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Chemograph analysis of two herbicides in a German karst aquifer

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The dynamic of spring discharge of mature karst aquifers shows after strong precipitation events: Karst spring discharge increases rapidly and strongly, the chemical composition of the spring water is altered and contaminants may be transported from the land-surface towards the spring with the percolating rainwater. Contrary to rapid water transport, high travel times have been observed for parts of the spring discharge, employing stable isotopes as indicators.
Monitoring the concentrations of Ca2+ and Cl- in spring water after a precipitation event one may observe the following: After a first increase, the concentrations of Ca2+ drop below the pre-event value, due to dilution with lowly mineralized rain water. On the other hand the concentrations of Cl- increase quickly and return to their background values nearly as fast. This difference in behavior arises from the different origins of these two inorganic ions. Ca2+ in spring water originates mainly from the dissolution of the carbonatic bedrock, while Cl- might be transported from the land-surface (e.g. from road salt) towards the spring.
To investigate the dynamic of water in the Gallusquelle catchment in southwest Germany a one year sampling campaign was conducted, using different herbicides as indicator compounds. Depending on discharge conditions the sampling interval varied between 3 hours and several days. Among others, the currently applied and chemically unstable metazachlor was observed together with atrazine, which is prohibited since more than 20 years in Germany.
While the detection frequency of atrazine in the spring water samples was nearly 100%, the concentrations ranged only up to 5.2 ng/L. On the other hand, the currently applied metazachlor was only detected in 30.7% of the samples, but its maximum concentration was 71.9 ng/L.
An interesting feature was the different temporal concentration pattern of the two investigated herbicides: After precipitation events the concentration of metazachlor in spring water increased rapidly to relatively high values and dropped below the detection limit after a short period of time. Its general concentration pattern is comparable to Cl-. Atrazine on the other hand, shows a concentration pattern, comparable to Ca2+. After a first increase, the concentration of atrazine dropped below the pre-event value.
Concluding, one may state: While metazachlor is introduced into the aquifer system with percolating rainwater after precipitation events, the source for atrazine is most likely situated within the aquifer storage itself, e.g. in the fissured rock matrix.