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

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Keywords: multivariate analysis, geostatistics, GIS, monitoring network

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 km²). 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, $CaCO_3$ 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.

1. Introduction

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

The spatial distribution of trace elements over large national or continental areas has been studied for a long time in order to establish geochemical baseline (Chen et al., 1991; McGrath and Loveland, 1992; Salminen, 2005; Shacklette and Boerngen, 1984). More recently, national and continental soil monitoring networks have been set up in Europe to determine 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 km² 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).

- Cd, found in phosphate fertilizers and manure spread on soils (Belon et al., 2012). This element presents a high health risk as a carcinogen (IARC, 1993).
- Cu, widely used in vineyard areas and present in the manure spread. This element affects the microbial life of the soil due to its biocidal action (Ranjard et al., 2008).
- Cr, resulting from industrial activities (e.g. effluents from tanneries) and which can be found in soils due to irrigation. It is also brought into the soil by manure spreading. This element presents a health risk because it is carcinogenic in its hexavalent form.
- Ni, brought into the soil by manure spreading, due to mining activities or as a by-product associated with other types of pollutants such as PAHs (Barcan and Kovnatsky, 1998; Belon et al., 2012; Zehetner et al., 2009). This element is not very phytotoxic and presents less health risk than the elements above. However, anthropogenic contributions to soils can be significant (Rooney et al., 2007).
- Pb, from mining, industrial and road traffic emissions. Its accumulation in the food chain induces a significant health risk (lead poisoning).

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

2. Materials and methods

2.1 Study area

The area includes the Nouvelle Aquitaine region, which is the largest agricultural region in France (39,000 km² of usable agricultural area) and the department of Gers. The agricultural production of this area is varied (field crops, livestock farming, viticulture and arboriculture).

105 The area also includes large forest areas (28,000 km²) 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 (Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}) with
137 cobaltihexamine chloride (AFNOR, 1999). $CaCO_3$ 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 %) / $HClO_4$ (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 × IQR

154 (2) Upper whisker = Q3 + 1.5 × 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 γ (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

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

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

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

$$(4)\quad \sum_{j=1}^{n} N(h) \left(\hat{\gamma}\left(\overline{h_j}\right) - \gamma\left(\overline{h_j}\right) \right)^2$$

Where $\gamma\left(\overline{h_j}\right)$ is the experimental value of the semivariance, and $\hat{\gamma}\left(\overline{h_j}\right)$ is the modeled value of the semivariance. The geostatistical calculations were carried out with the gstat library and the R software (Pebesma, 2004). The ratio between the nugget and the total variance (hereinafter called nugget/variance ratio) was calculated in order to have a relative assessment of the nugget effect (expressed in %), which is more explicit than the absolute value and enables comparisons. The anisotropy was studied from a semivariance map with two direction 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, $CaCO_3$, 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 $CaCO_3$ for principal component 2 (PC2); coarse
240 silt, $CaCO_3$, 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).

It can be also observed:

- In Figure 3A, the concentrations of Cr, Fe, Ni and the clay content correlate positively. This suggests a rather geogenic origin of Cr and Ni. Indeed, the materials resulting from the degradation of rocks rich in Cr and Ni are also rich in clays. Thus Cr, Ni and clays would remain bound after the weathering of these rocks and transfer to the soil (Cheng et al., 2011; Kierczak et al., 2007). This was observed in a previous study (ASPITET) on trace elements in soils in France (Baize, 1997).

- In Figure 3B, Cd concentrations, $CaCO_3$, pH and CEC also correlate positively. In the study region, soils with high $CaCO_3$ content, pH, and CEC are limestone soils. The association between Cd and certain carbonate minerals could therefore explain this correlation, as it was already observed in natural environments (Chada et al., 2005; Martin-Garin et al., 2002). This association is the result of the carbonate dissolution reaction, where Cd^{2+} would replace Ca^{2+} to form $CaCO_3$-$CdCO_3$ or $CdCO_3$ (Papadopoulos and Rowell, 1988). The introduction of Cd into soils by amendments based on calcium carbonates and phosphate fertilizers is also a possible source of Cd in soils (Senesil et al., 1999).

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

3.3 Spatial and geostatistical analysis: factors influencing spatial distribution

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

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

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

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

3.4. Statistical approaches: representativeness and limits

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

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

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

4. Conclusion

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

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

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

Acknowledgments

This study was supported by a French Scientific Group of Interest on soils: the "GIS Sol", (involving the Ministry for an Ecological and Solidary Transition (MTES), the French Ministry of Agriculture (MAA), the French Agency for Energy and Environment (ADEME), the French Research Institute for Development (IRD), the French National Institute of Geographic and Forest Information (IGN), the National Institute for Agronomic Research (INRAE)) and Bordeaux Sciences Agro. Thanks are expressed to Claudy Jolivet, Céline Ratié and Line Boulonne of unit INRAE US1106 InfoSol. We thank the three anonymous reviewers for their comments that helped to improve this article.

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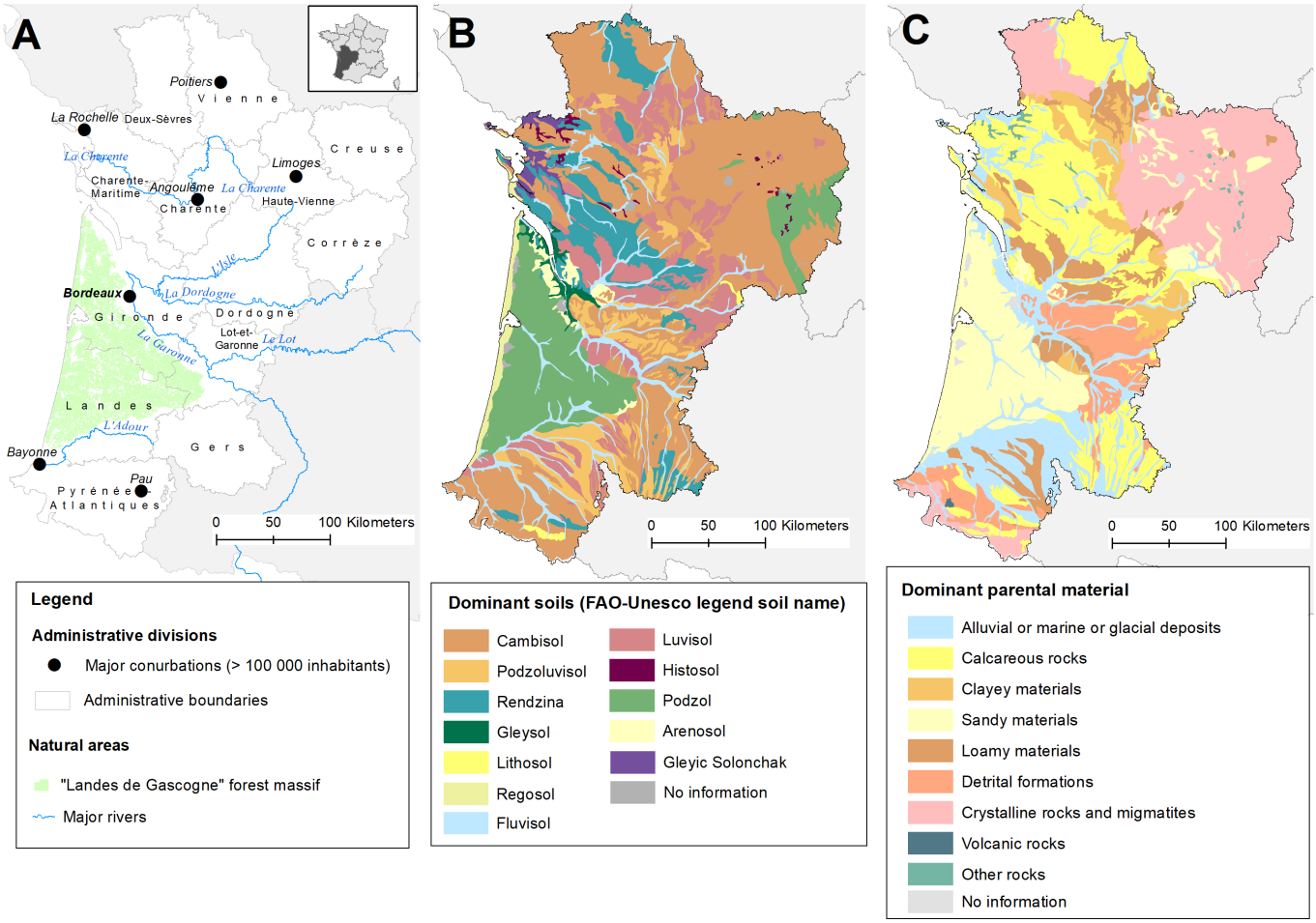
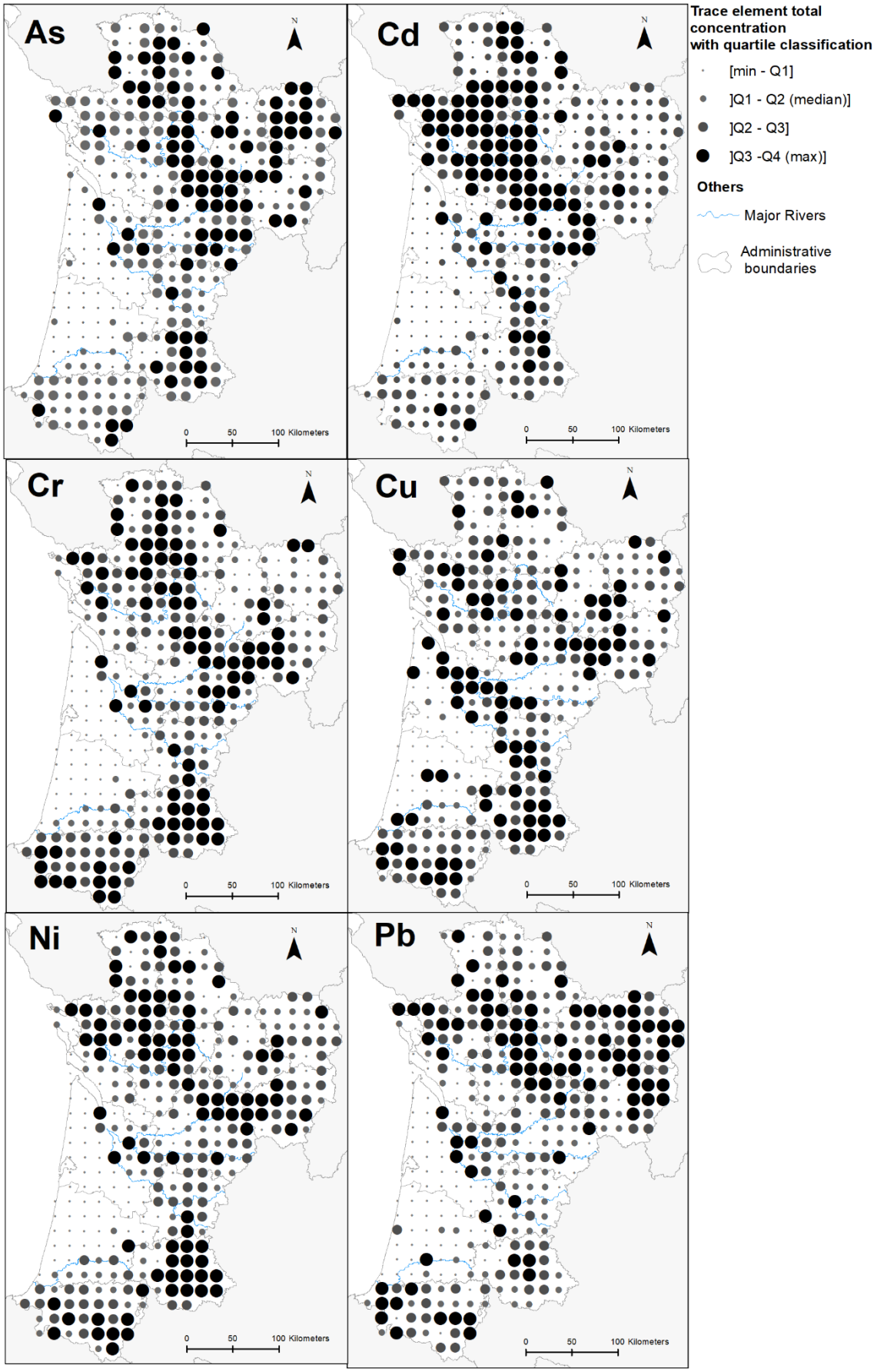
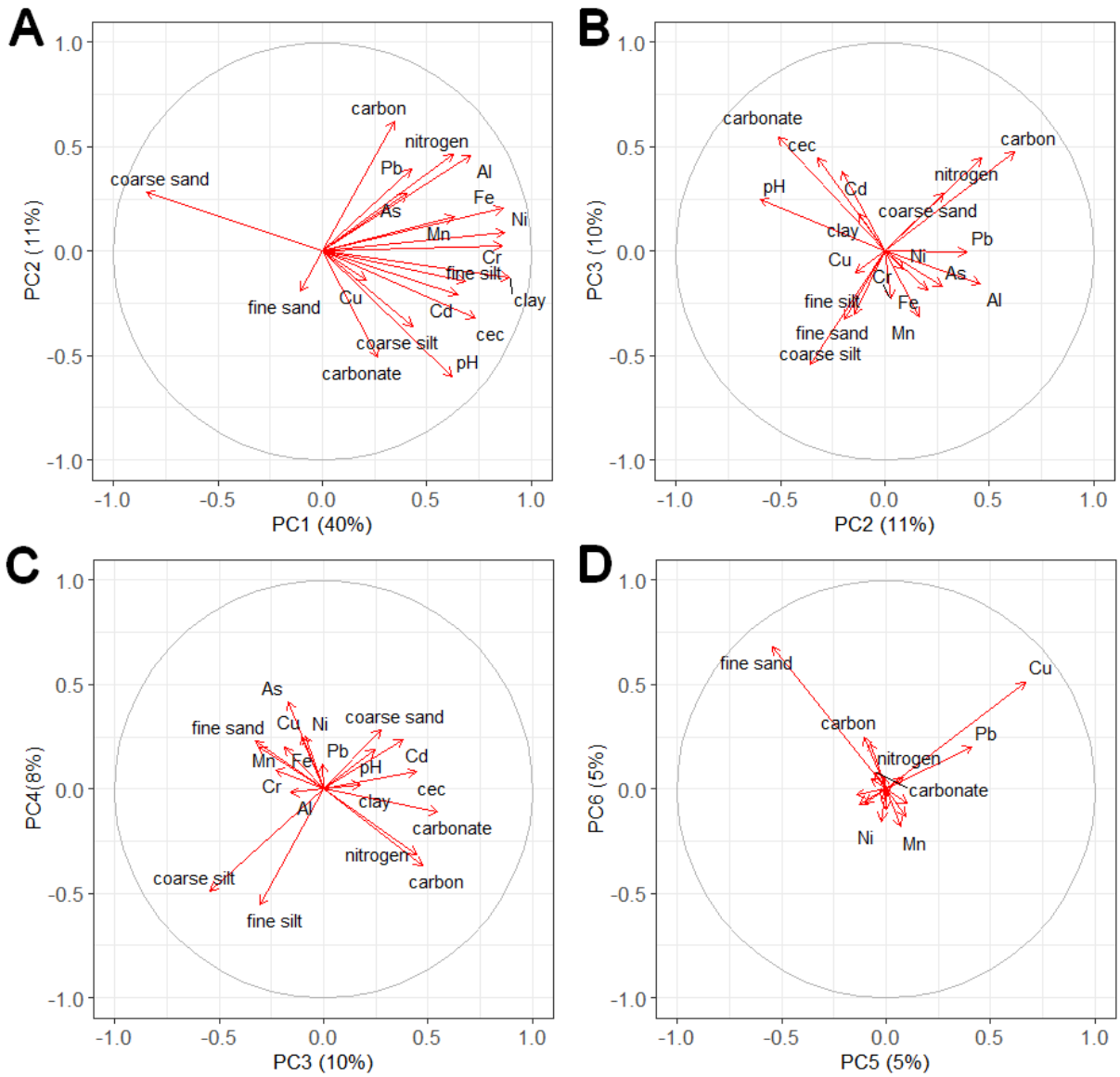


Figure 1: A) Map describing the administrative divisions of the study area and major natural areas. B) Map of dominant soils from the Soil Geographical Data Base of France (BDGSF) at scale 1:1000000 (INRA, 2018). C) Map of the dominant parent material from the BDGSF.

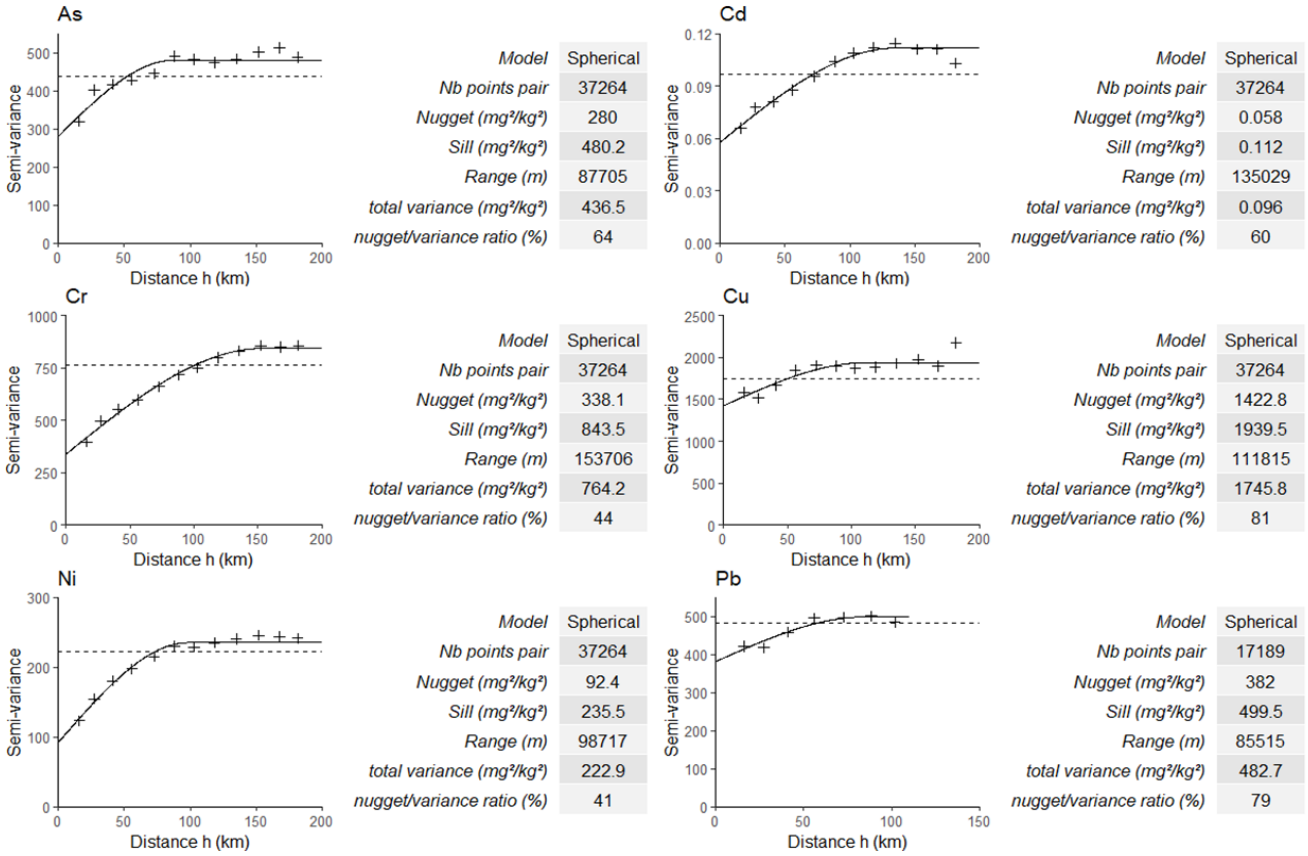


649 Figure 2: Point distribution of As, Cd, Cr, Cu, Ni and Pb concentrations with classification by quartile in
650 the topsoil of southwestern France.



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.

654



655

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).

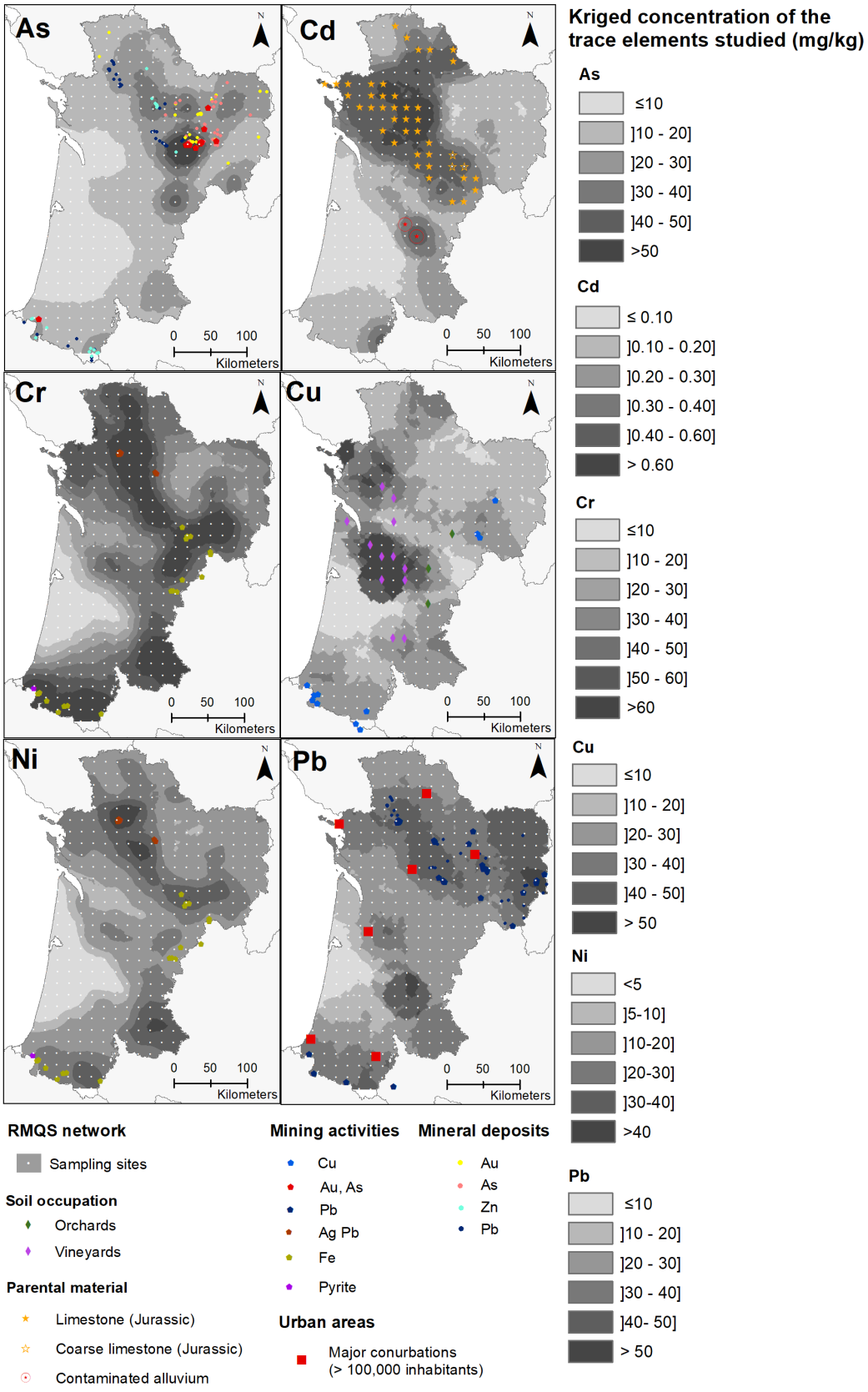
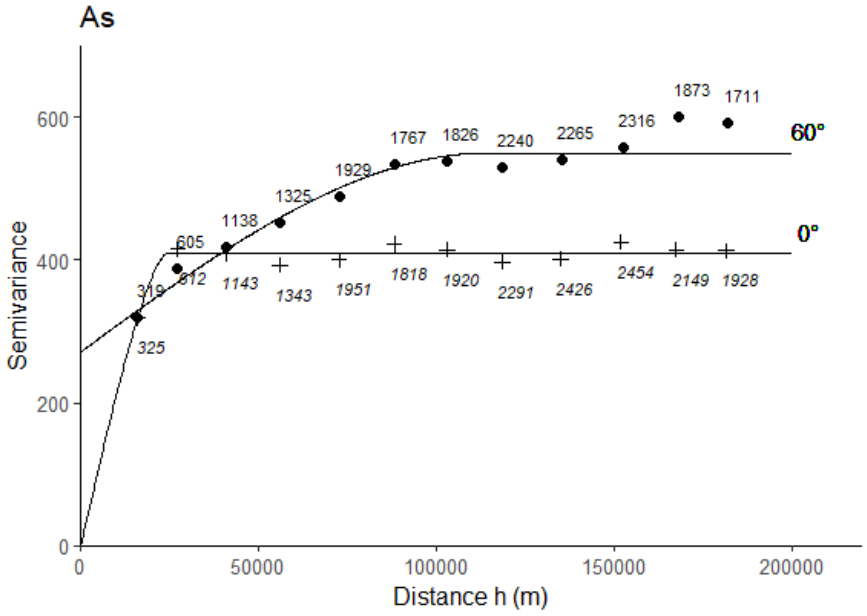


Figure 5: Maps with kriged concentrations of studied trace elements, and geographic information describing soil occupation, geology, mineral deposits and mining activities over the SWF. Soil occupation and geological data are shown on maps over sampling sites and originate from site description and geological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



Angle (degrees)	0	60
Model	Circular	Spherical
Nb points pair	20360	19314
Nugget (mg²/kg²)	0.0	271.5
Sill (mg²/kg²)	408.7	549.9
Range (m)	24014	114652

668

669

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
Median (national)	***12.0***	***0.20***	***53.2***	***13.9***	***19.3***	***27.8***
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
National upper whisker	***36.7***	***0.65***	***121.7***	***42.8***	***61.5***	***62.0***
Number of values (region) > regional upper whisker	25	40	6	36	7	16
Number of values (region) > national upper whisker	***30***	***35***	***4***	***42***	***5***	***23***

677 Table 2: Descriptive statistics of granulometry, pH, $CaCO_3$, carbon, nitrogen, total Al, Fe and
678 Mn of the 356 soil samples.
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Variable	*unit*	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
$CaCO_3$	*g/kg*	0.5	0.5	0.5	2.05	706
pH		4	4.9	5.8	7.4	8.4
CEC	*cmolc/kg*	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	*mg/kg*	5	195.8	485.5	738.5	4870

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681

Supplementary materials:

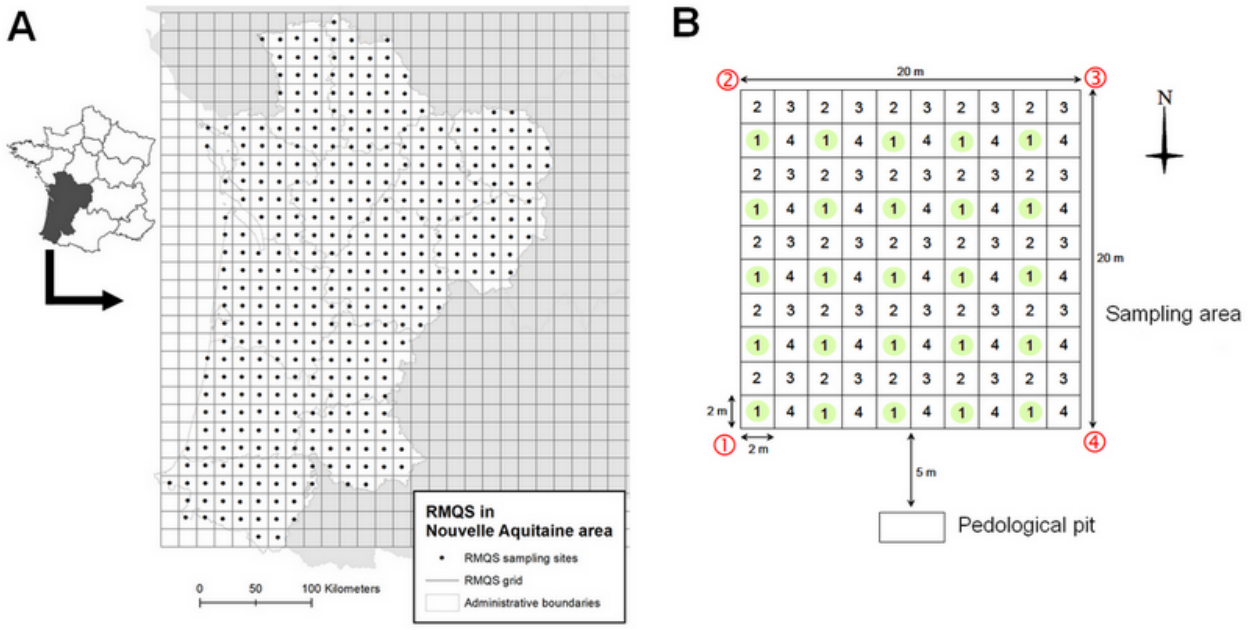

Figure S1: A) Location of RMQS sampling sites in the survey area. B) Illustration of the sampling process applied on the RMQS sites. Modified from Jolivet et al. (2006). During the first campaign. samples were taken from the subsquares numbered 1.

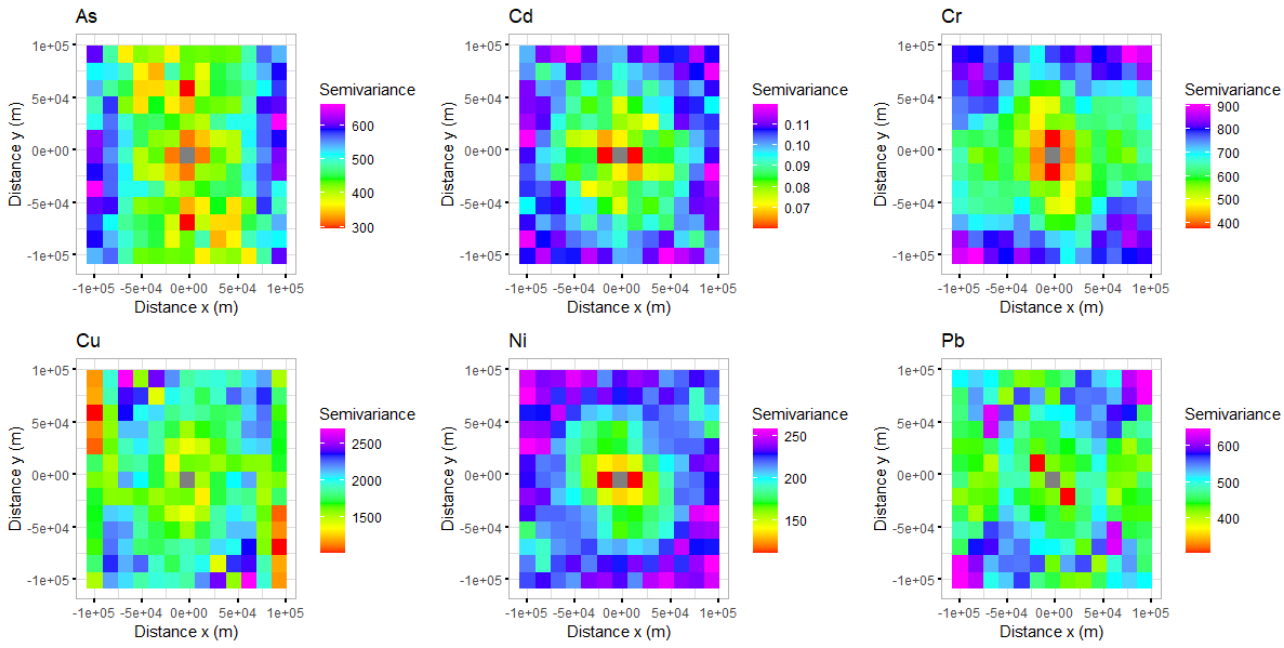

Figure S2: Experimental bidirectional variograms shown as a raster with a 16.000 m wide tile. The X-axis represents west-east direction and the Y-axis represents north-south direction.

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	**10.52**	0.72	1.57	0.03	0.00001	0.93
fine silt	**6.17**	0.96	4.61	**21.54**	1.00	0.51
coarse silt	2.45	**5.89**	**14.87**	**16.78**	0.61	0.29
fine sand	0.14	1.68	5.38	3.69	**29.26**	**46.64**
coarse sand	**9.30**	3.60	3.78	**5.59**	0.86	1.72
cec	**7.03**	4.69	**10.07**	0.47	0.01	0.11
pH	5.05	**16.47**	3.09	2.42	0.01	0.33
carbonate ($CaCO_3$)	0.92	**11.85**	**15.10**	0.84	0.29	0.65
carbon	1.57	**17.64**	**11.37**	**9.48**	1.04	**6.21**
nitrogen	5.09	**9.83**	**10.03**	**6.89**	0.61	4.87
Fe	**9.79**	1.90	1.75	2.78	1.58	0.54
Mn	5.21	1.24	4.91	2.89	0.48	3.30
Cd	**5.46**	1.98	**7.26**	3.95	0.05	0.24
Al	**6.60**	**9.66**	1.23	0.02	0.49	0.25
Cu	0.58	0.91	0.55	4.37	**44.10**	**26.41**
Pb	2.35	**7.12**	0.00	0.95	**16.59**	4.09
As	2.13	3.46	1.43	**12.21**	1.92	0.08
Ni	**9.97**	0.38	0.40	4.52	0.06	2.38
Cr	**9.68**	0.03	2.59	0.59	1.03	0.45

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