A methodological approach for the identification of sulphate sources in the Portoscuso area (south-western Sardinia)

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ABSTRACT

Several detrimental effects due to intense industrial activities affect the groundwater of the Portoscuso area (SW Sardinia, Italy) such that the Italian Government has designed the whole territory as a contaminated site of national interest (D.M., March 12, 2003). Groundwater pollution is a crucial environmental issue in this area, where a volcanic ignimbrite succession up to 500 m thick outcrops, locally covered by sand deposits of variable thickness. Groundwater upgradient to the industrial district shows sulphate concentrations exceeding the background value of 450 mg/L calculated for the area (Vecchio et al., 2011). In order to verify the origin of sulphate, multidisciplinary investigations were carried out on the geochemical features and stable isotope ratios in groundwater.

Keywords: groundwater, sulphate contamination, isotopes

METHODS

A 3D hydrogeological conceptual model was elaborated for the aquifers. Two hydrogeological and hydrogeochemical surveys were carried out in 2015 and 2018, including a piezometric and chemical-physical survey of 122 piezometers, which allowed defining the main flow direction of groundwater. Forty-seven piezometers were sampled for the geochemical investigations and analysis of δ^2H, $\delta^{18}O$ of water. Twenty samples of the 2015 campaign were selected based on sulphate concentration to perform investigation on dissolved stable isotopes of sulphate ($\delta^{34}S_{SO4}$ e $\delta^{18}O_{SO4}$) up gradient and down gradient from potential sources of pollution. Three samples of rain were collected upstream and downstream of the industrial area considering the prevailing winds from NW, for a complete geochemical and isotopic characterization. The sampling of rainwater was carried out by ARPA Sardegna according to the method set out in Annex IV appendix 2 of Presidential Decree 203/88.
The δ^2H_{H2O} and $\delta^{18}O_{H2O}$ were measured using Wavelength-Scanned Cavity Ringdown Spectroscopy (L2120-i, Picarro). The isotopic characterization of $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ was carried out at the University of Barcelona, Spain. The samples were prepared precipitating the sulphate as $BaSO_4$. The $\delta^{34}S_{SO4}$ analysis was performed with an elemental analyzer coupled in continuous flow with a Finnigan Delta C IRMS mass spectrometer (Carlo Erba). The $\delta^{18}O_{SO4}$ was analysed in duplicate

samples using a ThermoQuest elementary high temperature conversion analyser coupled in continuous flow with a Delta X IRMS Finnigan MAT mass spectrometer. This method was also applied to the rain samples. Only for 2 rain samples was possible precipitate sufficient $BaSO_4$ to determine sulphate isotopic composition.

RESULTS

The stable isotopic composition of the water (δ^2H_{H2O}, $\delta^{18}O_{H2O}$) shows that most of the samples lie between the SIMWL (Southern Italy Meteoric Water Line, Giustini et al., 2016) and the GMWL (Global Meteoric Water Line), highlighting the meteoric origin of the recharge waters.

However, some samples align along a straight line crossing the δ^2H and $\delta^{18}O$ values measured by Mongelli et al. (2013) for the sea waters of northern Sardinia. This suggests the presence of salinization processes due to marine intrusion.

For the interpretation of $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$, data were plotted together with the isotopic composition of the main sulphate sources (Mongelli et al., 2013; Petitta et al., 2011) (Figure 1), and the main flow direction in the aquifer was taken into account. It appears that the origins of the sulphate are various and influenced by several factors. Part of the sulphate sources is likely of natural origin (sea spray and decomposition of marine organic matter) and part of anthropic origin (e.g. dissolution of sulphides probably coming from the waste rock from coal exploitation, atmospheric sulphate of industrial origin). Mixing processes likely occur in groundwater.

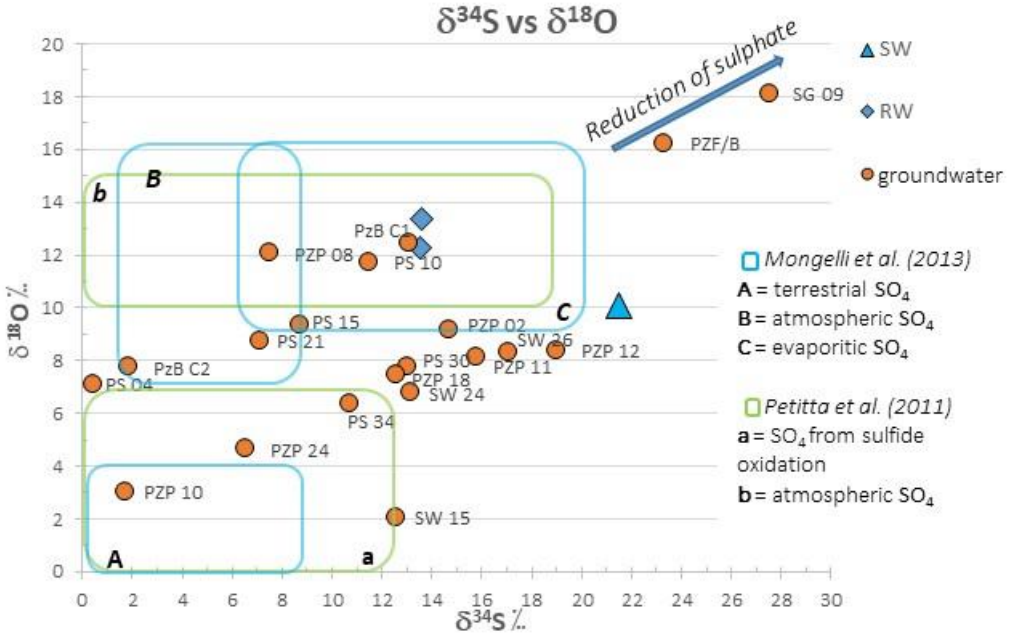

Fig. 1 - Sulphur against oxygen isotopic composition of sulphate in groundwater and rain waters (RW) from the Portoscuso area. Sea Water (SW) isotopic composition from Mongelli et al. (2013) is also provided.

CONCLUSIONS

The integrated approach of hydrogeological, geochemical and stable isotope analyses have provided information on the origin of sulphate in the groundwater of the Portoscuso area. It appears that the origins of the sulphate are various and influenced by several factors, both natural and anthropogenic. Further investigations on the isotopic composition of atmospheric particulate and leachate from waste rocks are running in order to verify the presented hypothesis.

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