Geoenvironmental Study of Groundwater in the Fundão Area - Portugal

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Abstract. The area of implementation of the Cova da Beira’s irrigation system, due to its geographical situation and its sustainable socio-economic development requires the execution of geo-environmental studies, focusing on the behaviour of a set of variables with important ecological significance. This study is aimed to characterize the distribution patterns of variables in groundwater samples and their characterization in terms of chemical quality. Hence, an exploratory data analysis was performed in order to characterize the overall sample, followed by a stage in which a multivariate analysis was carried out through a dimensionality reduction technique (analysis of main components). The study of the dynamics of natural processes, anthropic and its influence on the dispersion, fixation and (re)mobilization of chemical elements, has contributed decisively to the optimization of the diagnostic strategy and the environmental management as well.

1. Introduction
This work aims to answer some questions about groundwater characterization in the Fundão area, starting with a set of 20 groundwater analyzes collected specifically for this work, focusing on the behavior of a set of chemical elements included in the Environmental Protection Agency's "List of Priority Pollutants"[1].

The quantitative and qualitative importance of groundwater is a factor of extreme importance for the socio-economic development of the region in which this study is inserted.

Water for the purposes of agronomy is closely linked to processes of infiltration, storage and circulation both superficial and underground.

The contamination of the environment by chemical elements of multiple origins implies the occurrence of these elements in form assimilable or easy immobilization in concentrations above the advisable or admissible levels.

Among the chemical elements of concern are the pesticides, fertilizers, sewage sludge, irrigation water, etc. The areas where this type of contamination usually appears are areas of high industrial deployment and high agricultural development [2].

The fundamental objective is the geoenvironmental characterization of groundwater, at a local scale, in the area of the Cova da Beira Irrigation Project.
For the accomplishment of this work were also defined some objectives namely:

- Calculate, analyze and interpret the sample characteristics;
- Describe the variability of the data with a smaller number of uncorrelated variables;
- Explain through a smaller number of factors the correlations between variables.

2. Characterization of the Study Area
The municipality of Fundão is located in the District of Castelo Branco, in the central region and in the sub-region of Beira Baixa called Cova da Beira. It is in this area that the city of Fundão is implanted, at the northern foot of the Mountain of Gardunha, leaning against the Mount of S. Brás at an altitude of 497 meters.

Of the municipalities that constitute the Cova da Beira area, the municipality of Fundão is the one with the lowest environmental performance value [3]. Thus, the municipality of Fundão constitutes, an excellent case of geoenvironmental study.

Sustained use of river systems, soils and aquifers requires the identification of problems and their assessment, with a view to developing scientific foundations to support the proper management of the environmental impacts of human interventions.

For the detailed characterization of the study area, it is essential to obtain data on geology, climatology, hydrology and possible anthropic influences, in order to estimate the natural variability and to differentiate natural concentrations of contamination / pollution levels [4].

Water for the purposes of agronomy and forestry, is closely linked to processes of infiltration, storage and circulation both superficial and underground. Thus, its quantitative and qualitative importance is a factor of extreme importance for the socioeconomic development of the region in which this study is inserted.

2.1 Geographical Location
The study area is located in the central region of Portugal. It is inserted between the Mountain of Estrela in the northwest and Mountain of Gardunha in the south. Topographically it is a slightly undulating plain, with heights varying between 400 and 500 meters [5].

2.2 Geology
According to the geotectonic division, the area is located in “Zona Centro Ibérica”. It is characterized by the existence of Fundão's hercinic plutonite among the most recent hercinic batholiths of Castelo Branco and Guarda.

The plutonite of the Fundão is intruded in a strip of the Schist-Gravel Complex, constituted by alternating shales and gravels. The metamorphic halo surrounds the plutonite, so it is discordant to the schists.

2.3 Climate
The current climate of the study area presents characteristics of a temperate climate with mediterranean characteristics, being named, according to the classification of Koppen [6], by Csa (C - temperate climate, s - temperature of the hottest month > 22 ° C). The classification fits perfectly into the two major climatic domains of the national territory, calculated by Mendes and Bettencourt [7].
The months of higher precipitation and relative humidity are those of November, December, January and February, while the months of July and August record the lowest precipitation. The lowest average monthly temperatures occur in January and the highest in July and August.

2.4 Hydrographic Network
In the whole area, the hydrographic network is well developed, dendritic type and with a high drainage density. From the geological point of view, the substrate is essentially constituted by granite schist and gravel rocks, which are assigned low infiltration values and consequently high surface runoff rates [8].

2.5 Underground Flow Network
According to Carvalho [8], the piezometric surface is of the radial hyperbolic type [9]. Since the flux is a perpendicular vector at each point to the equipotential surface, the flow network presents a fan distribution, appearing as nuclear zones of dispersion the topographically higher points. The water table follows the topography of the site.

2.6 Hydrochemistry
According to Carvalho [8], from the hydrochemical point of view, the groundwater of the study area can be classified into two groups, one with predominantly calcium chlorosulfate intermediates and the other with predominantly sodium/potassium bicarbonate intermediates.

3. Sampling
In a geoenvironmental study, methodologies for identification and quantification of contaminants/pollutants are compulsory, examples of which are sampling methods, sample preparation, as well as instrumental methods of chemical analysis.

Twenty samples of groundwater were collected during the months of September and October. Sampling was performed in large diameter wells [10], scattered throughout the study area (Figure 1).
The samples were analyzed for the following parameters: Copper, Lead, Zinc, Nickel, Manganese, Iron, Chromium, Magnesium, Potassium, Sodium, Phosphorus, Calcium, Nitrites, Ammonium, Bicarbonates, Nitrates, and Sulphates.

4. Exploratory Data Analysis
4.1 Sample Characteristics Using Univariate Statistical Analysis
Table 1 presents some sample characteristics for the 20 groundwater samples analyzed.

|        | Cu  | Pb  | Zn  | Ni  | Mn  | Fe  | Mg²⁺ | K⁺  | Na⁺  | P   | Ca²⁺ | NO₂⁻ | NH₄⁺ | HCO₃⁻ | NO₃⁻ | SO₄²⁻ |
|--------|-----|-----|-----|-----|-----|-----|------|-----|------|-----|------|------|------|-------|------|-------|
| Average| 0.5 | 0.1 | 0.5 | 0.005 | 0.1830 | 0.0115 | 0.5 | 15.5930 | 0.1795 | 11.7110 | 2.12 | 7.607 | 0.034 | 0.182 | 30.2 | 2.264 | 16.65 |
| Median | 0.5 | 0.1 | 0.5 | 0.005 | 0.1550 | 0.0100 | 0.5 | 12.7650 | 0.1850 | 11.2800 | 2.00 | 5.2350 | 0.0300 | 0.0500 | 12.5000 | 2.2200 | 16.0000 |
| Standard deviation | 0 | 0 | 0 | 0 | 0.0987 | 0.0048 | 0 | 9.8486 | 0.09627 | 2.81054 | 0.72446 | 5.75202 | 0.01231 | 0.27422 | 37.6823 | 0.13543 | 11.1273 |
| Range | 0 | 0 | 0 | 0 | 0.37 | 0.02 | 0 | 31.88 | 0.34 | 11.45 | 2.50 | 18.30 | 0.04 | 0.92 | 145.00 | 0.44 | 39.00 |
| Minimum | 0.5 | 0.1 | 0.5 | 0.05 | 0.07 | 0.01 | 0.5 | 1.34 | 0.02 | 4.90 | 1.50 | 1.62 | 0.03 | 0.03 | 1.00 | 2.22 | 2.00 |
| Maximum | 0.5 | 0.1 | 0.5 | 0.05 | 0.44 | 0.03 | 0.5 | 33.22 | 0.36 | 16.35 | 4.00 | 19.92 | 0.07 | 0.95 | 146.00 | 2.66 | 41.00 |

From the analysis of Table 1, it can be observed that in the case of Copper, Lead, Zinc, Nickel and Chromium do not have any valid sample characteristics, since the values that resulted from the chemical analyzes are all below the limit of quantification.

Concentrations of Manganese vary between 0.07 and 0.44. This variable presents an average of 0.1830 higher than the median (0.1550). Asymmetry shows a positive value.

For the Iron variable, concentrations range from 0.01 to 0.03 and show a small variability around the mean (0.0115).

Magnesium presents a slightly positive asymmetry with a range of values of 31.88.

Potassium concentrations in the analyzed samples presented a minimum of 0.02 and a maximum of 0.36, presenting an average of 0.1795 lower than the median (0.1850).

Sodium is the only analyzed variable that presents a negative asymmetry. The mean (11.7110) is slightly higher than the median (11.2800).

Phosphorus has an amplitude of values of 2.50 with a small variability of values in relation to the mean.

For the variable Calcium an average value of 7.6070 is observed, presenting a standard deviation of 5.75202. It presents a slightly positive asymmetry.

Nitrates present the same values for the 1st quartile, 2nd quartile and 3rd quartile (0.03).
In the case of the Ammonium variable concentrations vary between 0.03 and 0.95. It presents a positive asymmetry (1,950) and a slight variability of values around the mean value.

Bicarbonates present an average value of 30.2 and a positive asymmetry (1,688).

The Nitrate variable shows a positive asymmetry (2,888). It presents the same values in the 3 quartiles since only 2 samples have different values of 22,200, namely samples number 12 and 14.

With respect to the variable Sulphates, it has a minimum value of 2.00 and a maximum value of 41.00. The variability of the values is low around the mean value (16.6500).

All variables present a positive asymmetry with the exception of the variable Sodium; In all variables it is observed that the variability of the values around the mean is small.

4.2 Sample Characteristics Using Bivariate Statistical Analysis

In order to identify the correlations between the different variables analyzed, the Pearson correlation method was used. Table 2 presents the Pearson correlation values for a significant correlation at the 0.05 level.

| Pearson Correlation | Mn   | Fe   | Mg2+ | K+  | Na+ | P       | Ca2+ | NO2- | NH4+ | HCO3- | NO3- | SO42- |
|---------------------|------|------|------|-----|-----|---------|------|------|------|-------|------|-------|
| Mn                  | 1    | 0.469 | -0.005 | 0.512 | -0.230 | 0.664 | 0.019 | 0.284 | 0.251 | 0.488 | 0.300 | -0.331 |
| Fe                  | 0.469 | 1    | 0.228 | 0.516 | -0.032 | 0.243 | 0.515 | 0.245 | 0.586 | 0.438 | 0.245 | -0.193 |
| Mg2+                | -0.005 | 0.228 | 1    | 0.458 | 0.826 | 0.395 | 0.826 | 0.505 | 0.233 | 0.579 | 0.505 | 0.745 |
| K+                  | 0.512 | 0.516 | 0.485 | 1    | -0.275 | 0.500 | 0.500 | 0.126 | -0.035 | 0.675 | 0.126 | 0.162 |
| Na+                 | -0.230 | -0.032 | 0.826 | 0.275 | 1    | 0.134 | 0.545 | 0.356 | 0.077 | 0.370 | 0.356 | 0.743 |
| P                   | 0.664 | 0.243 | 0.395 | 0.500 | 0.154 | 1    | 0.207 | 0.415 | -0.038 | 0.571 | 0.415 | 0.213 |
| Ca2+                | 0.019 | 0.515 | 0.826 | 0.500 | 0.545 | 0.207 | 1    | 0.333 | 0.312 | 0.509 | 0.333 | 0.433 |
| NO2-                | 0.284 | 0.245 | 0.505 | 0.126 | 0.356 | 0.415 | 0.333 | 1    | 0.322 | 0.652 | 1.000 | 0.364 |
| NH4+                | 0.251 | 0.586 | 0.233 | -0.035 | 0.077 | -0.038 | 0.312 | 0.322 | 1    | 0.205 | 0.322 | 0.022 |
| HCO3-               | 0.488 | 0.438 | 0.579 | 0.675 | 0.570 | 0.571 | 0.509 | 0.652 | 0.205 | 1    | 0.652 | 0.354 |
| NO3-                | 0.284 | 0.245 | 0.505 | 0.126 | 0.356 | 0.415 | 0.333 | 1.000 | 0.322 | 0.652 | 1    | 0.364 |
| SO42-               | -0.331 | -0.193 | 0.745 | 0.162 | 0.743 | 0.213 | 0.433 | 0.364 | 0.022 | 0.354 | 0.364 | 1    |

The variable Mn presents low correlation values, lower than 0.664 in modulus. It is slightly positively correlated with the variables K+ and P and presents a null correlation with the variables Mg2+ and Ca2+.

The Fe variable is slightly positively correlated with the variables K+, Ca2+ and NH4+.

The variable Mg2+ is positively correlated with the variables Na+, Ca2+ and SO42- and has a null correlation with the variable Mn.

The variable K+ is slightly positively correlated with the variable HCO3-.

The Na+ variable is correlated with the variables Mg2+ and SO42-. In the case of the variable P, it presents correlation values greater than 0.5 for the variables Mn and HCO3-.

The variable Ca2+ is correlated with the variable Mg2+ and presents a null correlation with the variable Mn.

The variable NO2- is slightly positively correlated with the variable HCO3-.

The variable NH4+ is not correlated with any variable, however presenting the value of 0.586 with the variable Fe.

The variable HCO3- is slightly positively correlated with the variables Mg2+, K+, P, NO2- and NO3-.

The variable NO3- is slightly positively correlated with the variable HCO3-.

The variable SO42- presents a positive correlation with the variables Mg2+ and Na+.

From the observation of table 2 we can also observe that in the global sample the correlations have low values, lower than 0.826.
4.3 Sample Characteristics Using Multivariate Analysis

In order to explore the data using multivariate analysis, the principal component analysis (PCA) method was used. This study is based on 20 samples and 12 variables. The Cu, Pb, Zn, Ni and Cr variables were excluded because they had a null variability around the mean. In order to try to clarify the relationships between variables, we created a matrix generated from the binomial total number of samples versus variables (20 x 12).

It starts from a set of 12 variables and it is intended to find a new set of uncorrelated variables, the main components. These are a linear combination of the original variables. Thus, a smaller number of these variables may explain a significant percentage of the variability of the data. If the explanation were total, we would have to use the 12 major components and the study would be unnecessary.

The determination of the principal components to be retained generally follows an empirical criterion on the basis of the eigenvalues greater than 1 [11].

Table 3. Coordinates of the active variables in the factorial axes

| Variable | 1   | 2   | 3   | 4   |
|----------|-----|-----|-----|-----|
| Mn       | 0.382 | 0.828 | -0.059 | -0.222 |
| Fe       | 0.498 | 0.572 | -0.600 | 0.563 |
| Mg²⁺     | 0.855 | -0.421 | -0.156 | 0.113 |
| K⁺       | 0.616 | 0.308 | -0.650 | -0.017 |
| Na⁺      | 0.623 | -0.643 | -0.132 | 0.038 |
| P        | 0.606 | 0.350 | -0.191 | -0.511 |
| Ca²⁺     | 0.738 | -0.189 | -0.246 | 0.432 |
| NO₂⁻     | 0.752 | 0.018 | 0.058 | -0.233 |
| NH₄⁺     | 0.363 | 0.240 | 0.464 | 0.651 |
| HCO₃⁻     | 0.856 | 0.208 | -0.061 | -0.169 |
| NO₃⁻     | 0.752 | 0.018 | 0.583 | -0.233 |
| SO₄²⁻     | 0.556 | -0.711 | -0.047 | -0.127 |

Table 4. Own values and percentage of variance explained, for each of the factorial axes

| Axis | Own Value | % Variance Explained | % Cumulative Variance |
|------|-----------|----------------------|-----------------------|
| 1    | 5,109     | 42.574               | 42.574                |
| 2    | 2,464     | 20.531               | 63.105                |
| 3    | 1,471     | 12.257               | 75.362                |
| 4    | 1,424     | 11.868               | 87.229                |
| 5    | 0,520     | 4.330                | 91.560                |
| 6    | 0,358     | 2.982                | 94.541                |
| 7    | 0,721     | 2.262                | 96.803                |
| 8    | 0,197     | 1.638                | 98.441                |
| 9    | 0,123     | 1.027                | 99.469                |
| 10   | 0,044     | 0,366                | 99.835                |
| 11   | 0,020     | 0,165                | 100,00                |
| 12   | 2,082E-16 | 1,735E-15            | 100,00                |

The retention of the first four factorial axes explaining 87.229% of the total variance. (Using this method, the "dimensionality" of the problem, 12 original variables, was reduced to 4 "latent" variables). Factorial axis 1 explains the variables Mg²⁺, K⁺, Na⁺, P, Ca²⁺, NO₂⁻, HCO₃⁻, NO₃⁻ and SO₄²⁻. Factorial axis 2 explains the variables Mn, Fe, as opposed to the variables Na⁺ + and SO₄²⁻. Factorial axis 3 explains the variable K⁺. Factorial axis 4 explains the variable NH₄⁺.
Figure 2 shows the projection of the different variables in the first main plane, not having projected the variables that have a correlation coefficient with less than 0.5.

Figure 2. Projection of the different variables in the first main plane

The first main plane consisting of the main axes 1 and 2 contains 63.105% of the information contained in the correlation matrix.

Axis 1 explains the association (P and K⁺), whose origin is to be attributed to the agricultural activity of the region and the association (NO₂⁻ and NO₃⁻), whose origin is due to the agricultural activity practiced in the region. This axis also explains the variables SO₄²⁻, Na⁺, Ca²⁺ and Mg²⁺ that shows the natural quartz of the groundwater of the region.

Axis 2 separates the agricultural and farming component of the component that shows the natural chemical matrix of the groundwater of the studied area.

Axis 2 explains the association (Mn and Fe), whose origin is to be found in the geological complexity of the region.

5. Conclusions

The application of univariate statistics allowed us to characterize the "behavior" of the variables under study. In all the variables it is verified that the variability of the values around the mean is small and that with the exception of the variable Sodium, all the variables present a positive asymmetry.

The Pearson correlation method allowed us to define the correlations between the different variables. In the overall sample, these correlations are generally low.

The application of the Statistical Analysis of Major Components technique to the overall data allowed us to study the intercorrelation between the variables analyzed and to establish the distribution structure of these variables. The projection of the variables in the first factorial plan, allowed to test the connection of the variables and to separate those of essentially lithological character (Mn and Fe), those of essentially hydrochemical character (SO₄²⁻, Na⁺, Ca²⁺ and Mg²⁺) and those of essentially anthropogenic character (P, K⁺, NO₂⁻ and NO₃⁻). The application of the PCA also allowed the identification of the hydrogeochemical image of the agricultural component (P and K⁺) and of the agricultural component (NO₂⁻ and NO₃⁻) practiced in the study area.

The low concentration of the variables in the analyzed samples could be attributed to several factors, namely at the time of sampling at the end of the dry period (September and October), the low infiltration
values characteristic of the study area, the non-use of groundwater for irrigation, which may increase the dilution of concentrations, and the environmentally sustainable practices of agricultural and livestock farming in the studied area.

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