SPATIAL VARIABILITY OF SOME GROUNDWATER CHARACTERISTICS IN THE STATE OF BAHIA, BRAZIL

F. Negrão[1], E. Vidal Vázquez[2], J. Paz-Ferreiro[2], I.B. de Oliveira[1]

[1]Departamento de Engenharia Ambiental, Escola Politécnica, Universidade Federal da Bahia, Campus da Federação, 40210-630, Salvador, Bahia, Brasil.
[2]Edafología y Química Agrícola, Facultad de Ciencias, Universidade da Coruña, Campus Zapateira s/n, 15071, Coruña. E-mail: evidal@udc.es

RESUMEN. El Estado de Bahía, situado en el noroeste de Brasil, se caracteriza por una gran variedad desde el punto de vista del clima, la geología y la hidrogeología. Si bien el litoral es tan lluvioso que soporta una vegetación natural de tipo bosque Atlántico, el 68% del territorio es semiárido y árido. En dicho estado se pueden reconocer cinco grandes dominios hidrogeológicos, asociados a los siguientes materiales: sedimentos terciario-cuaternarios, sedimentos mesozoicos, karst, metasedimentos y rocas cristalinas ígneas y metamórficas. Se utilizaron datos tomados en 3322 pozos para analizar, a escala estatal, la variabilidad espacial de pH, sólidos totales en disolución (TDS), cloruros, dureza, nitratos, fluoruros y un índice de calidad del agua (QI) obtenido de los anteriores. De acuerdo con los valores de TDS y cloruros, muchos de los acuíferos del estado de Bahía, sobre todo los de las zonas áridas, contienen agua salada, no apta para el consumo humano y, en ocasiones, ni tan siquiera para el riego. También se detectaron niveles excesivos de nitrato y fluoruros que afectan a pequeñas áreas. Según el índice de calidad elaborado, el 39.8% de los pozos contenían agua no potable. El análisis de semivariogramas puso de manifiesto una elevada correlación espacial de TDS, cloruros y fluoruros, mientras que la de la dureza y contenido en nitratos era media y la del pH era baja. Los mapas de krigeado permitieron comprobar que, en general, las aguas de los dominios sedimentarios y metasedimentarios eran de calidad buena u óptima, mientras el riesgo de encontrar agua de calidad no adecuada para el consumo humano e incluso para riego es superior en los dominios kárstico y cristalino.

ABSTRACT. The State of Bahia, located in the Northwest of Brazil, is known for its diversity in terms of climate, geology and hydrogeology. Although litoral regions are very humid and support Atlantic forest, 68% of the territory is semiarid or arid. Five main hydrogeological domains have been distinguished in this state, depending on the following materials: Tertiary-Quaternary cover sediments, Mesozoic sediments, Calcareous (Karst), Metasediments and Crystalline, i.e. metamorphic or igneous rocks. A data set resulting from analysis of samples taken from 3322 wells was used to assess all over the state the spatial variability of pH, total dissolved solids (TDS), chloride, hardness, nitrate, fluoride and a groundwater quality index (QI) obtained from the former parameters. Following TDS and chloride contents many parts of the state, particularly in the dry areas, are underlain by high saline groundwater, which is not recommended as drinking water and even for irrigation purposes. Also excessive nitrate or fluoride levels were detected, but they occurred only locally. According with our quality index, 39.8% of the sampled groundwater was no potable. Semivariogram analysis showed strong spatial dependence for TDS, chloride and fluoride, whereas it was moderate for hardness and nitrate and low for pH. Following inspection of kriging maps it was apparent that, in general, optimal and good water quality was associated to sediment and metasediment domains, whereas de risk of improper water quality for drinking and even irrigation purposes was higher at the karstic and crystalline domains.

1.- Introduction

The relationship between groundwater composition and environment depends on both, natural and anthropogenic factors. Water dissolves minerals from the rocks with which it comes in contact. Therefore, groundwater acquires its natural composition in accordance with the hydrogeological scenario, which, in turn, depends on the climate, topography and rock properties (i.e. hydraulic properties, chemical composition). Although the vadose zone filters out particulate matter, such as leaves, soil, and bugs, dissolved elements can still occur in large enough concentrations in groundwater and could cause problems. So, groundwater quality can be affected by industrial discharges, urban activities, agriculture and disposal of waste. For example, contaminants from leaking fuel tanks or fuel or toxic chemical spills may enter the groundwater and contaminate the aquifer. Also, pesticides and fertilizers applied to lawns and crops can accumulate and migrate to the water table. The physical properties of an aquifer, such as thickness, rock or sediment type, and location, play a large part in determining whether contaminants from the land surface will reach the groundwater.

Groundwater quality is estimated from physical, chemical, and biological parameters. Typically, water quality is concerned with its chemical and biological quality, since most groundwater is adequate regarding turbidity, colour, taste, and odour, i.e. physical quality. Groundwater is less susceptible to bacterial pollution than surface water because the soil and rocks through which it flows screen out most of the bacteria, even if bacteria occasionally find their way into ground water in dangerously high concentrations. A first approach to groundwater quality can be made using major element and ion concentrations. The list of the dissolved constituents in groundwater is rather large, but it can be divided into three groups: major constituents, minor constituents, and trace elements. The most common (major constituents) dissolved mineral elements and ions are: sodium, calcium, magnesium, potassium, chloride, bicarbonate, and sulphate, which make up over 99% of the solute content.

Geostatistics, based on the theory of regionalized variable, is the primary tool of spatial variability analysis. Geostatistcal methods of interpolation are optimal in the sense that they yield unbiased estimates with minimal estimation variance. Variogram estimation and modeling is extremely important for structural analysis and for interpolation (e.g. Journel and Huijbregts, 1978; Samper and Carrera, 1996; Vieira, 2000). Fitted semivariograms can then be used to produce maps of the investigated property by "kriging". The main advantage of this technique is that the estimation error, known as the kriging variance, gives valuable information about the reliability of the interpolated values over the area of interest.

Groundwater is a vital natural resource for the reliable and economic provision of potable water supply in both the urban and rural environment in many parts of the world. This is the case in the Bahia State, Brazil, characterized by contrasting climatic and hydrogeological conditions, so that in the driest regions aquifers play a fundamental role both, for the provision of potable water supply and for irrigation of agricultural land. Moreover, at the Bahia's State scale, aquifers are experiencing an increasing threat of pollution from urbanization, industrial development, agricultural activities and mining. Thus assessment of groundwater quality at different scales is widely required in this state and can be justified on broad environmental sustainability and narrower economic benefit criteria. In this work we analyzed a rather exhaustive data set comprising pH, total dissolved solids (TSD), chloride, hardness, fluoride and nitrogen from samples taken during 25 years from wells of all over the state. A quality index was calculated from these variables. The objective of our work was to assess patterns of spatial variability of the available chemical parameters and the quality index at the scale of the Bahia State.

2.- Material and Methods

2.1.- Study area

The State of Bahia, with a surface area of about 567,000 km^2, is located in Northeastern Brazil, on the Atlantic coast. A mountain chain, which is called the Chapada Diamantina, crosses this state from North to South. In some parts, the Diamantina Tableland region has the shape of flat top plateaus with abrupt edges (Chapadão). This chain divides Bahia in two clearly distinct geographical zones.

Within this state, geographical regions, vegetation, climate and geology show a big contrast. Natural vegetation is represented by the Atlantic forest at the costal regions, the extensive savanna formation known as "cerrado" at the far interior and the xeric shrubland and thorn forest known as "caatinga" at the fabled semiarid and arid "sertão" region. Climate is Tropical. Mean yearly temperatures of Bahia State range from 19.2 to 26.6ºC. Noteworthy, monthly amplitudes of mean temperatures are smaller than 3ºC. Climates within the state are mainly diversified by rainfall that varies from about 360 to 2000 mm year^{-1}. So, according with Thornthwaite's classification (Negrão, 2008) six basic climate types are distinguished: Humid, Humid to Subhumid, Subhumid, Subhumid to Dry, Semiarid, and Arid. The humid areas with >800 mm year^{-1} rainfall are located at the East (along the Atlantic coastal line) and West of the state and in the higher domains of the mountainous Diamantina Tableland. The semiarid and arid zones, mainly in the central and North areas of the state, cover 68% of the territory; so, the North of Bahia, at the border with Pernambuco and Alagoas States is the most dry region with yearly rainfall < 400 mm.

Table 1. Surface area of the main hydrogeological domains in the Bahia State, Brazil.

Hydrogeological domain	Surface area (km^2)
Tertiary-Quaternary cover	88273
Mesozoic Detritic sediments	115086
Calcareous	77574
Metasediments	84330
Crystalline	201668

Also the rock formations are widely varied. From the hydrogeological point of view five main domains can be distinguished, (Guerra and Negrão, 2006; Negrão, 2008). First, the domain of recent Tertiary-Quaternary embodies two main subdomains corresponding to shallow and deep aquifers with a surface area of 73556 and 14717 km^2, respectively. Under arid and semiarid climate this domain has been intensively used for drink water and irrigation. Second, the Mesozoic sediment domain, which cover about 20% of the State surface area and mainly consists of detritic sediments. This domain is also characterized by a great porosity and, in general, it is located in rainy areas, so that it stores the most important groundwater reserves. Aquifers such as Tucano, Recôncavo, Extremo Sul and Urucuaia belong to this domain. Third, the calcareous o karst domain is subdivided into two subgroups with < 800 and > 800 mm/year rainfall, which occupy 23391 and 54532 km^2, respectively. Fourth, the Metamorphic domain (i.e. metasedimentary), covering 14.8% of the Bahia surface is mainly characteristic of the central "Chapada Diamantina", thus belongs to areas with > 800 mm/year rainfall. Finally the Crystalline domain, embracing 35.5% of the state surface area, corresponds to intrusive and metamorphic felsic rocks such as granite, gneiss, migmatite and granulite; again two subdomains are distinguished with precipitations > 800 and < 800 mm/year (Negrão, 2008).

2.2.- Available data set

Water samples were taken from 3322 well open in the period from 1973 to 2006 and analyzed for pH, TDS, chlorine, hardness, nitrate and fluoride following standard methods (CERB, 2007).

A quality index (QI) was obtained by lineal combination of values derived the above mentioned six measured parameters. The weight of each parameter in the QI was estimated from rules, which take into account drinking water quality standards (Oliveira et al., 2004; Negrão, 2008). The quality index ranked each well from 0 to 100. Water was considered as optimal, good, acceptable and no potable for QI values of 80-100, 52-80, 37 to 52 and 0 to 37, respectively.

2.3.- Statistical and Geostatistical Analysis

Data sets were initially analyzed by descriptive statistics, and the mean, variance, standard deviation, coefficient of variation, maximum, minimum, skewness, and kurtosis were obtained using the STAT software (Vieira et al., 2000).

A detailed description of geostatistical methods has been provided by a number of authors, i.e. Matheron (1962), Journel and Huijbregts (1978), Vieira et al. (1983), Samper and Carrera (1996), Goovaerts (1997), etc. Briefly, geostatistical analysis is based on the assumption that measurements separated by small distances are more likely to be similar to each other than those farther apart (i.e. spatial autocorrelation exists). This assumption can be verified through examination of semivariograms, a statistical tool used to measure the between-sample autocorrelation. Sample semivariograms were calculated using the expression:

$$\gamma^*(h)=\frac{1}{2\,N(h)}\sum_{i=1}^{N(h)}[Z(x_i)-Z(x_i+h)]^2 \qquad (1)$$

where: $\gamma^*(h)$ is estimated semivariance, $N(h)$ is the number of pairs of points separated by h, $Z(x_i)$, $Z(x_i + h)$ values of parameter separated by a vector (h).

In this way, for each variable a graph was obtained that showed the amount of variance between points as a function of distance Following authorized recommendations the cross-validation technique was utilized when modelling a semivariogram (Vieira, 2000).

Spatial dependence was expressed by the SD parameter (degree of spatial dependence), which was defined as the proportion of structural variance (C_1) in relation to the sill threshold (C_0 + C_1), following Cambardella et al. (2004). Ordinary kriging was used for interpolation at unsampled locations and for prediction of the error variance.

3.- Results and discussion

3.1.- Statistical analysis

Table 2 lists summary statistics for pH, total dissolved solids (TDS), chloride, hardness, nitrate and fluoride of the 3322 analyzed wells. The range of pH varied between minimum 3.6 and maximum 10.8. Water that is basic can form scale; acidic water can corrode. High pH causes a bitter taste; water pipes and water-using appliances become encrusted and it also depresses the effectiveness of the disinfection of chlorine. Low-pH water will corrode or dissolve metals and other substances. According to U.S. Environmental Protection Agency criteria (US-EPA, 2011), water for domestic use should have a pH between 5.5 and 9. Following this rule, pH was adequate, very high or very low for 97.9%, 1.3% and 0.0% of the wells, respectively.

Table 2. Summary statistics of the analyzed chemical parameters for 3322 wells (Std. = standard deviation, C.V. = coefficient of variation, TDS = Total dissolved solids).

	pH	**TDS**	**Cl^-**	**Hardness**	**NO_3^-**	**F^-**
		mg/L				
Maximum	10.8	47098	19916	42900	188	92
Minimum	3.6	8	1	3	0	0
Mean	7.7	2494	973	1141	6.3	0.8
Median	7.7	844	176	447	0.9	0.5
Std.	0.7	4518	2076	2152	13.0	2.0
C.V.	9.0	181	213	189	206	247

Dissolved solids occur naturally but also enters environment from man-made sources, and can still occur in large concentrations in groundwater, even if the vadose zone works as a filter. The total mass of dissolved constituents is referred to as the total dissolved solids (TDS) concentration. TDS is a measure of the dissolved “salts” or minerals in the water, even if it may also include some dissolved organic compounds. In water bodies, the total negative charge of the anions tends to equal the total positive charge of the cations. A higher TDS means that there are more cations and anions in the water. With more ions in the water, the water’s electrical conductivity (EC) increases. By measuring the TDS concentration, we can indirectly determine its electrical conductivity. At a high TDS concentration, water becomes saline.

A huge range of TDS values, from 8 to 47098 mg L^{-1}, was measured over the 3322 wells in Bahía. Water with a TDS above 500 mg L^{-1} is not recommended for use as drinking water (EPA secondary drinking water guidelines). Water with a TDS above 1,500 to 2,600 mg L^{-1} (EC greater than 2.25 to 4 mmho cm^{-1}) is generally considered problematic for irrigation use on crops with low or medium salt tolerance. Water from 64.1% of the wells contained TDS above the threshold of 500 mg L^{-1}, thus was not considering suitable for drinking. Moreover, for 21.8% of the studied wells TDS values were above 2800 mg L^{-1}, not adequate even for irrigation purposes, because such excessive levels cannot be tolerated by most cultivated plants.

Low to moderate concentrations of chloride ions add palatability to water. Excessive concentrations, of course, can make water unpleasant to drink. Chloride concentrations ranged from 1 to 19916 mg L^{-1}. There was a very significant relationship between TDS and chloride. As chloride content is balanced by sodium content, these results confirm that many parts of the State are underlain by highly saline ground water that has no uses or only very limited uses.

The US-EPA Secondary Drinking Water Regulations (2011) recommend a maximum concentration of 250 mg L^{-1} for chloride ions. Water from 42.5% of the wells contained chloride concentrations higher than this threshold.

Water that contains high concentrations of calcium and magnesium is said to be hard. The hardness of water is expressed in terms of the amount of calcium carbonate-the principal constituent of limestone or equivalent minerals that would be formed if the water were evaporated. The hardness over the State of Bahía also showed an enormous range of variation, from 3 to 42900 mg L^{-1}. Water is considered soft if it contains 0 to 60 mg L^{-1}, moderately hard from 61 to 120 mg L^{-1}, hard between 121 and 180 mg L^{-1}, and very hard if more than 180 mg L^{-1}. Very hard water is not desirable for many domestic uses. Note that hard water can be softened at a fairly reasonable cost.

Groundwater was very hard in 68.3% of the wells. Hardness was over 120 mg L^{-1} in 75.5% of the wells and over 60 mg L^{-1} in 84.8% of the wells. Therefore, groundwater can be considered soft for only 15.2% of the wells in Bahia State.

Nitrate occurs naturally in mineral deposits, soils, freshwater systems, the atmosphere, and biota. Also, it enters the environment from fertilizer, feedlots, and sewage. The highest levels of nitrate in groundwater are found under extensively developed rural areas. According with the standards of the World Health Organization (WHO) and the European Community (EC), the maximum contaminant level of nitrate in drinking water is given to be 50 mg/L. For the US Environmental Protection Agency (EPA), such nitrate level is 44 mg L^{-1} in drinking water. The guide level of nitrate for the EC is 25 mg L^{-1}.

In the Bahia State levels of nitrate varied from 0 (i.e. below the detection limit) to 188 mg L^{-1}. Nitrate mean and median values were 6.3 and 0.9 mg L^{-1}, respectively, indicating a much skewed frequency distribution. These results suggest that the quality of groundwater has been degraded only locally, where nitrate contents exceed 50 mg L^{-1}. Water sampled at 1.72% of the studied wells was above this nitrate threshold and even 0.21% of the wells were above the 100 mg L^{-1} level. Conversely, 51.9 % of the wells contained less than 1.0 mg L^{-1} nitrate.

Maximum allowable F^- levels, following drinking water US-EPA standards are as high as 4.0 mg L^{-1}, whereas for the Brazilian authority concentrations higher than 0.5 mg L^{-1} should be avoided. Measured F^- concentrations ranged from 0 to 92 mg L^{-1}. Only 1.99% of the sampled well showed levels higher than 4 mg L^{-1}, which was locally associated with rock composition.

The statistical results for the quality index were as follows: 13.7% optimal (QI > 80), 32.1% good (52 < QI < 80), 14.4% acceptable (37 < QI < 52) and 39.8 % no potable (0 < QI < 37). Suboptimal levels of quality are moistly associated with high chlorine and TDS levels.

3.2. - Patterns of spatial variability

Sample semivariograms were calculated from 0 to 270 km and for this interval semivariance increased as a function of the distance until a stable sill was reached in the seven data sets studied (data not shown). For larger distances, however trends were observed. Therefore, models were fitted for this interval.

Results of semivariogram modelling, including model type and semivariogram parameters (sill, nugget and range of spatial dependence) are summarised in Table 3. All the experimental semivariograms could be adjusted quite well, over the spatial scale of interest, by models with a nugget component (C_0) plus a spatial component (C_1) with a range of spatial dependence from 49 to 160 km. Spherical models best fitted the experimental semivariograms of most of the variables; the exception was pH, which was fitted by an exponential model.

The nugget variances were all below 47.5%, except for pH which showed a smaller spatial continuity at close distances, with a nugget of 75.2%.

Table 3. Semivariogram parameters for the studied chemical variables and for water quality index . (C_0 = nugget effect; C_1 = sill; a = range, km; Expon. = exponential model; Spher. = spherical model).

Variable	**Model**	**C_0**	**C_1**	**$C_0/(C_0+C_1)$**	**a (km)**
pH	Expon.	0.3	0.1	75.2	91
TDS	Spher.	$50x10^5$	$180x10^5$	21.7	150
Cl-	Spher.	$10x10^5$	$38x10^5$	20.8	155
Hardness	Spher.	$15x10^5$	$42x10^5$	26.3	160
$NO3^-$	Spher.	250.0	276.0	47.5	49
F^-	Spher.	8733.5	42745.8	17.0	70
QI	Spher.	278.3	642.4	30.2	138

Following Cambardella et al. (1994) the spatial dependence, SD = $C_0/(C_0+C_1)$ is considered strong for ratios lower than 25% and it is moderate for values between 25% and 75%. It follows that TDS, Cl^- and F^- exhibited a strong spatial dependence, which indicates, in general, good spatial continuity at close distances between sampled points, whereas SD was moderate for hardness, NO_3^- and quality index and low for pH. Therefore, the available sampling scheme captured large proportions of the spatial variance both for all the studied variables with the exception of pH.

Hydrogeological data sets all over the world frequently display a positive skewed frequency distribution, as in our study case. Samper and Newman (1989) recommended log-normal transformation for skewed data sets before semivariogam analysis and kriging. We have found a stable sill, provided experimental semivariances were calculated until 170 km, and therefore the lognormal transform was not performed. In spite of this, other methods, i.e., lognormal kriging, stratified kriging (as it is possible to compute semivariograms for each different domain) or co-kriging probably could improve our interpolation results. Further research is needed to asses if kriging standard error can be reduced when using these methods.

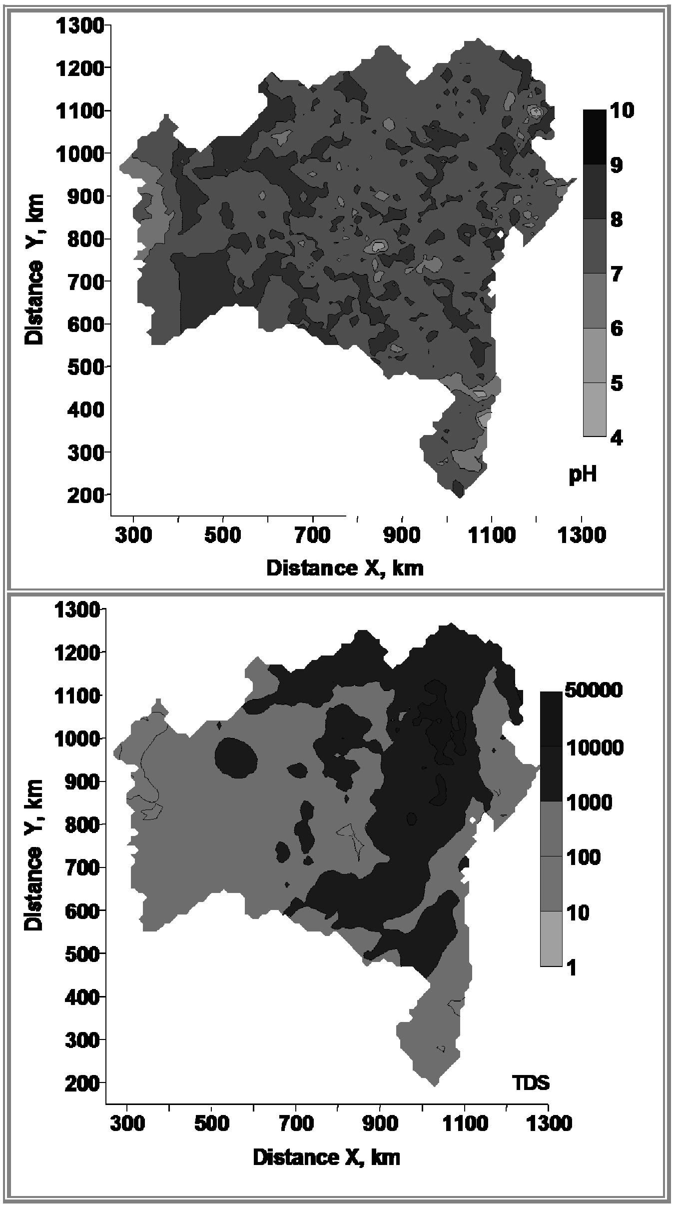

Fig. 1. Kriging maps of pH (up) and TDS (down).

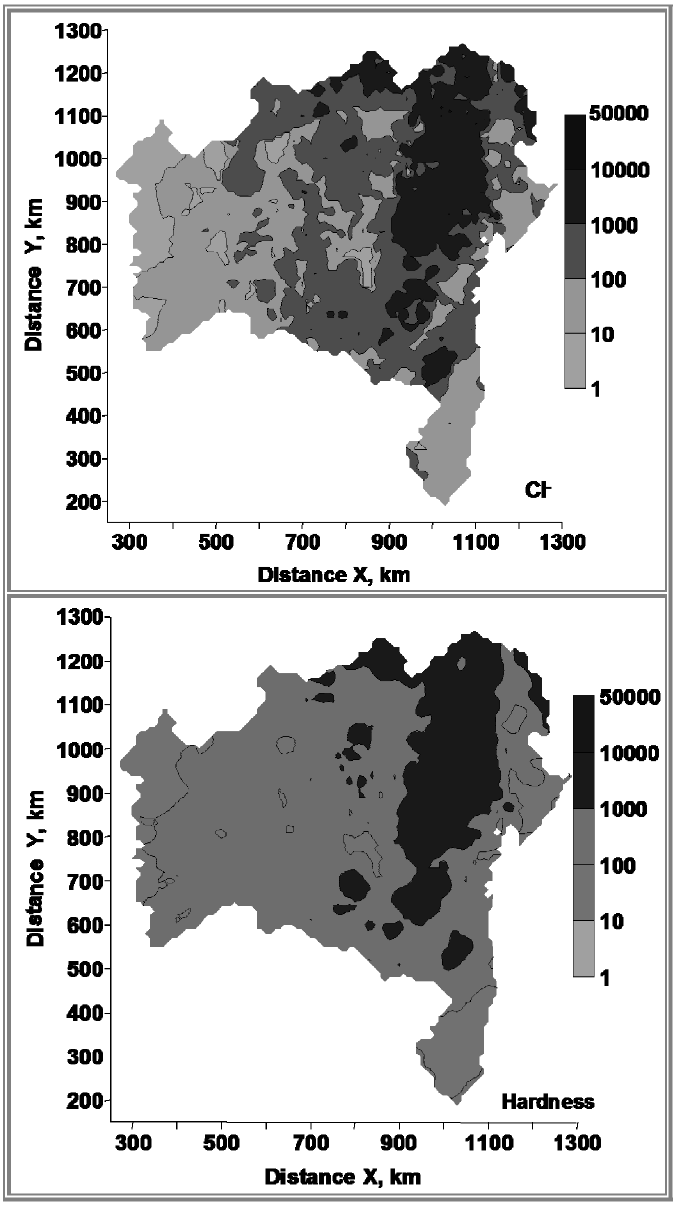

Fig. 2. Kriging maps of Cl^- (up) and hardness (down).

Selected kriging maps of the studied variables are shown in Fig.s 1 to 4. The map of pH, (Fig. 1) is very patchy all over the different hydrogeological domains. Consistent with the statistical results, the kriging map show that in most of the areas pH values range from 6.0 to 9.0, so that wells with water above 9.0 or below 6.0 are very localized.

Kriging maps for TDS, chloride and hardness (Fig.s 1 and 2) show evident similitude, with maximum values in the Crystalline domain, mainly under arid conditions. TDS in most of the surface area between 100 and 1000 mg L^{-1}, but frequently (and mainly in dry areas) it increases to the range between 1000 and 1000 mg L^{-1}; even TDS patches with values higher than 10,000 mg L^{-1}can be mapped. In most of the state chloride and hardness are in the ranges from 100 to 1000 and 1000 o 10,000 mg L^{-1}except for some areas at the costal and the western borders. As levels > 10,000 mg $L^{-1}$for chloride and hardness are not apparent; these maps suggest TDS may be the most sensitive parameter for assessing groundwater salinity at the scale of the.

Again consistent with the statistical results, nitrate map (Fig. 3) shows that the most frequent classes are those from 0 to 1 mg L^{-1} and 1 to 10 mg L^{-1}. In the main agricultural areas nitrate levels of the groundwater can be above the 10 mg L^{-1}threshold. The area with nitrate concentrations higher than 50 mg L^{-1}, i.e. the maximum allowed for drinking water is very localized at the Iricé aquifer in the karstic domain.

Finally the kriging contour map for the quality index (Fig. 4) best summarizes all the available information for the Bahia's aquifers. Regions with optimal and good groundwater are found mainly at the west cost, the most Western border and mountains of Chapada Diamantina.

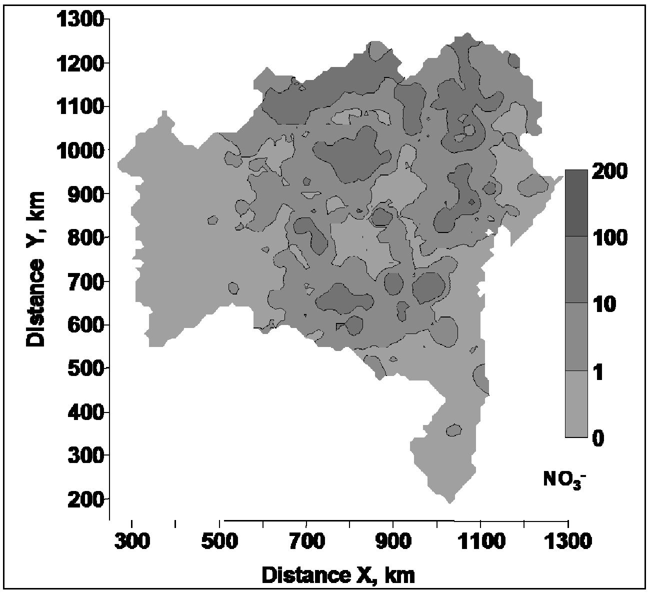

Fig. 3. Kriging map of NO_3

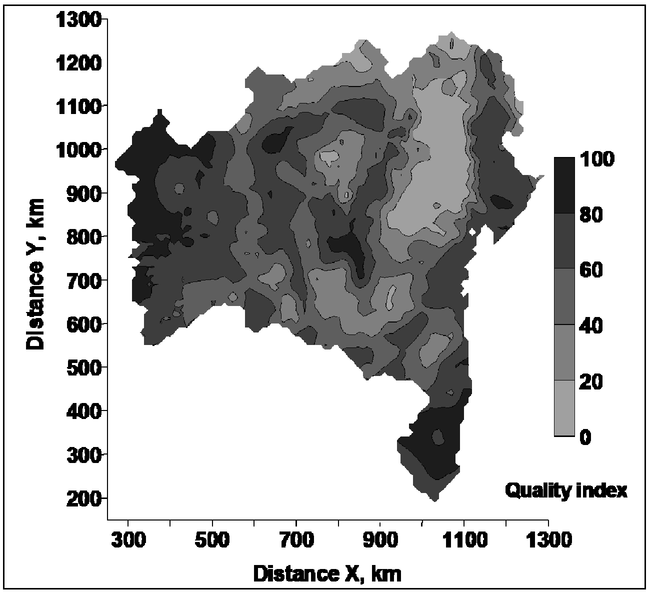

Fig. 4. Kriging map of groundwater quality index.

Most of the rocks in this region are sediments or metasediments. Between these areas groundwater quality is impaired following the intensity and dryness and the characteristics of the hydrogeological domains. Therefore, crystalline arid subdomain, followed by karst domain under semiarid showed the higher risk of improper water quality. This can be attributed to limited recharge and high rates of evaporation, which concentrates salts and carbonates.

4.- Conclusions

Levels of TDS and chloride in groundwater of the Bahía State (Brazil) showed important areas are underlain by groundwater with high saline content, not recommended for use as drinking water and even for irrigation. Locally also groundwater is not suitable for domestic use due to high nitrate and fluoride levels. The patterns of spatial dependence of the studied variables were described by a nugget component plus a structure. TDS, chloride, hardness, nitrate, fluoride and quality index were fitted to a spherical model, whereas pH was fitted to an exponential model. These variables were mapped by ordinary kriging. Further research is needed to assess performance of other forms of kriging, such as log-normal or stratified kriging. Karstic and crystalline hidrogeological domains in the driest regions of the state showed the lowest groundwater quality. In general under semiarid and arid climate risk of groundwater quality degradation was much higher.

5.- References

Cambardella, C.A.; Moorman, T.B. and Novak, J.M. 1994. Field-scale variability of soil properties in central Iowa soils. *Soil Science Society of America Journal*, Madison, v.58, p.1501-1511, 1994.

CERB (Companhía de Engenharía Rural da Bahia). 2007. Banco de dados Hidrogeológicos do Estado da Bahia. Salvador de Bahia. Brasil.

Oliveira, I.B.; Negrão, F.I. and Rocha, T.S. 2004. Determinação do índice de qualidade da água subterrânea (IQAS) com base nos dados de poços tubulares do estado da Bahia. (Área Piloto: Recôncavo). In: Anais do II Congreso Nacional do Meio Ambiente. Salvador, Bahia, Brasil. 8 pp.

Goovaerts, P. 1997 *Geostatistics for natural resources evaluation*. Applied Geostatistics series. New York: Oxford University Press. 483 pp.

Matheron, G. 1962. *Traité de géostatistique appliqué*, Tome I; Tome II: Le Krigeage. Editions B.R.G.M: Paris, 1962.

Negrão, F.I. 2008. *Hidrogeología do Estado da Bahia: Qualidade, Potencialidade, Disponibilidade, Vulnerabi-lidade e Grau de Poluição*. Tesis Doctoral.UDC. 186 pp.

Samper Calvete, F.J. and Carrera Ramírez, J. 1996. *Geoestadística. Aplicaciones a la Hidrología Subterránea*. CIMNE. Barcelona. 2ª Edición. 485 pp.

Samper, F.J. and Neuman, S.P. 1989. Estimation of Spatial Covariance Structures by Adjoint State Maximum Likelihood Cross-validation: 3 Application to Hydrochemical and Isotopic Data. *Water Resources Research*, Vol 25, nº 3, 373-384.

United States Environmental Protection Agency (US-EPA). 2011. Drinking water contaminants. National Primary DW Regulations and National Secondary DW Reg.http://water.epa.gov/drink/contaminants/index.cfm.

Vieira, S.R.; Hatfield, J.L.; Nielsen, D.R. and Biggar, J.W. 1983. Geostatistical theory and application to variability of some agronomical properties. Hilgardia, v. 51, 291-375 pp.

Vieira, S.R. 2000. Geoestatística em estudos de variabilidade espacial do solo. In: Novais, R.F.; Álvarez, V.H.; Schaefer, G.R. (Ed.). *Tópicos em Ciência do Solo*. Viçosa: Sociedade Brasileira de Ciência do Solo. v.1, p. 1-54.