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## Pitfalls, questions and solutions when sampling water for stable isotope analyses along complex riverine systems

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The second largest city in Romania (Cluj-Napoca) is supplied with drinking water originating from the upper basin of Somesul Mic river (SMR). As part of an ongoing project, we aim to investigate the origin, flow and quality of water consumed in the city by collecting monthly river, lake, tap and groundwater and performing physical, chemical and stable isotope analyses (d18O and d2H in water, and d13C in DIC). However, owing to the different types of water bodies to be sampled and the local climate, with freezing conditions for up to six months in the upper basin, the results of the analyses might indicate time and space specific conditions, rather than the general hydrologic conditions we were targeting. Thus, we have modified our approach, and have devised a secondary sampling strategy in order to address these issues.

We present here a sampling strategy that aims to disentangle between different factors controlling the stable isotope composition of surface waters under different geomorphologic and climatic conditions and minimize the risk of introducing unwanted biases. Briefly, we have sampled water under both freezing and non-freezing conditions from the rivers and lakes along the main trunk of SMR and measured d18O (and d2H) in water, as well as d13C in DIC. Our data shows that the presence of ice strongly affects that stable isotope composition of river and lake water (as a result of strong kinetic processes resulting from the specifics of water solidification) and the results of these measurements are meaningless when trying to understand the connections between the various water bodies. Contrary, d13C in DIC was less affected by the freezing processes, a finding mirrored by the chemical values of the water. However, the later were strongly influenced by local geomorphologic conditions, both in summer and winter. In lakes, sampling at different locations on the surface and at different depths resulted in a wide range of stable isotope ratios for O and H, unrelated to values measured in the inflowing and outflowing streams. Overall, our data suggest that monthly stable isotope values of river and lake water along a flow path are difficult to interpret in terms of residence and transit times and mixing of sources. Thus, in regions where freezing is recurrent, kinetic fractionation processes have a contribution to the “final” stable isotope composition of water that is higher than that resulting from other (hydrological) processes. Contrary, more valuable data was obtained when the stable isotope composition of surface waters was compared with that of precipitation water, allowing for possible identification

of moisture sources and pathways feeding the local water bodies. We conclude that in order to generate valuable data, quality control must first start with designing site-specific protocols for sampling and stable isotope analyses of water and factors altering the "sought-for" values should be considered first before interpreting the results.

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