



Pearl mussel shell oxygen-18 as a long term hydrological recorder: a proof-of-concept based on Secondary Ion Mass Spectrometry

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Stable isotopes as tracers in catchment hydrology are now a commonly used tool for stream water source apportionment and soil water flow paths identification. One area where stable isotopes have been particularly effective has been for transit time analysis. In this application, time series of precipitation isotope composition are compared with time series of stream water isotope composition and the degree of damping in the seasonal cycle can be quantified via convolution with many new model approaches recently developed. But regardless of the approach used, the limiting step in such analyses is the length of streamflow record and the spatial completeness. Precipitation isotope time series now extend over several years and even decades in some settings. However, stream water isotope composition time series are short, with very few data sets spanning over more than a few years. This is a problem as many systems are undergoing changes in land use, climate, etc. What is needed in this context are datasets across a wide variety of headwater streams and for long durations. A major restriction in this respect remains the time and labor intensive collection of such data.

Here we propose to reconstruct decades of isotope signatures in stream water from freshwater mussels, more specifically the freshwater pearl mussel *Margaritifera margaritifera*. We have explored the potential for Secondary Ion Mass Spectrometry (SIMS) to quantify oxygen isotope ratios in pearl mussel shell growth bands. Our SIMS based proof-of-concept work differs from conventional shell analysis: as opposed to most routine protocols for isotopic measurements (e.g. drilling, shell crushing), the SIMS technique allows in-situ high accuracy isotopic measurements along shell growth bands (e.g. 15 μm SIMS beam spot size vs. several hundreds of μm for a drill bit diameter).

Via our SIMS based proof-of-concept work we have been able to show that the seasonality in annual sequences in freshwater pearl mussel shell material is possible for *Margaritifera margaritifera*. We found consistent $\text{d}18\text{O}$ signatures in six successive growth lines. We found similar average and median $\text{d}18\text{O}$ values for precipitation, stream water and shell material. Amplitudes in the isotope signal were highest in precipitation, while both $\text{d}18\text{O}$ signatures in stream water and shell material were characterized by a significant damping.

The spatial resolution offered by SIMS is large enough to seize isotopic variations within a single growth year. This qualifies the SIMS technique for analyzing isotopic signatures of O in shell material with a view to re-construct historical series of in-stream isotope signatures. As living archives of past environmental conditions in stream water, pearl mussels – or any other freshwater mussel – offer huge potential for considerably extending the current set of data (e.g. included in the International Atomic Energy Agency Global Network of Isotopes in Rivers). The freshwater mussel isotope archives may eventually serve to both, extend the existing records of isotopic signatures in stream water and provide isotope data for non-monitored rivers.