Available online at http://geology.uaic.ro/auig/
Analele Stiintifice ale Universitatii "Al. I. Cuza" din Iasi
Seria Geologie 58 (2) (2012) 53–62

AUI GEOLOGIE

Spatial modelling of quality parameters for the shallow groundwaters of the Moldavian Platform

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Abstract

The aim of the present study is to estimate the continuous spatial distribution for certain quality (contents of Na^+, K^+, Mg^{2+}, SO_4^{2-}, HCO_3^- and TDS) related to the shallow groundwaters of the Moldavian Plateau. The analysis of covariance (ANCOVA), starting from 71 measurement points, was chosen for this purpose. The potential predictors for the spatial variation of groundwater quality that our study takes into account are the following: X and Y coordinates of points, digital elevation model (DEM), terrain slope, topographic wetness index, de Martonne aridity index, land use, surface lithology and soil classes. Compared to other methods, the analysis of the covariance has the advantage of allowing the integration of the qualitative variables as predictors. The results show that 32–45% of the spatial variation of the analysed parameters is explained by ANCOVA models, using as main predictors the de Martonne aridity index, terrain slope, X coordinate (the west-east spatial trend), land use and soil classes.

Keywords: groundwater quality parameters, analysis of the covariance, Moldavian Platform.

Introduction

Groundwater is one of the important sources of water for both domestic and industrial use. In the Moldavian Platform, the sedimentary aquifers constitute important sources of shallow groundwater. The purpose of the present study is to derive continuous spatial distributions for several groundwater quality parameters starting from a sample of the 71 measurement points. In order to convert the discrete spatial distributions into continuous ones, a spatial interpolation method must be chosen. There is a wide variety of such methods, ranging from simple mathematical interpolators (e.g. inverse distance

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weighting) to complex statistical methods (e.g. regression – kriging). The present study employs the analysis of covariance (ANCOVA) due to the fact that the latter is capable of integrating qualitative predictors.

The study area belongs to the Moldavian Plateau, covering a total surface of 5124 km^2. Its southern limit is represented by the border of Vaslui County, the western limit by a line joining the localities of Târgu Frumos, Hârlău and Botoşani, the northern limit by the Botoşani – Ştefăneşti road, while the eastern one is represented by the Prut river. The Moldavian Plateau is under the influence of a temperate-continental climate. The average annual precipitations are quite reduced (475–550 mm), and the mean annual air temperature varies between 8 and 9.5°C.

Geological setting

From a geological viewpoint, the perimeter studied is characterized by the presence of Badenian, Sarmatian, Meotian and Quaternary deposits. The upper Badenian deposits are exposed across a small area, in the north, along the bank of the Prut river. The subdivisions of the Sarmatian which occur throughout the Moldavian Platform belong to the Buglovian, Volhinian, Basarabian and Chersonian. These deposits appear successively, arranged by age, from north to south, and they consist of clays in the Jijia Plain and ootilic limestones and sandstones in the Central Moldavian Plateau. Meotian deposits occur across the same surface as the Chersonian ones, but at higher altitudes in the southern part of the Moldavian Platform. The Quaternary includes terrace and alluvial deposits belonging to the river network crossing the platform. From a lithological point of view, it is made up of sands and gravel, silts and clays (Ștefan, 2009).

The underground bodies of water identified belong to the porous and permeable type, accumulated within Sarmatian, Meotian or Quaternary deposits. The upper boundary of the unconfined aquifers varies naturally, being dynamically linked to the water level in the rivers, the amounts of rainfall and the inflow from the terraces (Panaitescu, 2008).

Materials and methods

The analysis of covariance (ANCOVA) is basically a combination between linear regression and the analysis of variance (ANOVA). The main advantage of this approach lies in its ability to integrate the effect of qualitative variables such as land use, soil classes, lithology etc. Generally, this integration is in the form of indicator (dummy) variables (Hengl et al., 2004), which assume the value 1 if a qualitative variable has a significant effect upon the dependent variable, and 0 otherwise.

The computation of the statistical models was carried out using the XLSTAT 2010 trial version software (Addinsoft). The results were subsequently applied in the GIS environment using the ArcGIS 9.3 (ESRI) software package.

A sample of 71 measurement points, located along floodplains, terraces and interfluves (Fig. 1), was used in the present analysis. These data were gathered based on the water samples collected between 1969 and 2007, the drillings carried out within the state-owned hydrological network area, managed by the Prut-Bârlad Water Basins Administration, and the research data supplied by the scientific literature available (Dragomir, 2009; Catrina, 2008). All the measurements of the samples that came from the national system monitoring, for water quality indicators, were carried out in the Chemical Laboratory of the "Romanian Waters" National Administration – Prut – Barlad Water Branch, Iasi. For the determination of the targeted indicators, standardized methods of analysis were uses: STAS 9187/84 (for fixed residue); STAS 361-90 (for calcium); STAS 6674-77 (for magnesium); EPA 9038/1986 (for sulfate); SR ISO 9297/2001 (for chloride).

Initially, the data were selected and statistically analysed in order to carry out a hydrogeochemical characterization of the waters. The findings were validated by checking the anion–cation balance in agreement with the acceptance criteria used by Murray and Wade (1996, Tab. 1). The ionic balance check is based on a percentage difference between the total cation forms and the total anion forms, defined as follows:

$$\% \text{ difference} = 100\ (\Sigma\text{cations} - \Sigma\text{anions})/(\Sigma\text{cations} + \Sigma\text{anions})$$

where the ions are in units of meq/L.

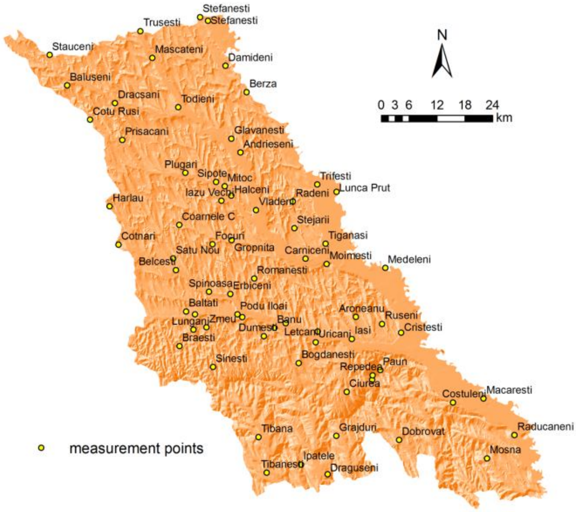

Fig. 1 Measurement points from the study area.

Table 1 Criteria proposed for the acceptance of analytical data (Murray and Wade, 1996)

Anion sum (meq/L)	Acceptable difference (meq/L)
0–3	± 0.2%
3–10	± 2.0%
10–800	± 2.5%

For the present study, the quality indicators taken into account are the major ions (Na^+, K^+, Mg^{2+}, SO_4^{2-}, and HCO_3^-) and the total dissolved solids (TDS).

The potential predictors for the spatial variation of groundwater quality that the present study focuses on are the following: the X and Y coordinates of points (according to Gauss-Kruger coordinate system), the digital elevation model (DEM), the terrain slope, the topographic wetness index, the de Martonne aridity index, the land use, the surface lithology and the soil classes. The DEM was computed from the elevation data available, extracted from the 1:50,000 scale topographic map, at a spatial resolution of 10×10 m (Ștefan, 2009). Starting from the DEM, the terrain slope (SL) and the SAGA-GIS topographic wetness index were generated. The de Martonne aridity index (AI) was com-

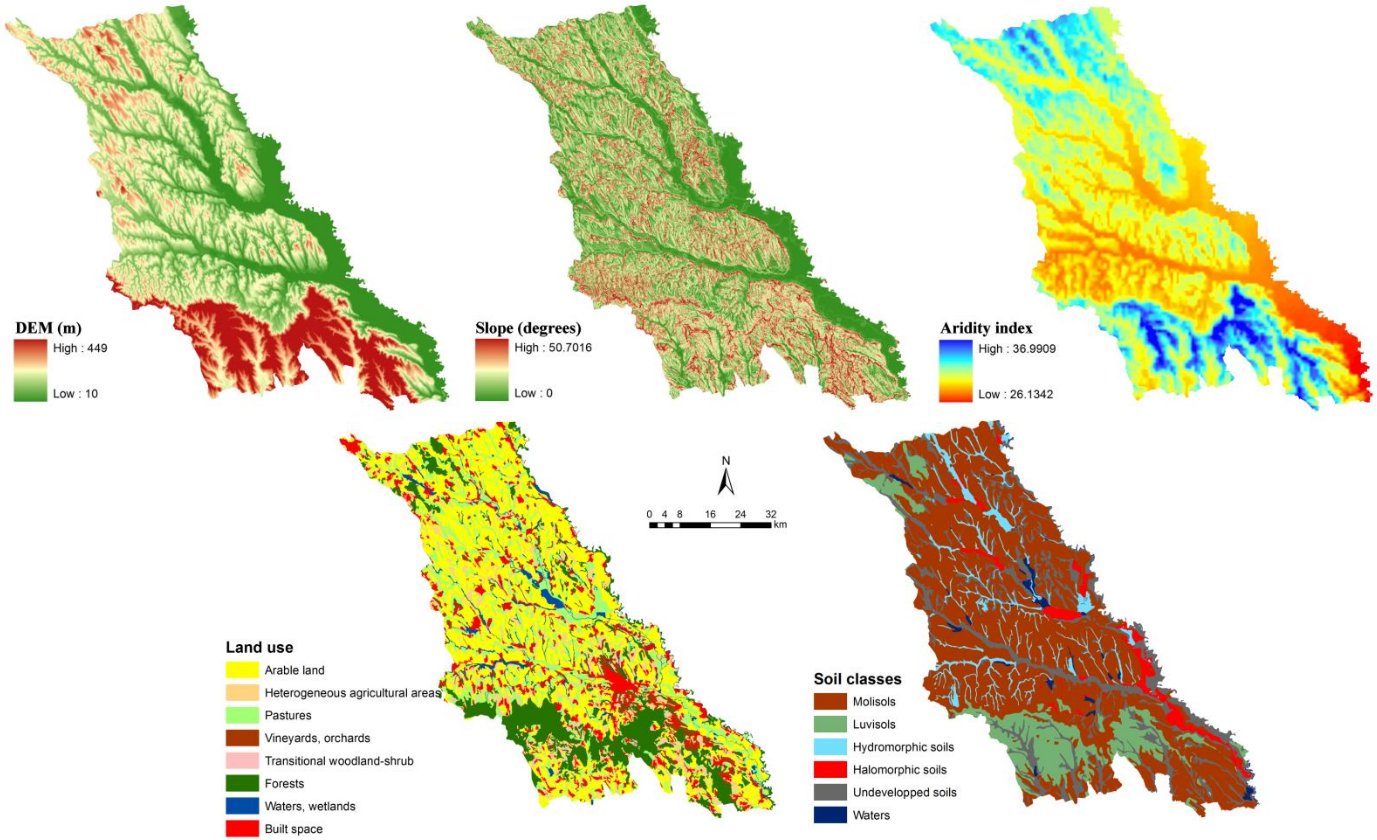

Fig. 2 The predictors which entered the ANCOVA equations.

puted based on the mean annual temperatures and precipitations, which were resampled from the Worldclim raster database (Hijmans et al., 2005) at a spatial resolution of 50×50 m. The land use categories were extracted from the Corine Land Cover (CLC) 2000 database, while the information regarding surface lithology and soil classes was acquired from the 1:200,000 scale geological and soil maps. The predictors which entered the ANCOVA equations are shown in Figure 2.

For certain groundwater parameters (Na^{+} + K^{+}, SO_4^{2-}, TDS), a logarithmic transfor-mation was necessary prior to the statistical analysis, in order to meet the normality requirements of ANCOVA models. An example is illustrated in Figure 3.

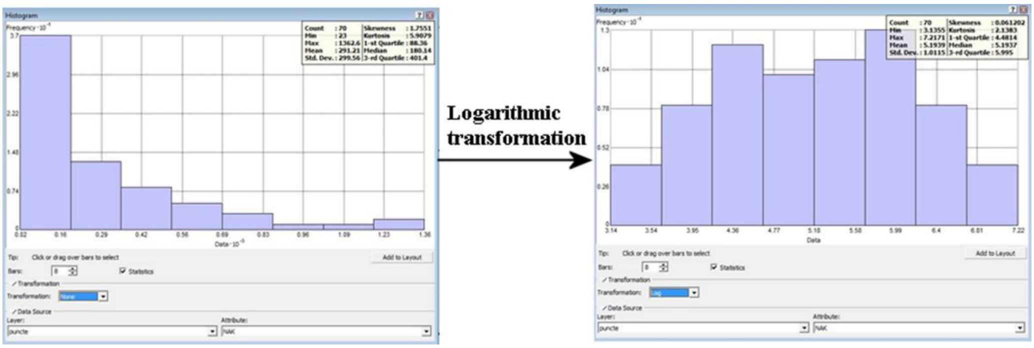

Fig. 3 An example of the logarithmic transformation.

Results

1. Water chemistry

The shallow groundwaters was grouped into: 1) groundwaters belonging to the alluvial plains and the terraces of the lower and middle course of the Prut river and its tributaries; 2) groundwaters belonging to the interfluves of the Moldavian Plain; 3) groundwaters belonging to the alluvial plain and the terraces of the upper Bârlad river and its tributaries from the northern part of the Central Moldavian Plateau. Table 2 shows certain descriptive statistics for the groundwater parameters belonging to the groups above.

The groundwaters was hydrogeochemically characterized using the Piper diagrams that reveal the following features:

- The groundwaters from the alluvial plains and the terraces of the lower and middle course of the Prut river and its tributaries are the bicarbonate type, including the bicarbonate-sulfate, bicarbonate-chlorine and mixed subtypes (Fig. 4). The sulfate-bicarbonate facies is characteristic for the groundwater from the alluvial deposits situated along the middle and upper course of Jijia, the lower course of Sitna, the middle and lower course of Bahlui and the floodplain formed by the Prut and Jijia rivers downstream of the Medeleni village. 65% of the cationic hydrogeochemical facies are of the sodium type. The magnesium type is less frequent and it characterizes the Bahlui deposits at Banu, Dumeşti and Uricani. The calcium facies is very rare, being encountered in the alluviums deposited by the Prut between the villages of Dămideni şi Cârniceni.
- The groundwaters from the the interfluves of the Moldavian Plain belong to the bicarbonate-sulfate hydrogeochemical facies (Fig. 5). The mean content of the ions Ca^{2+} and Na^{+} (Tab. 2), as well as the high correlations between these cations and SO_4^{2-} and HCO_3^{-}, constitute evidence of the cationic exchange which takes place

between the bicarbonate-calcium waters and the Sarmatian clays, which retain Ca^{2+} and release Na^{+}. The intake of elements supplied by calcite (especially in the structural plateau areas) or gypsum solubilisation is not to be disregarded, either.

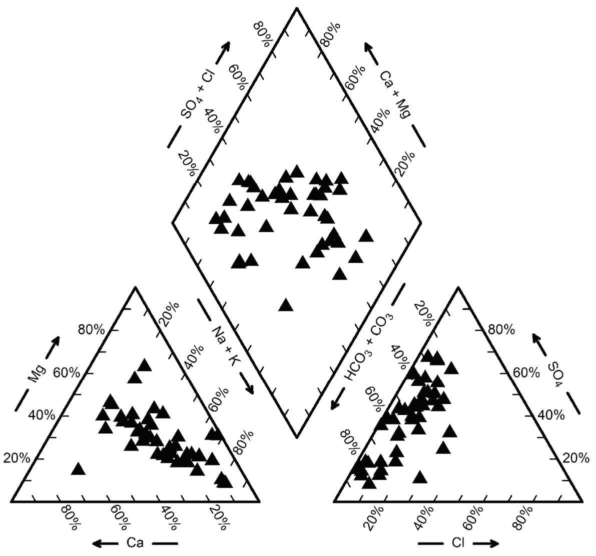

Fig. 4 Piper diagram for the groundwater belonging to the alluvial plains and the terraces of the lower and middle course of the Prut river and its tributaries.

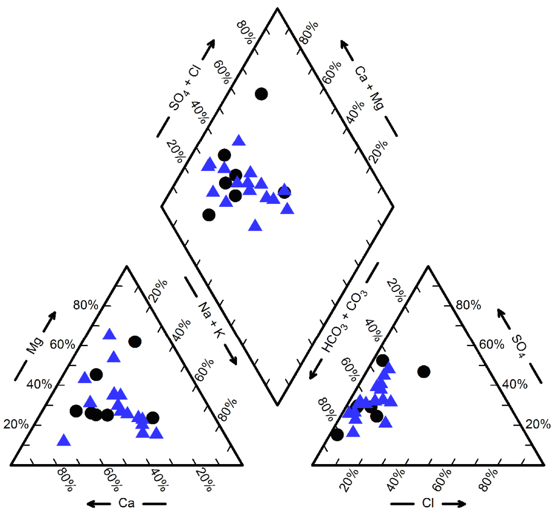

Fig. 5 Piper diagram for the groundwater belonging to the interfluves of the Moldavian Plain (circle symbol) and to the alluvial plain and the terraces of the upper Bârlad river and its tributaries (triangle symbol).

- Most of the groundwaters from the alluvial deposits of the upper Bârlad river and its tributaries belong to the bicarbonate and bicarbonate-sulfate anionic types (Fig. 5). The Ca^{2+} cation has the highest content. The explanation lies in the fact that the aquifers are supplied by waters flowing along slopes which display a limestone and/or sandstone layer in the upper part. Another source of Ca^{2+} is represented by gypsum solubilisation, as confirmed by the high correlations between the ions of this mineral (Ștefan, 2009). Furthermore, these aquifers exhibit high and very high correlations between Na^+ and SO_4^{2-}, HCO_3^-, as well as between Ca^{2+} and Cl^-

The total dissolved solids (TDS) in the groundwater from the study area range between 273 and 4306.14 mg/L, with a mean value for each group of waters. Based on these values, shallow groundwater samples in the study area vary from fresh (TDS < 1000 mg/L) to brackish (1000<TDS<10000 mg/L).

2. Statistical spatial models

The spatial variation of the *sodium* and *potassium* content is described by the following equation:

$$NaK = 8.768 - 0.0000065 \times X - 0.031 \times SL - 0.105 \times AI + 0.427 \times CLC\text{-}231$$

The application of the equation in the GIS environment has led to the spatial model in Figure 6. According to the ANCOVA model, which explains 38% of the variance of dependent variables, there is a general decreasing trend in the sodium and potassium content from west to east. Moreover, the content increases along with the aridity of the climate, due to the enhanced evapotranspiration. The relation with the slope indicates that gentle slopes and flat terrains are characterized by higher sodium and potassium contents, which is due to the fact that the ion content is generally higher throughout the floodplains. The model has also revealed that the content is higher where the land is used as pasture (CLC-231). The standardized ANCOVA coefficients show that these 3 factors have fairly equal influences upon the dependent vari-ables, slightly more pronounced in the case of the west-east trend and the aridity index.

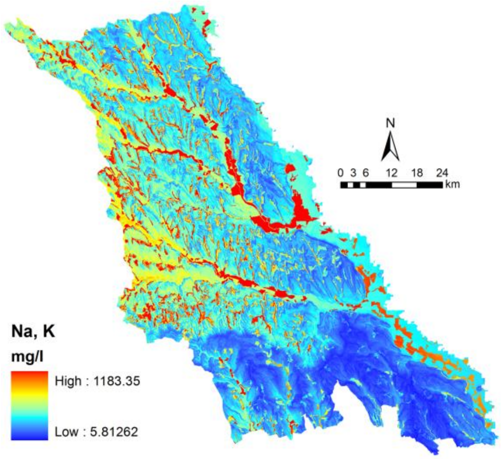

Fig. 6 The spatial variation of the *sodium* and *potassium* content.

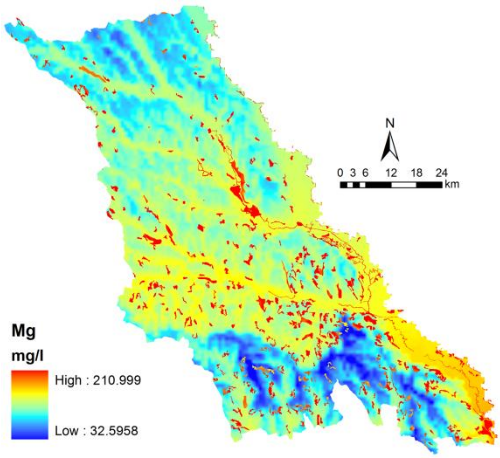

Fig. 7 The spatial variation of the *magnesium* content.

In the case of the *magnesium* content, the histogram is quasi-normal and, therefore, a logarithmic transformation was not necessary. The ANCOVA model integrates one quantitative variable (the aridity index) and 2 qualitative variables, namely land use and soil classes, as follows:

$$Mg = 277.325 - 7.265 \times AI + 38.271 \times CLC\text{-}242 + 100.744 \times CLC\text{-}511 + 23.363 \times SOIL\text{-}6$$

The model, which explains 38% of the spatial variance of magnesium, shows that the magnesium content of the groundwater increases in drier areas. It is also higher throughout floodplains (CLC-511) and under agricultural areas, especially those with complex cultivation patterns (CLC-242), namely a mixture of arable lands and other agricultural terrains (orchards, vineyards). Moreover, the magnesium content is generally higher under hydromorphic soils (SOIL-6). The spatial model obtained using the equation above is shown in Figure 7. Among the factors analysed, the land use classes are the most important ones, followed by the aridity index.

The spatial variation of the *sulfate* content (Fig. 8) is very similar to that of the sodium and potassium contents, the two variables being well correlated:

$$SO_4 = 8.277 - 0.00000507 \times X - 0.109 \times AI + 0.458 \times CLC\text{-}231 - 0.937 \times CLC\text{-}411$$

The model explains 32% of the spatial variance of sulfates. We notice the same west-east decreasing trend, higher values being recorded in drier areas and under pastures. Apparently, the magnesium content is lower under wetland vegetation, which is, however, questionable, given the fact that only one point from the sample corresponds to this land use category. According to the standardized regression coefficients, the most important factor is the aridity index.

The model obtained for the *bicarbonate* content (Fig. 9) explains 45% of the spatial variance and is described by the following equation:

$$HCO_3 = 4572.007 - 0.00478 \times X - 12.713 \times SL - 44.240 \times AI - 99.143 \times SOIL\text{-}1$$

The same west-east decreasing trend as in the cases of the sodium, potassium and sulfate contents, only in a more pronounced form, can be noticed for this variable. Once again, the aridity of the climate plays an important role in explaining the spatial distribution of the bicarbonate content. Furthermore, the values of this parameter are higher on gentle slopes or flat terrains and lower where the soils belong to the Molisols class (SOIL-1). The explanation lies in the fact that these soils (mostly Chernozems) retain most of the carbonates in the lower part of their profiles, which is related to the aridity of the climate not allowing a continuous percolation of the soils down to the groundwater.

In the case of the *total dissolved solids (TDS)* (Fig. 10), the ANCOVA model explains 35% of the variance of this parameter by means of 4 predictors: the X coordinate, the slope, the DEM and the soil (Molisols class), as follows:

$$TDS = 5.698 - 0.00000449 \times X - 0.0171 \times SL - 0.000964 \times DEM - 0.168 \times SOIL\text{-}1$$

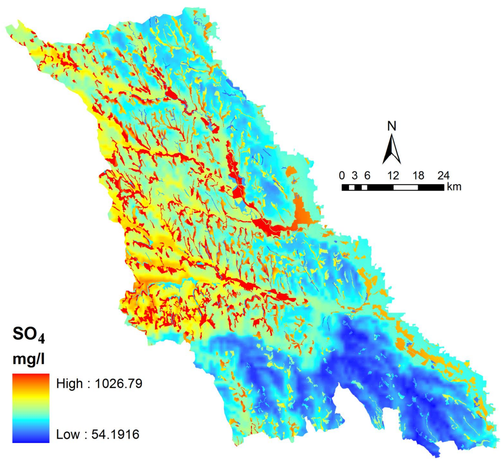

Fig. 8 The spatial variation of the *sulfate* content.

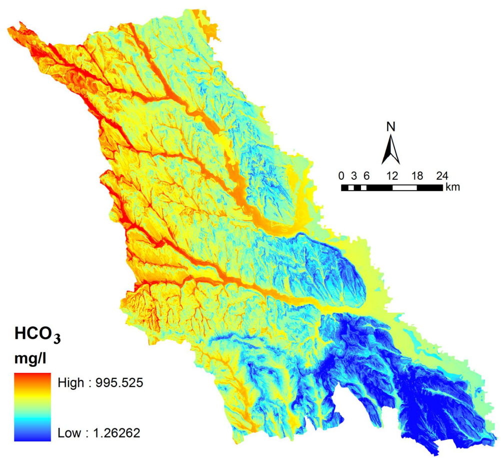

Fig. 9 The spatial variation of the *bicarbonate* content.

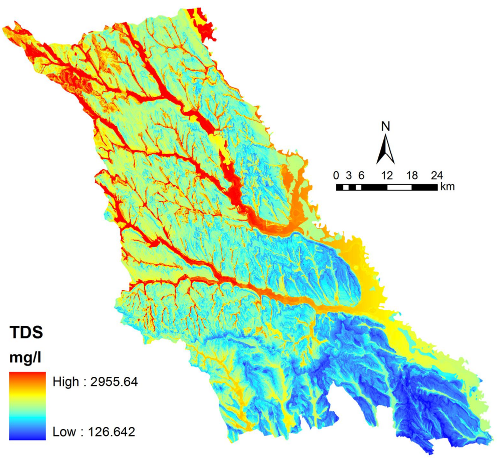

Fig. 10 The spatial variation of the *total dissolved solids*.

Again, the general west-east variation, the inverse relation with the slope, and the lower values under molisols, are all noticed. The inverse relation with the altitude is partially an effect of the aridity of the climate, which is enhanced at lower altitudes, and partially an effect of the lithology, which is dominated by limestones and sandstones at higher elevations in the southern part of the region.

Conclusions

The predictors that play the most important role in explaining and rendering the spatial variation of the groundwater quality parameters in the study area are the de Martonne aridity index, the terrain slope, the X coordinate (the west-east spatial trend), the land use and the soil classes. There is some amount of uncertainty regarding the influence of these predictors, uncertainty which derives from the fact that some of them are well correlated. Certain qualitative predictors could, however, be reclassified in order to reduce the uncertainty. For instance, CLC classes 511 and 411 could be grouped together, as they are both related to the presence of waters and wetlands. The statistical models computed explain 32–45% of the spatial variance of the parameters analysed. Their quality could be further improved by coupling the ANCOVA with the ordinary kriging of the residuals. Compared to other methods, the analysis of the covariance has the advantage of allowing the integration of qualitative variables as predictors.

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Received November, 2012
Revised: November, 2012
Accepted: December, 2012