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Chapter – 21

USE OF WATER QUALITY INDEX TO EVALUATE THE INFLUENCE OF ANTHROPOGENIC CONTAMINATION ON GROUNDWATER CHEMISTRY OF A SHALLOW AQUIFER, LOURES VALLEY, LISBON, PORTUGAL

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ABSTRACT: A significant industrial development, associated with a demographic expansion, occurred during the last decades of the XX century, in Loures valley, a region located in the vicinities of Lisbon, the capital city of Portugal. This was accompanied with an important modification of land use and occupation patterns, mainly the decrease of the agricultural land.

One of the main consequences was the deterioration of the groundwater chemistry observed in the shallow aquifer associated to Trancão river, a subsidiary of Tagus river.

Factorial Correspondence Analysis has been used to build a water quality index, for evaluating the impact of the anthropogenic factors on groundwater of the shallow aquifer. By analysing the kriged maps of the values of the index, it was possible to identify the areas more sensitive to the anthropogenic impact.

KEYWORDS: Groundwater Contamination, Water Quality Indices, Decision Making, Multivariate Data Analysis, Factorial Correspondence Analysis, Kriging

1 INTRODUCTION

Serious efforts have been made to combat groundwater contamination across the European Union (EU), mostly through the implementation of national and international policies. The Water Framework Directive (WFD) - Directive 2000/60/EC - establishes a legal framework to protect and restore clean water across Europe and ensure its long-term and sustainable use. The WFD defines good status of groundwater - the goal for 2015 - in terms of both quantity and chemical status.

For this purpose the EU has adopted the Directive 2006/118/EC on the protection of groundwater against pollution and deterioration as the Directive cited: *having regard to the need to achieve consistent levels of protection for groundwater, quality standards and threshold values should be established, and methodologies based on a common approach developed, in order to provide criteria for the assessment of the chemical status of bodies of groundwater*.

The WFD recognize also the importance of groundwater and surface waters interactions and the necessity to protect groundwater and their dependent ecosystems from anthropogenic activities.

There is a growing need to develop robust methodologies to evaluate aquifer vulnerability and groundwater pollution risk to support the decision makers in the Water National Plans, especially to fill the gap between the scientists and the people that need to deal with the gathered information. Among these tools are the so-called water quality indices which will be shown in this article.

Such indices are developed with the aim of rapidly combining a large quantity of chemical information of a water sample into a single value and thereby facilitate spatial and temporal water quality monitoring. The use of these indices as an aggregation and communication tool can be extremely useful, particularly when considering the possibility of incorporating drinking water or other standards frequently used in pollution policies (Stigter *et al*., 2006)

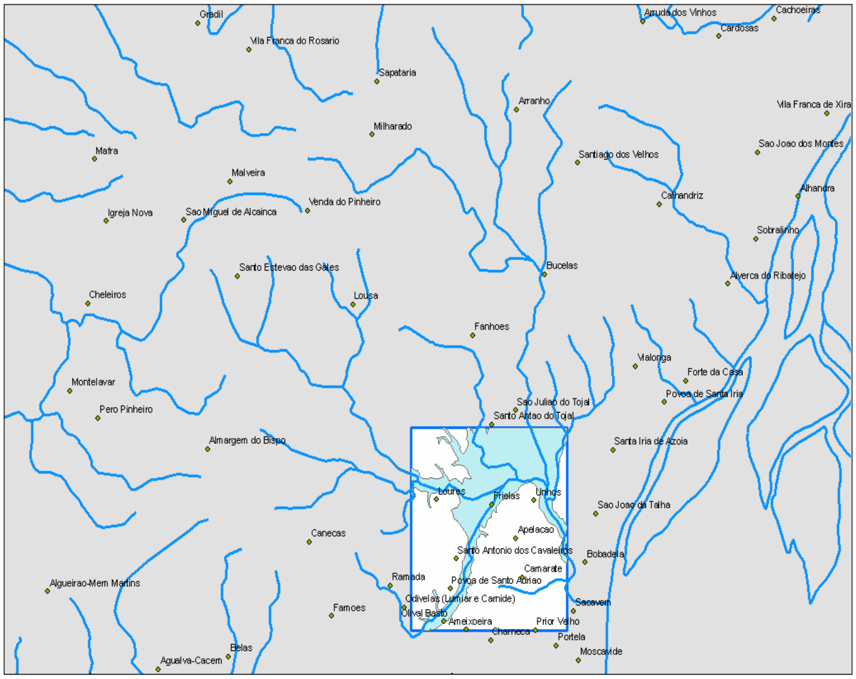


Figure 1 – Location of the area under study with the indication of the hydrographic network

2 STUDY AREA

2.1 Hydrogeological Setting

The study area (Figure 1) is located a few kilometres north-east of Lisbon on the right bank of the Tagus river. It is a shallow alluvium aquifer in Trancão river, where the alluvial deposits were removed from the geologic formations of the catchment's area of the river and deposited in an area that is periodically invaded by the estuarine brackish water of Tagus river.

The geologic formations found in the Trancão river basin ranged from Jurassic to Holocene (Figure 2) and are, according to Zbyszewski et al. 1981, the following ones: (1) limestones and marls formations from the Jurassic and Cretaceous; (2) a estuarine sequence with alternated marine and continental facies from Miocene; (3) a Palaeogene continental sedimentary formation ("Formação de Benfica"); (4) a Neo-cretaceous volcanic basaltic complex ("Complexo Vulcânico de Lisboa"); (5) fluvial deposits forming terrace levels from the Pleistocene (Zêzere 1991); (6) a Holocene alluvium, characterized by a sequence of sandy and clayey lenticular beds with lateral and vertical facies variation, presenting a great granulometric variety.

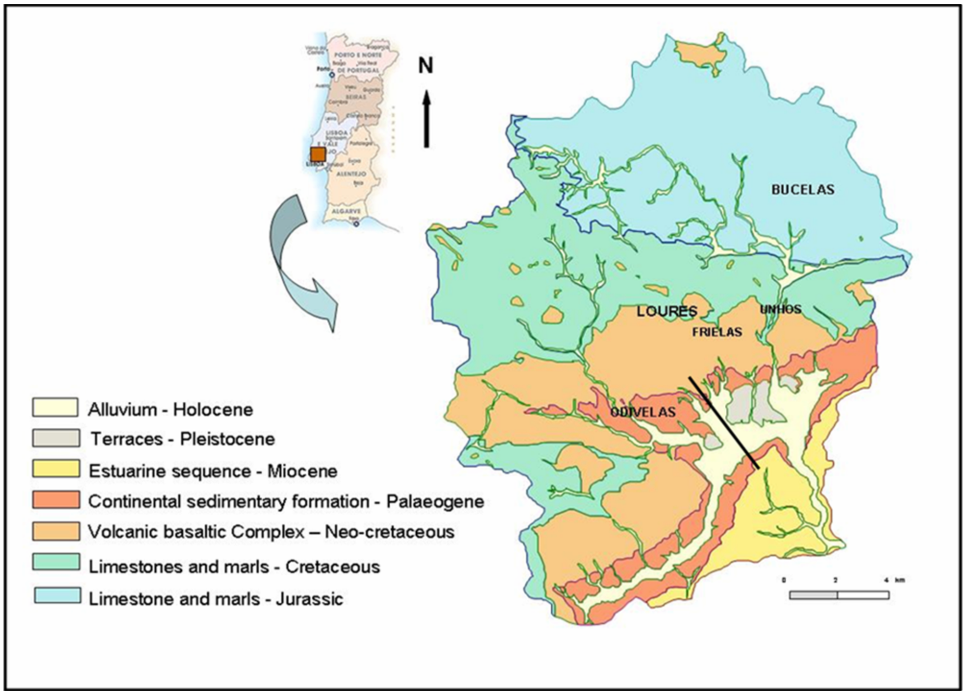


Figure 2 – Location of the area under study and simplified geological sketch of Loures region and Trancão river basin (adapted from Zbyszewski *et al*. 1981).

The Loures alluvium is mainly composed by sediments originated in the surrounding "Formação de Benfica" and "Complexo Vulcânico de Lisboa" formations. The "Formação de Benfica" is the continental sedimentary formation

(Palaeogene) mainly composed by conglomerates, sandstones, siltstones, and mudstones. The “Complexo Vulcânico de Lisboa” is a volcanic complex (neo-cretaceous) characterized by very weathered basaltic flows and pyroclastic deposits.

The floodplain of Loures is a depressed area to which converge various watercourses, including Trancão river, a subsidiary of Tagus river (see Figure 1).

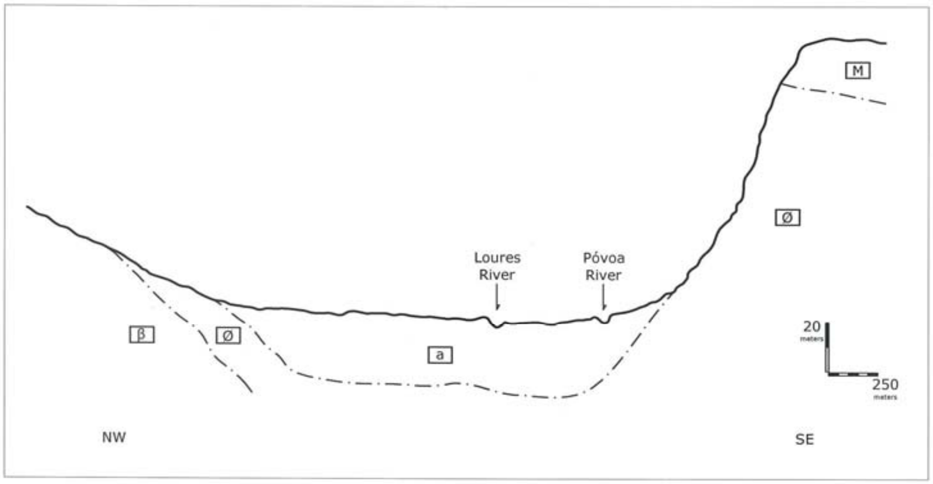


Figure 3 Geological cross-section (NW-SE) of Loures valley (see its location in Figure 2) showing the thickness, relation with the water courses and the boundaries with other formations. a Holocene - alluvium (**Shallow aquifer**); M Miocene; Ø Palaeogene – “Formação de Benfica”; β Neo-Cretaceous – “Complexo Vulcânico de Lisboa”; — · — stratigraphic limit.

The Loures alluvium forms a continuous unconfined aquifer that is hydraulically connected with the surface water. Its thickness and boundary conditions as well its hydraulic contact with the watercourses are schematically shown in Figure 3. There is a lack of information about hydraulic parameters, leakage coefficients and mass transport parameters, which invalidate any tentative to study the groundwater flow and pollutant transport by numerical modelling. Only a rough conceptual model can be established. An isopiezometric map of the region shows (Figure 4) that groundwater flows in the direction of the main water courses with very low hydraulic heads values (from 2 to 6 m). The aquifer is exploited for irrigation by several dug wells.

2.2 Pollution sources

During the last decades of the XX century, the increase of population in the vicinities of Lisbon has contributed significantly for the augmentation of domestic sewage, which, combined with the low levels of wastewater treatment and the reduced dilution power of the watercourses, contributes to the deterioration of the water quality of Trancão river and associated shallow aquifers.

The water from that river is mainly used for irrigation purposes and its quality is also severely threatened by the discharges from industrial activities.

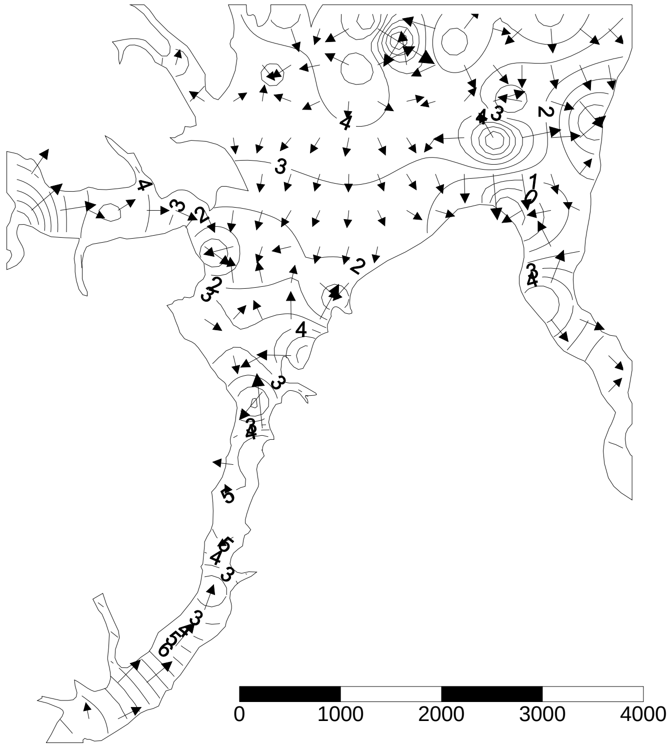


Figure 4 – Iso-piezometric map and groundwater flow main directions in the shallow aquifer of Loures valley (distances in meters).

One of the most polluted activities is the pig farm industry, which units are mainly located in the NW of Loures. The number of animals is estimated to be around 20.000, which are responsible for about 200 m^3/day of non-treated wastewater flow. The second more important industry is slaughterhouses, located primarily in NE and NW of the area, with the third place occupied by the chemical industries located mainly in SW part (Figure 4).

3 MATERIALS AND METHODS

3.1 Sampling

In order to characterize the magnitude of anthropogenic impact in the groundwater, the results of physic-chemical analyses of water, sampled from 36 shallow wells, during 3 sampling campaigns were used (Silva, 2003). The location of these wells can be seen in Figures 5A and 5B.

The first campaign refers to data collected in a wet year during the summer season; the second campaign refers to data collected in the same year, during the winter season and the third campaign refers to data collected in the next year, a dry year, during the summer season.

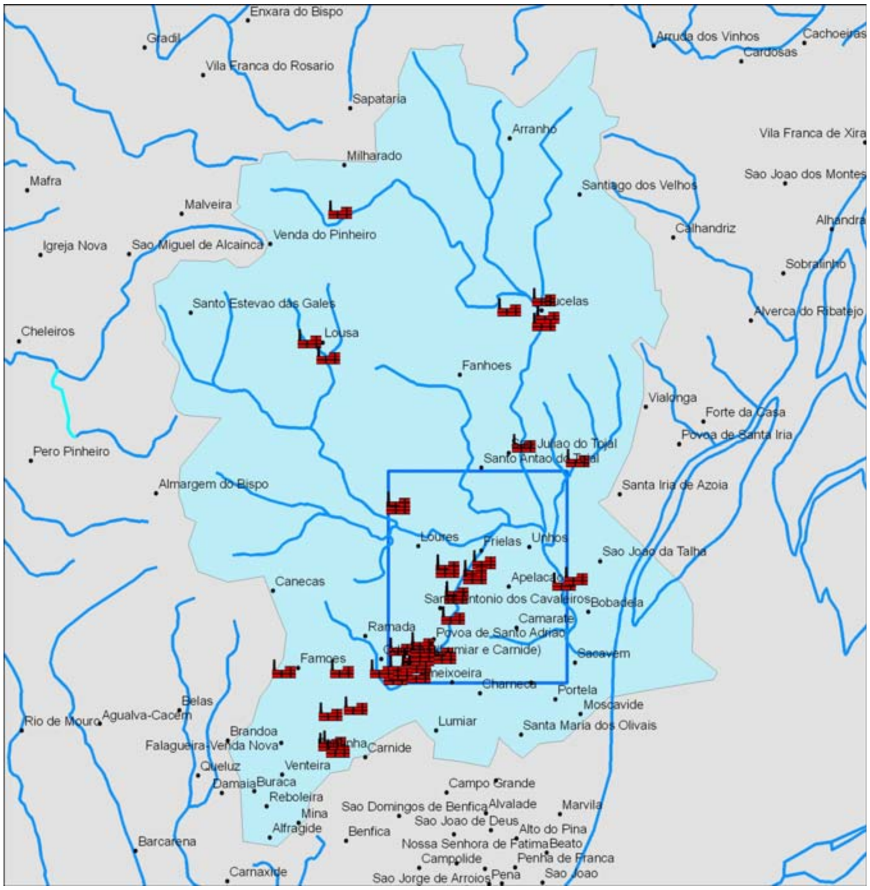


Figure 5A – Location of the main pollution sources in Loures valley

The list of monitored parameters are EC (electrical conductivity), pH, major anions (HCO_3, SO_4, Cl, F), major cations (Na, K, Ca, Mg) and trace elements (Al, Cr, Mn, Fe, Ni, Cu, As, Se, Br, Sb, Hg, Pb).

EC and pH were measured *in situ*. The water samples, collected for chemical analysis, were filtered, using a 0.45 µm cellulose membrane filter and stored in double capped HDPE bottles, one acidified with concentrated nitric acid for cations analyses and trace elements, and the other was reserved un-acidified for anions determinations.

The analyses of the major elements were performed at the Water Laboratory of Geology Department of the Faculty of Sciences of Lisbon, using the following methods: atomic absorption for Na, K and Mg; colorimetric methods for Ca; ion chromatography for anions; and potentiometric titration for alkalinity. The minor and trace elements were analyzed abroad at Actlabs Laboratories (Canada) by ICP-MS.

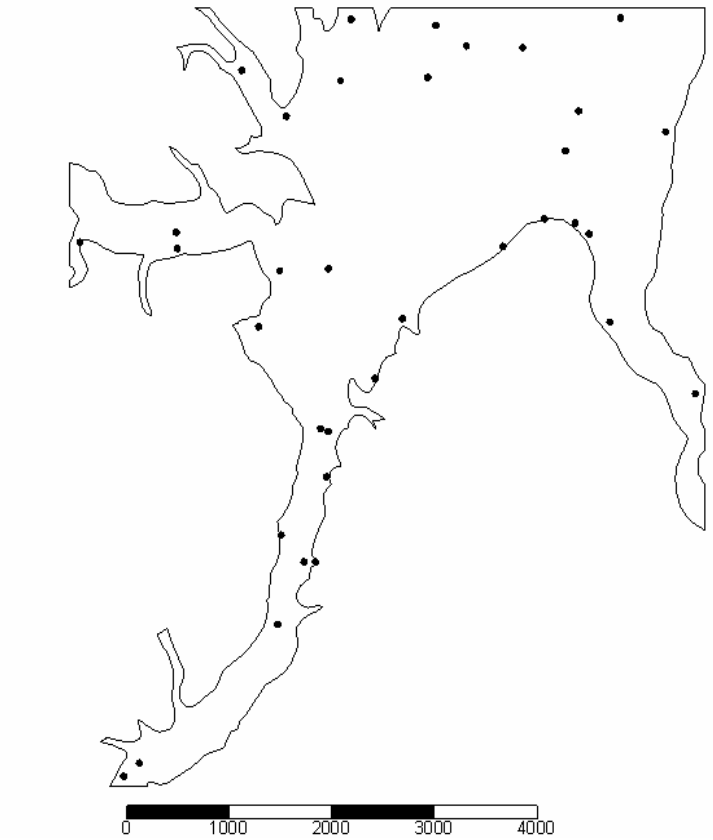


Figure 5B – Location of the 36 shallow wells where groundwater samples were collected (distances in meters).

3.2 Statistical Analysis

Table 1 displays the basic statistics of the variables sampled during the 1st campaign, as well the maximum limits for drinking water human supply, e.g. the parametric value (PV).

Results show that although the median value of EC is less than the PV, the maximum value is much greater than the PV.

Concerning major anions, only HCO3 and F medians are higher than the PV, while only the maximum values of the remaining parameters go beyond those limits.

Concerning major cations, all the elements have their median below the PV and their maximums greater than the corresponding PV.

Concerning the trace elements, the medians of Mn and Br are greater than the PV, while Fe, Cu and Ni have maximum values higher than that threshold.

Statistical analysis shows also that pH, SO_4, Na, Mn, Fe, Ni, Cu, Sb and Pb present highly skew coefficients (> 2.0).

Table 1. Basic statistics of hydrochemical variables from groundwater of Loures shallow aquifer, collected during the 1st campaign and parametric values concerning water quality to human consumption

Variable	Units	PV	Min	Max	Average	Median	St. Dev.	Skewness
EC	µS/cm	2500 (ii	703,00	4290,00	1730,56	1414,50	886,80	1,56
pH		≥6,5 & ≤9 (ii	6,40	8,18	6,91	6,82	0,32	2,08
HCO_3	mg/L	200 (iii	261,08	1071,00	558,60	541,70	192,22	1,05
SO_4	mg/L	250 (ii	26,85	2361,00	168,73	90,13	381,00	5,75
Cl	mg/L	250 (ii	46,25	1105,90	265,84	144,84	272,69	1,78
F	mg/L	1,5 (ii	0,50	5,10	1,91	1,61	1,08	1,43
Na	mg/L	200 (ii	35,50	985,00	226,25	128,90	235,26	2,01
K	mg/L	12 (i	0,40	67,40	15,11	6,95	18,24	1,53
Ca	mg/L	100 (ii	1,08	196,00	81,04	72,80	45,91	0,65
Mg	mg/L	50 (ii	10,45	106,40	45,10	44,00	22,45	0,64
Al	µg/L	200 (ii	1,60	70,00	22,54	18,05	16,33	1,85
Cr	µg/L	50 (ii	1,30	22,50	6,88	4,20	5,64	1,33
Mn	µg/L	50 (ii	1,14	761,10	132,88	51,13	194,35	2,02
Fe	µg/L	200 (ii	11,80	2914,50	215,95	71,40	499,94	4,82
Ni	µg/L	20 (ii	0,66	28,81	4,38	3,13	5,33	3,55
Cu	µg/L	2 (ii	2,57	61,14	8,88	5,96	10,04	4,39
As	µg/L	10 (ii	0,41	8,48	2,82	1,67	2,42	1,20
Se	µg/L	10 (ii	0,55	10,49	3,00	1,88	2,72	1,58
Br	µg/L	25 (ii	155,00	4090,00	1056,72	495,50	1085,49	1,62
Sb	µg/L	5 (ii	0,00	0,69	0,14	0,07	0,19	2,06
Hg	µg/L	1 (ii	0,00	0,30	0,04	0,02	0,08	1,91
Pb	µg/L	25 (ii	0,00	6,56	1,05	0,61	1,39	2,24

i) Maximum admissible value of Portuguese legislation, Dec.Lei 236/1998

ii) Parametric value of Portuguese legislation, Dec.Lei 306/2007

iii) Median value for natural waters (Turekian, 1977)

Table 2 displays the basic statistics of the variables sampled during the 2nd campaign, as well the PVs for drinking water human supply.

Comparing results of Table 2 with the ones displayed in Table 1 the main conclusion is that in general the groundwater quality has deteriorated. This is particularly visible in the medians of EC, pH, major cations and anions and in the great majority of the trace elements. Also the skew distributions of the variables increase, 14 against 9 observed in the 1st field survey.

Table 2 Basic statistics of hydrochemical variables from groundwater of Loures shallow aquifer, collected during the 2nd campaign and parametric values concerning water quality to human consumption.

Variable	Units	PV	Min	Max	Average	Median	St. Dev.	Skewness
EC	µS/cm	2500 (ii	900,00	7760,00	1893,36	1411,00	1379,77	2,86
pH		≥6,5 & ≤9 (ii	6,40	8,06	6,93	6,89	0,39	1,30
HCO_3	mg/L	200 (iii	29,28	750,30	399,75	386,13	159,81	0,07
SO_4	mg/L	250 (ii	1,95	329,90	110,76	110,90	57,13	1,36
Cl	mg/L	250 (ii	68,50	1894,20	334,03	140,05	455,99	2,69
F	mg/L	1,5 (ii	0,86	5,38	2,09	1,73	1,02	1,63
Na	mg/L	200 (ii	52,30	1767,00	267,16	131,85	344,73	3,16
K	mg/L	12 (i	1,00	105,50	16,00	8,80	20,75	2,83
Ca	mg/L	100 (ii	11,20	208,00	87,60	81,60	43,03	0,51
Mg	mg/L	50 (ii	9,98	120,60	49,40	44,80	24,85	1,02
Al	µg/L	200 (ii	16,80	1816,90	99,14	35,55	297,51	5,81
Cr	µg/L	50 (ii	2,20	63,30	11,84	7,25	12,56	2,78
Mn	µg/L	50 (ii	1,73	4722,75	703,92	318,76	1009,76	2,27
Fe	µg/L	200 (ii	69,70	12850,30	832,40	138,25	2213,50	4,92
Ni	µg/L	20 (ii	1,10	33,64	5,96	4,62	6,26	3,04
Cu	µg/L	2 (ii	1,98	9,62	5,10	5,00	1,87	0,52
As	µg/L	10 (ii	0,57	19,06	3,48	1,73	4,18	2,19
Se	µg/L	10 (ii	0,96	26,26	4,74	2,27	5,53	2,58
Br	µg/L	25 (ii	224,00	9260,00	1391,06	597,00	1914,78	2,84
Sb	µg/L	5 (ii	0,03	0,60	0,12	0,08	0,11	3,05
Hg	µg/L	1 (ii	0,00	0,00	0,00	0,00	0,00	
Pb	µg/L	25 (ii	0,53	74,68	6,80	4,05	12,55	4,83

i) Maximum admissible value of Portuguese legislation, Dec.Lei 236/1998

ii) Parametric value of Portuguese legislation, Dec.Lei 306/2007

iii) Median value for natural waters (Turekian, 1977)

Table 3 displays the basic statistics of the variables sampled during the 3rd campaign and the corresponding PV.

Comparing results of Table 3 with the previous one we conclude that the groundwater quality has reached more acceptable limits for human water supply purposes. In fact, with the exception of HCO3, Cu and Br, all the medians of the remaining variables are lower than the correspondent PV, although some maximums continue to be higher than that limit.

Table 3 Basic statistics of hydrochemical variables from groundwater of Loures shallow aquifer, collected during the 3rd campaign and parametric values concerning water quality to human consumption.

Variable	Units	PV	Min	Max	Average	Median	St. Dev.	Skewness
EC	µS/cm	2500 (ii	660,00	4640,00	1465,67	1269,00	757,04	2,60
pH		≥6,5 & ≤9 (ii	6,79	8,73	7,40	7,29	0,44	1,48
HCO_3	mg/L	200 (iii	196,42	983,32	512,08	504,47	166,18	0,69
SO_4	mg/L	250 (ii	35,00	241,90	99,71	89,05	48,44	1,21
Cl	mg/L	250 (ii	42,40	1505,50	201,79	107,80	267,90	3,73
F	mg/L	1,5 (ii	0,02	1,12	0,23	0,16	0,24	2,39
Na	mg/L	200 (ii	33,00	1024,00	177,89	111,70	185,99	3,17
K	mg/L	12 (i	0,65	51,00	11,69	7,90	12,07	1,83
Ca	mg/L	100 (ii	17,60	151,20	79,47	81,60	35,65	0,22
Mg	mg/L	50 (ii	9,92	80,80	40,31	37,93	17,82	0,36
Al	µg/L	200 (ii	0,00	586,80	38,60	0,00	105,82	4,36
Cr	µg/L	50 (ii	2,70	36,70	8,66	5,70	7,26	2,51
Mn	µg/L	50 (ii	1,06	3963,07	359,37	40,17	729,17	3,83
Fe	µg/L	200 (ii	62,50	5333,00	420,63	183,50	875,19	5,35
Ni	µg/L	20 (ii	0,00	27,31	4,55	2,99	5,68	3,30
Cu	µg/L	2 (ii	3,83	63,96	14,20	12,77	9,39	4,39
As	µg/L	10 (ii	0,57	9,70	2,36	1,42	2,19	1,64
Se	µg/L	10 (ii	0,77	17,87	3,86	2,56	3,32	2,65
Br	µg/L	25 (ii	151,00	4143,00	808,67	506,00	828,50	2,51
Sb	µg/L	5 (ii	0,00	0,68	0,13	0,11	0,12	3,38
Hg	µg/L	1 (ii	0,00	0,09	0,03	0,03	0,02	0,47
Pb	µg/L	25 (ii	0,56	21,12	2,40	1,35	3,61	4,34

i) Maximum admissible value of Portuguese legislation, Dec.Lei 236/1998
ii) Parametric value of Portuguese legislation, Dec.Lei 306/2007
iii) Median value for natural waters (Turekian, 1977)

3.3 Building a Water Quality Index

The method used here to create a Water Quality Index (WQI) is based on a multivariate statistical approach

The procedure involves three important steps, namely: (1) selection of the parameters to be included in the index; (2) standardisation of the parameters and (3) the aggregation of the parameters.

The type and number of parameters selected depends mainly on the purpose of the index construction and the availability of data.

In the present case the WQI is created to monitor the impact of industry on the groundwater quality and its consequences for consumption, which implies that some of the referred parameters will be left out while others are added.

The parameters selected were pH, SO_4, Cl, F, Na, Ca, Mg, Al, Cr, Mn, Fe, Ni, Cu, As, Se, Br, Sb, Hg, Pb, HCO_3 and K.

The current PV were defined according to different national directives and are indicated for each parameter in the Tables 1, 2 or 3

In order to obtain WQI values, the parameters involved in the pollution index have to be standardised.

The method used here (Pereira et al., 1993, Stigter et al., 2007) subdivides each variable into three classes as exemplified in Figure 6, for the variables SO_4, Cl and F : the 1st class contained the values that are below the PV, the 2nd class, the values between PV and 2x PV and the 3rd class the values higher than 2 X PV.

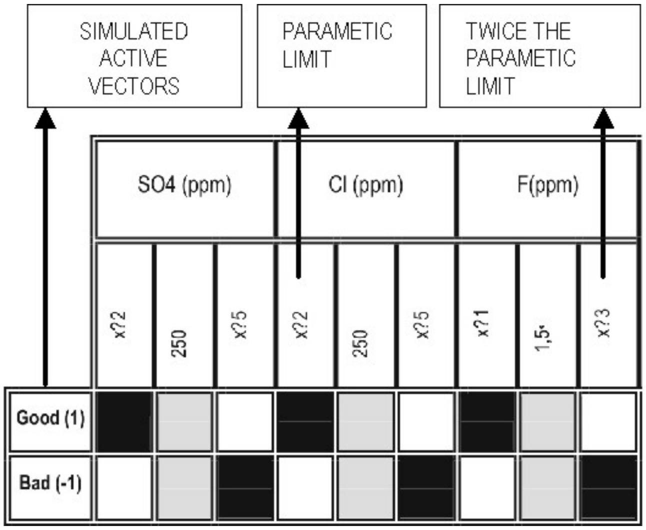
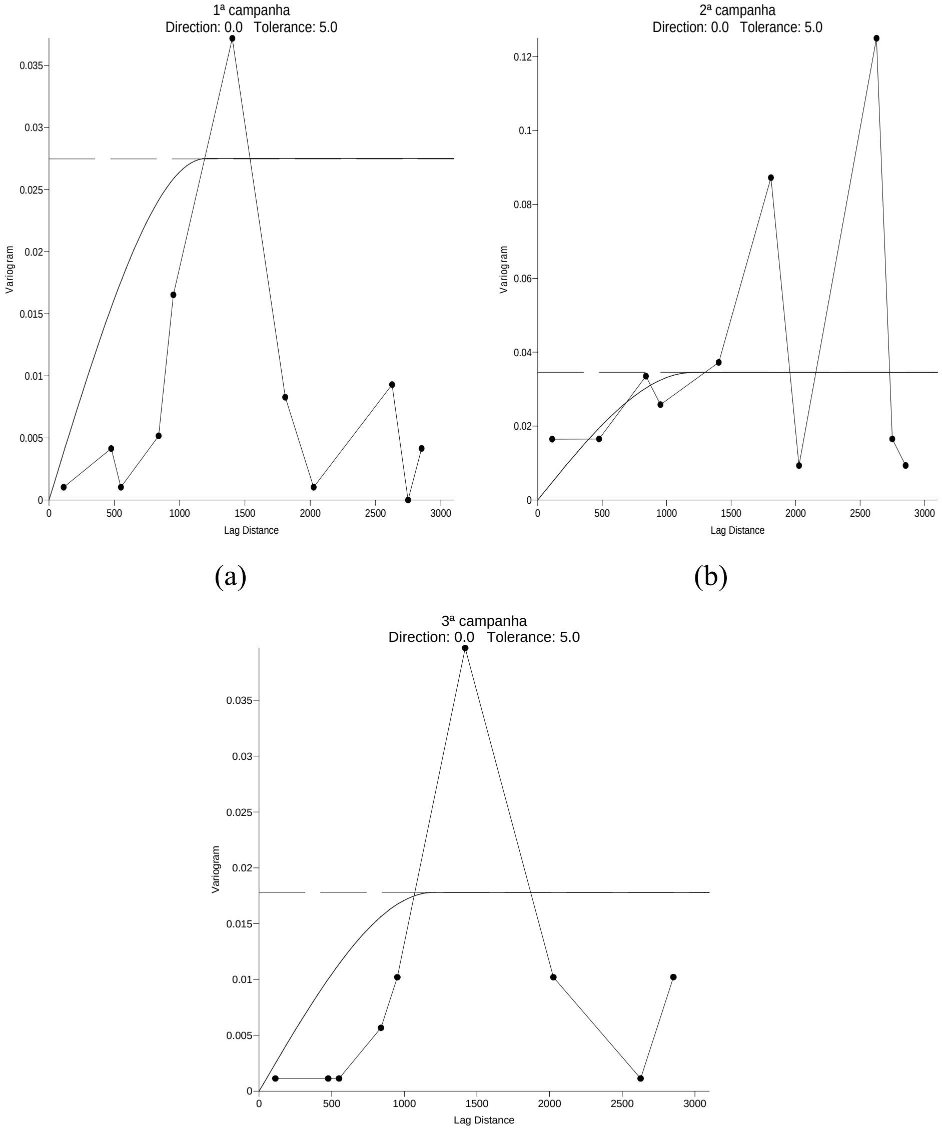


Figure 6 – Example of standardization procedure used for building the WQI

Standardisation of the variables occurs by applying a simply binary codification system to the samples: 0 if sample does not belong to class, 1 if it does.

Aggregation of the standardised parameters into the final index value is performed by using a multivariate statistical approach based on the principle of correspondence factor analysis (CFA). Developed by Benzécri in the early sixties (Benzécri 1977), CFA belongs to a group of factor extraction methods whose main objective is to discover the underlying pattern of relationships within a data set. This is basically done by rearranging the data into a small number of uncorrelated "components" or "factors" that are extracted from the data by statistical transformations. Such transformations involve the diagonalisation of the some sort of similarity matrix of the variables, such as a correlation or variance-covariance matrix (Pereira and Sousa 2000). Each factor describes a certain amount of the statistical variance of the analysed data and is interpreted according to the intercorrelated variables. The main advantage of CFA is that symmetry is conferred to the data matrix (Pereira and Sousa, 2000), thus permitting the simultaneous study of correlations within and between variables and samples.

A detailed discussion of the theory behind CFA goes beyond the scope of this article, but its application in the present case is rather straightforward. The first step involves the definition of two standard water samples; one of very high and the other of very low quality (see Figure 6)



(a) (b)

(c)

Figure 7. Experimental variograms and fitted spherical models of WQI: (a) 1st campaign; (b) 2nd campaign; (c) 3rd campaign

The high quality standard sample (the ´good´ pole) has concentrations of all parameters below the corresponding PV, whereas in the low quality sample (the ´bad´ pole) concentrations always exceed the 2 x PV.

By this procedure, each real sample analysis is located in an arbitrary scale defined by these two extreme poles, by the bias of the CFA supplementary projection.

The resulting scores correspond to the final index values, which range between -1 and 1.

The new variable obtained by this method is defined as a Regionalized Variable and consequently additive by construction, since the barycentric principle of CFA guarantees that two samples with given profiles in the variable can be replaced by a new individual, whose profile is given by the coordinates of the centre of gravity of the two original samples (Benzécri 1982).

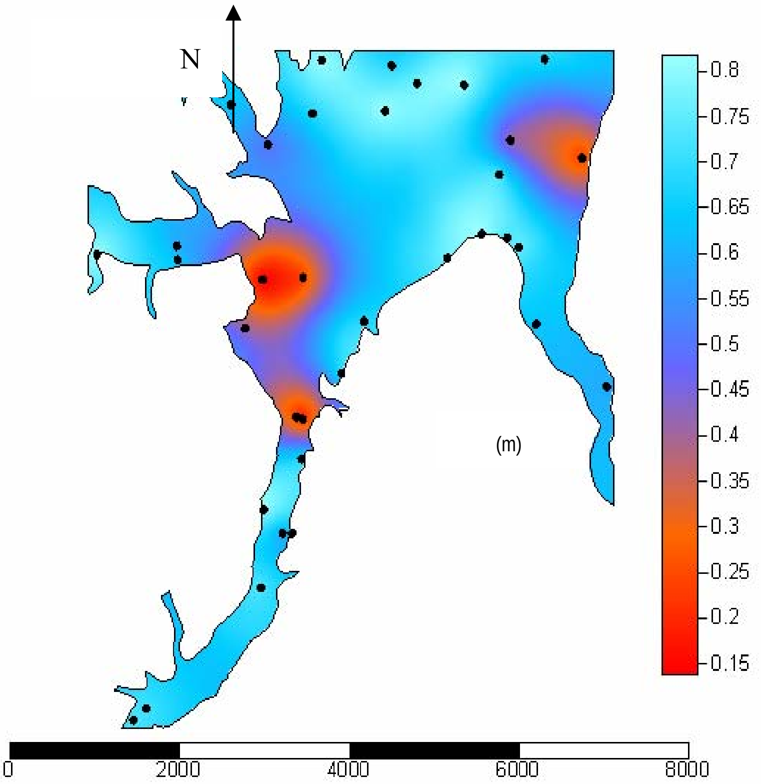


Figure 8 – Groundwater pollution index map – 1st campaign (distances in meters).

So, WQI maps can be created through interpolation of the obtained values. First the structure of the spatial distribution of the indices in each study area is analysed by looking at their experimental variograms. After fitting a spherical variogram model, the maps are created using an ordinary kriging interpolation algorithm.

4 RESULTS AND DISCUSSION

After the calculation of the indices for the 3 campaigns using the parameters observed in the 36 wells, experimental variograms were calculated through the groundwater main flow direction, e.g. W-E . The variograms were fitted by spherical theoretical models with a range of 1200 m (Figure 7)

Figures 8, 9 and 10 show the spatial distribution of the indices, interpolated by ordinary kriging algorithm, where low index value classes correspond to high groundwater pollution areas.

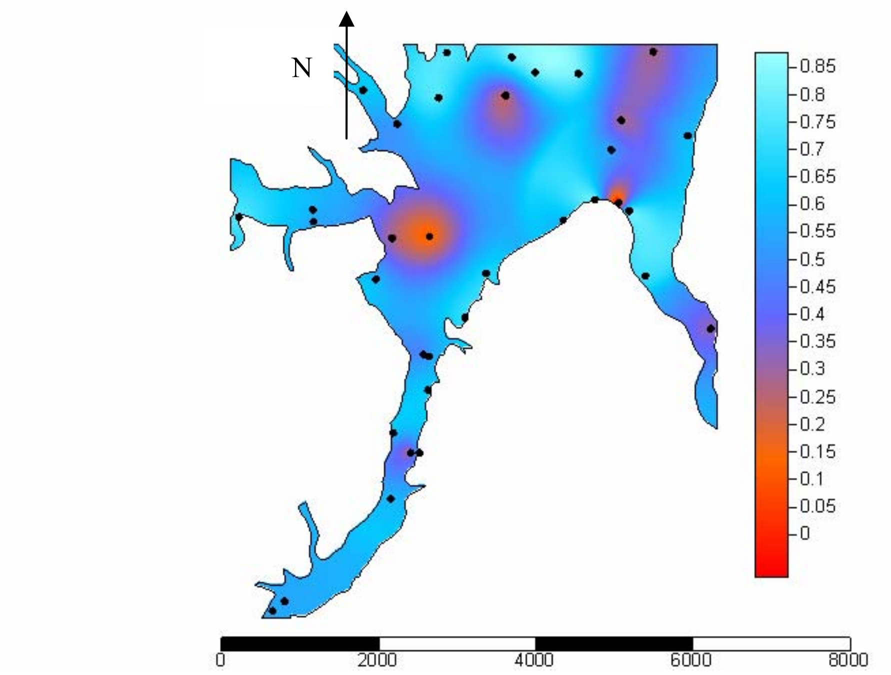


Figure 9 – Groundwater pollution index map – 2nd campaign (distances in meters).

The map obtained for the first campaign (Figure 5), carried out during the summer season of the wet year, shows three focus of high pollution, with restricted dissemination zone that may correspond to intense punctual discharges of industries. In this period of the year, groundwater flow is slow and the pollutants tend to remain in the vicinity of the origin source with no dispersion.

The map obtained for the second campaign (Figure 6), during the winter season of a wet year, shows a more diffuse picture of groundwater pollution in the area where there is a great density of industries, e.g. the NW area. In this period, due to the increase of aquifer recharge, groundwater flow is faster, and consequently the pollutants are dispersed in a wider area.

Finally the map obtained for the third campaign (Figure 7), during the summer period of the dry year, due to the decrease of groundwater velocities, shows that the dissemination of pollutants is restricted to local areas where punctual discharges of industrial wastewater occur.

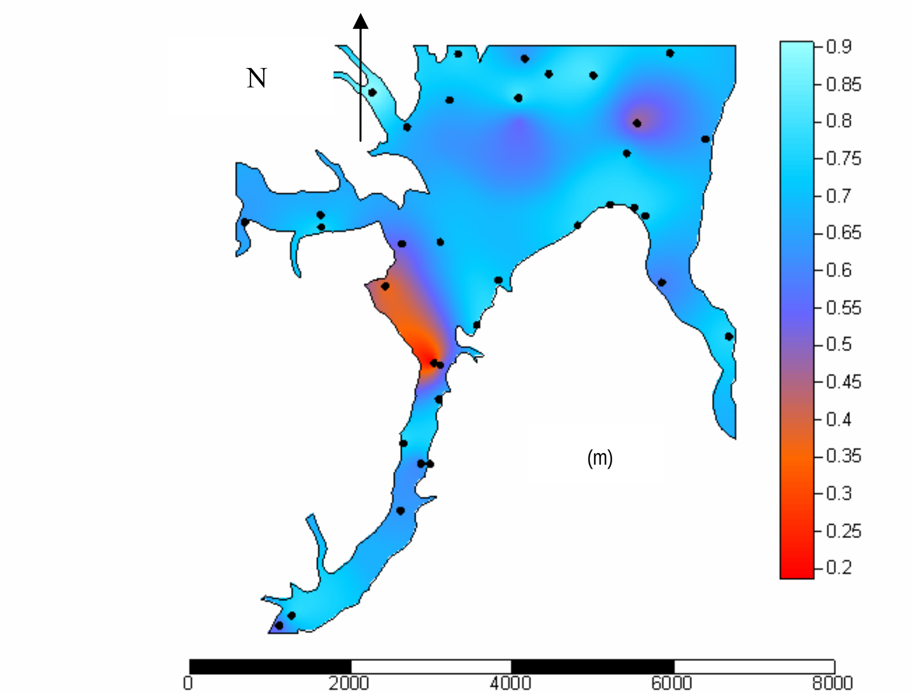


Figure 10 – Groundwater pollution index map – 3rd campaign (distances in meters).

5 CONCLUSIONS

A significant industrial development, associated with a demographic expansion, occurred during the last decades of the XX century, in Loures valley, a region located in the vicinities of Lisbon. Due to the increase of the various anthropogenic factors, surface and groundwater quality have been constantly deteriorated. This was particularly visible in Trancão River and other subsidiary water courses of Tagus River and in the shallow alluvium aquifers associated with them.

The use of WQI, which combines a large quantity of chemical information of a water sample into a single value, facilitate spatial and temporal water quality evaluation of the area threatened by the industrial and domestic wastewaters. Results obtained from 3 sampling campaigns carried out during 2 years show that the chemical composition of the groundwater is strongly influenced by the precipitation regime as well the dispersion pollution plumes patterns.

6 FURTHER DEVELOPMENTS

Future studies should be focus in various items such as the reinforcement of the monitoring network, the improvement the knowledge of the hydraulic characteristics of the alluvium aquifer, the stream-aquifer interaction by estimating the value of leakage coefficient, an analysis of the water consumption of the end-users as well a proper characterization of the pollution sources. These tasks will be fundamentally to model the groundwater flow and transport in the aquifer. All these data and model results will help the interpretation of the Water Quality Indices in different areas, reducing the level of uncertainty of the decision makers.

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