



Comparison of different methods to assess natural background levels in groundwater bodies in southern Europe

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The assessment of the natural background levels (NBLs) of a substance or element is important to distinguish anthropogenic pollution from contamination of natural origin in groundwater bodies. NBLs are the result of different atmospheric, geological, chemical and biological interaction processes during groundwater infiltration and circulation. Rainfall composition, water-rock interactions in both vadose and saturated zone, exchanges with other water bodies and residence time also contribute to determine the groundwater natural composition. Nowadays there are different methods to assess NBLs but the main concern is that they may provide different results.

In the European legislative context, the Groundwater Directive (2006/118/EC) requests to EU Member States to derive appropriate threshold values (TV) for several potentially harmful substances, taking into account NBLs when necessary, in order to assess the chemical status of groundwater bodies.

In the framework of a common project between Italy (CNR) and Portugal (FCT), several groundwater bodies were taken into account in different regions of Italy (Latium and Campania) and Portugal. The general objective is the definition of a sound comprehensive methodology for NBL assessment at groundwater body scale, suitable to different hydrogeological settings through comparing diverse case studies and different approaches. The Italian case studies are located in volcanic or volcano-sedimentary geological contexts, where high concentrations of substances such as As, F, Fe, Mn among others in groundwater are well known. The Portuguese case studies are located in carbonate and porous media aquifers.

Several data sets were explored with the use of statistical as well as mathematical procedures in order to determine a threshold between natural and anthropogenic concentration. Today essentially two groups of methods are proposed, the first ascribed to the probability plots (PP method), the second based on the selection of the uninfluenced water samples corresponding the natural population (Pre-Selection method, "PS"). PPs are grounded on the principle that different sources generate different data populations which can be separated by statistical procedures. Aligned points indicate samples belonging to a single population that originated from a unique process, while changes in slope of the curves may indicate passages between different populations. The PS method proposes to select only those samples which are not, or very little, influenced by human activities, e.g. removing those with high nitrate or other markers of anthropic contamination. In the residual data set one value, usually one percentile is chosen as representative of the NBL, meaning that all concentrations exceeding that level should be ascribed to anthropogenic sources.

NBLs for several substances including As, F, Fe and Mn have been determined using both PS methods and probability plots in linear and logarithmic scale. The comparison of results shows, even for the same case study, a large range of values depending on the method used, on the pre-selection criteria, on the chosen percentile especially in case of strongly skewed distribution. The need for a sound methodology, to establish a formal value of the NBLs, is perceived especially from a legal point of view both at the national and European level.