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GROUNDWATER HYDROCHEMISTRY OF THE ÉVORA REGION OF PORTUGAL: GEOSTATISTICAL ANALYSIS

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ABSTRACT. This paper presents a geostatistical analysis of a set of hydrochemical data obtained in the region of Évora (Portugal). These hydrochemical data were selected from a larger set of samples collected in wells and springs located in crystalline rocks (gneisses, hornfels, micaschists, quartzodiorites and granodiorites).

The logarithmic transformation of all variables, except silica and pH, allowed the sample statistics to follow a Gaussian distribution more closely. Thus all subsequent analysis was performed on these transformed data.

The structural analysis of the physical-chemical parameters (conductivity, pH, bicarbonate, sulphate, chloride, nitrate, calcium, magnesium, sodium, potassium and silica) shows that the linear and spherical models, with "nugget", give satisfactory fits to the sample semivariograms.

Some variables exhibit a regional drift in the NW-SE direction which gives, as a consequence, variations in the range and/or sill values and, in some cases, even changes in the type of the semivariogram with the direction.

The spatial distribution studied by ordinary or universal kriging shows the presence of a strip, of NW-SE direction, with low values in all variables. This corresponds to a region of higher relief and lesser thickness of weathered material. Flat regions with lower altitudes have higher values of all parameters. The elevated randomness reflected in high values of nugget is interpreted as a consequence of anthropogenic factors, e.g. agricultural activities.

INTRODUCTION

The study area, which consists mainly of crystalline rocks, is characterized by scarce ground- and surface water resources. Despite the relative scarcity of groundwater, this resource is important for water supply for small population centers as well as for private use, agriculture and cattle supply.

For the hydrogeological characterization, 350 wells and springs were identified and some parameters, e.g temperature, pH, electric conductivity (EC) and redox potential were measured. From this set of points, 86 were selected in order to obtain a more complete hydrochemical picture. At these 86 points the following parameters were analyzed: CO_2, alkalinity, sulphate, chloride, nitrate, calcium,

magnesium. sodium, potassium and silica.

The factors which contribute to the hydrochemical characteristics can be related to anthropogenic activities or to water-rock interaction processes. The identification of these factors is important in order to forecast the hydrochemical behaviour. Multivariate methods and geostatistical analysis can contribute to a better identification of those processes.

GEOLOGICAL AND HYDROGEOLOGICAL SETTING

The study area is located in the Central-South region of Portugal, near the city of Évora (fig. 1) and is composed of igneous and metamorphic rocks, affected by the Hercynian orogeny. The area is a part of the Ossa-Morena zone, one of the subdivisions that have been described in the Iberian Peninsula (Chacón et al., 1983). The pre-Mesozoic rocks were affected by two deformations, the first one in middle/late Devonian and the second after late Devonian and before Westphalian D (Julivert et al., 1972). There is, in the region of Évora, a predominance of metamorphic rocks, including anathetic granular rocks (fig. 3). The dominant lithologies are gneisses, micaschists, amphibolitic schists, amphibolitic hornfels and crystalline limestone, surrounding a central area of igneous rocks with quartzodiorites, granodiorites and small areas of gabbrodiorites and aplite-pegmatitic rocks. There are also some quartz veins and sparse outcrops of basaltic rocks (Carvalhosa et al., 1969).

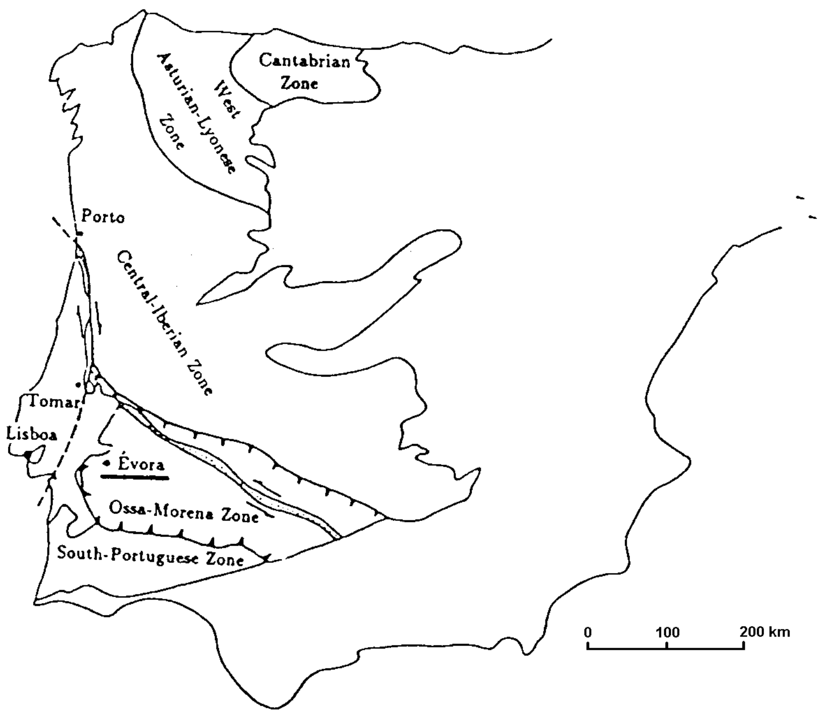

FIG 1. Map showing the location of the study area (Chacón et al., 1983).

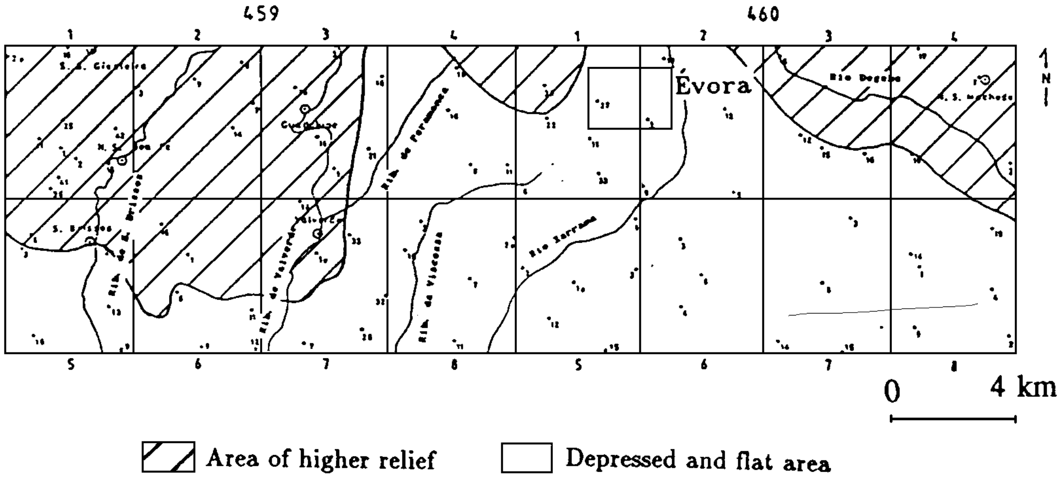

FIG 2. Relief, drainage network and location of sampling points.

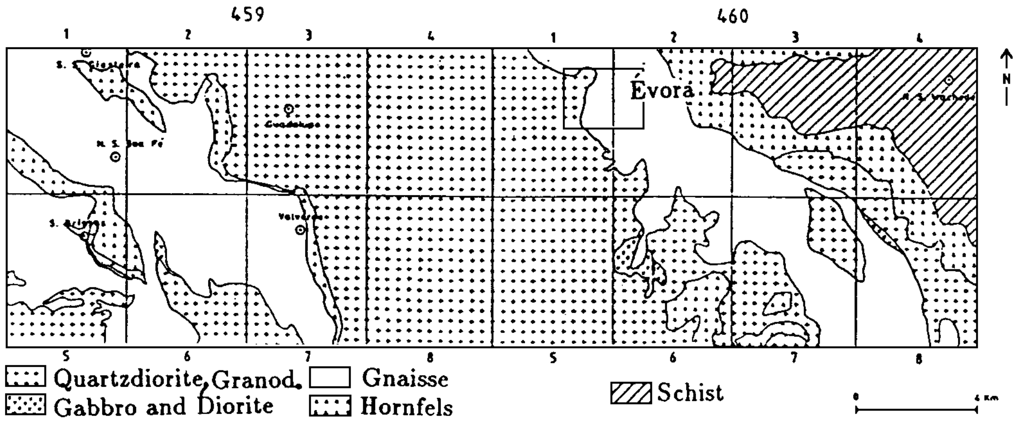

FIG 3. Geological setting of the region of Évora.

The geomorphology is characterized by an incipient drainage network (fig. 2) belonging to two drainage basins (Sado and Guadiana rivers).

The northwest and northeast areas are more elevated, the latter corresponding to the micaschist formation (fig. 2 and 3). The northwestern and western relief, corresponding to gneisses, quartzdiorites and granodiorites, is more influenced by tectonic factors than by lithology. Aplite-pegmatitic rocks form some hardness-related relief.

Hydrogeologically, all the different lithologies exhibit similar behaviour. The water circulation is effectively in the upper zone of weathered rock and in the deeper zone through fractures.

The small thickness of weathered superficial rock, in many places less than

two meters thick, makes the circulation of groundwater in this zone very dependent on the period of maximum precipitation, which occurs between November and April. During the hot, dry months the water circulates essentially through joints and deeper fractures that exist in the unweathered or slightly weathered rocks to depths of more than 100 meters.

In general, the micaschists have lower productivity than other lithologies (granodiorites, quartzodiorites, gneisses and hornfels). In the last four lithologies the alteration is stronger in flat and depressed areas, reducing the permeability due to the presence of argillaceous alteration materials. The chemical quality reflects this situation, the water of flatter areas being more mineralized than that of higher zones.

GEOSTATISTICAL ANALYSIS

Geostatistical analysis was applied to all the physical-chemical variables, except temperature. This analysis consists of several steps: statistical characterization of each variable, estimation of empirical semivariograms and fitting to the theoretical semivariograms, detection of drift, kriging and interpretation of results.

Except for pH and silica, which follow a normal distribution, all the other variables follow very nearly a log-normal distribution. A logarithmic transformation has thus been carried out for them. Table I lists the sample median, mean, standard deviation (S. Dev.), variance (Var.), coefficient of variation (C. Var.), skewness (Skew.) and kurtosis (Kurt.) for all variables used.

Table I. Sample Statistics of Hydrochemical Data

Parameter*	Log	Mean	Median	S.Dev.	Var.	C.Var.	Skew.	Kurt.
pH	No	6.988	7.020	0.646	0.417	9.24	0.688	4.799
EC	Yes	6.085	6.064	0.686	0.470	11.27	0.115	2.248
Ca	Yes	3.459	3.453	0.794	0.630	22.95	-0.279	2.484
Mg	Yes	2.904	2.957	0.833	0.693	28.67	-0.135	2.424
Na	Yes	3.677	3.599	0.646	0.417	17.56	0.252	2.144
K	Yes	0.580	0.642	0.750	0.562	129.38	-0.377	3.416
HCO_3	Yes	5.002	5.009	0.736	0.542	14.72	-0.451	2.421
SO_4	Yes	3.067	3.006	0.820	0.673	26.74	0.262	2.376
Cl	Yes	3.906	3.776	0.758	0.575	19.41	0.597	2.66
NO_3	Yes	3.984	3.952	0.739	0.546	18.54	0.155	2.424
SiO_2	No	24.2	23.3	9.826	96.55	40.68	0.142	2.345

* EC in μS/cm, other parameters in mg/L

In order to make a preliminary characterization of the variables in relation to stationarity, a trend surface analysis was carried out. A high correlation with the

regression model gives an indication of the probable presence of drift.

All the variables appear to fit to trend surfaces of the first degree. Bicarbonate, silica and sulphate are the variables that present the lowest correlation coefficients with the regression. The first two are not even significant at a level of 1 %.

In Table II the results of trend surface analysis applied to all the variables are presented. As can be seen, all the surfaces present a similar attitude, with increasing values from NW to SE. The best fit was obtained for Na, K, and NO,. The increase in degree was not significant in any case.

Table 11. Trend Surface Equations

Variable	Trend surface equation a_0	$+ \ a_1 * x$	$+ \ a_2 * y$	F[(a)]	r [(b)]
pH	7.90	0.02672	-0.03796	9.93	0.439
Ln (EC)	7.88	0.02895	-0.04577	11.02	0.458
Ln (Ca)	6.16	0.02578	-0.04703	6.37	0.365
Ln (Mg)	3.96	0.02908	-0.04168	6.65	0.372
Ln (Na)	6.71	0.03336	-0.05820	20.3	0.573
Ln (K)	2.90	0.04046	-0.02973	16.3	0.531
Ln (HCO_3)	8.90	0.01880	-0.04534	4.52	0.313
Ln (SO_4)	7.17	0.02356	-0.05230	5.5	0.342
Ln (Cl)	5.90	0.03004	-0.04825	9.49	0.431
Ln (NO_3)	2.86	0.03863	-0.04095	16.34	0.532
SiO_2	-56.3	-0.206	0.713	4.22	0.304

[(a)] F = ratio of explained variance over residual variance
[(b)] r = coefficient of correlation

Structural analysis

The structural analysis aims to evaluate the structure of a spatial random variable Z(x) by using a probabilistic function of autocorrelation known as a semivariogram:

$$\gamma(h) = 1/N(h)\ [Z(x_i + h) - Z(x_i)]^2$$

where N(h) is the number of data pairs $[Z(x_i + h), Z(x_i)]$, and h is a displacement vector.

The experimental semivariograms were estimated according to NE-SW and NW-SE directions. The average semivariograms and the theoretical semivariograms were also estimated.

The NW-SE direction was chosen because it is the average direction of the slope of the fitted trend surfaces. The NE-SW direction was chosen because it is orthogonal to the first one. The N-S and E-W directions were not selected because the study area is elongated in an E-W direction and it is not possible to estimate the semivariogram along the N-S direction with the same degree of accuracy as the other directions, as it has few pairs of points and does not allow the estimation of behaviour for distances greater than 10 km.

For most variables the experimental semivariograms fit to semivariograms of spherical type:

$$\gamma (h) = C + \omega (1.5 *(h/a) - 0.5 *(h/a)^3) \qquad h < a$$
$$\gamma (h)= C + \omega \qquad h \geq a$$

where, γ = semivariogram; h = distance; ω = sill; a = range; C = nugget.

pH, K and NO_3 fit to the semivariogram of linear type:

$$\gamma (h)= C + \omega h$$

These three variables are amongst those that show a better fit to a trend surface and have the characteristic of being almost isotropic. Only K has a small deviation in the ω value.

In variables that present an anisotropic structure, this effect can be reflected in variations in the theoretical model's parameters, or even in the type of the model. Thus, electrical conductivity, Ca and Na experimental semivariograms fit to spherical models, according to the NE-SW direction, and to linear models along the orthogonal direction. The average semivariograms are always of spherical type.

The combination of results allows one to detect specific types of behaviour that will be further described in more detail.

<u>pH</u>. The semivariogram is isotropic, of linear type, with parameters, C = 0.24 and ω = 0.0143. On the experimental semivariogram a decrease in the value of γ for a distance in excess of 25 km is observed. The same effect (hole effect?) is obtained in semivariograms of other variables and can be explained by the existence of two areas with similar characteristics 25 km apart.

<u>Electrical conductivity and calcium</u>. The semivariograms of the logarithms of these variables fit to spherical models with parameters, C = 0.15, ω = 0.35 and a = 8 km (EC); C = 0.20, ω = 0.47 and a = 6 km (calcium) on the NE-SW direction; and to linear models with parameters, C = 0.15, ω = 0.03 (EC); C = 0.3 and ω = 0.028 on the NW-SE direction. The mean semi-variograms fit to spherical models with parameters, C = 0.13, ω = 0.40 and a = 10 km (EC); C = 0.30, ω = 0.40 and a = 10.5 km (calcium).

<u>Silica</u>. This variable follows a normal distribution, ranging in value from 4.1 and 47.5

mg/L. The experimental semi-variogram fits to a spherical model with parameters, C = 70, ω = 25.4 and a = 5 km. Silica is the variable with the weakest structure, as is shown by its high nugget, 73.4% of sill, and its range which is inferior to all other variables.

Sodium. The experimental semi-variograms of the logarithms fit to a spherical model and do not show any discernible anisotropy. The parameters fitted are: C = 0.35, ω = 0.1 and a = 10 km.

Potassium. The experimental semi-variograms of logarithms of potassium fit to a linear model. A slight anisotropy can be observed, as the semi-variogram in the NE-SW direction has parameters, C = 0.03 and ω = 0.018, whereas the one in the NW-SE direction has parameters, C = 0.3 and ω = 0.22. The last set of parameters coincide with the parameters fitted to the average semi-variogram.

Nitrate. This variable has a structure very similar to potassium, suggesting that both are influenced by the same processes, most likely the use of fertilizers in agriculture. The semi-variogram is linear with parameters, C = 0.3 and ω = 0.02 and does not show any discernible anisotropy.

Magnesium, bicarbonate, sulphate and chloride. The experimental semi-variograms of all those variables fit to spherical models. All of them show a slight anisotropy. The fitted parameters are shown in Table III.

Table III

Variable	C	ω	a	direction
Magnesium	0.15	0.62	7	NE-SW
	0.15	0.85	20	NW-SE
	0.15	0.67	10	average
Bicarbonate	0.08	0.60	8.5	NE-SW
	0.16	0.44	12	NW-SE
	0.10	0.55	10	average
Sulphate	0.32	0.48	10	NE-SW
	0.20	0.60	13	NW-SE
	0.28	0.50	12	average
Chloride	0.30	0.27	9	NE-SW
	0.25	0.37	11	NW-SE
	0.25	0.37	11	average

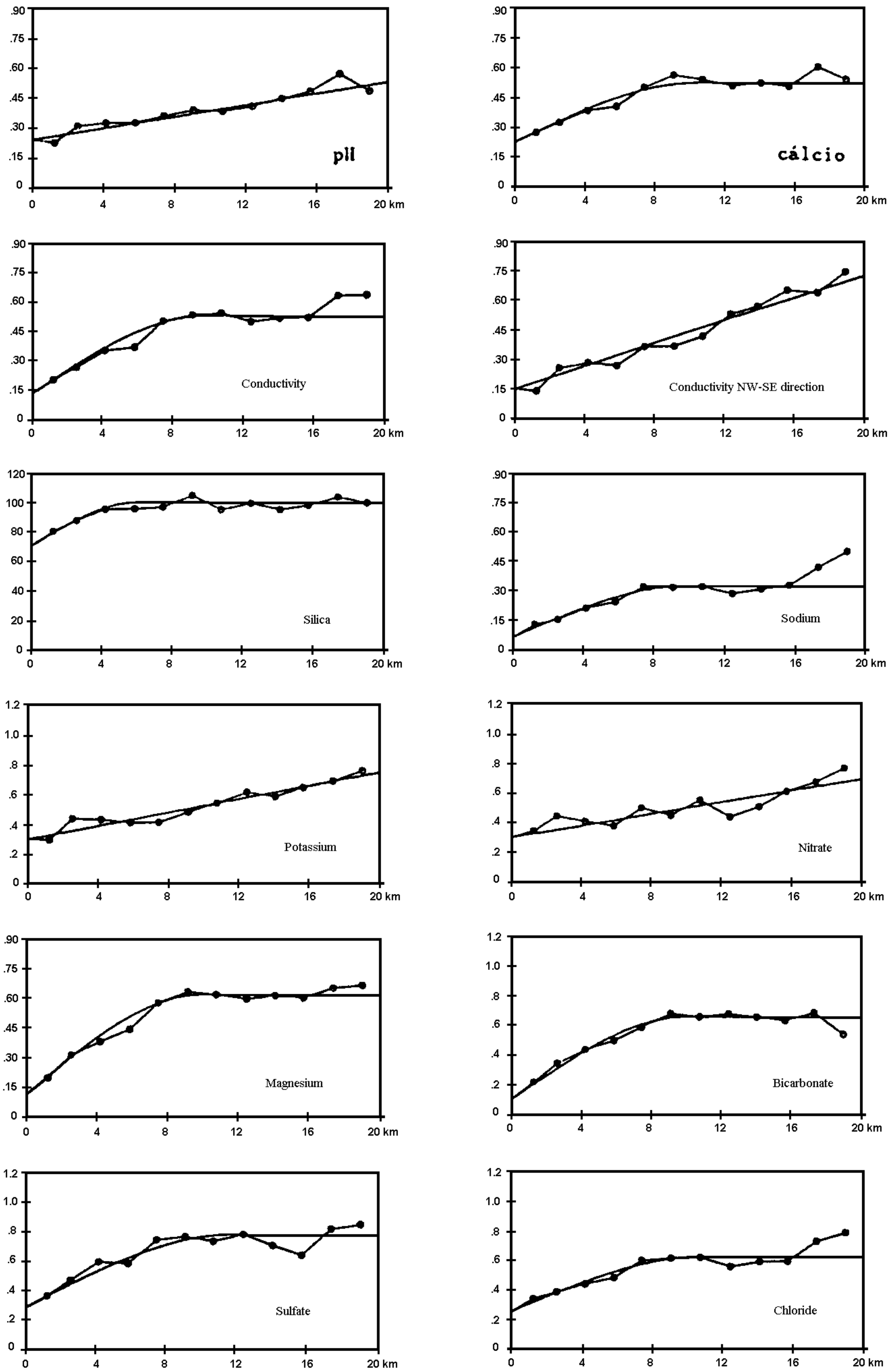

FIG 4. Semivariograms of the hydrochemical variables (γ(h) on Y axis, h on X axis).

Kriging

The spatial pattern of the variables was obtained from point estimates in a regular grid by kriging. We have considered, with drift, those variables with the best fit to a trend surface and which show significant anisotropy, i.e., logarithms of EC, Ca, Mg and Cl. For those variables universal kriging (UK) was used.

One difficulty in using UK is the estimate of the semivariogram, because in such cases the sample semivariogram gives a biased image of it (De Marsily, 1986). Here we have considered as representative the sample semivariogram obtained in the NE-SW direction, as this direction has minimum drift, being orthogonal to the direction of maximum depth of the trend surface. The calculations were carried out with the program UVKRIG (Carr, 1990). For the remaining variables, point estimates were made by ordinary kriging.

A validation was made by using the statistics' mean error, mean square error (RMS) and reduced mean square error. The correlation coefficients (r) between observed and estimated values were also used. Table IV shows the values of RMS and r.

Table IV

Variable	r	RMS
pH	0.4740	0.5724
EC	0.6583	0.5139
Ca	0.6047	0.6290
Mg	0.6629	0.6209
Na	0.6267	0.5071
K	0.4531	0.6705
HCO_3	0.6452	0.5615
SO_4	0.5138	0.7061
Cl	0.5084	0.6536
NO_3	0.3940	0.6877
SiO_2	0.2169	9.73

As can be expected, silica has the lowest coefficient of correlation due to its high nugget and low range. In all other variables the quality of the estimates increases significantly.

The spatial distributions of the variables (fig. 5) as estimated by kriging, show a similar pattern with the exception of silica. An inverse correlation can be observed between the values of the variables and the elevation of relief, as the higher values correspond to the flat and depressed areas. Such areas are either used for agricultural purposes or are in the neighbourhood of population centres. This can be seen in the tridimensional perspective of Na distribution (fig. 6a): a "valley" of low values of concentration with NW-SE, direction in the western, part of the map, and higher

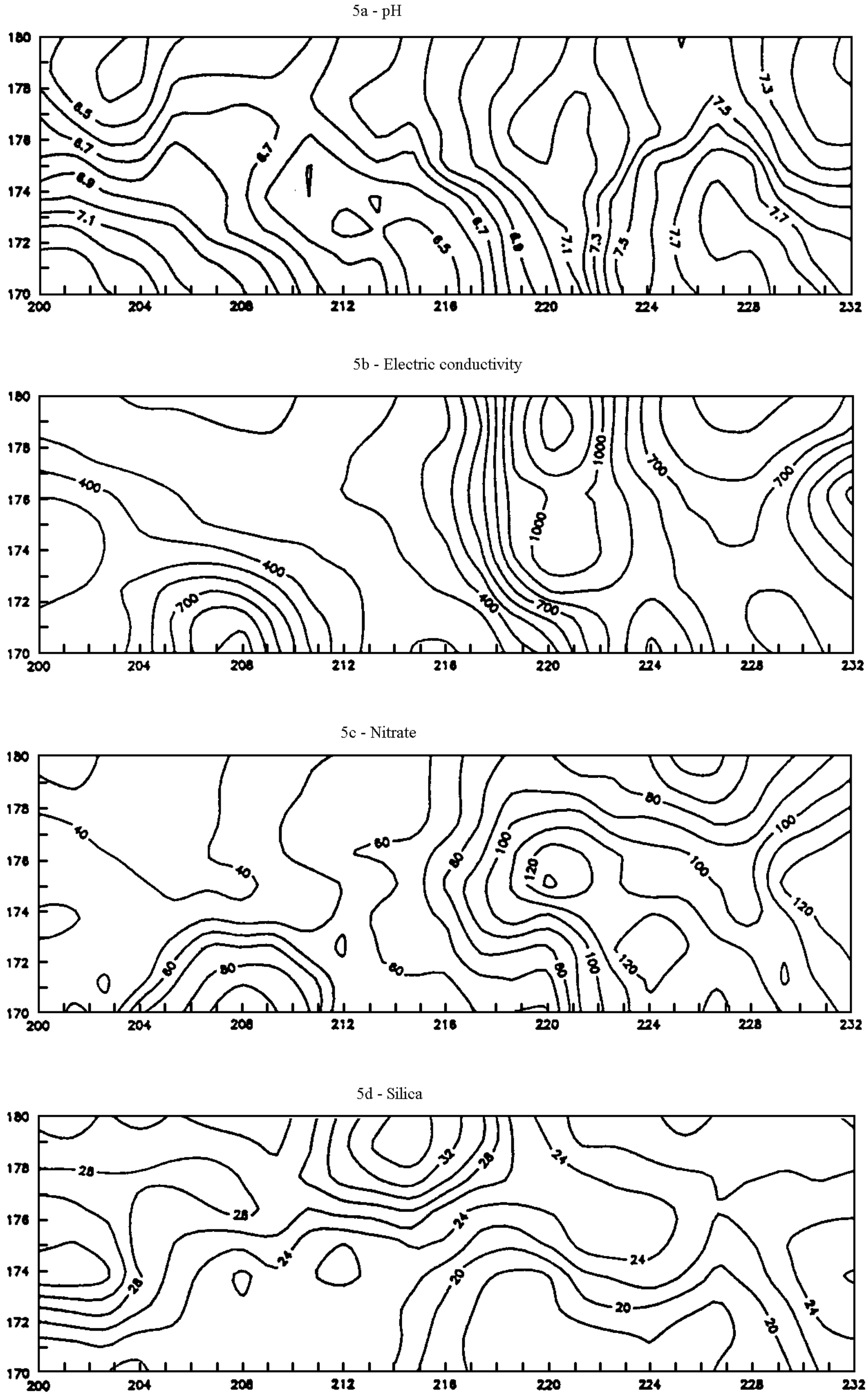

FIG 5. Map of kriging estimates

5a

5b

5c

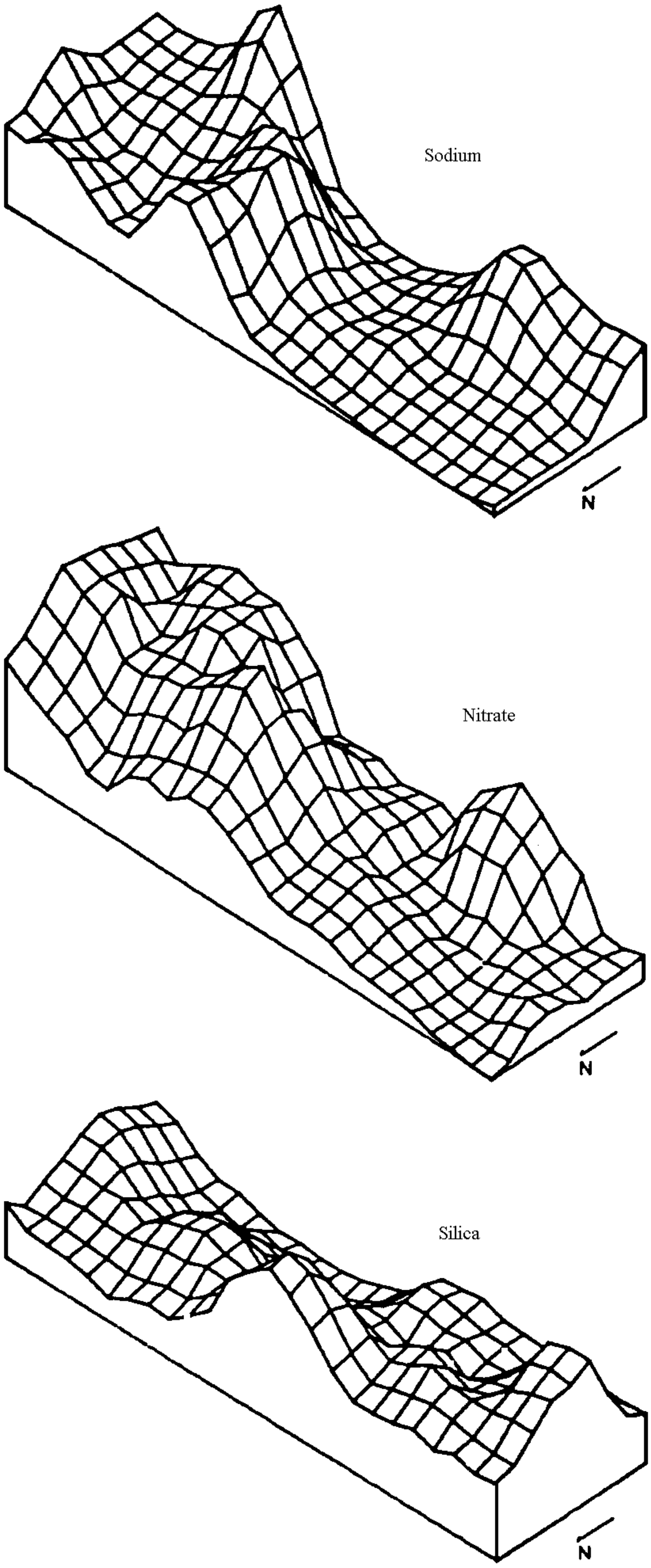

FIG 6. Tridimensional perspective of kriging estimates

values in areas of agriculture and human occupation. In the case of nitrate the distribution in the eastern sector is more homogeneous (fig. 5c and fig. 6b).

Silica presents a different pattern of distribution, the distribution is rather uniform in space and shows a weak structure. The higher values are associated with pegmatitic formations NW of Évora city, and the lower values to the flat SE areas (fig. 6c).

CONCLUSIONS

The patterns of spatial distribution and the relative statistical homogeneity allows the conclusion that anthropogenic factors have a stronger influence on the groundwaters' chemical composition than those related to water-rock interaction.

All the variables present some degree of spatial autocorrelation, as is indicated by their respective experimental semivariograms. The least structured variable is silica, which is characterized by an almost random behaviour.

Kriging, applied to the set of variables, shows that the spatial distribution of all the variables presents similar characteristics, with few differences, excepting silica, which has a more spatially uniform distribution with weak structure.

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