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Assessing background values of regulated parameters in groundwater bodies of Sardinia (Italy)

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Abstract

The groundwater bodies in the European Union should be classified on the basis of their chemical status according to the European regulations. To this purpose, the background values for electrical conductivity, chloride, sulfate, fluoride and lead in groundwater bodies hosted in carbonatic rocks in Sardinia (Italy) were estimated. Background values were dependent on geological (lithology and mineralization) and geographical (distance from the coast) features of aquifers. Results indicate that statistical methods should be integrated with hydrogeochemical investigations for a correct assessment of the background values.
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1. Introduction

The European Union (EU) has established rules (Dir. 2000/60/CE, 2006/118/CE, 2014/80/EU)) for the classification of the chemical status of groundwater bodies. The EU legislation has been implemented in Italy by the Legislative Decree (LD) 152/2006 and 30/2009 that established threshold values to be compared with monitoring data in order to assess the chemical status of each relevant groundwater body. When the natural background value of a parameter is higher than the threshold value established at national level, the background value replaces the threshold value in the specific groundwater body or groups of groundwater bodies. According to European rules, the natural background is the concentration of a substance in water corresponding to any anthropogenic alteration, or very minor alterations, with respect to undisturbed conditions. Statistical methods are commonly used to calculate the natural background and upper threshold values[1,2,3,4,5,6]. However, in order to properly classify the water bodies, it

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is imperative to have a comprehensive geochemical and hydrological understanding of aquifers, especially to avoid classification in bad status those water bodies that occur in natural hydrochemical facies.

In 2014, a cooperation agreement between the Sardinian Region (RAS) and the Department of Chemistry and Geology of the University of Cagliari was signed, and focused on the estimation of natural background levels in groundwater bodies, as well as on the optimization of groundwater monitoring programs in Sardinia.

2. Methods

Background values have been estimated for 114 groundwater bodies of Sardinia, identified and distinguished mainly on the basis of the dominant geological formations hosting the aquifers. The dataset included 1795 groundwater sampling sites and a total of 4138 chemical analyses. Combining geochemical (Piper diagrams and binary plots) and statistical (cumulative curves and box-plots) tools, and taking into account field observations and the occurrence of anthropogenic pressures, the water samples affected by anthropogenic inputs were identified, accordingly, they were excluded for the background calculation.

In this paper, 25 water bodies hosted in carbonatic aquifers were considered: 16 hosted in Mesozoic rocks and 9 in Paleozoic rocks where diffuse Pb–Zn mineralization occurs[7]. A total of 181 sampling sites, and respective water analyses, were selected on the basis of very minor anthropogenic alteration with respect to undisturbed conditions. The water bodies have extension in the range of 5 to 355 km^2. Most water bodies (n = 17) have extension < 50 km^2 with < 10 sampling sites available.

In order to taking into account the geochemical variability and to increase the statistical relevance, the water bodies were subdivided into three groups: Group 1 (NW Sardinia), Group 2 (E Sardinia) and Group 3 (SW Sardinia). Groups 1 and 2 are comprised of water bodies hosted in Mesozoic formations, while Group 3 includes water bodies hosted in Paleozoic formations. The location of water bodies and groundwater sampling sites are shown in Fig. 1.

The parameters considered in this paper are: electric conductivity, chloride, sulfate, fluoride and lead determined on 0.45 µm filtered aliquots. For each parameter, the background values were estimated both using the 95th percent value 4 and the median value plus two times the Median Absolute Deviation (MAD)[2,5]. Due to the large number of undetected concentrations, the detection limit (dl) value was used in calculations for lead concentrations below dl.

3. Results

The chemical composition of groundwater samples ranges from dominant calcium-magnesium-bicarbonate with low total dissolved solids (TDS < 0.5 g/L) to dominant sodium-chloride with relatively high TDS (Fig. 1). Table 1 shows the summary statistics calculated for the whole population (all samples) and for each groundwater group. The parameters considered occur in a wide range of values depending on the time of interaction between the water and the carbonatic rocks, as well as on geological and geographical factors. Among geological factors, the occurrence of evaporitic sediments plays a relevant role on water chemistry. Also, the water bodies located close to the coast are affected by sea spray.

It was observed that background values calculated by the Median+2MAD were generally lower than the values corresponding to the 95th percentile. At regional level, i.e. taking into account the whole population, the chloride concentrations exceed the national limit established by the Italian legislation, either assuming the 95th percentile or the Median+2MAD as background value. However, the observed variability in chemical composition should be taken into account when assessing background values. Among the water bodies hosted in Mesozoic carbonatic rocks, the group of waters located in NW Sardinia are distinguished due to the occurrence of Triassic levels. These levels contain evaporitic minerals, which solubility allows an increase in dissolved salts, and consequently in conductivity. In contrast, these Triassic levels are either lacking or negligible in the water bodies hosted in group of waters of E Sardinia, thus, the upper threshold values for conductivity and chloride are below the Italian limits.

The water bodies hosted in Paleozoic carbonatic rocks are distinguished by widespread occurrence of mineral deposits. The ores include a variety of sulfide minerals, with abundant galena. Therefore, the background value for lead in these water bodies results higher than the Italian limit. Also, the background value for fluoride is relatively high in Group 3 waters due to the frequent occurrence of fluorite in the mineral deposits.

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