



Combined use of multiple tracers to identify water flow dynamics and pollutant transport

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Assessing hydrological processes, water ages and mixing ratios is crucial for sustainable water management. The surface and subsurface heterogeneity necessitate the application of multiple tracers to quantify uncertainty when identifying the above mentioned processes and observational tools operating at high temporal resolutions are required. Although a variety of tracers exists, their interpretation can differ considerably due to the mentioned heterogeneity, underlying tracer assumptions, as well as sampling and analysis limitations.

For our urban hydrological observatory, we used stable water isotopes (e.g., ^2H and ^{18}O), chlorinated solvents (e.g., perchloroethylene (PCE)), dissolved gas concentrations (e.g. He, Ar, Kr, N_2 , and O_2), dye and heat tracers, chemically (persistent) anthropogenic markers (e.g., artificial sweeteners) and ^3H and tritiogenic ^3He concentrations to assess water flow paths and mixing between artificially infiltrated surface water and groundwater. Moreover, we explain the origin and spatial distribution of PCE contamination found at our study site with our multi-tracer approach.

Especially, the recent developments of portable field-operated gas equilibrium membrane inlet mass spectrometer (GE-MIMS) systems provide a unique opportunity to measure dissolved gas concentrations, such as ^4He with a high temporal resolution at relatively low costs. Although the GE-MIMS are not capable of providing apparent water ages, ^4He accumulation rates are often obtained from $^3\text{H}/^3\text{He}$ ages and it has been shown that non-atmospheric ^4He concentrations determined in the laboratory (e.g., by static (noble gas) mass spectrometry) and by field-based (GE-MIMS) methods closely agree. This agreement allowed us to establishing an inter-relationship between $^3\text{H}/^3\text{He}$ apparent water ages and the non-atmospheric ^4He excess (e.g., calibrating the ^4He excess in terms of residence time).

We demonstrate that the ^4He excess concentrations derived from the GE-MIMS system serve as an adequate proxy for the experimentally demanding laboratory-based analyses. We combined the obtained water ages with hydrochemical data, water isotopes ($\delta^{18}\text{O}$ and $\delta^2\text{H}$), and PCE concentrations to understand water flow dynamics and applied a developed Bayesian model to a tracer set, which includes the ^4He analyzed on-site to determine water-mixing ratios. We demonstrate that important information about flow and transport during changing boundary

conditions (e.g., infiltration rates) can only be identified with a high temporal resolution data set and that the gained information from multiple tracers and methods offered more insight and accuracy than from a single tracer.