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The role of lithology on the spatial and temporal variability of river water geochemistry in a pre-Alpine catchment

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The complexity of a riverine system and its catchment is expressed by the spatial and temporal variability of the geochemical composition of the surface waters. In particular, the solute chemistry and δ^{18}O-δD isotopic composition highlight mixing between distinct water end-members and can be a powerful tool to discriminate the contribution from different geological formations. The Posina River and its tributaries cover an area of 116 km^2, located at the foothills of the Central-Eastern Italian Alps and represent an interesting case study to understand hydrogeochemical processes in a catchment featuring a complex lithology (characterized by Triassic volcanic and carbonate rocks). In this work, we collected monthly water samples from the Posina River and its main tributaries for three years (2015-2017). Temperature and electrical conductivity were measured in the field by portable probes, and major elements and water stable isotopes were analysed by ion chromatography and laser spectroscopy, respectively. Moreover, trace elements were analysed by Inductive-coupled Mass Spectrometry in a subset of samples collected in different seasons, in order to highlight the effects of different lithologies occurring within the catchment. The electrical conductivity varied between an average value of 176 μS/cm and 281 μS/cm along the main course of the river, with sharp variations after the main confluences with the tributaries. The analyses of major elements (i.e. Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, SO_4^{2-}) highlight that, although Ca-HCO_3 hydrochemical facies is the most common, differences can be found in tributaries where volcanic rocks (mainly rhyolites and dacites) are predominant. For example, the average Na concentration (4 mg/L) observed in a tributary that flows mainly on volcanic rocks is higher than the one found in the Posina River (average of 1.6 mg/L at the outlet). These differences are supported by trace elements such as Sr, Rb and Li and the relative ratios (Sr/Rb, Sr/Li) that characterize the main lithologies in the catchment. The concentration of metals (Fe, Al, Mn, Ti), significantly increases during flood events. This was plausibly related to the remobilization of labile metals that precipitate as oxide/hydroxides during baseflow condition, but anthropogenic inputs related to human activities should be also considered. Stable isotopes data of riverine waters are consistent with the Global and the Local Meteoric Water Line. At the seasonal scale, river water isotopic composition had a small temporal variability, while during large rainfall-runoff events responded accordingly to the input of rain water. In conclusion, water stable isotopes, combined with geochemical data provide useful insights on weathering processes along the riverine profile and mixing processes with tributaries with different origins during dry and wet periods.