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1 **Rare earth elements in French stream waters – revisiting the**
2 **geochemical continental cycle using FOREGS dataset**

3

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5

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12

13

14 **Abstract**

15 The geochemical behavior of rare earth elements (REE) has been investigated mainly in
16 geological systems where these elements represent the best proxies of processes involving the
17 occurrence of an interface between different media. This behavior is assessed according to
18 REE concentrations recorded along the REE series normalized with respect to upper
19 continental crust. In this study based on a field approach, the geochemical behavior of REE
20 was investigated in French stream waters. This study is based on FOREGS (Forum of
21 European Geological Surveys) Geochemical dataset that consists on a sampling at regular
22 mesh on all Europe. In France, 119 stream water samples were extracted in drainage basins
23 $<100 \text{ km}^2$. The aim of the study is that of describing the spatial variation of REE and finding
24 the hydro-topo-geochemical factors that affect their distribution by means of a Multivariate
25 Factorial Kriging.

26 On the basis of their atomic number and of the results of a preliminary Principal Component
27 Analysis three REE have been selected (La, Eu and Lu) and five physicochemical properties
28 (pH, organic carbon, carbonates, Fe, Mn). A cokriging has been applied that shows a similar
29 spatial organization of REE: higher values are especially observed in the Aquitaine basin. In
30 order to investigate more deeply on the different sources of variation acting in the study area,
31 a factorial cokriging is applied. The first 2 regionalized factors have been estimated to give a
32 synthetic description of the studied process at the different selected spatial scales. At higher
33 spatial scales (250 km) environmental parameters like Fe, carbonates, pH, supposed to be
34 ascribed to the rock's nature or to other geological larger scale processes (i.e., hydrographic
35 network and topography), have shown to affect REE distribution. At short range, only Eu and
36 Mn weigh more, which are ascribed to the process of liberation of Mn oxides in rivers that
37 also release the REE sorbed onto these oxides.

38 **Keywords** lanthanide, river water, organic matter, Fe and Mn oxides

39 1. Introduction

40 Rare earth elements (REE) represent a group of fifteen elements, which share common
41 physiochemical properties and therefore often occur together (McLennan and Taylor, 2012).
42 Over the past fifteen years, REE became of critical importance to many green-technology
43 products but also for medical applications, and therefore are of great economic interest (e.g.,
44 (Tepe et al., 2014; Guyonnet et al., 2015). In this context as highlighted by Kulaksız and Bau
45 (2013), the continuous development of new technologies and new substances has led to
46 strongly increased release of REE into natural waters, although their toxicological effects and
47 the potential implications for the ecosystem are often not fully understood. But in aquatic
48 systems, REE concentrations are low compared to their concentrations in rocks with regards
49 to their slight solubility (e.g., Noack et al., 2014). Therefore, it appears important first, to
50 assess and to fully understand the occurrence and fate of aqueous REE in an environment
51 where REE release from the anthroposphere may be considered as negligible.

52 In aquatic systems, solution and interface chemistry appears to be the major factor
53 controlling the REE concentration (e.g., Elderfield et al., 1990; Sholkovitz, 1995). Rare earth
54 elements can form strong complexes with a number of different ligands. For convenience,
55 REE concentrations of continental waters are usually normalized to Upper Continental Crust
56 (UCC; McLennan, 2001), which produces smooth REE_{UCC} distribution patterns. The REE
57 patterns result from the combination of several processes able to induce their fractionation.
58 These processes are themselves controlled by several physicochemical mechanisms and
59 parameters. Three processes can be distinguished: (i) precipitation/dissolution, (ii) sorption
60 onto colloids and particles, and (iii) complexation in solution with organic and inorganic
61 ligands. The resulting REE pattern therefore corresponds to the REE pattern for mineral
62 sources that are modified by the sorption/complexation with ligands, colloids and particles.
63 This results in a wide range of diverse REE patterns, which can be characterized by a

64 depletion or enrichment degree of light REE (LREE) relative to heavy REE (HREE) or by
65 whether or not anomalies occur. Indeed, individual REE may show anomalous behavior in
66 natural waters: redox-sensitive Ce and Eu may show anomalies that may be used as redox-
67 and/or temperature-proxies (e.g., Bau, 1991; De Baar et al., 1988), and La, Gd and Lu may
68 show small anomalies due to subtle differences between the stabilities of REE complexes
69 (Bau, 1999; Byrne and Kim, 1990). In addition to these natural anomalies, anthropogenic
70 anomalies of Gd and, recently, La and Sm have been reported from natural waters (e.g.,
71 Kulaksız and Bau, 2013), and references therein).

72

73 To better understand the occurrence of aqueous metals and especially REE, the
74 FOREGS (Forum of European Geological Surveys) aims at providing a basis for formulating
75 policies and legislation concerning the management of harmful elements and to define their
76 corresponding safety levels (Salminen et al., 2005). A first attempt was performed in Italy,
77 Sweden and Europe by Imrie et al. (2008); Lado et al. (2008); Petrosino et al. (2013); Sadeghi
78 et al. (2013). These studies mostly focus on topsoil dataset and investigate the main factors
79 explaining REE variation in the soil solution; however, the FOREGS database contains
80 descriptions of other environmental media (stream and floodplain sediments, and stream
81 water). The database has been processed by Imrie et al. (2008); Lado et al. (2008), Petrosino
82 et al. (2013) and Sadeghi et al. (2013) by means of multivariate approaches to interpolate all
83 variables, metals or REE concentrations. They used factorial kriging for Imrie et al. (2008),
84 regression kriging for Lado et al. (2008) and inverse distance weighted interpolation and
85 principal component analysis for Sadeghi et al. (2013). The results associate spatial
86 distribution of elements with different factors operating at several scales. For example, Imrie
87 et al (2008) highlight four factors and amongst them (i) a short scale (72 km): concentrations
88 may be explained by parent material geology, land use and organic matter content; (ii) a

89 medium scale (296 km): concentrations may be explained by major structural division of
90 European continent and the distribution of calcareous rocks. Petrosino et al. (2013) show that
91 in Italy and Sweden, REE concentration in all sampling medias are related to the geological
92 context. In the particular case of stream water, they found that Swedish waters are more
93 concentrated in REE than Italian waters. These authors relate high REE concentrations to
94 water acidity (linked to vegetation and felsic rocks). Whereas, in Italy, pH is higher and the
95 watershed are mostly composed of calcareous rocks which mostly explain the lower REE
96 contents as already highlighted by Johannesson and Burdige (2007) or Deberdt et al. (2002).

97

98 As the chemistry of stream waters is influenced by several landscape factors which are
99 related to geology, topography, climate, and vegetation (e.g., Andersson and Nyberg, 2009;
100 Gaillardet et al., 2014); the aim of this study is to further investigate the FOREGS dataset
101 focusing on France. A special attention will be given to REE patterns spatial distribution. For
102 such needs, the FOREGS stream dataset was processed by means of geostatistical methods,
103 especially by factor kriging analysis. These approaches have three steps described as follows:
104 (i) modeling the coregionalization of the set of variables, (ii) analyzing the correlation
105 structure between the variables by applying principal component analysis; (iii) cokriging
106 specific factors at each characteristic scale. The 14 REE concentrations available in the
107 dataset were all used as inputs, as well as some physicochemical properties: pH, carbonate
108 alkalinity, Fe, Mn and organic carbon. The obtained maps allow visualizing the factors which
109 integrate REE spatial variability. This variability is discussed with some landscape factors,
110 especially topography and upstream/downstream location.

111

112

113 **2. Materials and methods**

114 **2.1 The study area**

115 The geology of France results of a succession of events related to assembly and
116 disruption of Gondwana and Pangea megacontinents and climate changes. Geographically,
117 France has acquired a rugged topography giving it a wide range of outcropping terranes
118 spanning from Proterozoic to Cenozoic (Figure 1). France can be divided into four geological
119 terranes. (i) France is mostly covered by Mesozoic and Cenozoic deposits which correspond
120 to intracratonic sedimentary basins like Paris Basin or Aquitaine Basin (Biteau et al., 2006;
121 Guillocheau et al., 2000). These extensive areas have been scarcely deformed and are
122 characterized by small dip values and concentric rock deposits. The tabular structure involves
123 typical landscapes like alluvial plains, plateau and hills. In addition to intracratonic genesis,
124 other basins correspond to grabens formed during Alps orogeny (Rhein and Limagnes
125 graben). These units are generally depressions filled with Cenozoic sediments. (ii) These
126 Mesozoic and Cenozoic sedimentary units lay on a basement composed of Paleozoic and
127 Proterozoic rocks (Ballèvre et al., 2009; Faure et al., 2009). The basement is widely
128 metamorphic and magmatic and is surrounded by discordant Mesozoic sedimentary cover. It
129 constitutes the essential part of eroded mountain ranges like Vosges, Armorican Massif or
130 French Massif Central erected during Cadomian and Variscan orogeny (Ballèvre et al., 2009;
131 Faure et al., 2009). These reliefs have been strongly flattened by erosion, except to Vosges
132 and French Massif Central which have been resurrected again during Alps orogeny (Faure et al.,
133 2009). (iii) Alps and Pyrenees are recent mountain ranges still erecting since Upper
134 Cretaceous (Choukroune, 1992; Lagabrielle and Lemoine, 1997; Rosenbaum and Lister,
135 2005; Vissers and Meijer, 2012). These ranges form a complex association between meso-
136 cenozoic rocks which have been heavily deformed due to fault and folding action and

137 basement units. The resulting landscape is high mountains (Valla et al., 2011). (iv) Recent
138 volcanic ranges are located massively in the Massif Central (Michon and Merle, 2001). These
139 units are mainly composed of basalts, trachytes, and rhyolites, aged from Neogene (Cantal) to
140 Pleistocene (Chaîne des Puys).

141

142 **2.2 The FOREGS dataset**

143

144 The FOREGS program uses standardized field, analytical and quality control
145 procedures to produce reliable reproducible geochemical data over Europe (Salminen et al.,
146 1998). Therefore, the FOREGS initiated a program to construct a geochemical database with
147 the aim of compiling the first geochemical atlas of Europe (Fedele et al., 2008). The field
148 manual by Salminen et al. (1998) is the basis for a decade-long project, involving geochemists
149 from 26 countries, which led to the publication of the Geochemical Atlas of Europe (De Vos
150 and Tarvainen, 2006; Salminen et al., 2005) . As a result, a large geochemical database is now
151 available free for public use¹ (De Vos and Tarvainen, 2006; Salminen et al., 2005).

152

153 **2.2.1 Sampling strategy**

154

155 The FOREGS sampling grid (Salminen et al., 1998; Tarvainen et al., 2005) was based on
156 the Global Terrestrial Network (GTN) grid composed of 160 x 160 km cells and developed
157 for the purpose of Global Geochemical Baselines Mapping (Darnley et al., 1995). For each
158 cell, five randomly generated sites were selected, according to the following scheme:

- 159 - Point number 1 is located in the NE quadrant of the GTN grid cell;
- 160 - Point number 2 in the NW quadrant;

¹ <http://weppi.gtk.fi/publ/foregsatlas/index.php>

- 161 - Point number 3 in the SW quadrant;
162 - Point number 4 in the SE quadrant;
163 - Point number 5 is randomly located in anyone of the four quadrants of the GTN grid
164 cell.

165 As a result, France was divided into 25 cells and 119 sample sites were determined. Based on
166 former randomly generated points, five nearest small drainage basins of $<100 \text{ km}^2$ were
167 selected. For each cell, a larger drainage basin (area 1,000-6,000 km^2), to which the small
168 drainage basin is connected, was selected. The floodplain sediment samples were collected
169 either from a suitable point near its outlet with the sea or the confluence point with another
170 major river system. In this study, French stream water samples were selected. The dataset
171 consists of 119 sampling sites (one sample per site). However, 4 sites located in Corsica were
172 removed of the dataset to obtain a homogeneous spatial distribution. Samples were collected
173 during two periods of the winter: from November 1998 to December 1998; and from March
174 1999 to October 1999. Sampling during rainy periods and flood events was avoided.
175 According to FOREGS stream water sampling procedure, running stream water was collected
176 from the small, second order, drainage basins ($<100 \text{ km}^2$). Physico-chemical parameters (pH,
177 temperature and electrical conductivity) were measured at the site while several stream water
178 samples were collected. ICP-MS analyses were performed on a 100 mL sample filtered to
179 $0.45 \mu\text{m}$ (Salminen et al. 1998).

180

181 **2.2.2 Chemical analyses and quality controls**

182 As described in Sandström et al. (2005): stream water samples were acidified to 1%
183 v/v with nitric acid and stored at less than 8°C . The samples were analyzed by both
184 inductively coupled plasma quadrupole mass spectrometry (ICP-QMS) and inductively
185 coupled plasma atomic emission spectrometry (ICP-AES), using Perkin Elmer Sciex ELAN

186 5000A and Spectro Flame M instruments respectively, in accordance with the German norms
187 DIN 38406-29 (ICP-MS) and DIN 38406-22 (ICP-AES). Analyses were performed by BGR
188 (Bundesanstalt für Geowissenschaften und Rohstoffe, Hannover, Germany). The primary
189 chemicals used to prepare the calibration and quality control standards and reagents were of
190 analytical reagent grade. Multi-element standard solutions for calibration were prepared from
191 Claritas SPEX/Certiprep stock solutions. International certified reference materials (NIST
192 1640, NIST 1643d and SLSR-4) were included in every batch of 20 samples. Indium was
193 used as an internal standard. The accuracy of the methods for all determinants is better than
194 $\pm 10\%$, the bias is within $\pm 3\%$, and the repeatability at the 95% confidence interval is better
195 than 5% at concentrations an order of magnitude above the limit of quantification. Limits of
196 quantification for all cations and trace metals are given in Sandström et al. (2005).

197

198 **2.3 Geographic information system and multivariate geostatistical approach.**

199

200 Geographic information system (GIS) analysis was performed with ArcGis 10
201 software. Distance between sample site and outlet was calculated using the BD Carthage
202 (Sandre Eau France) dataset which is the French official dataset about hydrographic network.
203 Geological context of sampling sites was obtained by GIS intersection with 1/1,000,000
204 geological units (BRGM One Geology).

205 Concentrations of 14 REE and physicochemical properties (pH, carbonate alkalinity as HCO_3 ,
206 Fe, Mn and organic carbon) were used as inputs for the geostatistical method. Descriptive
207 statistics (mean, standard deviation sd, median med, and median absolute deviation MAD)
208 were performed on all variables and normality of data and homogeneity of variances were
209 verified. As data behave following a not normal distribution, non-parametric Kruskal-Wallis
210 tests were performed to quantify differences in variables within geological contexts.

211 The multivariate spatial data were analyzed by cokriging and Factor Kriging Analysis (FKA)
 212 which is a geostatistical method developed by Matheron (1982). The FKA consists of
 213 decomposing the set of original second-order random stationary variables $\{Z_i(x), i = 1, \dots, n; \}$
 214 into a set of reciprocally orthogonal regionalized factors $\{Y_v^u(x), v = 1, \dots, n; u = 1, \dots, N_s\}$
 215 where N_s is the number of spatial scales, through transformation coefficients a_{iv}^u (loadings
 216 components score) combining the spatial with the multivariate decomposition:

$$217 \quad Z_i(x) = \sum_{u=1}^{N_s} \sum_{v=1}^n a_{iv}^u Y_v^u(x)$$

218 The three basic steps of FKA are the following:

219 (i) Modeling the coregionalization of the set of variables, using the so called Linear Model of
 220 Coregionalization (LMC);

221 (ii) Analyzing the correlation structure between the variables, by applying Principal
 222 Component Analysis (PCA) at each spatial scale;

223 (iii) Cokriging specific factors at each characteristic scale and mapping them.

224

225 **2.3.1 Linear Model of Coregionalization**

226 The LMC, developed by Journel and Huijbregts (1978), considers all the studied
 227 variables as the result of the same independent physical processes, acting at different spatial
 228 scales u . The $n(n+1)/2$ simple and cross variograms of the p variables are modeled by a linear
 229 combination of N_s standardized variograms to unit sill $g^u(h)$. Using the matrix notation, the
 230 LMC can be written as:

$$231 \quad \Gamma(h) = \sum_{u=1}^{N_s} B^u g^u(h)$$

232 where $\Gamma(h) = [\gamma_{ij}(h)]$ is a symmetric matrix of order $n \times n$, whose diagonal and non-diagonal
233 elements represent simple and cross variograms for lag h ; $B^u = [b^u_{ij}]$ is called
234 coregionalization matrix and it is a symmetric semi-definite matrix of order $n \times n$ with real
235 elements b^u_{ij} at a specific spatial scale u . The model is authorized if the functions $g^u(h)$ are
236 authorized variogram models. In the LMC the spatial behavior of the variables is supposed
237 resulting from superimposition of different independent processes working at different spatial
238 scales. These processes may affect the behavior of experimental semi-variograms, which can
239 then be modeled by a set of functions $g^u(h)$. The choice of number and characteristics (model,
240 sill, range) of the functions $g^u(h)$ is quite delicate and can be made easier by a good
241 experience of the studied phenomena (Chilès and Guillen, 1984). Fitting of LMC is
242 performed by weighed least-squares approximation under the constraint of positive semi-
243 definiteness of the B^u , using the iterative procedures developed by Goulard (1989). The best
244 model was chosen, as suggested by Goulard and Voltz (1992), by comparing the goodness of
245 fit for several combinations of functions of $g^u(h)$ with different ranges in terms of the
246 weighted sum of squares.

247

248 **2.3.2 Regionalized Principal Component Analysis**

249

250 Regionalized Principal Component Analysis consists of decomposing each
251 coregionalization matrix B^u into two other diagonal matrices: the matrix of eigenvectors and
252 the diagonal matrix of eigenvalues for each spatial scale u through the matrix A^u of order $n \times$
253 n of the transformation coefficients a^u_{iv} (Wackernagel, 2003). The transformation coefficients
254 a^u_{iv} in the matrix A^u correspond to the covariances between the original variables $Z_i(x)$ and the
255 regionalized factors $Y^u_v(x)$.

256

257 **2.3.3 Mapping multivariate spatial information**

258

259 The behavior and relationships among variables at different spatial scales can be
260 displayed by interpolating the regionalized factors $Y^u_v(x)$ using cokriging and mapping them
261 (Castrignanò et al., 2007, 2000). The cokriging system in FKA has been widely described by
262 Wackernagel (2003).

263

264 **3. Results**

265 3.1 Relationships between stream data and geology.

266 Table 1 shows the descriptive statistics of all variables between the geological
267 contexts. The majority of the 115 samples is located in sedimentary areas (n=85), among them
268 40 are carbonate derived rocks, 9 chalks, 12 clays and 24 sand and sandstones. The others
269 are located in metamorphic (n=18), acidic plutonic (n=8) and acidic volcanic (n=3) contexts.
270 Most of physicochemical properties and selected REE show significant differences between
271 the geological contexts: pH, carbonate alkalinity, Fe, La and Lu. This suggests the influence
272 of surrounding rocks geology on water chemistry. Water samples taken from sedimentary
273 areas are characterized by higher carbonate alkalinity concentrations (from 69mg/L to 134
274 mg/L) and alkaline pH value (from 7.68 to 8.02) which is explained by carbonates presence in
275 sedimentary rocks. Higher Fe concentrations (176 mg/L and 224 mg/L respectively) are
276 observed in both acidic plutonic and metamorphic areas. Regarding La, Eu and Lu
277 concentrations, higher concentrations are observed in samples taken from metamorphic and
278 plutonic areas (0.1491 $\mu\text{g/L}$ and 0.1374 $\mu\text{g/L}$ for La, respectively) whereas lower
279 concentrations are derived from carbonate rocks (0.0280 $\mu\text{g/L}$ for La). This is consistent with

280 REE sources essentially located in metamorphic and magmatic rocks (from 50 to 100 mg/kg
281 for La; Henderson, 1984; McLennan, 1989) whereas REE content in carbonates is low (10
282 mg/kg for La; Turekian and Wedepohl, 1961).

283

284 3.2 Principal Component Analysis

285

286 The classical statistical technique based on the PCA has been applied in order to investigate
287 on the behavior of the variables in relation to the principal components. Since geochemical
288 data are compositional, every data set should be opened, prior to its statistical treatment, using
289 a preferred method from a variety of suggested methods (Sadeghi et al., 2014). In this study,
290 statistical PCA has been performed using the ln-transformed data sets (Pawłowsky-Glahn and
291 Buccianti, 2011). The generated results are given in Table 2. The PCA, performed in this
292 study, using ln-transformed data has successfully opened the data. Using PCA, two principal
293 components were extracted that cumulatively explained 90.6% of the total data variability and
294 with an eigenvalue greater than 1 (Table 2). The other components had an eigenvalue less
295 than 1 and were not used. Generally, the first components account for most of the variability
296 contained in the data set (Johnson and Wichern, 2002). In the case study the first two
297 principal components were used in the analysis, mainly due to the presence of such
298 correlations with the real properties, as shown in the circle of correlations presented in Figure
299 2. The circle of correlation shows the proximity of the variables inside a unit circle and is
300 useful to evaluate the affinity and the antagonism between the variables. Statement can easily
301 be made about variables which are located near the circumference of the unit circle. In our
302 case the first component is highly correlated with all REE and also Fe, while the Mn, OC, pH,
303 carbonate alkalinity are located a little further away from the circumference and appear to
304 have a different behavior. They all are correlated negatively with the F2. From an analysis of

305 the circle it is possible to see that all the HREE are positioned in the upper part and all the
306 LREE in the lower part of the semi circumference. Europium shows a slightly different
307 behavior as it is more detached from the circumference, and is close to Fe. From the PCA it
308 appears that the first regionalized factor explains the behavior of the REE and separates them
309 from the other elements. No substantial additional information is provided by the F2.

310

311 **3.3 Coregionalization analysis**

312 The variables are highly shifted from the Gaussian distribution so they were
313 normalized and standardized to mean 0 and variance 1. On the basis of the results of principal
314 component analysis, a choice has been made between the 19 variables. The chosen parameters
315 are Fe, Mn, carbonate alkalinity, organic carbon and pH for the physicochemical properties
316 together with La, Lu and Eu for the REE. La is representative of LREE, Lu of HREE and Eu
317 has been chosen because of his peculiar behavior (McLennan and Taylor, 2012). Using
318 GAMV of GSLIB library (Deutsch and Journel, 1992) the experimental variograms and
319 cross-variograms of the 3 REEs and Fe, Mn, carbonate alkalinity, organic carbon and pH has
320 been obtained with lag separation distance equal to 20 km. No relevant anisotropy was
321 observed in the variogram maps and the experimental variograms looked upper bounded. The
322 linear coregionalization model has been obtained using the LCMFIT2 program (Pardo-
323 Iguzquiza and Dowd, 2002) to fit the 36 experimental variograms. The LMC was fitted using
324 two spatial structures: a spherical model with a range of 120 km and a spherical model with a
325 range of 250 km. The linear coregionalization models (direct and cross-variograms) (not
326 shown) appear well spatially structured also due to the absence of the not-spatially correlated
327 component (nugget effect). The spatial cross-correlation is shown in Table 3. The
328 appropriateness of the LCM and the basic structures was evaluated with a cross-validation test
329 by calculating the mean error and the variance of standardized error, which were quite close

330 to 0 (varying between -0.033 and 0.0145) and 1 (varying between 0.9 and 1.2), respectively.
331 These results mean that the estimates were unbiased and the estimation variance reproduced
332 the experimental variance accurately.

333

334 **3.4 Factorial kriging**

335

336 Using FACTOR2d program (Pardo-Iguzquiza and Dowd, 2002) a factorial cokriging
337 is used to estimate the first 2 regionalized individual factors that, at the cost of an acceptable
338 loss of information, have given a synthetic description of the process in study at the different
339 selected spatial scales. As no nugget effect has been modeled, the short-range and long-range
340 components of the first two regionalized factors were selected. The long range component
341 (250 km) of the first two factors explains most variance (80.3% and 17.0%, respectively)
342 while the short range component explains just the 50.0% and 20.2% for F1 and F2
343 respectively, which is less representative. The long range component of the first factor shows
344 to be the most explicative as it is correlated with most of the elements positively, such as Fe
345 (0.796), La (0.814), Lu (0.603), organic carbon (0.639) and negatively with HCO_3^- (-0.607),
346 pH (-0.648) (Table 4). The F1 at long range synthesizes the long range variability of the
347 whole elements with a localized higher value zone in the central and south-eastern part. The
348 short range component (120 km) of the first factor is mostly correlated with Eu (0.773) and
349 Mn (0.687). Europium shows a different behavior being mostly explained by the F1 at the
350 short spatial scale. However, in order to get more precise information about its structure,
351 additional data should be collected to infer the variability at a smaller spatial scale. As far as
352 the F2, it does not show to be correlated at all with the REE but it is correlated more with the
353 physico-chemical parameters, such as with the pH at small spatial scale (0.580).

354

355 **3.5 Cokriging**

356

357 Cokriging was applied to the transformed data to obtain the estimates which were then
358 back-transformed to express them in the original variables. The spatial maps of the eleven
359 variables were obtained by cokriging on a 10 km × 10 km square grid. Figures 3, 4 and 5
360 represent, respectively, the first regionalized factor at short range and at long range, the 3
361 selected REEs and the 5 physicochemical properties. From an analysis of the cokriged maps
362 it is possible to see that REE exhibit all similar spatial distributions, with extended higher
363 values in the south-western part, in correspondence with the depression of Aquitaine basin
364 (low area surrounded by higher land and usually characterized by interior drainage). Other
365 zones of localized higher value correspond with the Alpine valley corridors of the Rhône, the
366 hydrographic network of the Seine basin, hydrographic network of the Loire with its
367 effluents. Another zone of higher values is localized in correspondence of the Oise basin, in
368 the Paris basin. The anisotropy (SW-NE for the southern part and NW-SE for the northern
369 part of France) showed in the maps of REE is coherent with the direction of propagation of
370 rivers except for the Aquitaine basin where the high concentrations are due to the interior
371 drainage of the low area. Organic carbon and Mn show similar behavior having higher zone
372 values concentrated in the same areas of the REE, while carbonate alkalinity and pH, show a
373 totally contrasting behavior with the rest of the variables (being negatively correlated).

374

375 **4. Discussion**

376 4.1. Assessment of factor kriging analysis

377

378 The long range component of the first factor shows to be the most explicative (80.3% of the
379 variance) as it synthesizes the long range variability of most of the elements (Fe, La, Lu,

380 organic carbon, carbonate alkalinity and pH) with a localized higher value zone in the central
381 and south-eastern part. Therefore at high spatial scales environmental parameters like Fe,
382 carbonates, pH, are supposed be ascribed to the rock's nature or to other larger scale processes
383 (i.e., river network). The structure of the hydrographic network is determined by a complex
384 of physicogeographic conditions especially by climate, by the topography, and by the
385 geological structure of the locality. Indeed, hydrographic network and topography have shown
386 to affect REE distribution (e.g., Kohler et al., 2014). The short range component of the first
387 factor explains just the 50.0% of the variance and is mostly correlated with Eu (0.773) and
388 Mn (0.687). So at short range, just the Eu and Mn weigh more, which are ascribed to the
389 process of Mn oxides release in rivers simultaneously with REE sorbed on these oxides
390 (Koeppenkastrop and De Carlo, 1993). Indeed, Mn oxides behave like Fe oxides, and as
391 evidenced by Steinmann and Stille (2008) saturation index of goethite decrease with transport
392 and resulting REE fractionation in the stream water.

393 To sum up, only the first regionalized factor corresponding to long range is
394 representative of the conjoint variability of the elements in study. The short range variability
395 has not proved to explain the behavior of the variables satisfactorily. The sampling scale
396 adopted is too wide and can give sufficient information for a correlation scale of hundreds of
397 kilometers. To be able to infer the variation at a smaller scale, further sampling on a finer
398 spatial scale would be needed.

399

400 4.2. Rare earth elements as tracer of hydrological transfer

401

402 Research results from past twenty years clearly show an influence of topography on
403 stream water chemistry. Moreover several authors have proved that topography was the
404 attribute that had the major influence on stream water chemistry (Andersson and Nyberg,

405 2009; Ogawa et al., 2006). The influence of topography is important because it controls the
406 water subsurface contact time (Beven and Kirkby, 1979; Dillon and Molot, 1997; McGuire et
407 al., 2005; Wolock et al., 1990). Topography is of great significance in hydrology, affecting
408 soil water content, flowpaths and residence times (Nyberg, 1995), and subsequently the
409 chemical composition of surface waters (Beven, 1986; Wolock et al., 1989). Such a feature
410 was thus tested on REE as previously shown by Köhler et al. (2014): in boreal catchments
411 REE export is mostly strongly controlled by landscape type. In continental systems,
412 percolation of rain water through the rocks will result in low-temperature chemical
413 weathering reactions that will slowly break down the primary minerals, possibly resulting in
414 mobility of the REE. The chemistry of groundwater is clearly very dependent on the
415 physicochemical environments through which it has passed.

416 A focus on the Garonne and Dordogne systems, in correspondence to the Aquitaine
417 basin characterized by higher values and anisotropy, emphasized this feature. Indeed, both
418 river systems originate in Massif Central, where low-temperature chemical weathering of
419 acidic magmatic rocks occurs. Moreover, topography is escarped and results in low residence
420 time. It is highlighted on figure 6, where REE patterns of considered samples depicted low
421 REE concentration and negative cerium anomaly. Positive europium anomaly can be
422 interpreted as a result of water rock interaction with feldspar from bedrocks (i.e., basalts;
423 Steinmann and Stille, 2008). Both river systems then encountered the Aquitaine basin, with a
424 more flat topography with higher residence time. It results in higher REE concentrations
425 (figure 6), with middle REE enriched patterns, corresponding to an organic sedimentary input.
426 Overall, spatial variability results in REE and organic carbon concentrations increase and a
427 pH decrease (figure 7).

428 Wetlands would play a key role in the regulation of REE concentrations in the
429 environment as earlier proposed (Davranche et al., 2014). Indeed REE are released in wetland

430 bound to colloidal organic matter as also observed in watershed or rivers (Shiller, 2010;
431 Stolpe et al., 2013). Moreover, figure 7 shows the global control of dissolved REE
432 concentrations by pH as previously highlighted for Nd by Johannesson and Burdige (2007) or
433 Deberdt et al. (2002). Indeed, pH can significantly influence the speciation and thus the
434 behavior of the REE (Pourret et al., 2007; Tang and Johannesson, 2003). A decrease in pH
435 will favor solution of the REE and thus their transport either as organic complexes or as free
436 ions. In figure 8, cerium anomaly in these two river water systems are reported as a function
437 of the distance to the outlet. Figure 8 shows that the two river water systems plot along a
438 single trend reflecting the Ce anomaly amplitude gradual reduction as the distance to the
439 outlet decreases. It must be noted that a few points (n=3) have a different behavior from this
440 trend and correspond to more organic water (associated to wetlands). As already proposed by
441 Pourret et al. (2010) the likely reason for the Ce anomaly amplitude gradual reduction
442 observed mainly relies on the fact that, in low permeability aquifers, water table generally
443 reaches organic soil horizons in bottomland domains, thus allowing incorporation of large
444 quantities of organic colloids in the aquifer bottomland part. This feature is not seen in the
445 aquifer upland part where the water table always remains far below the upper, organic-rich
446 soil horizons. Considering results from this study, it appears that the general feature of
447 shallow groundwaters flowing into aquifers developed onto low permeability bedrock
448 (Pourret et al., 2010) can be expanded to river water systems.

449

450 **5. Concluding remarks**

451

452 In order to further understand REE patterns spatial distribution, the FOREGS stream
453 dataset was processed by means of geostatistical methods. The obtained maps allow
454 visualizing the factors which integrate REE spatial variability. Cokriging shows a similar

455 spatial organization of REE: higher values are observed in the Aquitaine basin, more locally
456 in the Alpine valley corridors of the Rhone, and along some tributaries of the Loire and the
457 Seine. A factorial cokriging was applied to investigate more deeply the different sources of
458 variation acting in the study area. The first 2 regionalized factors have been estimated to give
459 a synthetic description of the studied process at the different selected spatial scales. At large
460 spatial scales (250 km) environmental parameters like Fe, carbonates, pH, are supposed be
461 ascribed to the rock's nature (plutonic, volcanic and metamorphic versus sedimentary) or to
462 other larger scale processes, such as hydrographic network and topography have shown to
463 affect REE distribution. The factor kriging analysis used in this study reveals the spatial
464 patterns of REE in stream water. REE are positively correlated to Fe and Mn and negatively
465 to carbonate alkalinity and pH. At short range, only Eu and Mn weigh more, which are
466 ascribed to the process of liberation of Mn oxides in rivers that also releases the REE sorbed
467 onto these oxides. This variability is discussed with some landscape factors, especially
468 topography and upstream/downstream location. However, the short range variability cannot
469 be explained satisfactorily by the adopted sampling as the sampling scale is too wide and can
470 give sufficient information for a correlation scale of hundreds of km. To be able to infer the
471 variation at a smaller scale, further sampling on a finer spatial scale would be needed.

472

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476

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672

673 **Figure and table captions**

674 Fig. 1 Simplified maps of (a) elevation and (b) geological units. |

675

676 Fig. 2 Principal component analysis: circle of correlations.

677

678 Fig. 3 First regionalized factor at short (structure 1) and at long range (structure 2).

679

680 Fig. 4 Cokrigged maps of (a) La, (b) Eu, and (c) Lu.

681

682 Fig. 5 Cokrigged maps of physicochemical properties (a) Fe, (b) HCO_3^- , (c) Mn, (d) organic
683 carbon, and (e) pH.

684

685 Fig. 6 Upper continental crust(UCC)-normalized REE patterns in samples from (a) Dordogne
686 river and (b) Garonne river (UCC values are from McLennan 2001).

687

688 Fig. 7 Concentrations of Nd in river samples as a function of pH (Garonne-Dordogne
689 watershed).

690

691 Fig. 8 Cerium anomaly as a function of distance to outlet (Garonne-Dordogne watershed).

692

693 Table 1 Descriptive statistics of selected REE and physicochemical properties.

694

695 Table 2 Principal component analysis: obtained components.

696

697 Table 3 Structural correlation coefficients.

698

699 Table 4 Correlation between factors and original variables.

Table 1 Descriptive statistics of selected REE and physicochemical properties (to be continued).

Geological context	n	pH				HCO ₃ (mg/L)				OC (mg/L)				Fe (µg/L)				Mn (µg/L)			
		mean	sd	med	MAD	mean	sd	med	MAD	mean	sd	med	MAD	mean	sd	med	MAD	mean	sd	med	MAD
acidic plutonic rock	8	6.99	0.42	7.00	0.20	30.12	31.74	18.17	5.24	5.02	3.28	4.05	1.80	176.48	114.55	150.00	81.05	16.24	10.69	13.75	6.95
acidic volcanic rock	3	7.03	0.85	6.70	0.30	31.14	8.61	34.00	3.95	1.82	0.77	1.85	0.73	74.90	30.96	83.00	18.00	11.42	6.07	10.20	4.15
Metamorphic rock (schist, gneiss...)	18	7.42	0.67	7.20	0.30	50.80	47.08	34.63	12.50	5.03	3.79	4.57	2.70	224.47	161.12	229.00	154.78	23.73	23.55	15.50	10.45
Carbonate sedimentary rock	40	8.02	0.67	8.10	0.10	230.87	114.18	277.98	65.84	2.89	3.70	1.97	0.90	46.78	68.82	18.23	9.60	17.45	28.19	3.61	3.24
Chalk	9	7.79	0.67	7.75	0.10	276.11	69.14	300.23	24.08	4.50	3.44	3.41	1.71	65.33	93.12	32.60	24.02	14.16	10.19	11.30	7.10
Clay	12	7.68	0.67	7.80	0.25	163.49	133.96	113.15	91.75	3.61	2.25	3.68	1.74	108.56	126.34	60.77	45.12	34.11	44.31	20.55	13.90
Sand and sandstone	24	7.80	0.67	8.00	0.20	174.60	130.85	131.67	106.31	4.35	2.96	3.80	1.95	137.25	211.21	37.40	28.39	25.73	28.36	15.71	11.18
no data	1																				
Kruskal-Wallis p-value		***				***				*				***							NS

***: p<0.001, **: p<0.01, *: p<0.05, NS = non-significant.

Table 1 Descriptive statistics of selected REE and physicochemical properties (continued).

Geological context	n	La (µg/L)				Eu (µg/L)				Lu (µg/L)			
		mean	sd	med	MAD	mean	sd	med	MAD	mean	sd	med	MAD
acidic plutonic rock	8	0.1491	0.0905	0.1490	0.0680	0.0083	0.0036	0.0070	0.0020	0.0031	0.0014	0.0030	0.0010
acidic volcanic rock	3	0.0717	0.0071	0.0730	0.0050	0.0040	0.0010	0.0040	0.0010	0.0013	0.0006	0.0010	< 0.001
Metamorphic rock (schist. gneiss...)	18	0.1374	0.1076	0.1250	0.0930	0.0095	0.0057	0.0080	0.0040	0.0031	0.0019	0.0030	0.0020
Carbonate sedimentary rock	40	0.0280	0.0441	0.0170	0.0130	0.0055	0.0043	0.0050	0.0030	0.0013	0.0009	0.0010	< 0.001
Chalk	9	0.0720	0.1333	0.0190	0.0090	0.0049	0.0069	0.0020	0.0010	0.0018	0.0016	0.0010	< 0.001
Clay	12	0.0850	0.1267	0.0380	0.0240	0.0080	0.0087	0.0050	0.0030	0.0020	0.0018	0.0010	< 0.001
Sand and sandstone	24	0.0941	0.1278	0.0340	0.0260	0.0080	0.0078	0.0050	0.0030	0.0025	0.0026	0.0010	< 0.001
no data	1												
Kruskal-Wallis p-value		***				*				***			

***: p<0.001, **: p<0.01, *: p<0.05, NS = non-significant.

Table 2[Click here to download Table: Table 2 armand jge.docx](#)

Table 2 Principal component analysis: obtained components.

Component	Eigenvalue	Variance (%)	Cumulative variance
F1	22.66	84.5	84.5
F2	1.62	6.1	90.6

Table 3

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Table 3 Structural correlation coefficients

Short range h = 120 km								
	Eu	Fe	HCO ₃	La	Lu	Mn	OC	pH
Eu	1.000							
Fe	0.640	1.000						
HCO ₃	-0.174	-0.227	1.000					
La	0.772	0.525	-0.474	1.000				
Lu	0.682	0.444	-0.409	0.568	1.000			
Mn	0.644	0.856	-0.156	0.533	0.315	1.000		
OC	0.735	0.409	0.000	0.251	0.364	0.400	1.000	
pH	-0.261	-0.181	0.403	-0.191	-0.331	-0.191	0.000	1.000
Long range h = 250 km								
	Eu	Fe	HCO ₃	La	Lu	Mn	OC	pH
Eu	1.000							
Fe	0.879	1.000						
HCO ₃	-0.987	-0.845	1.000					
La	0.734	0.958	-0.718	1.000				
Lu	0.865	0.995	-0.823	0.957	1.000			
Mn	0.109	0.561	-0.087	0.752	0.572	1.000		
OC	0.428	0.796	-0.355	0.858	0.802	0.873	1.000	
pH	-0.739	-0.922	0.750	-0.981	-0.920	-0.705	-0.752	1.000

Table 4

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Table 4 Correlation between factors and original variables.

<i>Short range h = 120 km</i>		
	Factor 1	Factor 2
Eu	0.773	0.146
Fe	0.493	0.106
HCO ₃	-0.256	0.437
La	0.441	-0.044
Lu	0.519	-0.148
Mn	0.687	0.183
OC	0.378	0.252
pH	-0.296	0.580
Explained variance (%)	50.0	20.2
<i>Long range h = 250 km</i>		
	Factor 1	Factor 2
Eu	-0.436	0.294
Fe	0.796	-0.074
HCO ₃	-0.607	0.452
La	0.814	0.104
Lu	0.603	-0.042
Mn	0.374	0.423
OC	0.639	0.393
pH	-0.648	-0.029
Explained variance (%)	80.3	17.0

Figure 1
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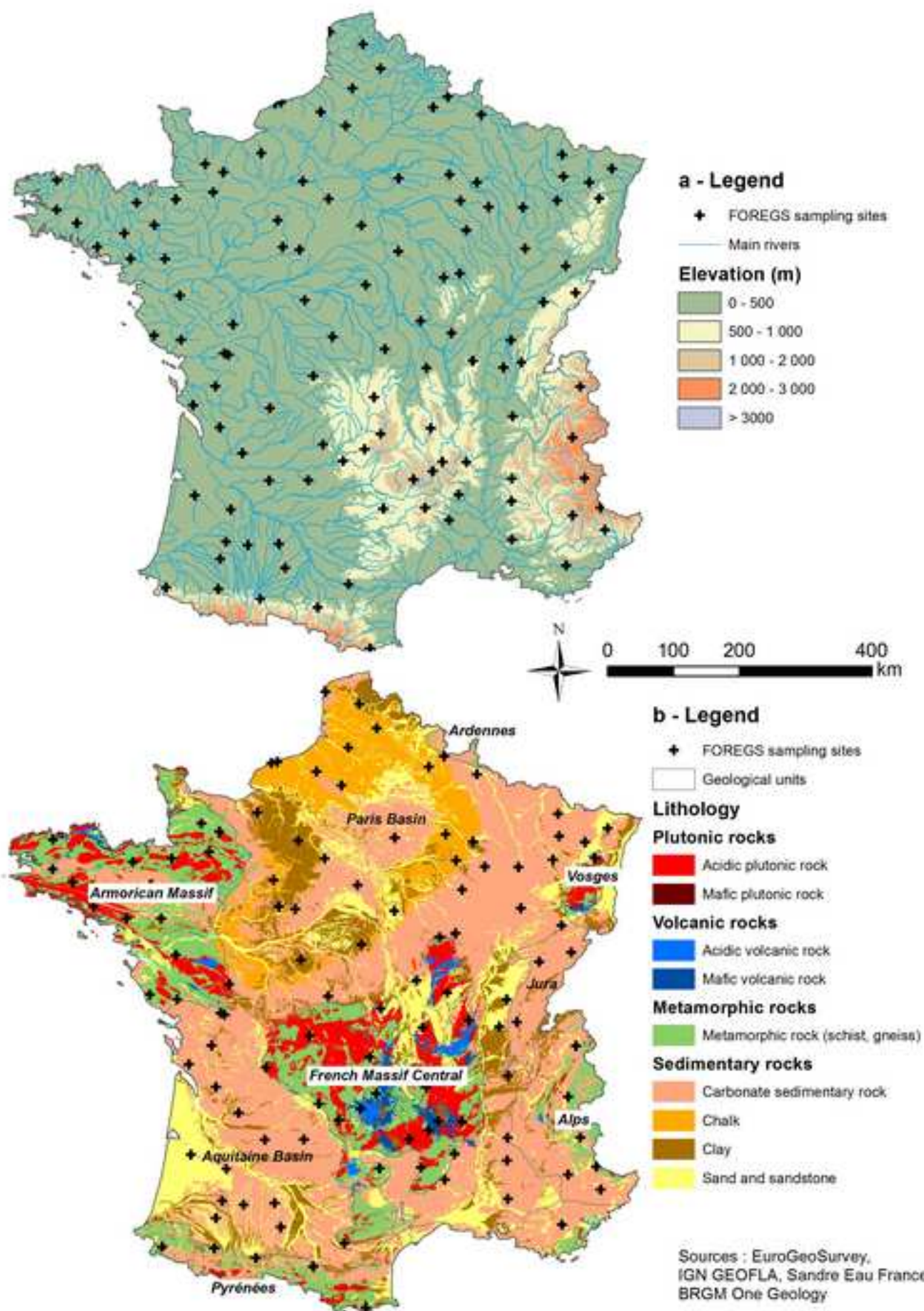


Figure 2

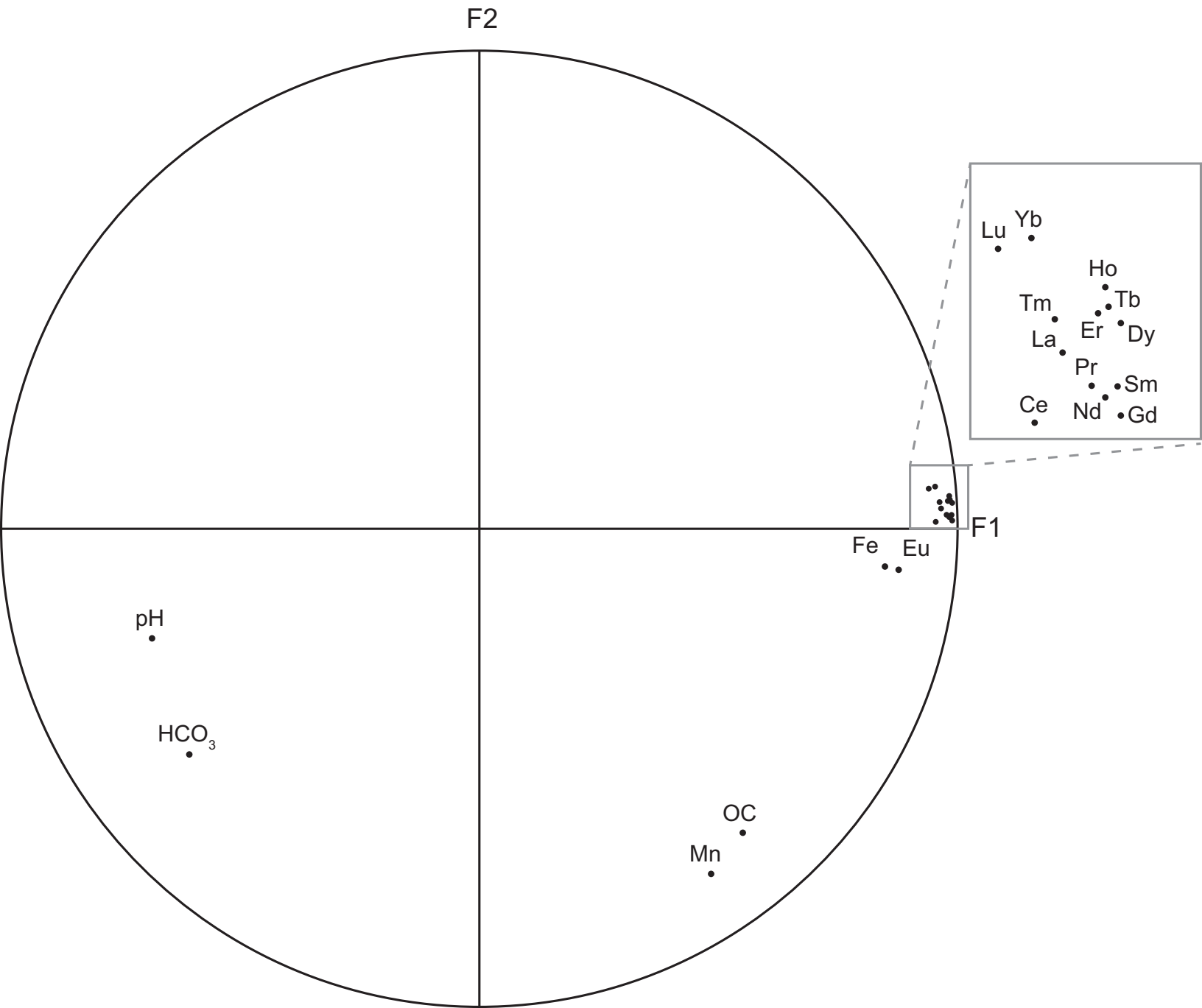


Figure 3
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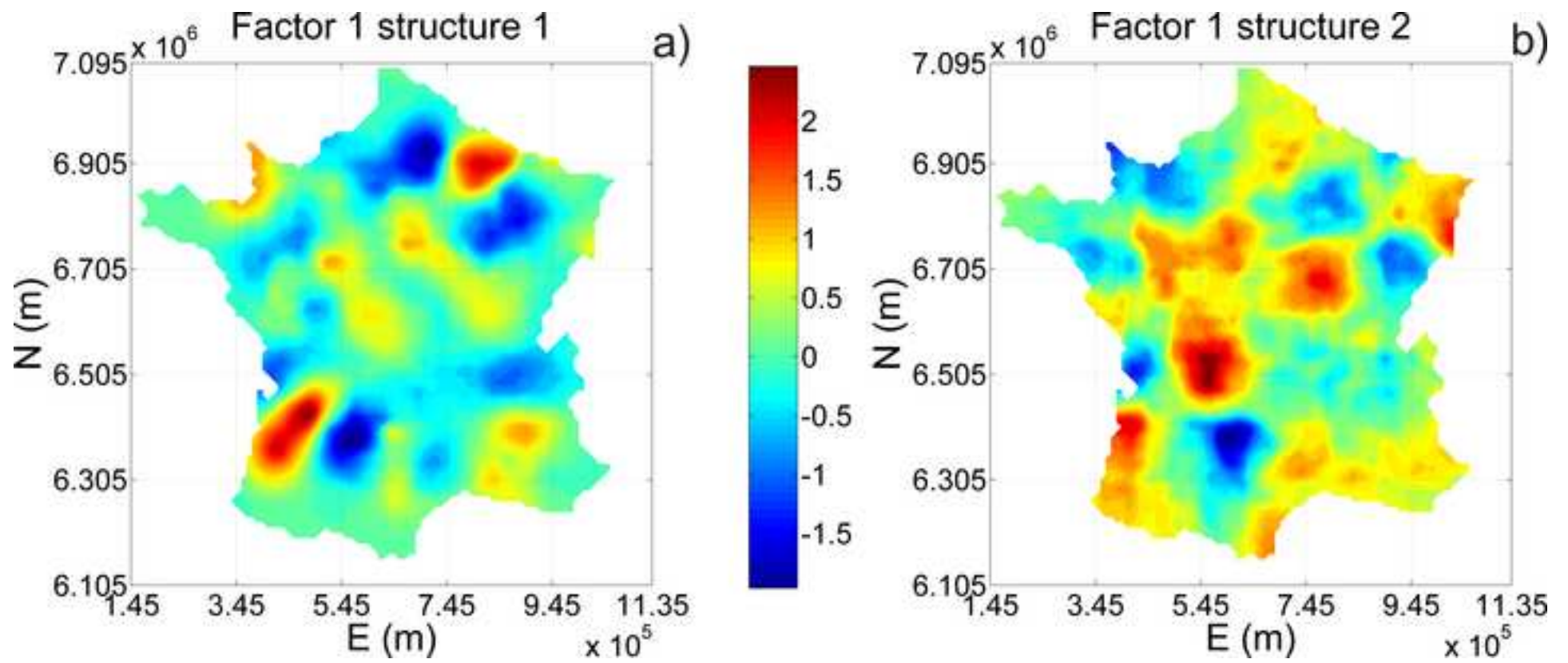


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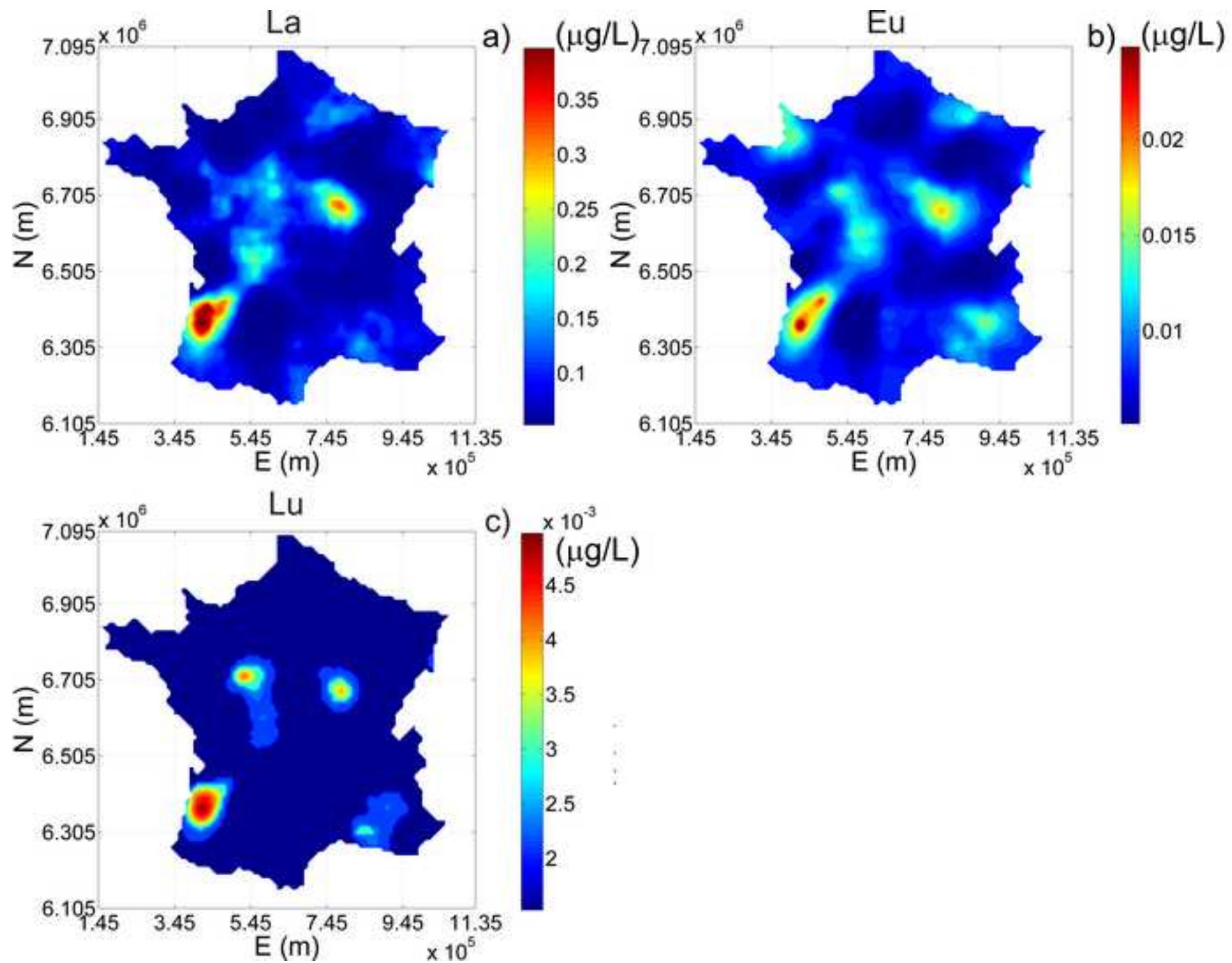


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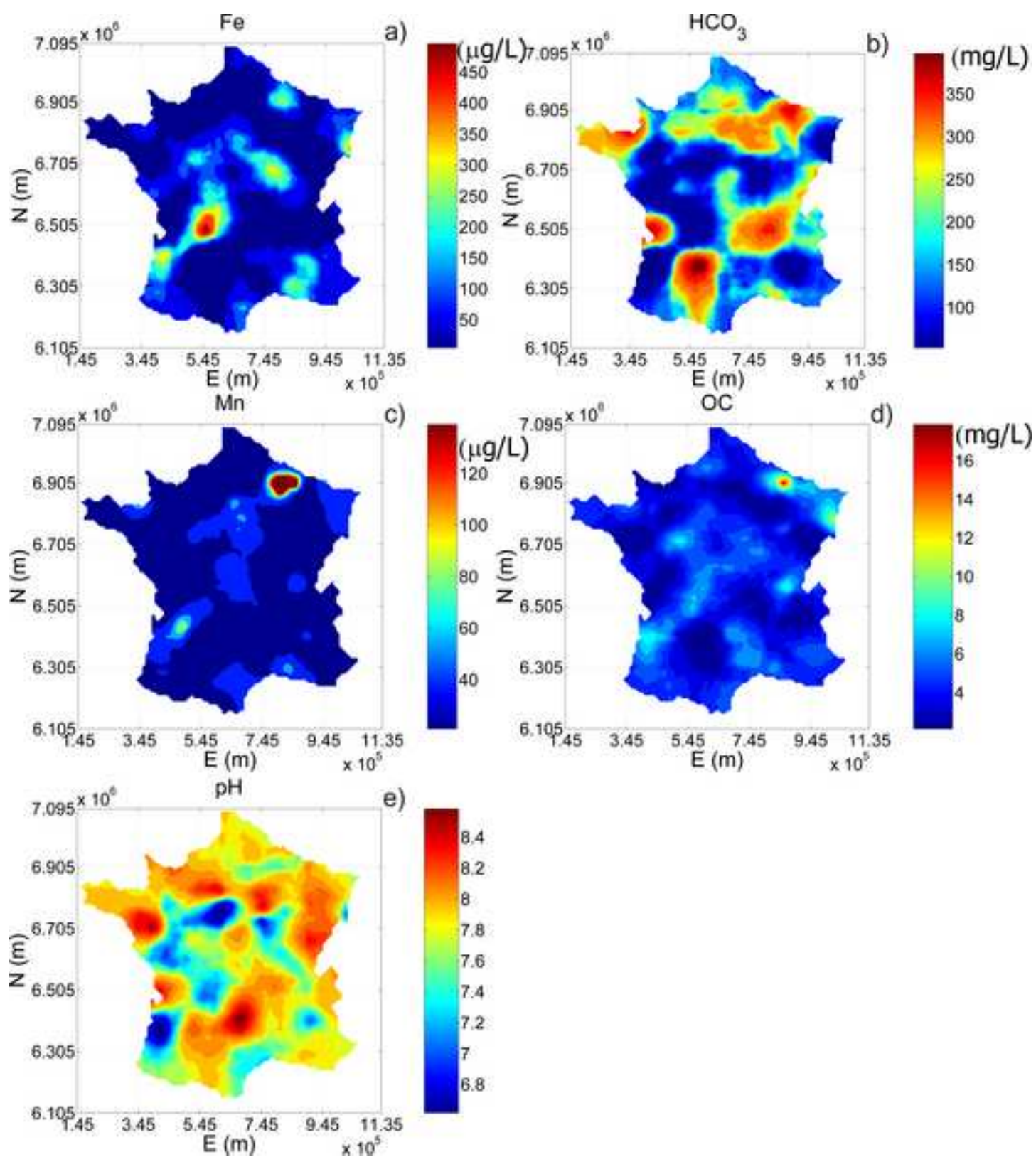


Figure 6

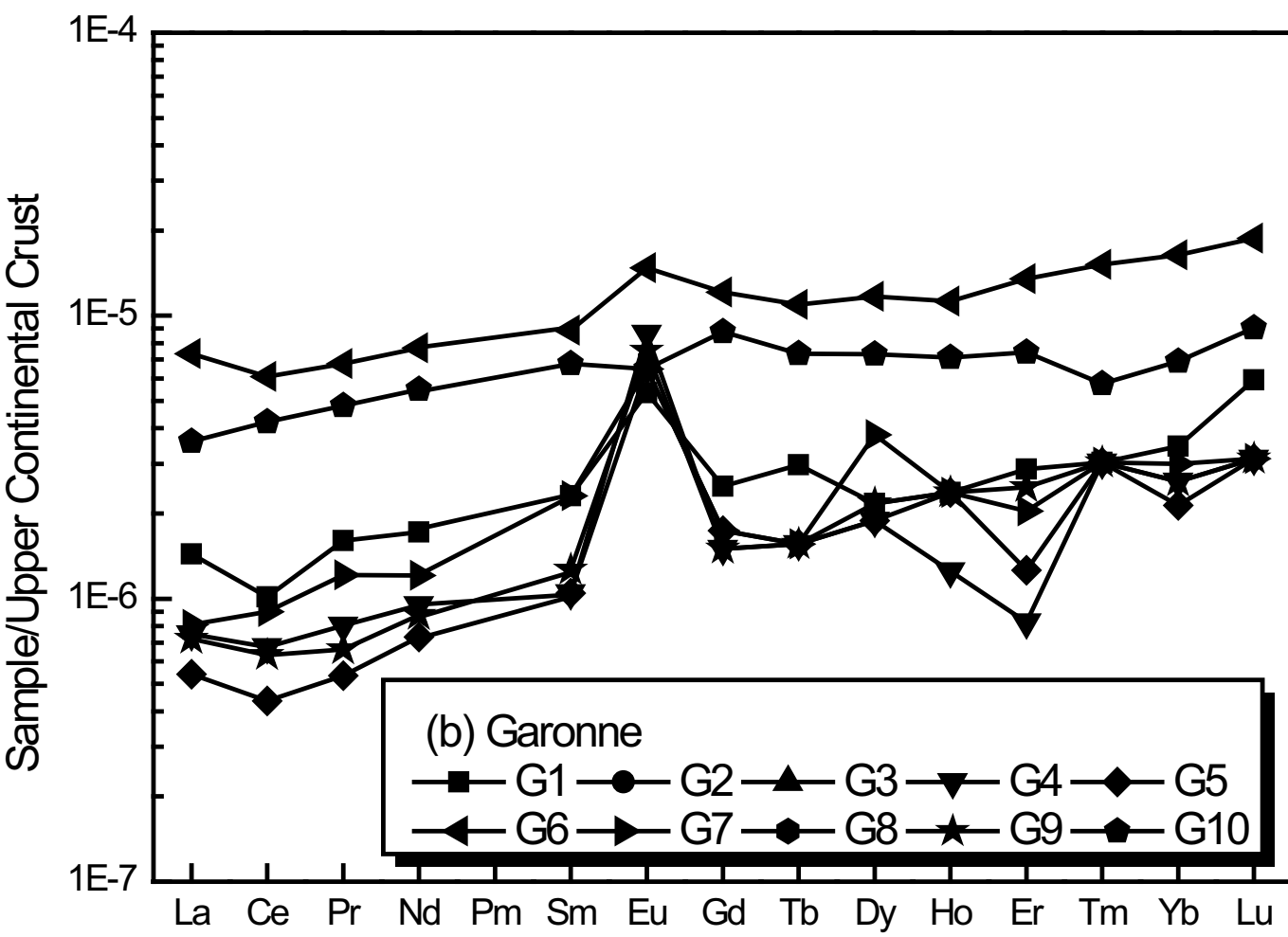
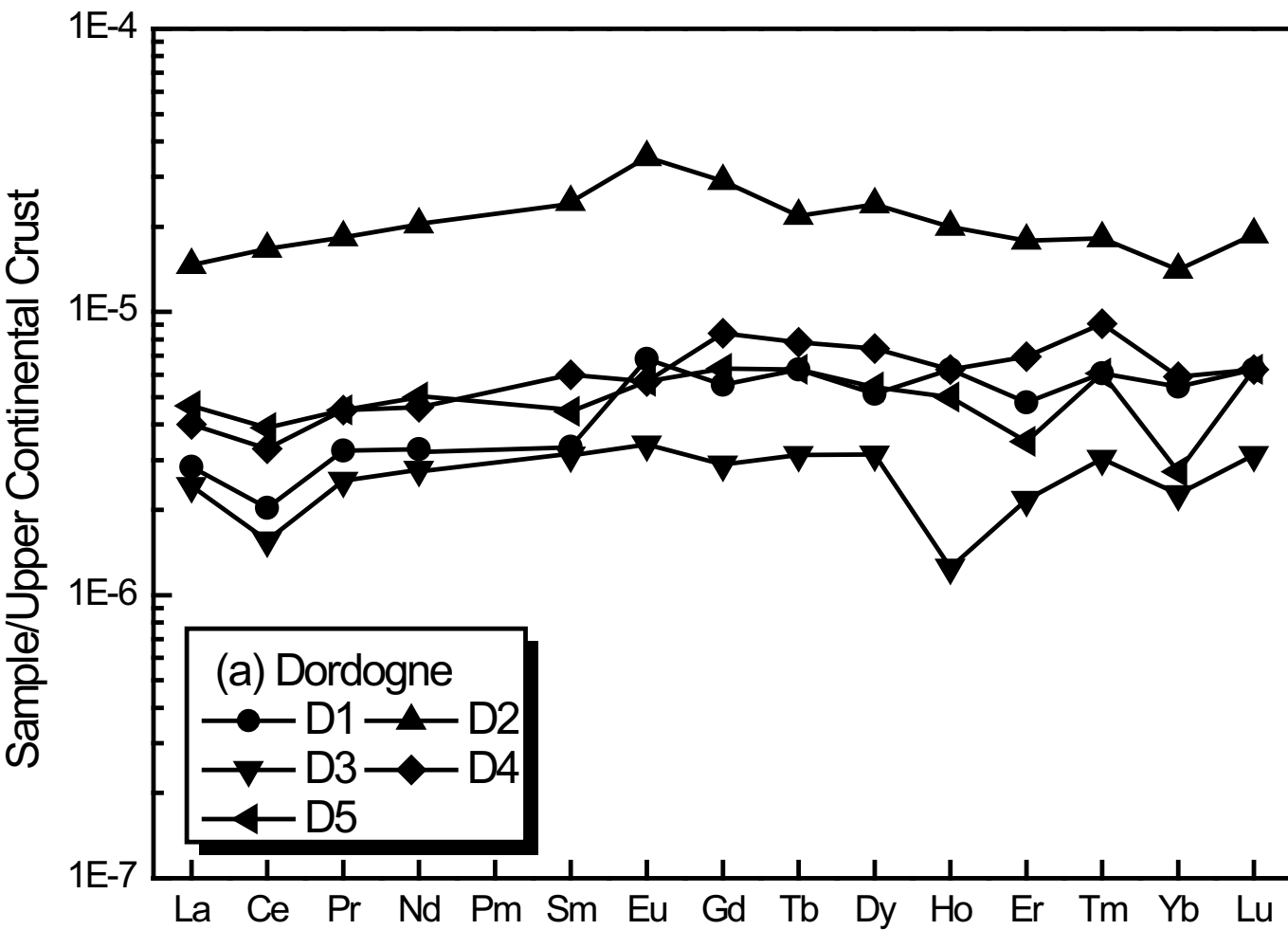


Figure 7

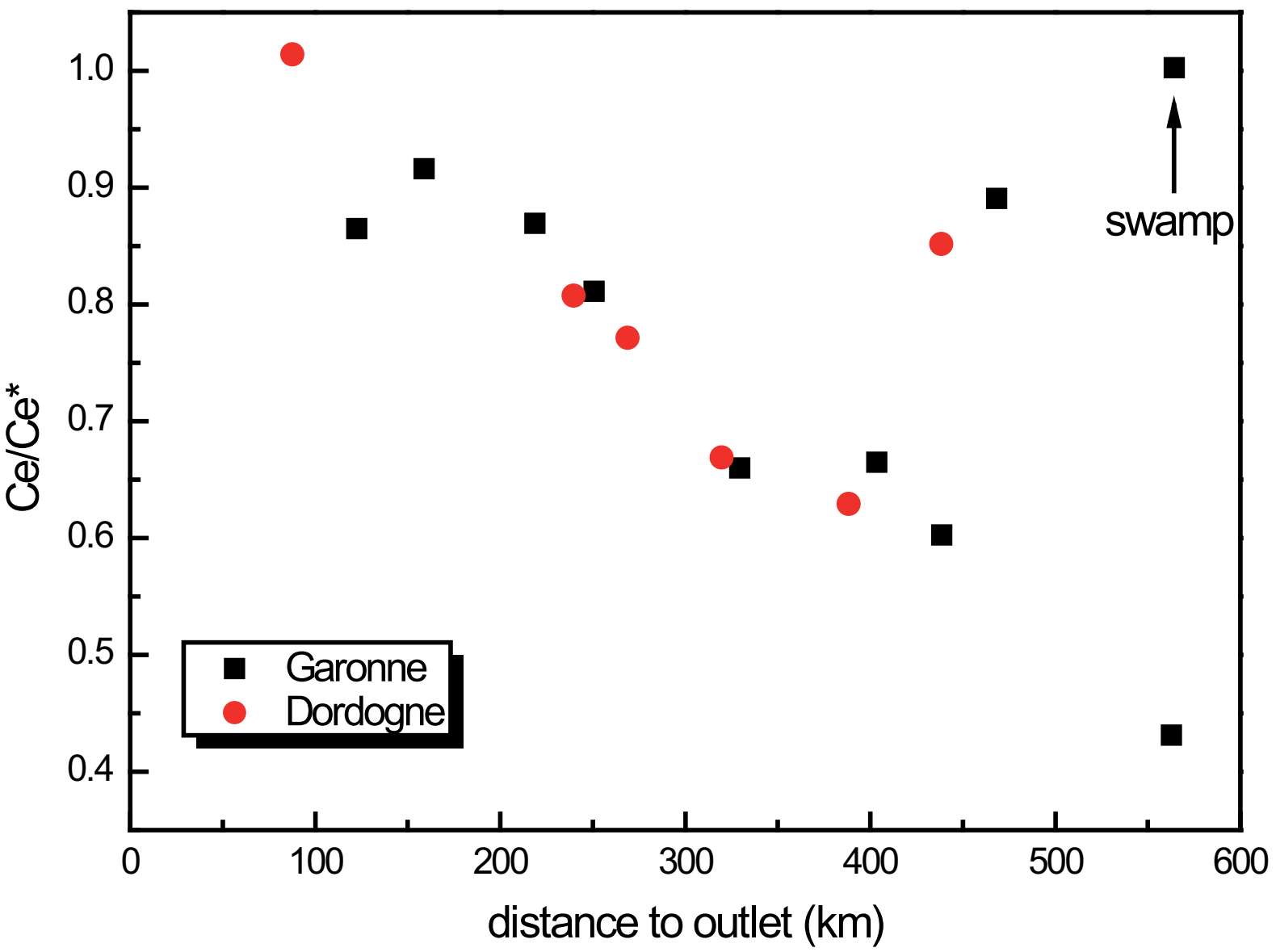
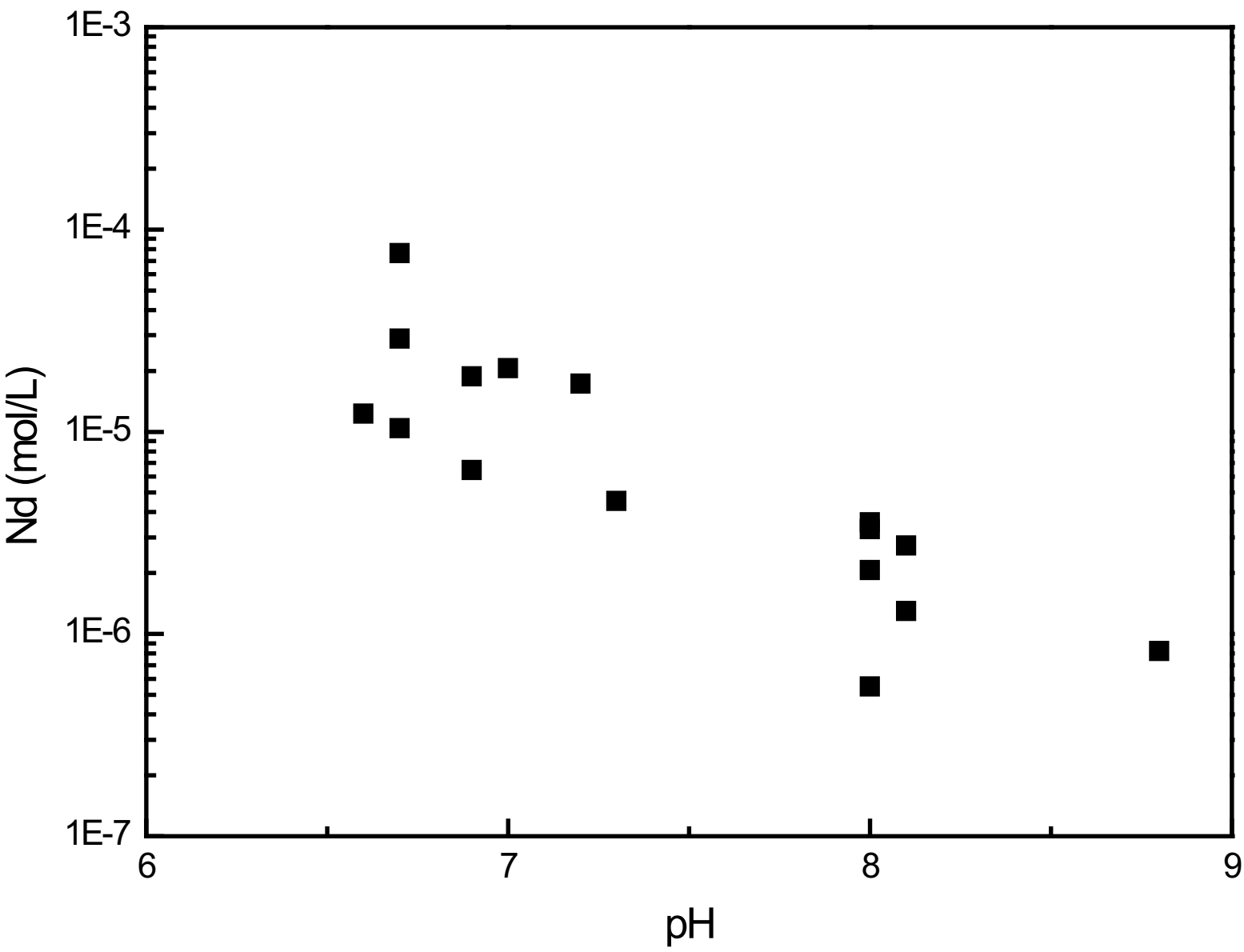


Figure 8



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