



## Persistence of S-metolachlor at the catchment scale investigated by compound-specific isotope analysis (CSIA)

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Pesticide pollution of agriculturally impacted ground and surface water is ubiquitous with concentrations exceeding drinkable water limits or environmental quality standards (EQS). In this context, Compound-Specific Isotope Analysis (CSIA) opens novel opportunities to follow-up pesticide persistence and degradation from agricultural soil to rivers at the catchment scale. While CSIA has been used for decades to investigate in situ degradation of legacy compounds at contaminated aquifers, its application to evaluate pesticide degradation and transport in soil and surface water is mostly lacking due to analytical and conceptual challenges. Here we show that degradation estimates of the herbicide S-metolachlor at the catchment scale based on a classical mass balance, accounting for the different catchment's compartments, were similar to those based on CSIA data. S-metolachlor CSIA based on carbon isotope ratios was carried out from soil samples collected monthly across the 120-km<sup>2</sup> Souffel catchment (Bas-Rhin, East of France) and from flow-proportional river samples collected at the outlet of the catchment from March 1 to October 1 2019. Based on CSIA data, 98% ± 20% of the S-metolachlor was degraded over agricultural season. This converged with estimates of S-metolachlor degradation (98.9 ± 4.7%; mean ± SD) obtained using the classical mass balance. Interestingly, degradation mainly occurred in soil, while only 12.3 ± 3.1% of S-metolachlor degraded in river on a total river length of 79 km. The wastewater treatment plants (WWTPs) contributed to 52 ± 18% of the total input mass of S-metolachlor in river. However, similar isotope signatures of S-metolachlor for diffuse and WWTP sources hampered the identification of pesticide sources. From 0.04 to 0.12% of the S-metolachlor applied was exported from the catchment during the agricultural season, which is similar to previous S-metolachlor exports estimated in other catchments. Although a little fraction of S-metolachlor was exported, 81% and 93% of the river samples exceeded the drinkable water limit (0.1 µg.L<sup>-1</sup>) and the EQS for S-metolachlor (0.07 µg.L<sup>-1</sup>), respectively. Overall, we anticipate that pesticide CSIA deployed systematically in agricultural catchments could help water managers to estimate pesticide persistence and sources to address regulatory and monitoring strategies.