Multivariate Analysis of Water Geochemical Data: A Case Study in the Chiavenna Valley (Central Alps, Northern Italy)

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Geochemistry of running and ground waters includes simultaneous measurements of many chemical and physical parameters and the application of multivariate methodologies is often a tool required for a large data set in order to explain the whole structure of the data base. This work presents an application example aimed to investigate water chemistry of about 200 samples collected from Chiavenna Valley (Northern Italy) by using this type of methodologies. Chiavenna Valley is a NNW-SSE elongated basin with a surface of about 700km² and geologically consists of schistose and para-gneiss and meta-granitoid crystalline rocks, sedimentary formations and a relatively well developed Quaternary cover (Sciesa, 1991). Preliminary investigations (Vaselli et al., 1999) of running and ground waters indicated that their chemical composition is mainly characterised by a Ca(Mg)-HCO₃ composition although Ca(Mg)-SO4 waters have been recognised in the central-northern part of the valley. With respect to the nitrogenated species (NO₂, NH_4^+ and NO_3^-), they show relatively low enrichments around the urbanised areas and tend to decrease dramatically after few hundreds meters apart. As far as the heavy metal concentration is concerned, the Chiavenna Valley can be considered a relatively pollution-free area characterised by small, possibly natural, enrichments in some toxic elements such as Sc, V, Mn, Cu, Zn, As, Ba, Pb and U. These conclusions have been achieved by using graphical methods, based on scatter plots that represent the information on both the sampling units and the variables in a single diagram. This allows the visual inspection of the position of one observation relative to another and the relative importance of each of the two variables to the position of any unit. However, when several variables have been determined a matrix array of scatter plots does not provide information on the simultaneous multiple relationships among all the variables and the samples.

In other words, the inspection is partial and a general overview on the samples and variables gathered gets difficult to be handled. Multivariate methodologies, and in this case biplot analysis, change the perspective and the data exploration starts from general (the data matrix) and tries to detect the presence of sub-compositions as a feature inherited from the whole structure. A biplot is a graphical explorative representation of the information in an n x p data matrix and the bi- refers to the two kinds of information contained in the data matrix: the information in the rows pertains to the samples or sampling units and that in the columns pertains to variables. The availability of a relatively large database on water chemistry for Chiavenna for which major, minor and trace constituents have been determined has allowed the application of biplot analysis and the detection of sub-compositions useful to describe the nature of these waters. On this ground, we could recognise 4 groups of waters with increasing water-rock interaction and mixing processes, as follows: i) precipitation-dominated waters; ii) rock-dominated waters; iii) mixing-dominated waters and iv) Permo-Mesozoic gypsum-bearing rock-dominated waters. In terms of heavy metal concentrations, the Chiavenna Valley waters seem to be closely related to these four groups. New simple diagrams to classify this water can be thus proposed and may represent an useful tool both to observe time water evolution inside the basin and to compare data collected from different areas.

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