in the Swiss Jura and Baize et al. (1999) in  
303 Bourgogne, where the Cd concentration was correlated with Jurassic age limestone. This  
304 interpretation is also relevant insofar as such limestone soils of the same geological age are  
305 present in the SWF, in particular in the departments of Dordogne and Charentes, i.e. in the  
306 centre and northwest of the region, respectively (Figure 5). Very high Cd concentrations were  
307 also found at two sites located on the alluvial deposits of the Garonne river (Figure 5). These  
308 anomalies can be explained by the historical cadmium contamination of the Lot-Garonne  
309 hydrological continuum that carries suspended matter directly from the Decazeville industrial  
310 basin following the extraction and processing of ores rich in Zn and Cd or indirectly due to  
311 the remobilization of sediments accumulated behind the dams of the Lot river (Audry et al.,  
312 2004; Coynel et al., 2009, 2007; Dabrin et al., 2009; Pougnet et al., 2019).

313 Cu has the highest nugget/variance ratio (81 %) and a large range (112 km), which can be  
314 explained by the anthropogenic input of this element in the vineyards of the region (Figure 5).  
315 Indeed, Cu has been used in viticulture in a mixture of copper sulphate and lime (Bordeaux  
316 mixture) to fight against downy mildew (*Peronospora viticola*) since the end of the 19th  
317 century (Ayres, 2004). This cultivation practice has led to diffuse soil contamination in  
318 French wine-growing areas and in particular in Gironde, as mentioned in previous studies  
319 (Baize et al., 2006; El Hadri et al., 2012). However, this contribution remains very  
320 heterogeneous depending on the vine management technique chosen by the winegrowers as  
321 well as the variability of the fungal pressure.

322 Cr and Ni have the lowest nugget/variance ratios (41 and 44% respectively). Less spatial  
323 variability than for the other trace elements therefore appears for distances <16 km. This  
324 suggests that the distribution of these two elements is mainly natural. This hypothesis would  
325 be supported on the one hand by the fact that Cr and Ni are known to be not very mobile in  
326 soils. On the other hand, these elements are usually found strongly adsorbed on the mineral  
327 components of the soil such as calcite, illite and montmorillonite (Businelli et al., 2004;  
328 Hickey and Kittrick, 1984; Mamindy-Pajany et al., 2013; Navarro-Pedreño et al., 2003). This  
329 is relevant given the positive correlation with clays found above. The Cr and Ni  
330 concentrations in SWF soils therefore appear to depend on the underlying bedrock, with high  
331 concentrations being found in soils from Jurassic and Cretaceous rocks (Figure 5). This  
332 dependence was already observed for the RMQS network at the national level (GIS Sol,  
333 2011). Similar results were found by the FOREGS program on French soils (Salpeteur and  
334 Maldan, 2011). If anthropogenic contaminations are possible, for example by spreading  
335 sludge or due to industrial discharges, then they are probably very localised and therefore not  
336 detected in the RMQS grid.

337 Pb has a high nugget/variance ratio (79%), with a lower range than the other elements (85  
338 km). Its regional spatial distribution shows high concentrations in the north and northeast of  
339 the region, with spots near large urban areas (Bordeaux, Bayonne, etc.) (Figure 5).  
340 Concentrations in the northeast of the region are believed to be mainly of mining origin  
341 (Courtin-Nomade et al., 2002; de Gramont and Braux, 1990). The spots close to large cities  
342 are likely due to the density of traffic and the use of leaded gasoline until 2000 in France. The  
343 work by Saby et al. (2006) led to a similar observation around the Paris urban area. Several Pb  
344 spots are also found in forests and Pyrenean passes. They could come from hunting activities,  
345 Pb shot being disseminated in soil samples (Mellor and McCartney, 1994; Tsuji and  
346 Karagatzides, 1998).

### 347 3.4. *Statistical approaches: representativeness and limits*

348 The relatively high nugget/variance ratios obtained with semivariograms indicate that local  
349 variations of TE concentrations cannot be detected by the 16x16 km grid. In other words, local  
350 “hot spots” of TE concentrations may not be detected. Therefore, the issue of the  
351 representativeness of the study on a regional scale could be raised. An analysis of the  
352 representativeness of the different grid sizes (32x32, 16x16, 8x8 km) to design the RMQS  
353 network was carried out (Arrouays et al., 2001). The analysis was based on the pair: soil type  
354 – soil use pair. Results showed that with a 16x16 km grid, only 2.5% of the pairs are not  
355 represented. In the SWF, the unrepresented part corresponds to small areas of vineyards and  
356 orchards, which could have a significant input of TE. Targeted densification of the grid (e.g.  
357 8x8 km) would help to better characterize these areas. However, this would also greatly  
358 increase the number of sampling sites and consequently the implementation cost of the  
359 network and the duration of the sampling.

360 In the present work we used upper whiskers as a first approach to detect anomalies in the TE  
361 distribution. This simple approach, using descriptive statistics, has been widely used in  
362 geochemical studies, including other studies based on the RMQS dataset (Redon et al., 2013;  
363 Saby et al., 2009; Villanneau et al., 2008). However, it needs to be completed from other  
364 approaches to discriminate between geogenic and anthropogenic anomalies. Saby et al. (2009)  
365 determined the spatial patterns of TE over the whole of France with a spatially constrained  
366 multivariate analysis method. The authors also identified the geogenic origin of Cd associated  
367 with Jurassic limestone and the anthropogenic origin of Cu associated with the vineyard. At a  
368 regional scale, Redon et al. (2013) combined the soil classification between calcareous and  
369 non-calcareous soils, with several statistical methods (upper whiskers, enrichment factor,  
370 PCA, linear regression) over the former Midi-Pyrénées region, adjacent to our study area. The  
371 authors obtained similar results to ours, with Cu anomalies associated with the vineyard, but



372 found Cd and Pb contamination in grazing land suggesting sources from organic fertilization.  
373 Finally, in the present work, we combined geostatistics and GIS that had the advantage of  
374 producing intuitive maps with both TE concentrations anomalies and their associated sources.

#### 375 **4. Conclusion**

376 The spatial distribution and variability of As, Cd, Cu, Cr, Ni, Pb for the south-western region  
377 of France could be determined on the basis of the RMQS systematic sampling grid. The  
378 regional median concentrations of these elements are close to the national values. However,  
379 regional anomalous concentrations were highlighted by comparing with regional and national  
380 whiskers taken as threshold values of anomaly and possible contamination. The origins of  
381 these trace elements in SWF soils were identified combining cartographic and geostatistical  
382 methods. Thus, As has a dual origin geogenic and anthropogenic, from gold deposit and  
383 mining activities. Cu and Pb have anthropogenic origins, either linked to a main activity like  
384 viticulture (Cu), or consecutive to several activities, mining, hunting and automobile traffic  
385 (Pb). Cd, Cr and Ni are mainly of geogenic origin at the regional scale. In most cases,  
386 contaminated areas are well demarcated. The Landes massif, with mostly sandy soils, contains  
387 little content of trace elements.

388 The investigation approach used, combining systematic monitoring network and geostatistical  
389 method, has thus shown its capability to detect contaminations in trace elements and to  
390 identify their origins on a regional scale. This is possible despite a relatively large grid (16x16  
391 km). This approach could therefore be transposable to countries with comparable surface  
392 areas. Systematic soil monitoring networks have a dual interest: on the one hand, the data  
393 acquired relating to soil quality can be used as a support element for national and regional  
394 territorial decisions. This may concern environmental protection, agroecological transition or  
395 food safety. On the other hand, these databases could be extended to other TE, not only those

396 monitored in the RMQS network but also to TE barely or not yet taken into account.  
397 Emerging contaminations in the soil could then be identified. This would help to support  
398 public decisions for the reduction and anticipation of pollution. This second point is  
399 particularly important given the development of new technologies leading to an increasing use  
400 of new elements (Alonso et al., 2012). These include the use of catalytic converters containing  
401 platinoids (Pd, Pt, Rh), smartphones containing rare metals (such as Nd or Y) or MRI contrast  
402 agents containing Gd (Lerat-Hardy et al., 2019; Schäfer et al., 1998). Finally, this type of  
403 network could also enable changes in soil quality to be monitored by the early detection of  
404 degradation that might be expected or not. A new campaign of soil sampling is ongoing for  
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415

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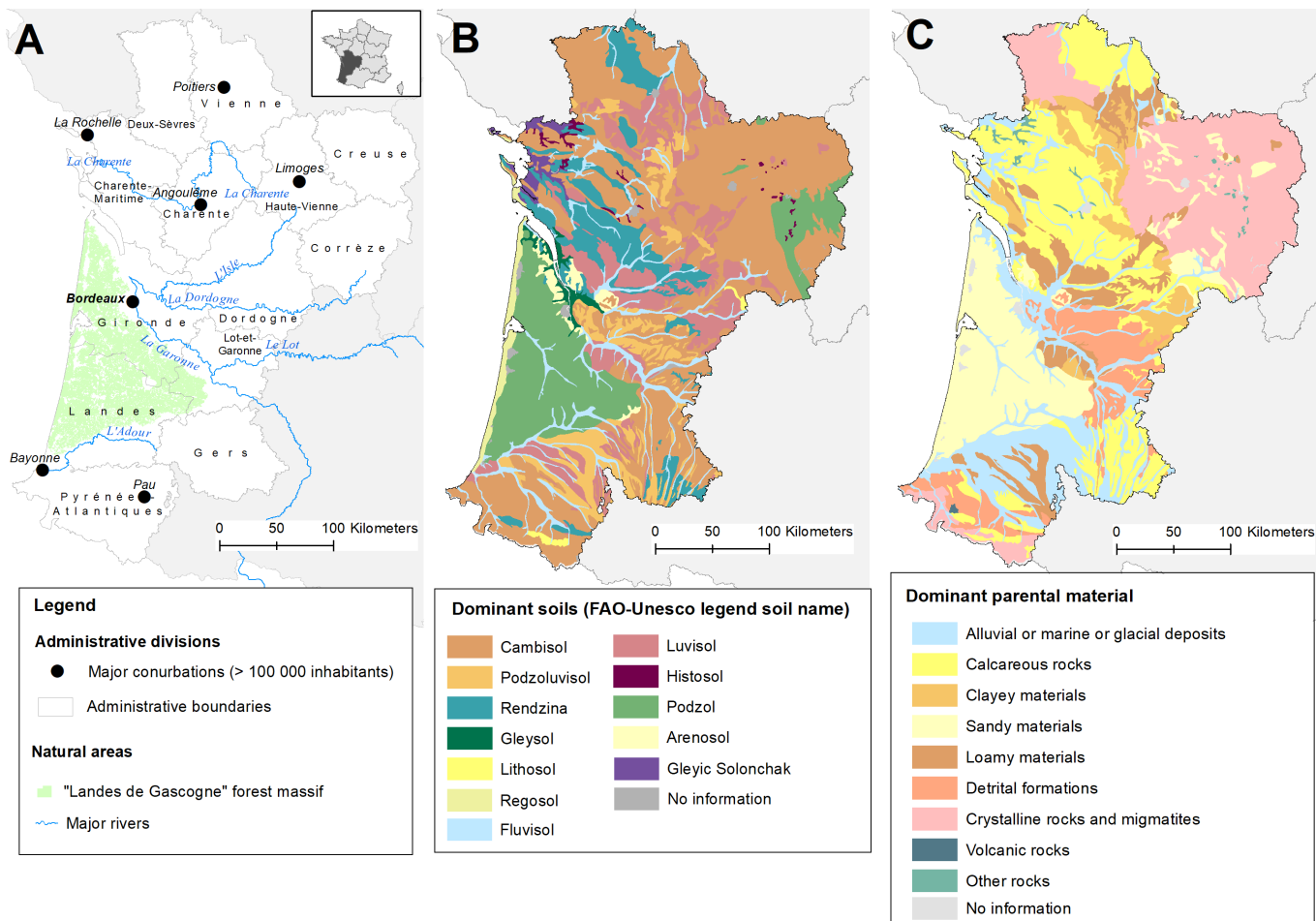
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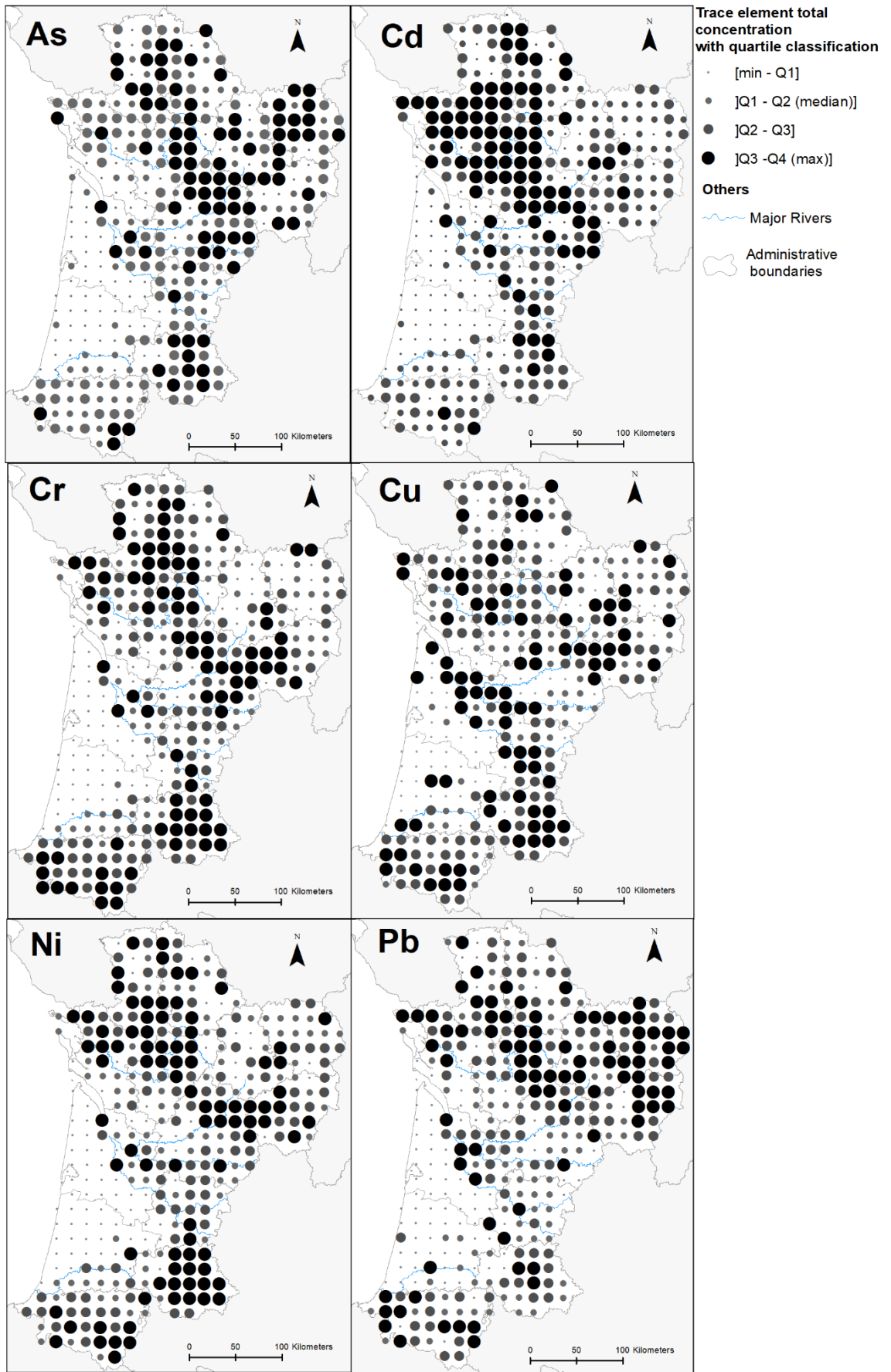
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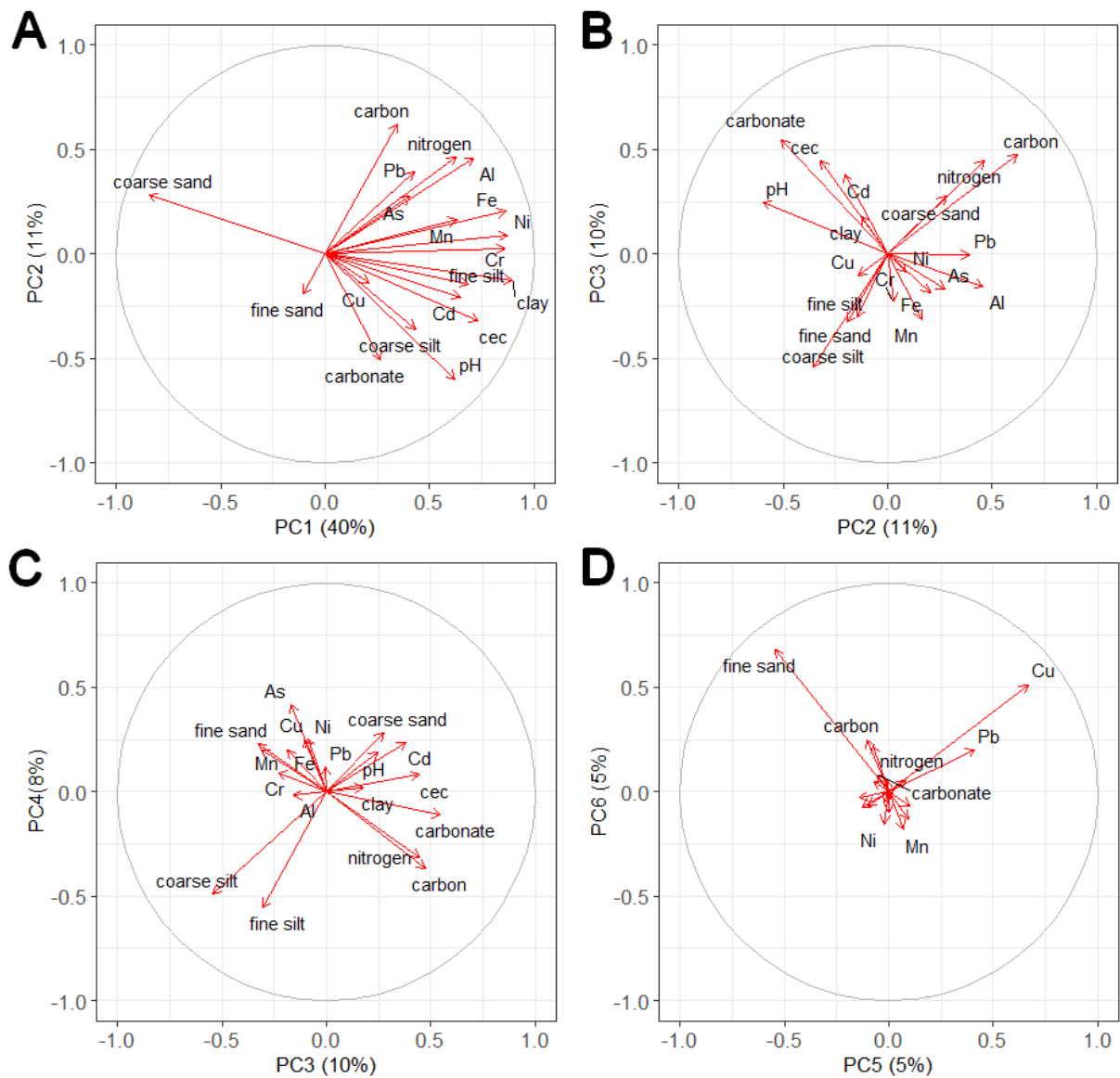




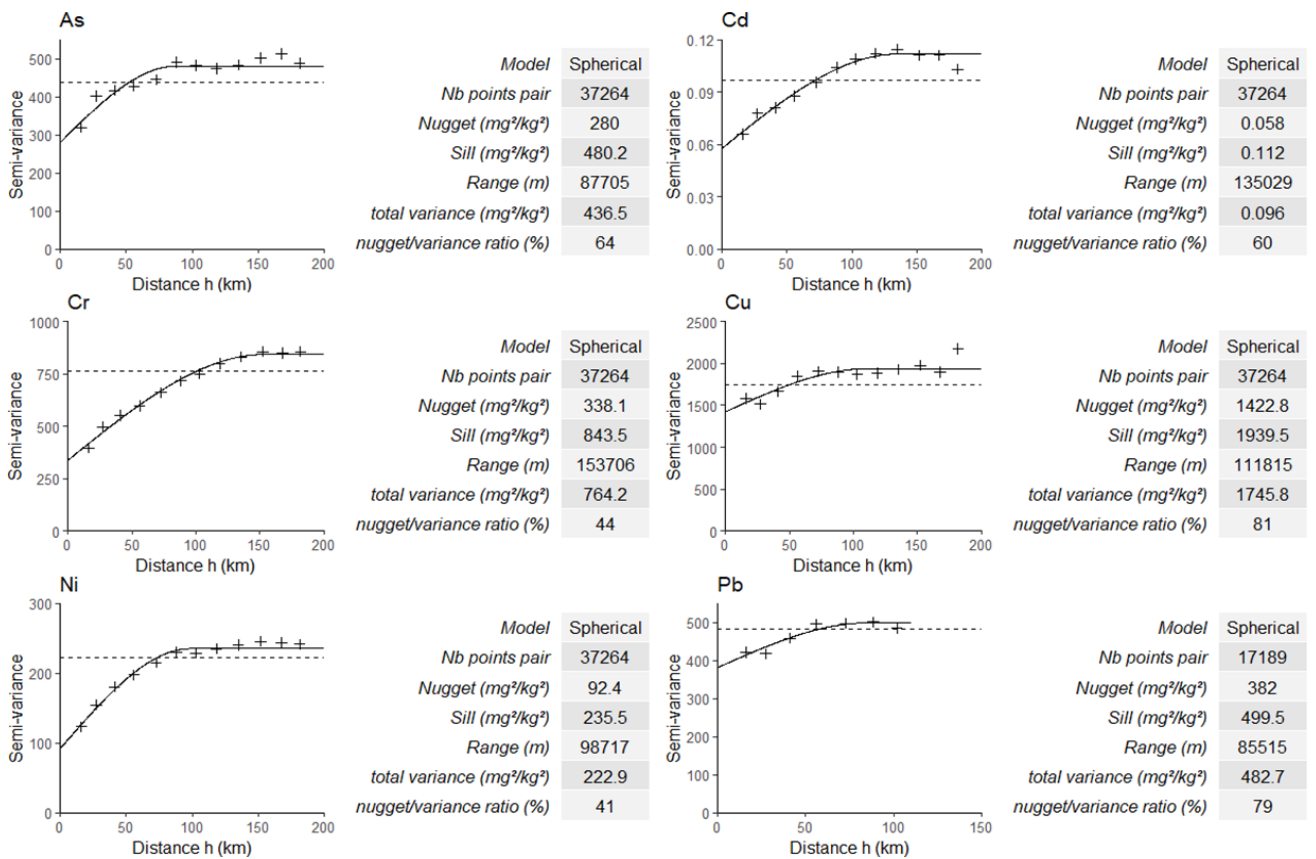
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 645 Figure 1: A) Map describing the administrative divisions of the study area and major natural areas. B) Map  
 646 of dominant soils from the Soil Geographical Data Base of France (BDGSF) at scale 1:1000000 (INRA,  
 647 2018). C) Map of the dominant parent material from the BDGSF.  
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649 Figure 2: Point distribution of As, Cd, Cr, Cu, Ni and Pb concentrations with classification by quartile in  
 650 the topsoil of southwestern France.

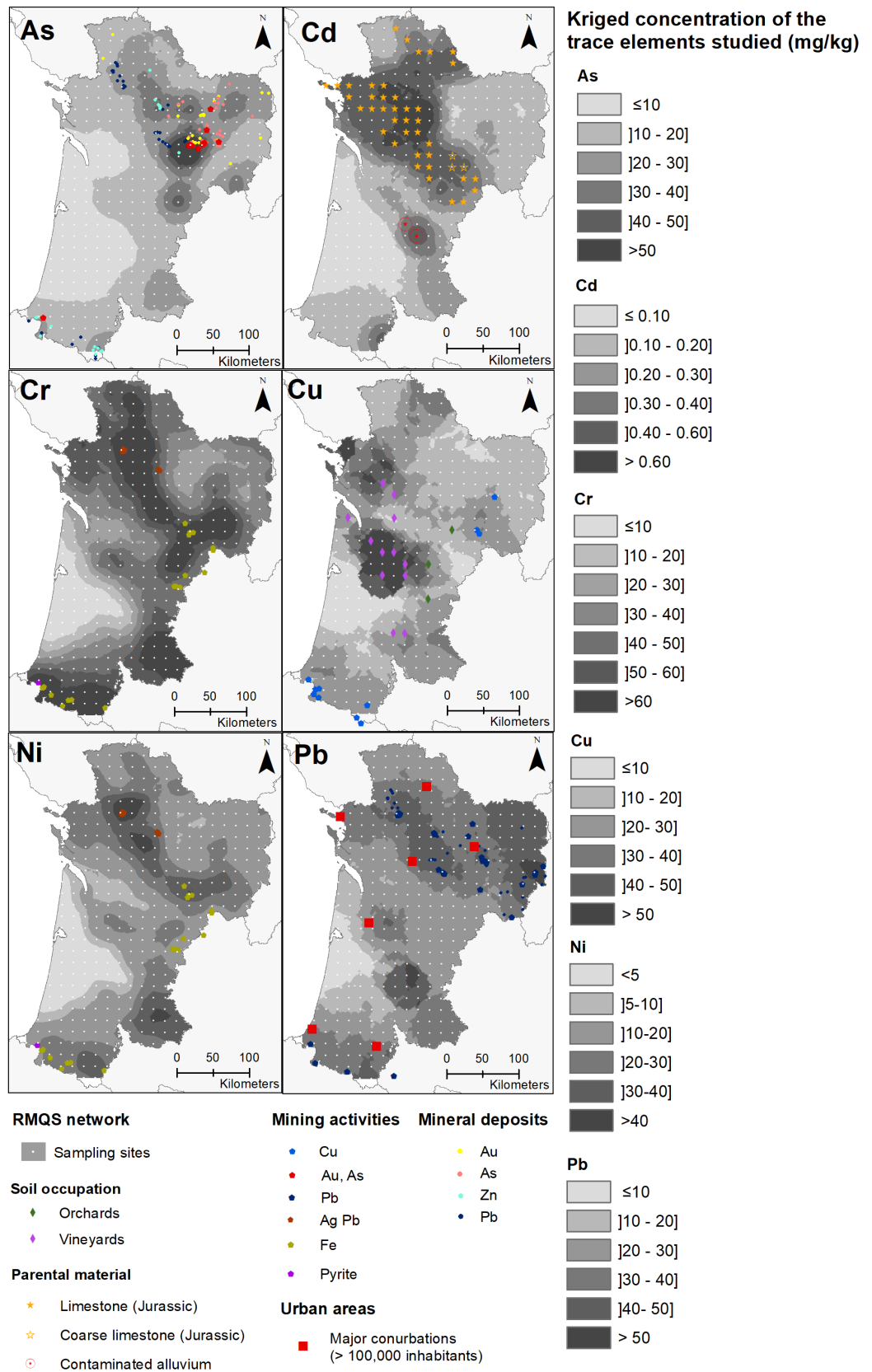


651 Figure 3: Variable factor maps of the principal components analysis. On each axis, in bracket,  
 652 the percentage of variance explained by the principal components (PC). A) PC 1 and PC 2; B)  
 653 PC 2 and PC 3; C) PC 3 and 4 D) PC 5 and PC 6.



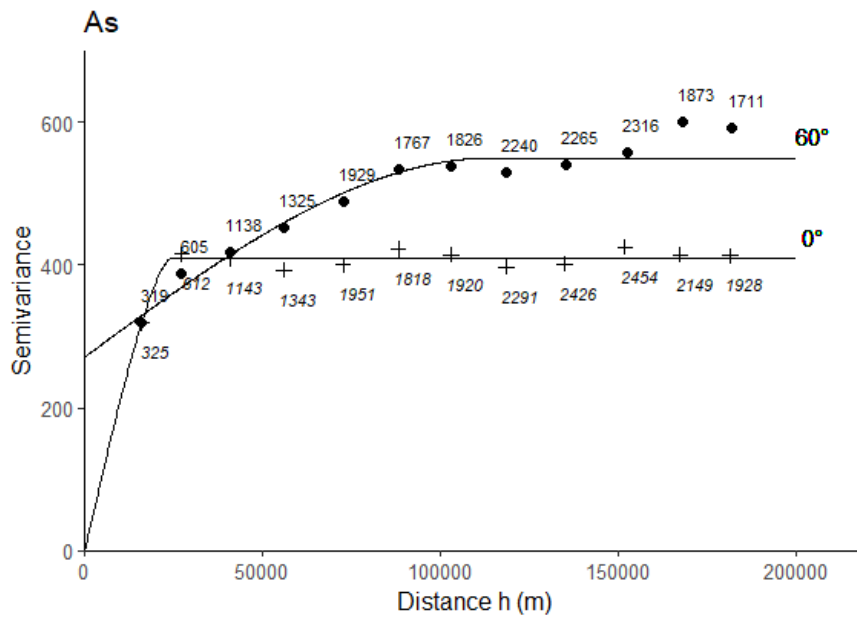
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656 Figure 4: Omnidirectional semivariograms, experimental (cross), and fitted with spherical model  
 657 (black line). Dashed line corresponds to the total variance. Pb experimental semivariogram is cut  
 658 from 100,000 meters because the semivariance decreases sharply after this distance. The data at the  
 659 top right of each graph describe the modeled semivariograms. For each semivariogram the number  
 660 (nb) of points pair is superior to 50 (Webster and Oliver, 1993).



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Figure 5: Maps with kriged concentrations of studied trace elements, and geographic information describing soil occupation, geology, mineral deposits and mining activities over the SWF. Soil occupation and geological data are shown on maps over sampling sites and originate from site description and geological maps, respectively (BRGM, 2005). Mineral deposits and mining activities data are shown on the maps at their exact location (BRGM, 2007).



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670 Figure 6: Directional semivariograms of As. Crosses represent 0° semivariance data, dots represent  
 671 60° semivariance data. For each semivariance value, the number of point pair is shown. The solid lines  
 672 represent the modeled semivariograms, with their descriptive parameters to the right of the figure.  
 673

674 Table 1: Descriptive statistics of As, Cd, Cr, Cu, Ni and Pb total concentrations in soils (in mg/kg) and  
 675 assessment of anomalous values at regional and *national* scales (Saby et al., 2019). Regional values  
 676 are included in the national dataset.

	As	Cd	Cr	Cu	Ni	Pb
Number of values (national)	2130	2144	2144	2144	2144	2144
Number of values (region)	356	356	356	356	356	356
Minimum (region)	0.39	0.01	1	0.5	0.5	3.1
Maximum (region)	209	2.1	168	491	73.6	261
1st quartile (region)	7.8	0.06	20.8	6.0	6.5	19
Median (region)	13.1	0.15	44	13.1	14.9	27.1
<b><i>Median (national)</i></b>	<b><i>12.0</i></b>	<b><i>0.20</i></b>	<b><i>53.2</i></b>	<b><i>13.9</i></b>	<b><i>19.3</i></b>	<b><i>27.8</i></b>
3rd quartile (region)	20.8	0.28	60.0	22.9	27.9	37.9
Regional upper whisker	41.2	0.60	118.6	48.3	60.0	66.3
<b><i>National upper whisker</i></b>	<b><i>36.7</i></b>	<b><i>0.65</i></b>	<b><i>121.7</i></b>	<b><i>42.8</i></b>	<b><i>61.5</i></b>	<b><i>62.0</i></b>
Number of values (region) > regional upper whisker	25	40	6	36	7	16
<b><i>Number of values (region) &gt; national upper whisker</i></b>	<b><i>30</i></b>	<b><i>35</i></b>	<b><i>4</i></b>	<b><i>42</i></b>	<b><i>5</i></b>	<b><i>23</i></b>

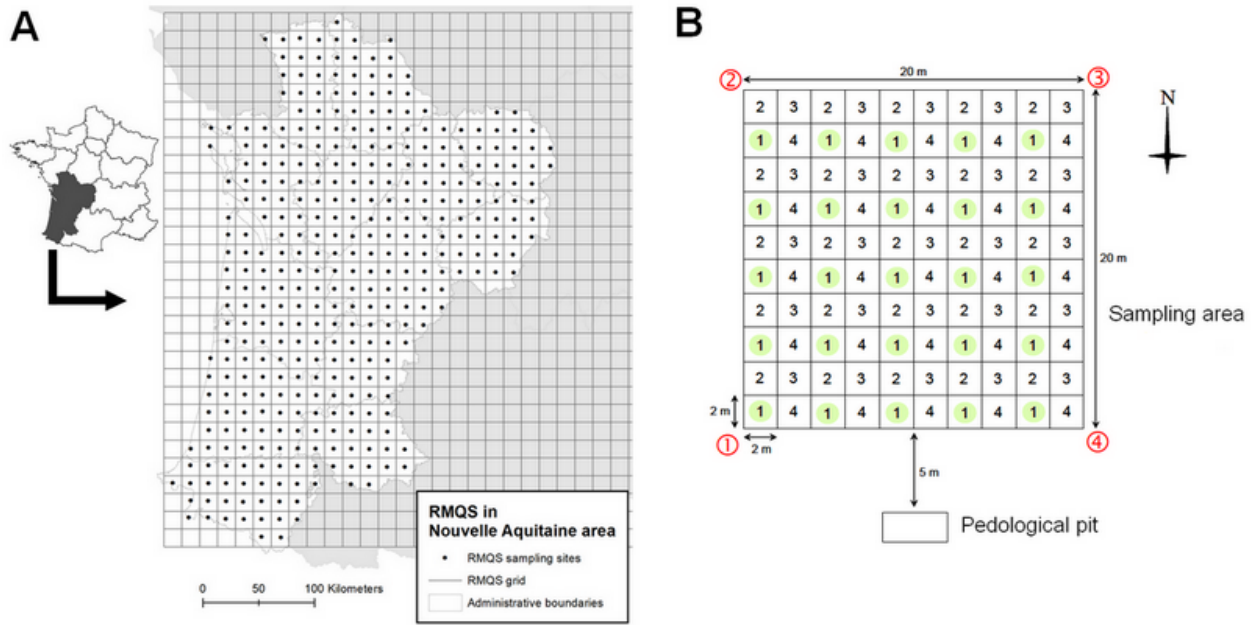
677 Table 2: Descriptive statistics of granulometry, pH, CaCO<sub>3</sub>, carbon, nitrogen, total Al, Fe and  
 678 Mn of the 356 soil samples.  
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Variable	<i>unit</i>	Min	1st quartile	Median	3rd quartile	Max
Clay	%	0.2	12.58	19.75	32.3	65.2
Fine silt	%	0.1	12.43	19.25	26.53	45.3
Coarse silt	%	0.1	6.7	11.05	16.6	38.6
Fine sand	%	0.5	8.28	12	16.13	59.8
Coarse sand	%	0.6	10.83	23.85	49.15	97
CaCO <sub>3</sub>	<i>g/kg</i>	0.5	0.5	0.5	2.05	706
pH		4	4.9	5.8	7.4	8.4
CEC	<i>cmolc/kg</i> <i>g</i>	0.25	3.84	6.61	17.33	50.6
Organic carbon	%	0.059	1.22	1.73	2.68	13.4
Total nitrogen	‰	0.03	0.94	1.50	2.3	9.79
Al	%	0.12	2.52	4.44	6.66	10.2
Fe	%	0.03	1.08	2.17	3.14	7.66
Mn	<i>mg/kg</i>	5	195.8	485.5	738.5	4870

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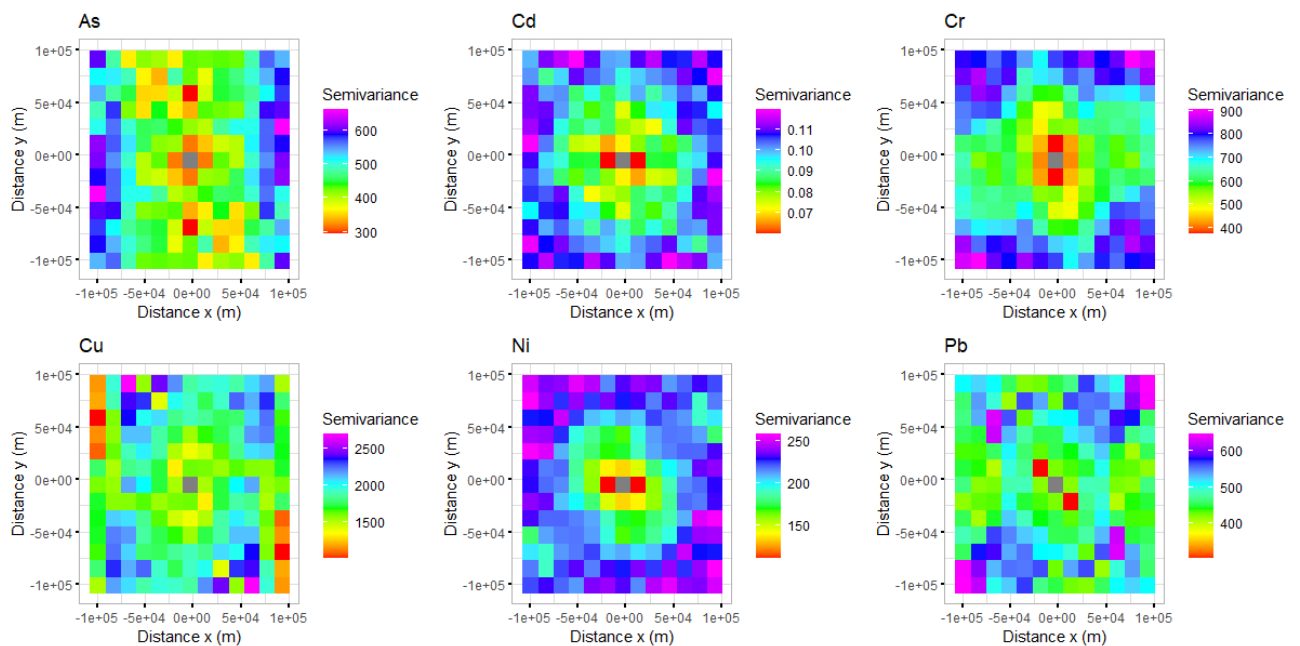
682 **Supplementary materials:**



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685 Figure S1: A) Location of RMQS sampling sites in the survey area. B) Illustration of the  
686 sampling process applied on the RMQS sites. Modified from Jolivet et al. (2006). During the  
687 first campaign, samples were taken from the subsquares numbered 1.

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691 Figure S2: Experimental bidirectional variograms shown as a raster with a 16.000 m wide tile.  
692 The X-axis represents west-east direction and the Y-axis represents north-south direction.

693 Table S1: Contribution of variables to each dimension of the PCA (%). The highest contributions  
 694 (>5.3%) are in bold.

Variables	PC 1	PC 2	PC 3	PC 4	PC 5	PC 6
clay	<b>10.52</b>	0.72	1.57	0.03	0.00001	0.93
fine silt	<b>6.17</b>	0.96	4.61	<b>21.54</b>	1.00	0.51
coarse silt	2.45	<b>5.89</b>	<b>14.87</b>	<b>16.78</b>	0.61	0.29
fine sand	0.14	1.68	5.38	3.69	<b>29.26</b>	<b>46.64</b>
coarse sand	<b>9.30</b>	3.60	3.78	<b>5.59</b>	0.86	1.72
cec	<b>7.03</b>	4.69	<b>10.07</b>	0.47	0.01	0.11
pH	5.05	<b>16.47</b>	3.09	2.42	0.01	0.33
carbonate (CaCO <sub>3</sub> )	0.92	<b>11.85</b>	<b>15.10</b>	0.84	0.29	0.65
carbon	1.57	<b>17.64</b>	<b>11.37</b>	<b>9.48</b>	1.04	<b>6.21</b>
nitrogen	5.09	<b>9.83</b>	<b>10.03</b>	<b>6.89</b>	0.61	4.87
Fe	<b>9.79</b>	1.90	1.75	2.78	1.58	0.54
Mn	5.21	1.24	4.91	2.89	0.48	3.30
Cd	<b>5.46</b>	1.98	<b>7.26</b>	3.95	0.05	0.24
Al	<b>6.60</b>	<b>9.66</b>	1.23	0.02	0.49	0.25
Cu	0.58	0.91	0.55	4.37	<b>44.10</b>	<b>26.41</b>
Pb	2.35	<b>7.12</b>	0.00	0.95	<b>16.59</b>	4.09
As	2.13	3.46	1.43	<b>12.21</b>	1.92	0.08
Ni	<b>9.97</b>	0.38	0.40	4.52	0.06	2.38
Cr	<b>9.68</b>	0.03	2.59	0.59	1.03	0.45

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