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Multivariate statistical analysis to characterize/discriminate between anthropogenic and geogenic trace elements occurrence in the Campania Plain, Southern Italy☆

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ABSTRACT

Shallow aquifers are the most accessible reservoirs of potable groundwater; nevertheless, they are also prone to various sources of pollution and it is usually difficult to distinguish between human and natural sources at the watershed scale. The area chosen for this study (the Campania Plain) is characterized by high spatial heterogeneities both in geochemical features and in hydraulic properties. Groundwater mineralization is driven by many processes such as, geothermal activity, weathering of volcanic products and intense human activities. In such a landscape, multivariate statistical analysis has been used to differentiate among the main hydrochemical processes occurring in the area, using three different approaches of factor analysis: (i) major elements, (ii) trace elements, (iii) both major and trace elements. The elaboration of the factor analysis approaches has revealed seven distinct hydrogeochemical processes: i) Salinization (Cl^-, Na^+); ii) Carbonate rocks dissolution; iii) Anthropogenic inputs (NO_3^-, SO_4^{2-}, U, V); iv) Reducing conditions (Fe^{2+}, Mn^{2+}); v) Heavy metals contamination (Cr and Ni); vi) Geothermal fluids influence (Li^+); and vii) Volcanic products contribution (As, Rb). Results from this study highlight the need to separately apply factor analysis when a large data set of trace elements is available. In fact, the impact of geothermal fluids in the shallow aquifer was identified from the application of the factor analysis using only trace elements. This study also reveals that the factor analysis of major and trace elements can differentiate between anthropogenic and geogenic sources of pollution in intensively exploited aquifers.

1. Introduction

Groundwater constitutes the main resource of fresh water for humans (Niu et al., 2017), and shallow aquifers are the most accessible and exploited resources for drinking purposes, even thou they are more susceptible to contamination than confined aquifers. Groundwater quality depends on both natural processes and anthropogenic activities (Foster and Chilton, 2003). Water–rock interaction, mineral dissolution, residence time of groundwater, flow paths, mixing among different water bodies and human exploitation are the main deterioration factors of groundwater quality (Belkhiri et al., 2010). Thus, to clearly define the ongoing hydrogeochemical processes within an aquifer is a challenging task, since large data sets and advanced methodologies are required. Multivariate statistical analysis such as the factor analysis (FA), the principal component analysis (PCA), the analysis of variance (ANOVA) and the cluster analysis, represent sound tools to detect and explain hydrogeochemical factors (Locsey and Cox, 2003) governing the chemical composition of groundwater (Corniello and Ducci, 2014). These statistical tools allow to discriminate between anthropogenic and geogenic sources (Cuoco et al., 2015b; Kim et al., 2009a; Mastrocicco et al., 2016; Pereira et al., 2003) and to manage large datasets without losing critical information and giving an

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accurate hydrochemical assessment of the studied aquifers (Voudouris et al., 2000). In contrast, chemical analysis, simple plots and correlation between different elements can provide limited understanding of the environmental distribution of contaminants (Einax et al., 1997). Nevertheless, the statistical tools and presentation methods are strongly dependent on the goals of each study and the quality and quantity of data available.

Recent studies focused on the capability of FA to identify hydrological processes for specific areas (Huang and Wang, 2017; Yang et al., 2016) and in different hydrological basins, under different hydrogeological conditions (Kazakis et al., 2017a). However, questions have arisen regarding the number of dissolved species that FA should include. Therefore, in order to test the response of FA using different combinations and number of dissolved species, the Campania Plain (CP) in Southern Italy was selected and studied since it hosts an aquifer characterized by a complex hydrochemical status, well represented in a large and consistent data set.

The CP is characterized by high spatial hydrogeological and geochemical heterogeneities. In fact, several processes due to the coexistence of different geological units and human activities affect the mineralization of groundwater, which is the primary water resource within the CP. Anthropogenic sources of pollution are mainly due to extensive urbanization, farming, agriculture practices and industries, while geothermal activities, volcanic products and saline sediments constitute the natural sources of geogenic pollution (Corniello et al., 2007). Indisputably, it is a challenge to characterize this complex and interconnected hydrochemical regime. Multivariate statistical analysis and advanced statistics constitute the most appropriate tool to be used even thou they require a large, robust and consistent dataset to be considered.

To summarize, the aim of this research is twofold: (i) to distinguish between natural and anthropogenic processes affecting groundwater focusing on trace elements and (ii) to test the response of FA using different combinations and number of dissolved species. A GIS environment was used to improve the visualization of the results for the multivariate statistical analysis and to depict water-rock interaction and anthropogenic processes in the study area.

2. Materials and methods

2.1. Study area

The Campania Plain (CP) is limited to the W by the Tyrrhenian Sea, to the N-NE by Massico Massif and Roccamonfina Volcano, to the S by the Phlegrean Fields and Mt. Vesuvio and to the E by the Maggiore, Tifatini and Avella Mountains (Fig. 1). The geological evolution of the graben hosting the CP begun in the upper Pliocene and proceeded during the Holocene with a critical extensive-tectonic stress (Casciello et al., 2006). The tectonic processes allowed the development of several volcanic centres (Roccamonfina, Phlegrean Fields and Somma-Vesuvio) located in the most depressed areas, at the graben borders (Rolandi et al., 2003). The carbonate bedrock of the Apennine chain is buried by marine clays and sands having the upper limit between 90 and 20 m below sea level, the overlying unit is made of Phlegrean volcano-clastites and volcanic sediments from others volcanic centres, made of trachytic-phonolithic pyroclastic materials, sands and cinerite reworked in subaqueous environment (De Vivo et al., 2001; Santangelo et al., 2017). The Holocene sediments, outcropping in the middle of the CP, are irregular successions of clays, silts and peat beds deposited by the Volturno River, while toward the coast dunes and sandbars are present (Amorosi et al., 2012). In the Southern part of the plain, the outcropping unit is an irregular succession of pozzolans, cinerites and sandy pyroclastites due to the Phlegrean Fields activity. The shallow aquifer of the study area is mainly hosted in the volcanic and alluvial sediments (section in Fig. 1), it is recharged by the local infiltration of rainwaters and fed by lateral inflows coming from karst and volcanic aquifers at the eastern and northern boundaries of the CP. The regional groundwater flow direction is from East to West (Allocca et al., 2007).

The CP covers approximately 700 Km^2 and has a population of more than 1 million inhabitants. The area shows a heterogeneous land use: (i) the urban area covers approximately 20% of the territory, (ii) the agricultural land is about 75% (where a variety of different crops are cultivated), and (iii) forests and pastures occupy the remaining territory, mainly on the ridges of the massifs surrounding the plain.

2.2. Sampling techniques

Within the boundaries shown in Fig. 1, 244 water samples were collected from agricultural, residential and municipal wells after purging at least three well volumes. Coordinates for all samples were recorded using a portable GPS. Electrical conductivity (EC), temperature (T) and pH values were measured in situ using a multiparameter Hanna Hi 991300 probe. All samples were prepared for laboratory analysis using 500 and 50 ml PET bottle. In the geochemical laboratory of the University of Campania “Luigi Vanvitelli” the major ions Ca^{2+}, Mg^{2+}, K^+, Na^+, Cl^-, SO_4^{2-}, NO_3^- were determined with a Dionex IC-120 ion chromatographer using four calibrations standards (0.5, 5, 25, 50 mg L^{-1}). Precision and accuracy were tested trough repeated measurements of certified standard solutions (MERK®) at different ion concentrations with a range comparable to that of the analysed samples. The relative percentage error for precision was 7% for Na^+, K^+ and Ca^{2+}, 5% for Mg^{2+} and SO_4^{2-}, and below 5% for other anions. A 100 ml aliquot of each sample, intended for HCO_3^- measurement, was titrated with certified 0.1 mol L^{-1}HCl. Trace elements (Fe, Mn, Zn, B, V, Li, U, Cr, Ba, Sr, As and Ni) were determined using an Agilent 7500 CE ICP-MS with intact interference reaction cell according to Cuoco et al. (2017b, 2013). Other elements were not considered since they have never been detected above the detection limit in the 244 samples considered. ICP-MS analyses were tested trough Interference Check Solutions (AGILENT®) in order to check the efficient functioning of the system. The instrumental drift was checked trough Y-Tb internal standard solution (AGILENT®). Accuracy and precision were checked following EPA method 200.8 and the relative percentage error for precision was less than 7%. The overall precision of the chemical analyses was checked by ionic balance, which was within ±5%.

2.3. Multivariate statistical analysis and graphical methods

In this study, the multivariate statistical analysis was chosen in order to determine the hydrogeochemical processes in the CP. More specifically, the statistical technique examines the relationship between variables detected in several samples, which represent a list of cases, and gives back a list of significant factors that assemble the initial variables. In this work, FA was applied under three different approaches: (i) using major ions (FA-A), (ii) using trace elements (FA-B), (iii) and using both (FA-C). Hence, the comparison of FA results can spotlight how processes that occur in the CP are described by different data sets. Moreover, natural and anthropogenic activities can be distinguished. The R-type FA was applied to reduce the large database (244 samples), organize data in groups with similar characteristics and identify the weight and score of each parameter. New and small groups of factors were created summarizing the initial variables (Anazawa and Ohmori, 2005;