

GEOCHEMICAL BACKGROUND VALUES IN AQUATIC SYSTEMS

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European (Dir. 2000/60/CE, 2006/118/CE, 2014/80/EU) and Italian (Legislative Decrees 152/2006 and 30/2009) regulations require the chemical classification of water bodies, as compared to threshold values established at national level. In undisturbed environments, chemical compositions of waters depend on a series of processes involving the interaction of water with mineral and gas phases. Such processes result in the natural composition of water, i.e. the background condition. According to European rules, natural background values of dissolved substances are defined as concentrations corresponding to any or very minor anthropogenic alterations, with respect to undisturbed conditions. Threshold values are derived from background estimates and correspond to the upper limits of background variations.

Hydrogeochemical background values depend on different factors, such as climatic conditions (temperature, rainfall input and rate), chemical and biological processes, reactivity of minerals with which the water comes in contact from recharge to discharge areas, residence time and mixing processes (Appelo and Postma, 2005). Therefore, background values in natural waters are usually characterized by large spatial variations at a range of scales (Edmunds et al., 2003). Human activities may alter background concentrations of constituents in the water. Inputs of pollutants to aquatic systems are often derived from inappropriate management of urban, agricultural, industrial and mining wastes. Specific pollutants, such as dissolved inorganic components, may derive from both natural and anthropogenic sources. Therefore, the knowledge of processes affecting water quality and the estimation of natural background ranges is crucial for distinguishing natural from anthropogenic sources of aqueous components.

From a regulatory point of view, the definition of threshold values is mandatory for the regional authorities that have to address a sustainable management of water resources. To this purpose, in order to properly classify the water bodies, it 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 hydrogeochemical facies.

Background ranges are generally estimated following statistical approaches. Calculations using the mean \pm 2SD (SD = standard deviation) have been frequently used to assess the background ranges, implicitly assuming a normal distribution of values (Matschullat et al., 2000). However, geochemical data are usually heavily skewed and rarely follow a normal distribution, therefore, using the mean \pm 2SD is considered inappropriate (Edmunds et al., 2003). The use of the median \pm 2MAD (MAD = Median Absolute Deviation) has been suggested for skewed geochemical data (Reimann et al., 2005). Integrating different estimators provides more reliable background and threshold estimates (Matschullat et al. 2000).

Chloride, sulfate and fluoride are regulated components in water destined to human consumption. Background values of these components were estimated integrating geochemical, hierarchical cluster (Templ et al., 2008) and Geographical Information System (GIS) methods.

The water chemistry was investigated on the basis of dissolved components Ca^{2+} , Mg^{2+} , Na^+ , K^+ , HCO_3^- , Cl^- , SO_4^{2-} and F^- . Background concentrations of chloride, sulfate and fluoride were estimated for each group of waters identified by cluster analyses. The GIS method was used for mapping and spatial visualization. This research was carried out in Sardinia (Italy). Because industrial activities and intensive agriculture occupy only minor parts in Sardinia, and the population is mostly concentrated in few towns, large areas are potentially unaffected by anthropogenic impacts. Such characteristics allowed to consider Sardinia a good site for assessing near-pristine conditions of water quality. The geological heterogeneity of the study area, i.e. aquifer lithology made up of siliciclastic to carbonate predominant rocks, with ages spanning from Cambrian to Quaternary, and a comprehensive dataset acquired from regional and local surveys, provided an additional value in estimating the background concentrations (Cidu et al., 2017).

Hierarchical cluster analysis allowed to identify hydrogeochemical groups of waters statistically distinguished (dataset: 1553 groundwater samples). Each water group was associated with the predominant lithology constituting the water bodies. Values of total dissolved solids (TDS) were a major distinguishing factor in principal clusters, whereas relative proportions of major cations and anions, and median nitrate and fluoride, distinguished the sub-clusters. Chloride and sulfate threshold values above regulations were observed respectively in water from sediments and volcanic rocks, and water interacting either with sulfides or gypsum (Table 1). These threshold values should be considered as upper limits in evaluating the good status of water bodies in Sardinia.

Table 1. Threshold values of chloride, sulfate and fluoride in principal clusters. Values in bold are above Italian limits of 250 mg/L (Legislative Decrees 152/2006)

Cluster	Predominant lithology in water bodies	Threshold values		
		Chloride mg/L	Sulfate mg/L	Fluoride mg/L
G1	Quaternary & Tertiary sediments	422	135	0.67
G2	Quaternary basalts & granitic rocks	155	59	0.45
G3	Quaternary & Tertiary sediments - volcanic rocks	1280	446	1.33
G4	Mesozoic & Paleozoic carbonatic rocks	180	103	0.64

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