



Modeling of isotope fractionation at the catchment scale: How promising is compound specific isotope analysis (CSIA) as a tool for analyzing diffuse pollution by agrochemicals?

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Concentration measurements are indispensable for the assessment of subsurface and surface water pollution by agrochemicals such as pesticides. However, monitoring data is often ambiguous and easily misinterpreted as a decrease in concentration could be caused by transformation, dilution or changes in the application of the pesticide. In this context, compound specific isotope analysis (CSIA) has recently emerged as a complementary monitoring technique. It is based on the measurement of the isotopic composition (e.g. $\delta^{13}\text{C}$ and $\delta^2\text{H}$) of the contaminant. Since transformation processes are likely accompanied by isotope fractionation, thus a change in this composition, CSIA offers the opportunity to gain additional knowledge about transport and degradation processes as well as to track pollutants back to their sources.

Isotopic techniques have not yet been applied in a comprehensive way in the analysis of catchment-wide organic pollution. We therefore incorporated fractionation processes associated with the fate of pesticides into the numerical flow and solute transport model HydroGeoSphere in order to assess the feasibility of CSIA within the context of catchment monitoring.

The model was set up for a hypothetical hillslope transect which drains into a river. Reactive solute transport was driven by two pesticides applications within one year and actual data for rainfall and potential evapotranspiration from a meteorological station in the Netherlands. Degradation of the pesticide was assumed to take place at a higher rate under the prevailing oxic conditions in the topsoil than in deeper, anoxic subsurface layers. In terms of CSIA, these two degradation pathways were associated with different strengths of isotope fractionation for both hydrogen and carbon atoms. By simulating changes in $\delta^{13}\text{C}$ and $\delta^2\text{H}$, the share of the oxic and the anoxic reaction on the overall degradation could be assessed.

Model results suggest that CSIA is suitable for assessing degradation of diffuse agrochemical pollutants in a relatively simple hydrological system. The simulated shifts in isotopic signals are within a range that could be detected with current isotope analytics. Concentrations in the stream vary significantly only for a short period during and after intense rainfall events. In contrast, CSIA values reveal longer response times such that isotopic shifts are likely to be detected in samples with a coarser temporal resolution. Rainfall events which result in fast lateral subsurface transport from the pollution source to the stream can be separated from those that lead to pollution migration through deeper subsurface zones with much longer travel times. Two-dimensional CSIA highlights an increasing importance of the oxic reaction in the topsoil during the wetter period of the year.

In order to examine to which extent CSIA is applicable for more complex hydrological systems, it is projected to simulate isotope fractionation in a 3-dimensional catchment featuring additional processes such as migration from several pollution sources or in-stream degradation.