



Compound-specific stable isotope analysis of herbicides in stream water: a combined monitoring and modeling approach to assess pollutant degradation at catchment scale

Stefanie Lutz (1), Ype Van der Velde (2), Omnia Elsayed (3), Gwenael Imfeld (3), Marie Lefrancq (3), Sylvain Payraudeau (3), and Boris Van Breukelen (1)

(1) Critical Zone Hydrology Group, VU University Amsterdam, Faculteit der Aard- en Levenswetenschappen, Amsterdam, Netherlands, (2) WU Environmental Sciences, Subdivision Soil Geography and Landscape, Wageningen University and Research centre, Wageningen, The Netherlands, (3) Laboratory of Hydrology and Geochemistry of Strasbourg (LHyGeS), University of Strasbourg/ENGEES, France

Compound-specific stable isotope analysis (CSIA) measures the isotopic composition of a compound, i.e. the relative abundance of light and heavy stable isotopes of an element contained in the compound (e.g. ^{12}C and ^{13}C). As degradation processes may induce a change in isotopic composition (i.e. isotope fractionation), CSIA allows distinguishing degradation from non-destructive processes such as dilution or sorption. CSIA can be combined with model-assisted interpretation to evaluate degradation of contaminants in the environment. Although CSIA methods have also been developed for diffuse pollutants such as pesticides and nitrate, they have not yet been continuously applied in monitoring of diffuse pollution in surface water.

Results of a virtual experiment of isotope fractionation at hillslope scale have suggested that CSIA qualifies as a feasible and useful complement to concentration measurements of diffuse pollutants (Lutz et al., 2013). We now present the first continuously measured concentration and carbon CSIA data of herbicides from a 49-ha agricultural catchment (Alsace, France). Stream concentrations of two chloroacetanilide herbicides, i.e. S-metolachlor and acetochlor, were highest ($65 \mu\text{g/L}$) following an extreme rainfall event in the first month after herbicide application, and subsequently decreased to background concentration level ($0.1 \mu\text{g/L}$). This decrease was accompanied by an increase of more than 2 ‰ in carbon isotope ratios, which was also observed in surface runoff samples from a plot experiment in the study catchment. The increase of carbon isotope ratios over time indicates the occurrence of herbicide degradation during transport to the stream, and thus demonstrates the advantage of CSIA over pesticide concentration measurements only.

Despite providing evidence of herbicide degradation, the field CSIA data do not allow for a comprehensive characterization of herbicide sources, fate and transport in the study catchment. Therefore, we developed a model of herbicide concentrations and isotope ratios at catchment scale that is based on the description of flow and transport by travel time distributions. The model simulates transient flow, herbicide degradation, and partial herbicide uptake by plants. By validating various formulations of herbicide transport and degradation against the measured CSIA data, we were able to analyze the role of surface and subsurface flow routes and identify dominant processes affecting herbicide degradation in the study catchment.