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GEOSTATISTICS AS A TOOL TO IMPROVE THE NATURAL BACKGROUND LEVEL DEFINITION: AN APPLICATION IN GROUNDWATER

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ABSTRACT

The UE BRIDGE project suggests calculating the Natural Background Level (NBL) as the 90th percentile of the distribution of the concentration data. This method is suited for large, spatially distributed datasets providing a regional value of NBL that could be higher than the Threshold Value (TV) set by every country. Therefore, the use of a unique regional NBL value, higher than TV, in dis-homogeneous areas from the hydro-geochemical perspective, could arise problems to distinguish between natural occurrences and anthropogenic contaminant sources. Hence, the goal of this study is to improve the NBL definition using the geostatistical approach, which allows reconstructing the contaminant spatial structure keeping in account geochemical and hydrogeological relationships. We retain this integrate mapping fundamental to evaluate the contaminant's distribution impact on the NBL value, giving indications to improve it. We decided to test this method on the Drainage Basin of Venice Lagoon (DBVL), an area in northeastern Italy notoriously affected by naturally occurring arsenic contamination, where the existing NBL is seven times higher than the TV. An available geochemical dataset collected by 50 piezometers was used

21 to reconstruct the spatial distribution of arsenic in the densely populated area of the DBVL. A
22 cokriging approach was applied exploiting the geochemical relationships among As, Fe and NH_4^+ .
23 The obtained spatial predictions of arsenic concentrations was divided into three different zones: i)
24 areas with an As concentration lower than the TV, ii) areas with an As concentration between the
25 TV and the median of the values higher than the TV, and iii) areas with an As concentration higher
26 than the median. Subsequently, following the BRIDGE suggestions, where enough samples were
27 available, the 90th percentile for each zone was calculated to obtain a local NBL (LNBL).
28 Differently from the original NBL, this local value gives more detailed water quality information
29 accounting the hydrogeological and geochemical setting, and contaminant spatial variation. Hence,
30 the definition of a LNBL could give more indications about the distinction between natural
31 occurrence and anthropogenic contamination.

32 **Keywords:** Local Natural Background Level (LNBL), cokriging (COK), Arsenic and Drainage
33 Basin to the Venice Lagoon (DBVL).

34 1. INTRODUCTION

35 The assessment of the groundwater quality and the impact of the human activities are important
36 worldwide challenges. Actually, the assessment of groundwater body qualitative status is related to
37 the definition of Natural Background levels (NBLs) and Threshold values (TVs). The first one is
38 mainly linked to the system's hydro-geochemical settings, while the second is associated to the
39 public health issue. The NBL definition is a well-known problem due to its complexity, its
40 challenging estimation and the delicate consequences on the environmental protection. The NBL of
41 an element or compound in groundwater represents the range of concentrations resulting from the
42 interaction of different natural atmospheric, geological, chemical and biological process during the
43 hydrological cycle, and it could be influenced by human activities (Edmunds and Shand, 2008;
44 Hinsby et al., 2008a; Reimann and Garrett, 2005). By defining the NBL, it is necessary to know the
45 extension and the hydro-geochemical characteristics of the groundwater body at risk, paying

attention to use data coming from the same aquifer body and collected far from anthropogenic sources of contamination, in order to obtain pristine water samples (Coetsier et al., 2009; Hinsby et al., 2008; Wendland et al., 2008). Many studies treat the problem of the NBL definition or the definition of new approaches to improve it (Coetsier et al., 2009; Ducci et al., 2016; Molinari et al., 2012; Preziosi et al., 2010; Rotiroti et al., 2013, 2015), since the NBL assumes importance discriminating the anthropogenic contamination from the natural occurrence. A first approach to estimate the NBL value into European groundwater bodies was suggested by Edmunds and Shand (2008), and it was based on a geochemical prospective rather than a statistical one. Actually, the European Community in accordance with the European “BRIDGE” project (Background cRiteria for the Identification of Groundwater thrEsholds) (Müller et al., 2006) suggests two main statistical method to estimate the NBL. The first approach, the “Component Separation” method (CP), is based on the distinguishable data distributions produced by the natural and anthropogenic sources that can be distinguished by a statistical analysis. In this approach, the observed concentration frequency distribution is fitted by the superimposition of two different distributions that represent the natural and the anthropogenic concentrations. Once estimate the distribution (shape and statistical parameters) of the natural component, the data following it will be used to estimate the NBL. On the other hand, the second method suggests a pre-selection of the data basing on some markers’ concentration that point an anthropogenic contamination out (e.g. nitrate, salinity, etc.). The basic idea of this method is that there is a correlation between the markers’ concentrations and the presence of an anthropogenic pressure. Thus, where the markers show concentration values over the pre-defined limits, the groundwater samples are excluded from the NBL estimation. Subsequently, for both methods, the NBL is estimated as the 90th or 97th percentile of the modified distribution of the concentration data (Coetsiers et al., 2009; Müller et al., 2006; Wendland et al., 2008b). These approaches give a unique NBL value for the entire area, which seems to be not capable to represent the local variation of the geochemical and environmental conditions. The definition of a unique NBL value for a large area, in fact, could make a considerable uncertainty

72 defining the contaminant's natural occurrence against an anthropogenic source. Considering both
73 the importance of the health problem related to the contaminant natural occurrence and the
74 complexity to define an exhaustive NBL value, this study aims to improve the NBL concept by
75 using geostatistical methodology such as cokriging predictor (COK). This method, like other types
76 of kriging, allows redefining the NBL as function of the spatial distribution of contaminant
77 concentration. However, the COK keeps also in consideration the relationships among the target
78 contaminant and other, geochemically related, dissolved species in groundwater. This methodology
79 is applied on the case of the Drainage Basin of the Venice lagoon (DBVL) notoriously affected by
80 both high natural and anthropic concentrations of arsenic. Furthermore, the Regional Agency for
81 Environmental Protection and Prevention of Veneto (ARPAV) through the "A.Li.Na" project
82 (ARPAV, 2014) estimated an arsenic NBL of 74 $\mu\text{g/L}$ that is seven times higher than the Threshold
83 Value ($\text{TV}=10 \mu\text{g/L}$) defined by the annex III in the Commission Staff Working report of the EU's
84 Groundwater Directive (GWD 2006/118/EC). However, the results of this project pointed out the
85 importance of a detailed and local NBL accounting the complex and laterally variable geological
86 and hydro-chemical settings. The results of our study could be useful to improve the definition of
87 the NBL because it exploit the knowledge about the spatial structure and uncertainty of the
88 naturally occurring contaminant into groundwater, giving a local detail that considers the
89 environmental background. In addition, they could be used by the stakeholders to perform a more
90 complete and explanatory plan for the environmental management.

91 **2. KNOWLEDGE ABOUT ARSENIC CONTAMINATION**

92 High arsenic concentrations in groundwater have been documented in several countries, such as
93 Bangladesh, India (McArthur et al., 2001; Nickson et al., 1998, 2000), Vietnam (Fendorf et al.,
94 2010), Hungary and the USA (Sorg et al., 2014; Welch et al., 2000). The natural occurrence of
95 arsenic in these countries is often linked to the alluvial plain systems, but high arsenic
96 concentrations can be found in volcanic environments or mining districts (e.g., Argentina, Chile,

97 Brazil, Ethiopia, Greece and Italy) (Nordstrom, 2003; Rango et al., 2013). In Italy, high natural
98 concentrations of arsenic in groundwater have been documented in volcanic aquifers of the central
99 and southern Italy related to the uprising of geothermal fluids (Baiocchi et al., 2011; Ducci et al.,
100 2016; Preziosi et al., 2010). Furthermore, in northern Italy, a high arsenic concentration can be
101 found in the alluvial aquifers of the Po Plain (Molinari et al., 2013; Rotiroti and Fumagalli, 2013;
102 Rotiroti et al., 2014; Zavatti et al., 1995) and the Venetian Plain (Carraro et al., 2013; Ungaro et al.,
103 2008). Few materials (e.g., gold or sulfide mineral deposits, volcanogenic sources, alluvial
104 sediments and organic matter) are currently recognized as significant sources of arsenic or drivers
105 for its mobilization in groundwater. Nevertheless, the occurrence of arsenic in groundwater could
106 be caused by anthropic activities, such as mineral extraction, industrial processes or fertilizer use.
107 Arsenic is a metalloid that has three oxidation states nevertheless the most common forms in
108 groundwater are the followings: the first is oxidized with an oxidation number (ON) equal to + 5,
109 whereas the second is reduced with an ON equal to + 3. The reduced form appears to be more
110 movable than the oxidized form in an aqueous medium, although both species have good mobility.
111 The arsenic toxicity is due to its affinity to Phosphorus (P) that could be replaced by arsenic (As) in
112 the metabolic processes of RNA and DNA synthesis. Arsenic is not widespread in the Earth's
113 continental crust but is commonly concentrated in sulfide-bearing mineral deposits associated with
114 Pyrite or Fe-hydroxides. Furthermore, many geothermal waters naturally exceed the TV of 10 µg/L.
115 As determined in many studies, arsenic often is adsorbed onto Fe-Mn oxides or hydroxides, as well
116 as into the organic matter (Baviskar et al., 2015; Carraro et al., 2015; McArthur et al., 2004, 2001,
117 Molinari et al., 2015, 2013; Nickson et al., 2000; Rowland et al., 2007). Dissolution of these
118 minerals in an acid-reducing environment causes the desorption processes that enable the release of
119 As in an aqueous medium, exceeding its threshold value (McArthur et al., 2016; Smedley and
120 Kinniburgh, 2002). Therefore, the organic matter could be a source of As, in addition to its role as a
121 redox driver (Rotiroti et al., 2014). In particular, the release of As in groundwater is influenced by
122 the variation of physical and chemical parameters, such as the Oxidation-Reduction Potential (ORP)

123 and pH (Smedley and Kinniburgh, 2002; Sorg et al., 2014), as well as the presence of elements and
124 compounds that can promote its release (e.g., NO_3^- , NH_4^+ , HCO_3^- , SO_4^{2-} , PO_4^{3-}) (Biswas et al., 2014).

125 **3. GEOLOGICAL AND HYDROGEOLOGICAL SETTINGS**

126 The study area is located in the middle-low Venetian Plain, including the Padua, Treviso and
127 Venice provinces. The area covers approximately 2038 km² with a topographic gradient ranging
128 from 0.6% to 0.1% near the Venice lagoon (Figure 1A, B). Two primary alluvial hydrogeological
129 units occur in the Venetian plain: a large unconfined aquifer extending 15-20 km in the upper
130 region of the plain from the foot of Prealps, and a multi-layered confined aquifer system in the
131 lower region of the plain towards the Adriatic Sea. These two units correspond, respectively, to the
132 upper and middle-lower plain environments. The plain spring's belt (named the "Fontanili" belt)
133 shows the transition from the upper plain to the lower plain, where the water table is very shallow
134 and locally intersects the topographic surface. From a geological perspective, the study area
135 comprises gravelly and sandy alluvial deposits in the upper region near the "Fontanili" belt and
136 silty-clayey deposits in the distal region (upper Pleistocene – Holocene) (Bondesan et al., 2004;
137 Fontana et al., 2004, 2008; Mozzi et al., 2003). These fine sediments often contain peat layers
138 formed in a floodplain environment, with a thickness of decimeters and a lateral extension of
139 kilometers. The Drainage Basin to the Venice Lagoon (DBVL) extends to the lower plain
140 environment, alternating silty layers with low permeability and sandy permeable layers, where the
141 primary aquifers are located (Cambruzzi et al., 2009; Dal Prà et al., 1992; Fabbri and Piccinini,
142 2013; Fabbri et al., 2011, 2013, 2016; Piccinini et al., 2015, 2016; Vorlicek et al., 2004) (Figure
143 1C). Anyway, the subsoil structure of the DBVL is heterogeneous, due to the complex alluvial
144 sedimentation processes that characterized the Brenta's alluvial plain (Trevisani and Fabbri, 2010)
145 and surely influences the spatial distribution of As-bearing materials. This is important because
146 Arsenic may be concentrated in sulfide-minerals, such as Pyrite (FeS_2), or adsorbed onto oxides or
147 hydroxides composing the fine portion of the alluvial sediments (Baviskar et al., 2015; Rowland et

148 al., 2007). Therefore, the peat layers play an important role in the arsenic release mechanism
 149 because the degradation of the organic matter controls the aquifer's redox conditions and the thus
 150 the dissolution of these As bearing minerals (Rotiroti et al., 2014).

152 **Figure 1.** A) The location of the Veneto region in Italy; B) The location of the study area in the
153 Veneto region, which covers the entire Brenta's Plain; C) A hydrogeological sketch of the low
154 Brenta's Plain along the "a-b cross-section"; D) The piezometer locations in the DBVL. All of the
155 piezometers are in the shallow aquifer, between 10 and 20 meter below ground level (BGL).

156 **4. MATERIALS AND METHODS**

157 **4.1.Dataset**

158 The data used in this work was obtained from the "A.Li.Na" project, which was developed to
159 estimate the natural background levels (NBLs) of As, Fe, Mn and NH_4^+ in the groundwater of the
160 DBVL, according to the pre-selection method suggested by BRIDGE project. The hydro-
161 geochemical sampling network (50 piezometers) was established with a variable spacing grid,
162 covering all of the investigated area (Figure 1D). The sampled piezometers, used for NBL
163 definition, are located far from the anthropogenic pollutant sources in order to obtain some pristine
164 water samples. The piezometers tap the shallow aquifer at a depth of 10 – 20 meters below ground
165 level (BGL). The hydro-geochemical parameters were collected during four seasonal surveys
166 conducted from 2013 to 2014. The groundwater sampling was performed according to the standard
167 protocols established by the Italian Environment Protection and Technical Services Agency (APAT,
168 2006). In addition, the physical parameters (e.g., pH, ORP, electric conductivity, temperature and
169 dissolved oxygen) were measured by a multi-parametric probe YSI mod. 556 MPS. The chemical
170 parameters were estimated in the laboratory through standardized methods. Arsenic and Manganese
171 were estimated by the UNI EN ISO 17294-2:2005 (revised by ISO 17294-2:2016) method, Iron by
172 the APAT CNR IRSA 3160 Man 29 2003 method and Ammonium by the APAT CNR IRSA 4030
173 A1 Man 29 2003 method (APAT, 2003). Furthermore, each sampling point was georeferenced in
174 the Gauss-Boaga coordinate system (Roma 1940 datum, West zone). According to BRIDGE
175 suggestions, the data were processed to estimate the average values from each available
176 concentration time series, in order to create an average dataset that depicts the average system

177 behavior. Therefore, an average dataset was determined, depicting. Afterwards, the concentration
 178 values below the limit of quantification (i.e., $\text{As} < 1 \mu\text{g/L}$) were changed to make the entire
 179 “A.Li.Na” dataset suitable for mapping purposes. In such a case, the As concentrations below this
 180 limit were set equal to $0.5 \mu\text{g/L}$. The DBVL shows high concentrations of arsenic in reducing
 181 environments and often in association with rich organic matter reservoirs (Carraro et al., 2015;
 182 Molinari et al., 2015; Rotiroti et al., 2014), according with the geological genesis of the area.
 183 Looking at the Figure 2, the major part of the arsenic data show an ORP values from 0 mV to -150
 184 mV and a pH between 7 and 8 according with the releasing as reduced forms.

185
 186 **Figure 2.** A Pourbaix diagram of Arsenic species built under the conditions of $T = 298.15 [^{\circ}\text{K}]$ and
 187 $P = 10^5 [\text{Pa}]$. The red dots represent the experimental data used for this study. The majority of the
 188 sample data falls into the arsenic reduced species stability field (Takeno, 2005).

189 4.2.Geostatistical methods

190 The arsenic concentration in groundwater is linked to complex hydro-geochemical processes not yet
191 well understood, hence its distribution in groundwater can be more usefully approached by
192 geostatistical methods than by deterministic ones (e.g., Inverse Distance Weighting and Natural
193 Neighbors). The geostatistical kriging predictor is based on a mixed model [1]:

$$\hat{Z}(\mathbf{u}_i) = R(\mathbf{u}_i) + m(\mathbf{u}_i) \quad [1]$$

194 where the predicted concentration $\hat{Z}(\mathbf{u}_i)$, at location $\mathbf{u}_i$, is composed of a residual component $R(\mathbf{u}_i)$
195 plus the mean $m(\mathbf{u}_i)$, representing, respectively, the stochastic component and the deterministic
196 component of the predicted geostatistical concentration. Moreover, the kriging method needs to
197 assume the stationary condition, considering the spatial correlation of the variable Z independent of
198 their spatial position ($\mathbf{u}_i$) but dependent only on the separation distance (h)(Bivand et al., 2008;
199 Isaak and Srivastava, 1989; Posa and De Iaco, 2009). Because the kriging predictor was built
200 according to Equation [1], the problem is to define the mean m dependent on the position ($\mathbf{u}_i$).
201 Depending on the mean characteristics, three types of predictors can be considered as follows: i)
202 Simple (co)kriging ($m(\mathbf{u}_i)=m$, the mean is known and constant), ii) Ordinary (co)kriging ($m(\mathbf{u}_i)=m$,
203 the mean is unknown but constant), and iii) Universal (co)kriging ($m(\mathbf{u}_i)$, the mean is not constant
204 but defined by a spatial function). In the context of this study, the more acceptable condition was a
205 mean that was constant within a moving search neighborhood but unknown, and thus, the selected
206 prediction was an ordinary kriging approximation of $\hat{Z}(\mathbf{u}_o)$.

$$\hat{Z}(\mathbf{u}_o) = \sum_{i=1}^n \omega(\mathbf{u}_i) Z(\mathbf{u}_i) \quad [2]$$

207 If auxiliary variables correlated to the primary variable are available, a cokriging approach can be
208 considered. Theoretically, it gives a prediction enhancement respect to ordinary kriging application.
209 Cokriging is based on the same principles of kriging but also uses correlated auxiliary variables (in
210 our case Fe and NH_4^+) to predict the primary variable (in our case As).

$$\hat{Z}(\mathbf{u}_o) = \sum_{i=1}^n \omega(\mathbf{u}_i) Z(\mathbf{u}_i) + \sum_{j=1}^n \tau(\mathbf{u}_j) V(\mathbf{u}_j) \quad [3].$$

211 As evidenced in Equation [3], the cokriging predictor uses a weighted linear combination of the
 212 principal variable $Z(\mathbf{u}_i)$ and of the auxiliary variables $V(\mathbf{u}_j)$ in the different position $(\mathbf{u}_i)$ and $(\mathbf{u}_j)$. In
 213 this manner, improving the principal variable prediction is possible. Using the matrix notation the
 214 cokriging system is written as

$$\mathbf{K}_{CK} \mathbf{L}_{CK}(\mathbf{u}) = \mathbf{k}_{CK} \quad [4].$$

215 Where $\mathbf{K}_{CK}$ is the $n(\mathbf{u}) \times n(\mathbf{u})$ matrix of data covariances, $\mathbf{L}_{CK}(\mathbf{u})$ is the vector of the weights $\omega(\mathbf{u}_i)$
 216 and $\tau(\mathbf{u}_j)$, $\mathbf{k}_{CK}$ represents the vector of data-to-unknown covariances. Basing on the [4], the
 217 cokriging weights required by the COK estimator [3] are obtained by multiplying the inverse of the
 218 data covariance matrix by the vector of data-to-unknown covariances:

$$\mathbf{L}_{CK}(\mathbf{u}) = \mathbf{K}_{CK}^{-1} \mathbf{k}_{CK} \quad [5].$$

219 Furthermore, to satisfy the stationary and unbiased conditions, the estimated weights from [5] have
 220 to undergo the following constraints:

$$\begin{cases} \sum_{i=1}^n \omega_i(u) = 1, \\ \sum_{j=1}^n \tau_j(u) = 0. \end{cases} \quad [6].$$

221 As reported in literature, cokriging method work better when the primary variable is less sampled
 222 respect to the auxiliary one. Furthermore, one could also use it when main and auxiliary variable are
 223 sampled in the same location (collocated cokriging) even if it gives lower prediction advantage than
 224 the classical application. Nevertheless, in our study we consider the collocated cokriging method
 225 because it produces a reduction on prediction error around 10% respect to OK. The geostatistical
 226 analysis was conducted in the R environment (R Core Team, 2015), in particular with the gstat
 227 package (Pebesma, 2004). The logical process (Figure 3) to estimate the arsenic spatial distribution

228 was composed of four primary steps: Exploratory Data Analysis, Variographic Analysis, Cross-
 229 validation, Ordinary cokriging.

230
 231 **Figure 3.** The flow chart of the classical logical process implemented in the geostatistical analysis.
 232 E.D.A = Exploratory Data Analysis, Var.A. = Variographic Analysis, X.V. = Cross-Validation,
 233 COK = Ordinary cokriging, Map. = Mapping the predicted principal variable.

234

235 5. RESULTS AND DISCUSSION

236 5.1. Geostatistical analysis

237 According to the goal of this study, the average dataset was considered. Initially, a study of the
238 correlations between arsenic and other related chemical components (i.e., iron and ammonium) was
239 performed. The robust correlation among As and other parameters indicated that the cokriging
240 (COK) approach might be appropriate. To evaluate the correlation, we used a Spearman's
241 correlation test and scatterplots. The Spearman's correlation test was selected because the
242 experimental data do not have a normal distribution and the relation among the variables is not
243 linear, so the Pearson's coefficient could be less exhaustive (Isaak and Srivastava, 1989). In that
244 case, the Spearman's test, basing on ranks correlation, allows evaluating the strength of the
245 correlation among the variables even if it is not linear. In addition, the scatterplot graphically
246 explores linear correlations. The relationships among As, Fe and NH_4^+ are illustrated in Figure 4 in
247 which the scatterplots show the poor linear correlation between two variables emphasized by the
248 local regression function LOESS (red line) and the numerical coefficients represent the Spearman's
249 ρ . The juxtaposition of these elements allow showing the poor relevance of the linear correlation on
250 our data. The Spearman's ρ is greater than 0.5 and statistically meaningful (p-value < 5%
251 significance level). Based on these relationships, we decided to use Fe and NH_4^+ as the auxiliary
252 variables in the COK prediction process of As. Subsequently, histograms, scatterplots explored the
253 statistical structure of the raw data. In this manner, estimating the statistical parameters of the data
254 (i.e., means, standard deviation, variance, skewness, etc.) was possible. Arsenic, iron and
255 ammonium data followed a lognormal distribution with positive skewness coefficients (3.13, 2.20,
256 1.87, respectively; Figure 5). The raw data were transformed to a normal score in order to perform a
257 COK prediction with lower error as possible. Furthermore, the normal score transformation allows
258 an easier back-transformation of the processed data, giving lower error respect to the use of log-
259 transformation.

Correlation Scatterplot Matrix (Spearman's rho)

260

261 **Figure 4.** A correlation scatterplot matrix based on Spearman's method, providing the ρ
 262 coefficients for the pairs As-Fe, As-NH₄⁺ and Fe-NH₄⁺. In the lower part of the matrix, the
 263 scatterplot related to the variable pairs are shown. They represent the poor linear correlation
 264 emphasized by the red line that represents the local regression function LOESS (Cleveland, 1979).
 265 The correlation coefficients ρ are shown in the upper part of the matrix. The used dataset is the
 266 average of the four surveys and the Spearman's correlation test was conducted with the
 267 experimental concentration variables.

268

269

270 **Figure 5.** The three histograms represent the distributions of the average data of As, Fe and NH₄⁺,
 271 respectively.

272 The second step of the geostatistical process was the Variographic Analysis of the transformed data.

273 The variogram $\gamma(h)$ describes how spatial continuity changes with the distance (h) and the direction.

274 In addition, the cokriging approach requires the variogram and the cross-variogram analyses. An

275 analysis of the surface variograms in Figure 6A did not reveal any anisotropy in the continuity

276 structures of the studied variables. Considering this, only omnidirectional variograms and cross-

277 variograms were considered (Figure 6B). A Linear Model of Co-regionalization (LMC) fits a

278 theoretical variogram model with both experimental variograms and cross-variograms. The LMC

279 provides authorized theoretical models of variograms and cross-variograms of two or more

280 variables so that the variance of any possible linear combination of these variables is always

281 positive (Isaak and Srivastava, 1989). The resulting theoretical variograms (Figure 6) were used

282 during the cokriging prediction. The variogram model used in this study was spherical both for

283 auto- and cross-variograms:

$$\gamma(h) = \begin{cases} nu + c; & |h| > a \\ nu + c \left[\frac{3}{2} \frac{|h|}{a} - \frac{1}{2} \left(\frac{|h|}{a} \right)^3 \right]; & |h| \leq a \end{cases} \quad [7].$$

284 where nu is the nugget effect, c represents the partial sill and a represents the range. The variogram

285 models referred to As, Fe and NH_4^+ , and the three cross-variogram models of As-Fe, As- NH_4^+ and

286 Fe- NH_4^+ are visible in Table 1.

287

288 **Table 1. The variogram and cross-variogram models used to predict the arsenic spatial**

289 **distribution.**

Variogram model	Parameter
$\gamma(h) = \begin{cases} 0.486 + 0.523; & h > 8000 \\ 0.486 + 0.523 \left[\frac{3}{2} \frac{ h }{8000} - \frac{1}{2} \left(\frac{ h }{8000} \right)^3 \right]; & h \leq 8000 \end{cases}$	[As]
$\gamma(h) = \begin{cases} 0.730 + 0.260; & h > 8000 \\ 0.730 + 0.260 \left[\frac{3}{2} \frac{ h }{8000} - \frac{1}{2} \left(\frac{ h }{8000} \right)^3 \right]; & h \leq 8000 \end{cases}$	[Fe]

$\gamma(h) = \begin{cases} 0.055 + 0.884; & h > 8000 \\ 0.055 + 0.884 \left[\frac{3}{2} \frac{ h }{8000} - \frac{1}{2} \left(\frac{ h }{8000} \right)^3 \right]; & h \leq 8000 \end{cases}$	$[\text{NH}_4^+]$
$\gamma(h) = \begin{cases} 0.581 + 0.148; & h > 8000 \\ 0.581 + 0.148 \left[\frac{3}{2} \frac{ h }{8000} - \frac{1}{2} \left(\frac{ h }{8000} \right)^3 \right]; & h \leq 8000 \end{cases}$	$[\text{As-Fe}]$
$\gamma(h) = \begin{cases} 0.034 + 0.521; & h > 8000 \\ 0.034 + 0.521 \left[\frac{3}{2} \frac{ h }{8000} - \frac{1}{2} \left(\frac{ h }{8000} \right)^3 \right]; & h \leq 8000 \end{cases}$	$[\text{As-NH}_4^+]$
$\gamma(h) = \begin{cases} -0.004 + 0.429; & h > 8000 \\ -0.004 + 0.429 \left[\frac{3}{2} \frac{ h }{8000} - \frac{1}{2} \left(\frac{ h }{8000} \right)^3 \right]; & h \leq 8000 \end{cases}$	$[\text{Fe-NH}_4^+]$

290

291

292 **Figure 6.** A) The surface variograms and cross-variograms. The surface variograms are shown in
293 the first column. B) The omnidirectional variogram and cross-variograms. The variograms are on
294 the diagonal, and the associated cross-variograms (referred to the average values of surveys) are
295 below the diagonal.

296 Following the above variogram analysis, a cross-validation procedure was applied. The cross-
297 validation tests the ability of the model to reproduce the spatial continuity structure by the
298 prediction of the used dataset. The cross-validation, applied on our data, gives a mean estimation
299 error equal to 0.001 $\mu\text{g/L}$, confirming the good prediction given by the chosen variogram model
300 (Isaak and Srivastava, 1989). Looking the Figure 7, it is evident the normality of the estimation
301 errors and the good reproduction of the experimental data, highlighting the model's goodness.
302 Furthermore, in our case, the cross-validation resulted in an acceptable normalized root mean
303 square error (nRMSE) equal to 13.3%, which is around 10% lower than the nRMSE obtained by the
304 ordinary kriging prediction on the same data. A similar nRMSE is likely linked to the presence of
305 punctual high values of arsenic (hot spots), influencing the prediction process. Generally, the
306 problems linked to the hot spots are common in environmental datasets.

307

308 **Figure 7:** Graphical representation of the arsenic residuals coming from the cross-validation
 309 process by assessing the goodness of the chosen spatial model. Moving from the upper left corner
 310 toward the lower right one, there are the probability density function of residuals, the distribution
 311 around the zero value, the QQ-norm plot and the scatterplot observed As vs. predicted As. In the
 312 last diagram, the red line represents the linear trend line (correlation coeff. = 0.67)

313 5.2.Arsenic distribution

314 Following the previous geostatistical analysis, an ordinary cokriging predictor was applied. The
 315 prediction process allowed mapping the arsenic distribution on the shallow groundwater of the
 316 DBVL (Figure 8). By improving the NBL concept and getting a more detailed value, we decided to
 317 consider the TV and the median (M) of the original dataset as thresholds to reclassify the
 318 distribution map. The reclassification process is necessary to identify the data that have similar
 319 arsenic values and then estimate some Local NBL following the 90th percentile method. In our case,
 320 the median was chosen because the “A.Li.Na” NBL value is several times higher than the TV and it
 321 seems adequate as intermediate threshold, separating the 50% of the data. However, the choice of
 322 the intermediate threshold is linked to both the dataset structure and the gap between the existing
 323 NBL and TV. In this way, we are able to define some sub-area in which estimate, effectively, some
 324 local NBL (LNBL) values (Table 2). A unique value of NBL does not seem to be realistic in
 325 regional environments with a large variation of concentrations.

326 **Table 2. Arsenic concentration classes used to evaluate the LNBLs.**

1 st	As ≤ 10 µg/L (TV)	Lower (LNBL _L)
2 nd	10 < As ≤ 31.4 µg/L (M)	Intermediate (LNBL _I)
3 rd	As > 31.4 µg/L	Higher (LNBL _H)

327

328 According to the above-described thresholds, the map in Figure 8 (related to the average values of
 329 the four surveys) shows that many zones (about 49% of the study area) exceeded the threshold
 330 value (TV) set in the Annex III of the Commission staff working document of the GWD
 331 2006/118/EC. In some of these zones (9% of the domain), the predicted values also exceeded the
 332 natural background level (NBL) of 74 µg/L suggested by the “A.Li.Na” project. In particular, in the
 333 central-western region of the area between the Padua and Venice provinces (including Piezometers
 334 9, 10, 20, 37, 40 and 44), the predicted arsenic concentrations were greater than the TV, ranging
 335 from 33.75 to 224 µg/L. Similarly, arsenic concentrations reached the maximum value of 95 µg/L in

336 the eastern region of the study area, near the Venice airport (Piezometer 15). Examining the ORP
337 overlaid post-map, the ORP values denoted a reducing environment in these areas, in agreement
338 with the results of several studies on the role of ORP in As release (Carraro et al., 2015, 2013; Dalla
339 Libera et al., In Press; McArthur et al., 2001; Molinari et al., 2015; Nickson et al., 2000; Rotiroti et
340 al., 2014). These reducing conditions occur also in some “green” and “yellow” zones but in this
341 case arsenic is low cause the As-bearing material are missing in the subsoil. Otherwise, analyzing
342 the available stratigraphic logs (Figure 9), the presence of peat layers is evident in the areas with
343 high concentrations, confirming the role of organic matter as a redox driver of As release (Dalla
344 Libera et al., In Press; Molinari et al., 2013; Nickson et al., 2000; Rotiroti and Fumagalli, 2013;
345 Rotiroti et al., 2014; Ungaro et al., 2008). From a hydrogeological perspective, a map analysis
346 suggested that the arsenic contamination disagreed with the groundwater natural drainage and did
347 not spread in accordance with the groundwater flow directions (NW-SE) (Fabbri, 2013).

Figure 8. Original prediction of arsenic concentration within the DBVL. This map shows the raw prediction results obtained by the COK method. The contour lines represent the arsenic concentration values basing on the COK prediction with an interval of 5 $\mu\text{g/L}$. The bold lines are the main contours.

Figure 9. The reclassified arsenic prediction, obtained from the raw prediction in figure 8, and the ORP post-map. The stratigraphic log shows some peat layers corresponding to the zones with high arsenic values. The red boxes highlight the peat layers.

5.3. Implications for water and environmental management

Groundwater arsenic pollution in alluvial systems can result from natural processes, such as weathering, the interaction between groundwater and mineral deposits or the degradation of organic matter deposits (e.g., peat layers). The distinction between anthropogenic and natural sources of contamination is important for approaching the contamination issues. Therefore, the evaluation of an NBL value plays an important role in highlighting anthropogenic pollution. The methods, suggested by the EU BRIDGE project, provide a statistically representative value for the entire study area but does not take into consideration the spatial distribution of the data. Our approach suggests a Local Natural Background Levels (LNBLs), combining the 90th percentile concept and the spatial data distribution and defining two or three classes (depending to the difference between TV and NBL), in which we can estimate the LNBLs. In this way, the errors between the natural

occurrence and the man-made pollution are minimized. By considering a unique NBL value for the entire area, an incorrect distinction between natural occurrence and pollution could occur. For example, in zones with a concentration lower than the NBL, we risk accepting an external pollution as a natural occurrence. However, in an area belonging to a higher class, we risk misinterpreting a natural occurrence as pollution. Therefore, we suggest calculating a local NBL using only the data inside the areas, defined by concentration classes established using a geostatistical prediction (e.g., the green areas in Figure 6 with predicted values between 0.5 and 10 $\mu\text{g/L}$). This step could be easily conducted if the number of available data is significantly adequate in each class ($n \geq 30$) (Müller et al., 2006). If the number of data is lower than 30, the sampling network should be enhanced. Referring to the DBVL area, all three identified zones have a number of piezometers fewer than 30 in the “A.Li.Na” sampling network. Therefore, a significant calculation of the LNBL was not performed. However, in the green areas (about 51% of the study area, Figure 9) with a predicted arsenic concentration between 0.5 to 10 $\mu\text{g/L}$ (TV), 24 piezometers are available. For example, in these areas, the LNBL was estimated to be equal to 6.68 $\mu\text{g/L}$, according to the BRIDGE project method. Such a result shows that the LNBL value is not only much lower than the “A.Li.Na” NBL value (74 $\mu\text{g/L}$) but is also lower than the TV (10 $\mu\text{g/L}$).

6. CONCLUSIONS

The results presented in this paper show how a geostatistical spatial approach allows for the application of the 90th percentile method (NBL) in a more critical way. The map of the natural distribution of arsenic allows for the identification of critical areas, highlighting where the As values exceed the TV. In particular, this result illustrates the usefulness of calculating a local NBL (LNBL) related to the different defined areas. Using the cokriging approach, the definition of LNBLs takes advantage of the arsenic spatial distribution and the geochemical relationships among arsenic and other related parameters. In fact, the correlations between arsenic and auxiliary variables, such as Fe and NH_4^+ , are taken into consideration for cokriging prediction. The results of

393 this study highlight the critical issues related to the application of a single NBL value at the regional
394 scale. Through the BRIDGE suggestions, the European GWD proposes a NBL value without
395 considering the spatial distribution of the parameter concentration or the geochemical relations
396 among the correlated parameters. The LNBL concept aims to reduce the error associated with the
397 distinction between the natural occurrence of arsenic and anthropogenic pollution. By defining a
398 LNBL for every class of concentration, monitoring the anthropogenic pollution events is easy,
399 particularly for the lower and intermediate classes (see Table 2). In addition, the proposed approach
400 might be applied to a global view of the study area, informing decisions about water and
401 environmental management and improving the characterization plan necessary to evaluate
402 potentially contaminated sites. Finally, the suggested approach is easily applicable to estimate the
403 LNBL of any kind of elements or compound deriving from natural processes, both in groundwater
404 and soil.

405 **Author Contributions**

406 The manuscript was written through contributions of all authors. All authors have given approval to
407 the final version of the manuscript.

408 **Notes**

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