PROPOSAL FOR AN INTEGRATED METHOD OF NATURAL BACKGROUND LEVELS ASSESSMENT IN GROUNDWATER

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Inorganic potentially toxic elements in groundwater may derive from both natural processes and anthropogenic activities. Natural background levels are often defined to distinguish any anthropic contribution and eventually assess the environmental status of groundwater bodies, as requested by the Water Framework Directive. The geochemical approach for the NBL assessment requires the identification of groundwaters free from the human impact, using markers such as nitrates/ammonia in oxidising/reducing environments, organic compounds, isotopes, etc. The statistical approach involves the separation of uninfluenced and influenced populations by means of statistical procedures. In this study, we compare different study cases in the Plio-Pleistocene volcanic province of Latium (central Italy) with the aim of integrating the two approaches for the definition of the NBL.

After the validation of the total dataset, redox facies were distinguished on the grounds of Eh (> 100 mV) and O_2 (> 3 mg/L). In the geochemical approach, the influenced samples were discarded using NO_3/NH_4 (oxidising/reducing facies) to obtain the "pre-selected dataset". Instead of a fixed threshold for nitrates (e.g. 10 mg/L or 50 mg/L), we used a local threshold identified with the statistical techniques, representing the upper limit of the ambient (i.e. no longer pristine) nitrate background, provided it does not exceed 50 mg/L. For reducing facies, NH_4 (up to 0.5 mg/L) should be used.

Then, the natural background levels of As, F, Mn and SO_4 were estimated as follows. When data approximate one normal population, we assume that they all refer to the background population and the maximum value is proposed as NBL. When one or more outliers exist, we assume they represent different populations and processes. Regardless their anthropic or natural origin, the outliers usually represent localised phenomena, which differentiate from the background, and should be treated as such. Hence, the NBL was set at the boundary between the basal population and the outliers, identified with statistical techniques such as "box & whisker", probability plots, and others. However, when the outliers are certainly to be ascribed to natural processes, they should be considered when assessing the local NBL for monitoring purposes.

The geochemical approach and the diverse statistical methods applied, have provided often very variable results, with differences even of one order of magnitude in the defined NBLs, in particular for manganese. Hypothesis on normal distribution of data has been the main criterion for the final choice of NBLs. The values obtained for As and F are broadly comparable among the study cases and are always above the EU Drinking Water standards, while Mn and SO_4 show rather different NBLs, largely below the limits of the Italian legislation for the groundwater body chemical status definition.

The integration between multiple methods allows for a reasonable assessment of the natural

background levels in the study cases. The proposed procedure maintains the advantages of the pre-selection method (simplicity and reproducibility), minimising the main critical points, such as the choice of the nitrate threshold for the pre-selection of samples and the choice of the percentile to be adopted as NBL.