Rare earth elements in French stream waters -revisiting the geochemical continental cycle using FOREGS dataset

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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 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

1. Introduction

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

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

depletion or enrichment degree of light REE (LREE) relative to heavy REE (HREE) or by

whether or not anomalies occur. Indeed, individual REE may show anomalous behavior in

natural waters: redox-sensitive Ce and Eu may show anomalies that may be used as redox-

and/or temperature-proxies (e.g., Bau, 1991; De Baar et al., 1988), and La, Gd and Lu may

show small anomalies due to subtle differences between the stabilities of REE complexes

(Bau, 1999; Byrne and Kim, 1990). In addition to these natural anomalies, anthropogenic

anomalies of Gd and, recently, La and Sm have been reported from natural waters (e.g.,

Kulaksız and Bau, 2013), and references therein).

To better understand the occurrence of aqueous metals and especially REE, the

FOREGS (Forum of European Geological Surveys) aims at providing a basis for formulating

policies and legislation concerning the management of harmful elements and to define their

corresponding safety levels (Salminen et al., 2005). A first attempt was performed in Italy,

Sweden and Europe by Imrie et al. (2008); Lado et al. (2008); Petrosino et al. (2013); Sadeghi

et al. (2013). These studies mostly focus on topsoil dataset and investigate the main factors

explaining REE variation in the soil solution; however, the FOREGS database contains

descriptions of other environmental media (stream and floodplain sediments, and stream

water). The database has been processed by Imrie et al. (2008); Lado et al. (2008), Petrosino

et al. (2013) and Sadeghi et al. (2013) by means of multivariate approaches to interpolate all

variables, metals or REE concentrations. They used factorial kriging for Imrie et al. (2008),

regression kriging for Lado et al. (2008) and inverse distance weighted interpolation and

principal component analysis for Sadeghi et al. (2013). The results associate spatial

distribution of elements with different factors operating at several scales. For example, Imrie

et al (2008) highlight four factors and amongst them (i) a short scale (72 km): concentrations

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

2. Materials and methods

2.1 The study area

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

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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 use[1] (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;

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[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 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 km²). 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   0.45µm (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   ±10%, the bias is within ±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 $\{Z_i(x), i = 1,\ldots, n; \}$

214 into a set of reciprocally orthogonal regionalized factors $\{Y^u_v(x), v = 1,\ldots, n; u = 1,\ldots, N_s\}$

215 where N_S is the number of spatial scales, through transformation coefficients a^u_{iv} (loadings

216 components score) combining the spatial with the multivariate decomposition:

217 $$Z_i(x) = \sum_{u=1}^{N_S} \sum_{v=1}^{n} a^u_{iv} Y^u_v(x)$$

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 $$\Gamma(h) = \sum_{u=1}^{N_S} B^u g^u(h)$$

232   where $\Gamma(h) = [\gamma_{ij}(h)]$ is a symmetric matrix of order n × 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 × 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**

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250   Regionalized Principal Component Analysis consists of decomposing each

251   coregionalization matrix $\boldsymbol{B}^u$ into two other diagonal matrices: the matrix of eigenvectors and

252   the diagonal matrix of eigenvalues for each spatial scale u through the matrix $\boldsymbol{A}^u$ of order n x

253   n of the transformation coefficients a^u_{iv} (Wackernagel, 2003). The transformation coefficients

254   a^u_{iv} in the matrix $\boldsymbol{A}^u$ correspond to the covariances between the original variables $Z_i(x)$ and the

255   regionalized factors $Y^u_v(x)$.

256

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 $Y_v^u(x)$ 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

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 sandstoness. 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 µg/L and 0.1374 µg/L for La, respectively) whereas lower
279 concentrations are derived from carbonate rocks (0.0280 µg/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 (Pawlowsky-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

13

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

3.5 Cokriging

355

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

4. Discussion

375

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 sedimendary) 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

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 mean	sd	med	MAD	HCO3 (mg/L) mean	sd	med	MAD	OC (mg/L) mean	sd	med	MAD	Fe (µg/L) mean	sd	med	MAD	Mn (µg/L) 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 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 Structural correlation coefficients

	Eu	Fe	HCO$_3$	La	Lu	Mn	OC	pH
			Short range h = 120 km					
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 Correlation between factors and original variables.

Short range h = 120 km		
	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
Long range h = 250 km		
	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

a - Legend

+ FOREGS sampling sites
— Main rivers

Elevation (m)

- 0 - 500
- 500 - 1 000
- 1 000 - 2 000
- 2 000 - 3 000
- \> 3000

b - Legend

+ FOREGS sampling sites
☐ Geological units

Lithology

Plutonic rocks
- Acidic plutonic rock
- Mafic plutonic rock

Volcanic rocks
- Acidic volcanic rock
- Mafic volcanic rock

Metamorphic rocks
- Metamorphic rock (schist, gneiss)

Sedimentary rocks
- Carbonate sedimentary rock
- Chalk
- Clay
- Sand and sandstone

Sources : EuroGeoSurvey,
IGN GEOFLA, Sandre Eau France
BRGM One Geology

Figure 2

a) Factor 1 structure 1

b) Factor 1 structure 2

Figure 4
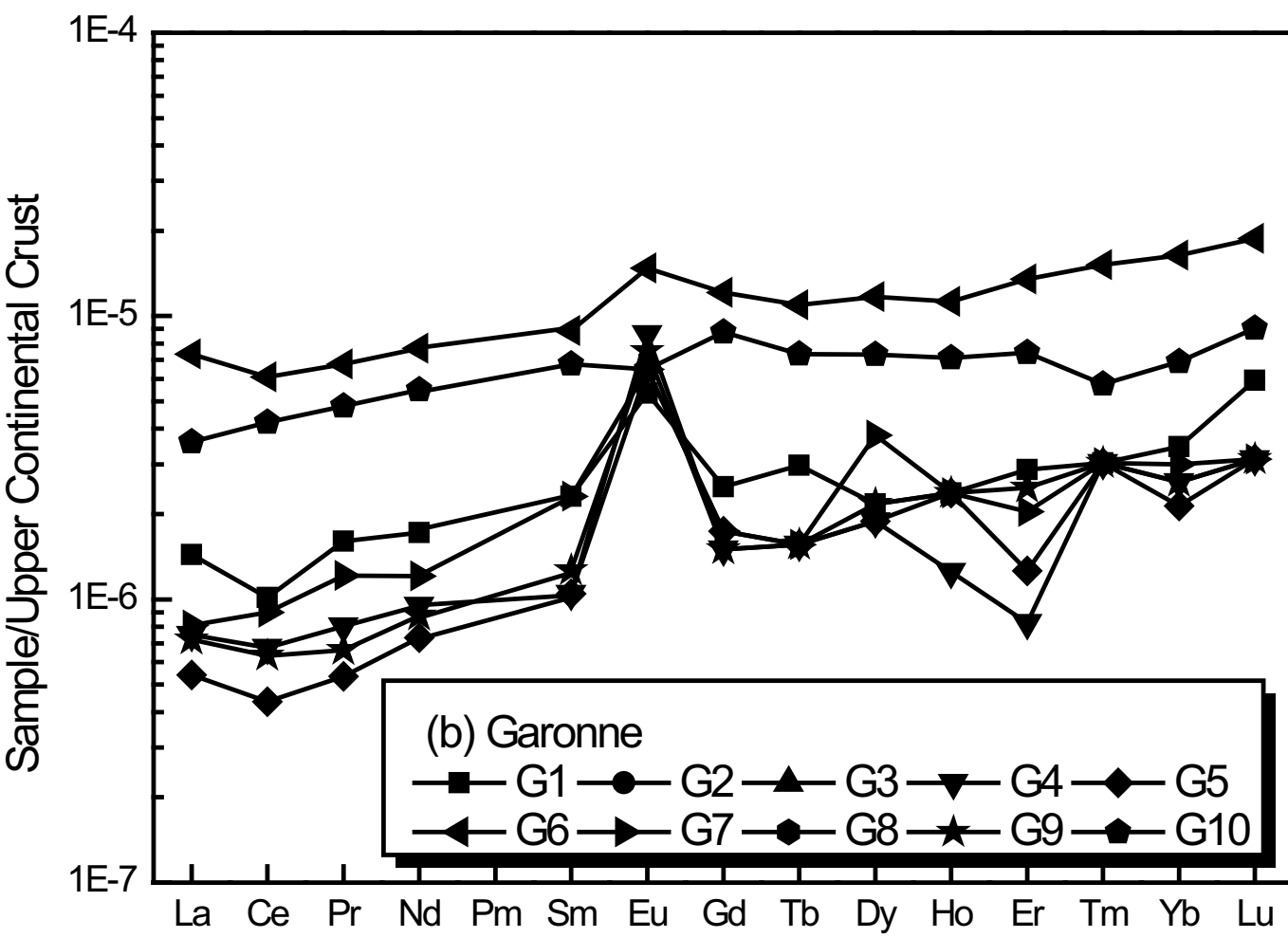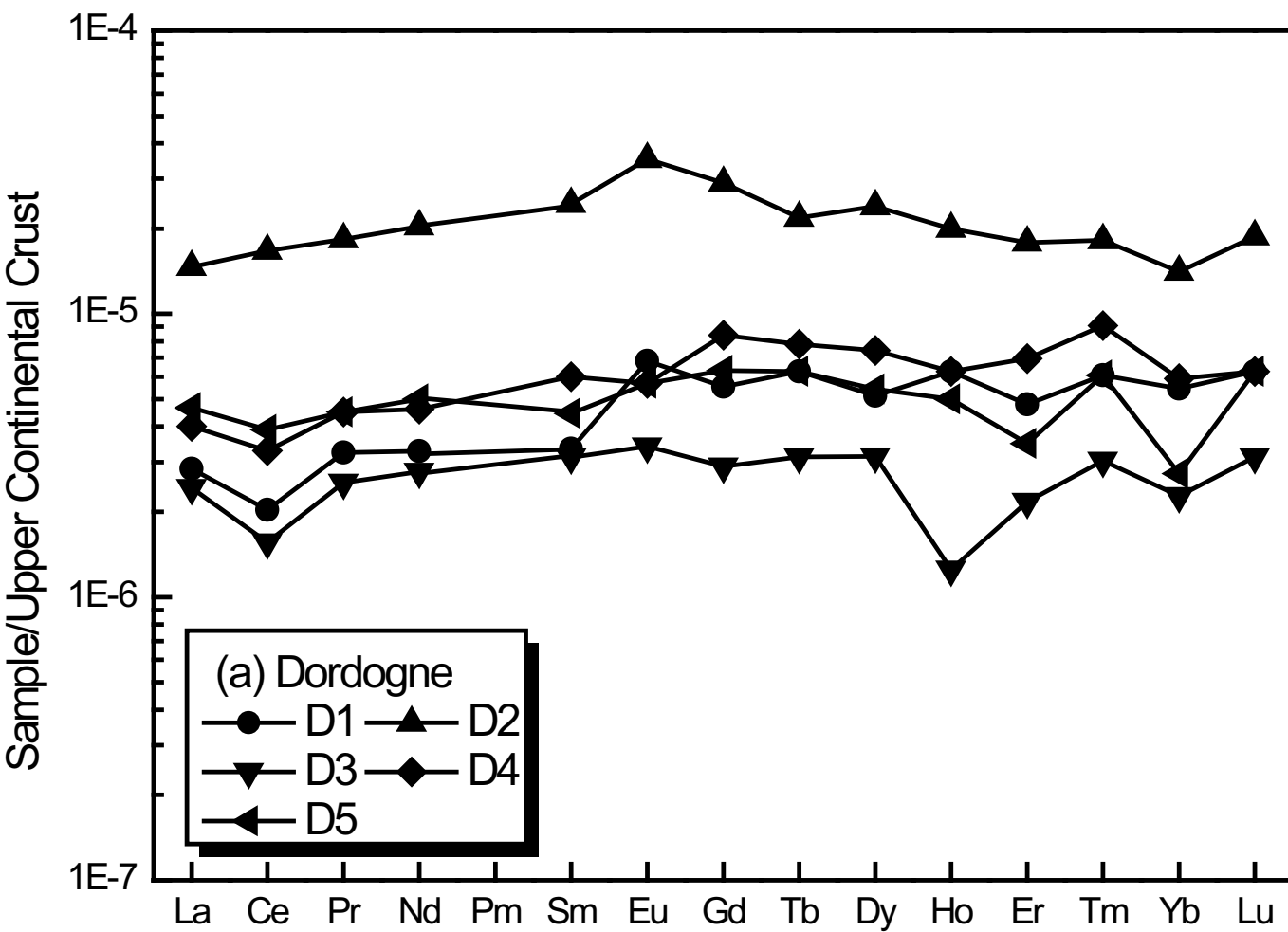**Click here to download high resolution image**
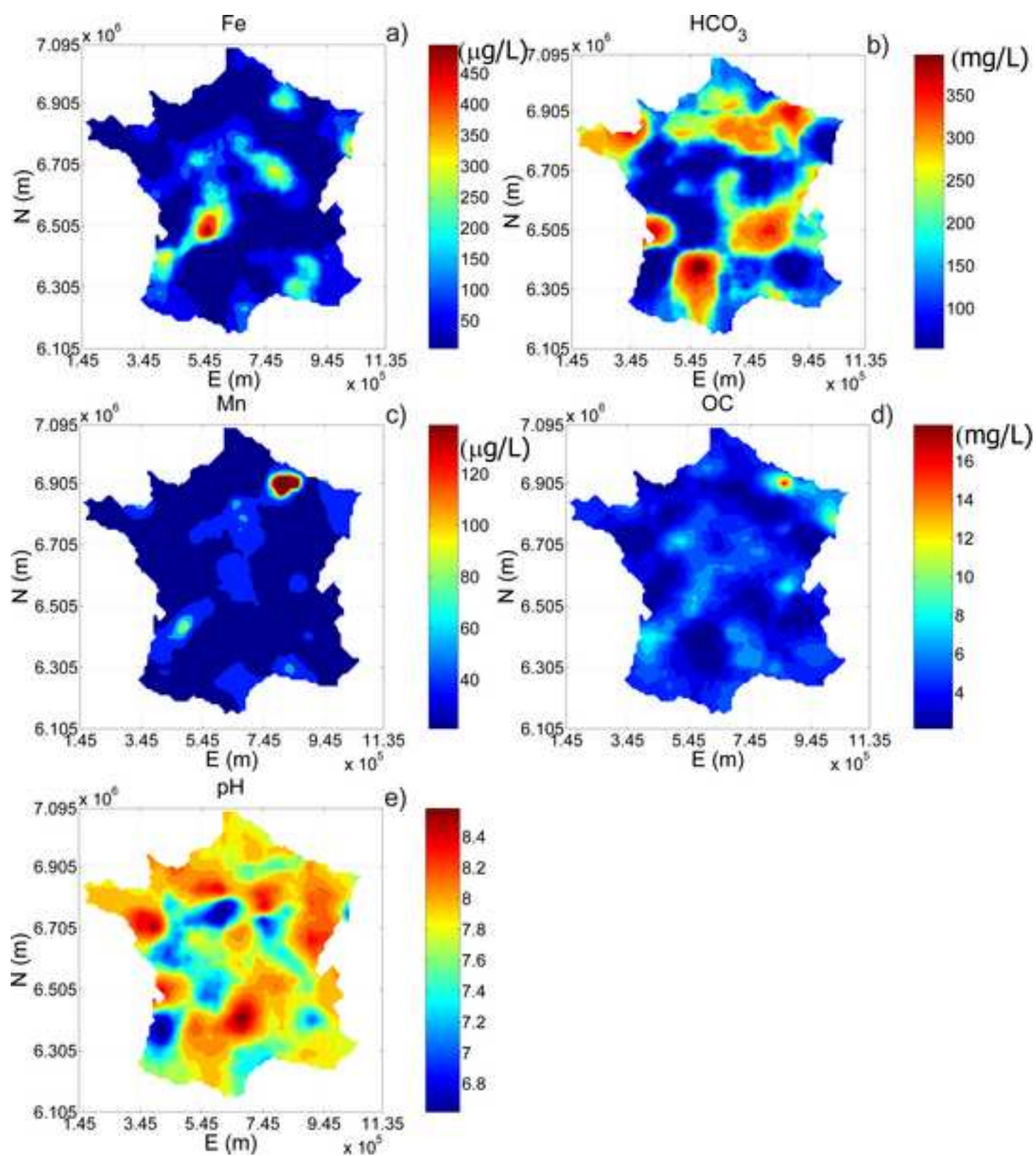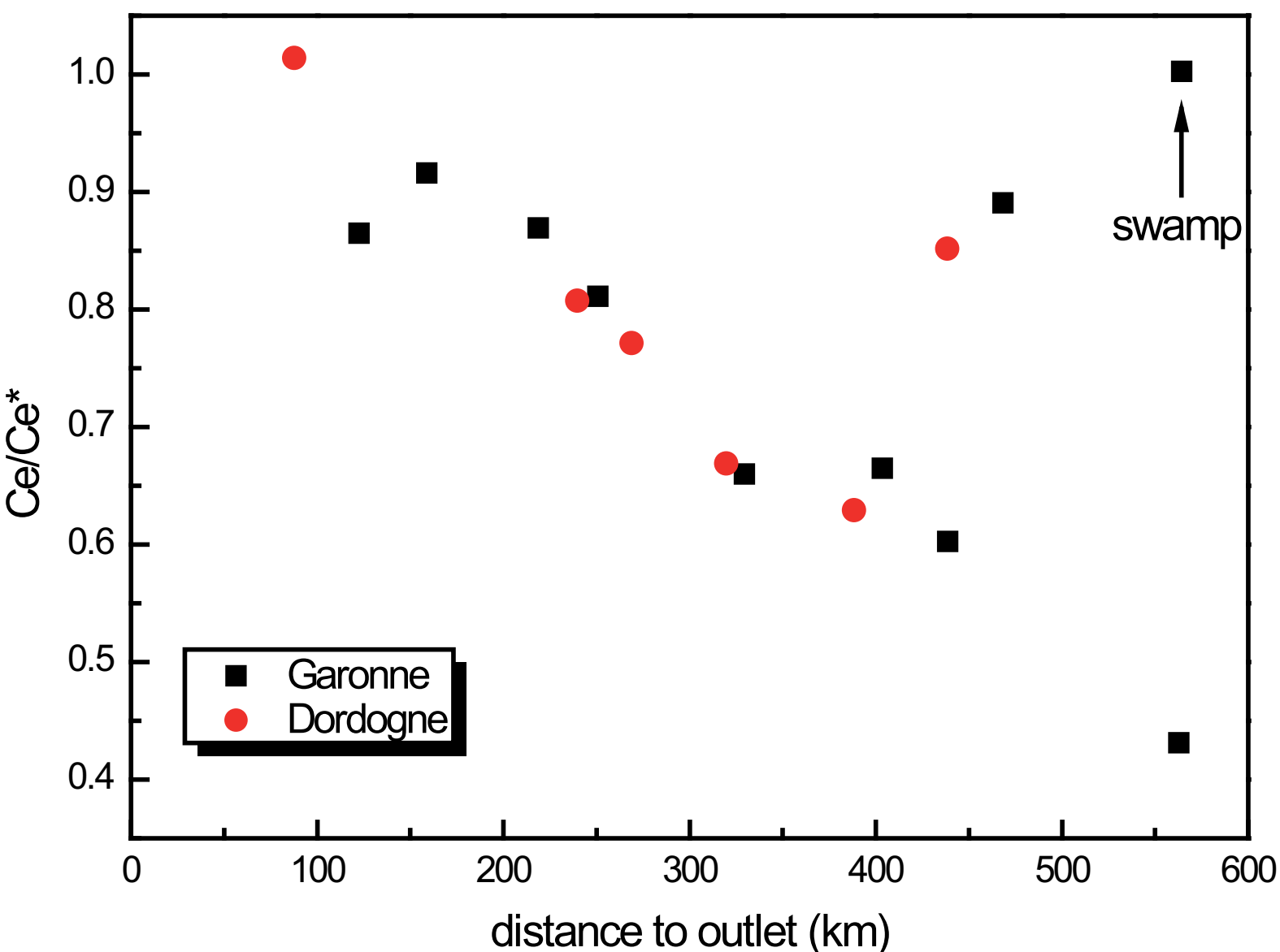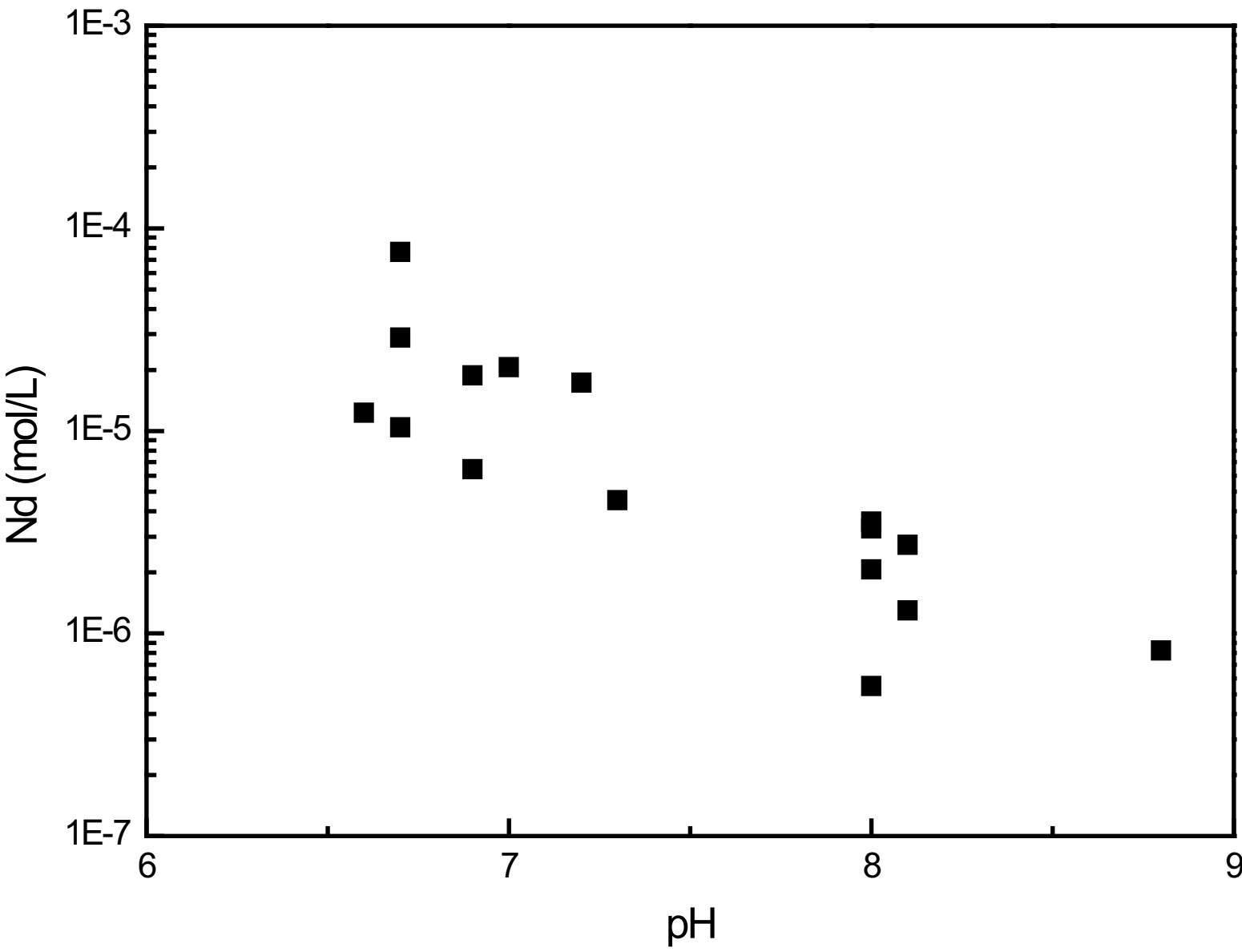
Figure 6

Figure 7

Figure 8

Authorship Confirmation

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As corresponding author I, Olivier Pourret, hereby confirm on behalf of all authors that:

1. This manuscript, or a large part of it, <u>has not been published, was not, and is not being submitted to</u> any other journal. If presented at a conference, the conference is identified. If published in conference proceedings, <u>the publication is identified below</u> and substantial <u>justification for re-publication</u> must be presented.

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