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Comparison of different stable hydrogen isotope-ratio measurement techniques for tracer studies with deuterated water in the unsaturated zone and in groundwater.

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Stable isotopes of the water molecule have proved to be extremely useful tracers in the unsaturated zone and in groundwater. However, the use of the natural fluctuations of these isotopes as tracer signal is often limited, because the variations in isotope ratios are too small or (and) the input function is unknown. In such cases the application of isotopically enriched water as tracer could be very useful. Water enriched with the isotopes ^{18}O, ^{3}H and Deuterium have been used by several scientists around the world to describe ground-water flow (Gaspar, 1987). We have used deuterated water as a reference tracer several times, mainly in karst aquifers (Benischke et al., 2003) but also in the saturated and unsaturated zone of porous groundwater aquifers. The objective of these experiments was to compare different types of tracers and their behaviour during transport as well as the degree to be classified as conservative or non-conservative. Deuterated water has advantages over ^{18}O-enriched or depleted water, however, in that it has a smaller natural abundance in nature and it is much more affordable. It has the advantage over tritium in being non-radioactive (Becker and Coplen, 2001). Other advantages of deuterium as a groundwater tracer are that it is non toxic and the sampling is very easy. The main disadvantage of the deuterium was for a long time the expensive and time consuming analysis.

With the development of new hydrogen isotope-ratio measurement techniques, it is now possible to measure hydrogen with automated dual-inlet methods or in continuous-flow mode in full automatic way. Examples of stable hydrogen isotope-ratio measurement techniques currently are in use include the equilibration of water with hydrogen gas in the presence of a platinum catalyst (Horita et al., 1989), reduction of water to H_2 using Cr metal in automated dual-inlet (Gehre et al., 1996) or continuous-flow mode (Morrison et

al., 2001) and high temperature continuous flow pyrolysis using a carbon based reactor (Begley and Scrimgeour, 1997).

We have used three of these techniques and evaluated the advantages and disadvantages of the different methods for the application of deuterated water in groundwater tracing. The best analytical precision (<1‰) has been achieved with the automated equilibration of water (3mL) with H_2 gas in the presence of a platinum-based catalyst. However, the method is time consuming and not very useful to analyse a big number of samples in a short time. With continuous-flow isotope ratio mass spectrometry using chromium as the reducing agent we were able to measure a sequence of 100 samples per day with good analytical precision (1-2‰). The memory effect was negligible for samples in the natural abundance range of 1.5‰ δD-values. The lowest precision (2-3‰) was obtained by high temperature continuous-flow pyrolysis using a carbon based reactor. In addition, a clear memory effect was observed when waters with very different δD-values were analyzed sequentially. In result of our investigations the on-line continuous-flow reduction of waters with chromium as reactive reactor component has a number of significant advantages over automated equilibration and on-line carbon-based pyrolysis. However, using some modifications of the reactor design, the memory of a carbon based reactor can be reduced to values below 1.5 % (Gehre, 2004).

Comparing deuterium with other groundwater tracers we found that Deuterium and Bromide have showed the highest degree of conservativeness, whereas Na-Fluorescein and moreover Sulphorhodamine G have showed significant retardation as it was expected (Benischke et al., 2003). A direct comparison was difficult due to the different sensitivity of the analytical procedures, because sensitivity of dye tracer analytics as well as Bromide and Deuterium analytics differ from each other over several order of magnitudes. We found that the minimum detectable concentration of deuterium in practice is about 0.1 mg/L above background. Similar values have been reported by Becker and Coplen (2001).

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