Evaluation of chloroacetanilide herbicides in wetland sytems using enantiomer- and compound-specific isotope analysis

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Chloroacetanilide herbicides are widely used in the European Union and the United States to control annual grasses. The transport and the degradation of metolachlor, alachlor and acetochlor were evaluated in different wetland systems using several analytical approaches, including the quantification of parent compounds and their degradation products, as well as enantiomer- and compound-specific isotope analysis.

In lab-scale wetlands (0.02 m^2), mass dissipation averaged 61 ± 14%, 52 ± 12% and 29 ± 19% for acetochlor, alachlor and metolachlor, respectively. Degradation of the chloroacetanilide herbicides into ethanesulfonic acid (ESA) and oxanilic acid (OA) prevailed after day 70. Enantiomeric fractionation (EF) for *rac*-metolachlor was 0.480 ± 0.005 in the rhizospheric zone, indicating enantioselective biodegradation. CSIA of chloroacetanilides in the wetlands revealed carbon isotope fractionation for alachlor (ε_{bulk} = -2.0 ± 0.3‰) and acetochlor (ε_{bulk} = -3.4 ± 0.5‰), indicating *in situ* biodegradation.

In planted bed wetlands (7 m^2), degradation of the chiral herbicide *S*-metolachlor was evaluated under different hydrological regimes (batch vs. continuous flow). Dissipation rates > 93% in the batch system combined with CSIA confirmed that *in situ* biodegradation of *S*-metolachlor occurred under alternate oxic-anoxic conditions ($\Delta\delta^{13}C_{inlet-outlet}$ = 1.2‰). OXA prevailed in the batch flow wetland, whereas ESA prevailed in the continuous flow system, indicating distinct degradation pathways under these two conditions. No significant enantiomeric fractionation of *S*-metolachlor occurred in the wetlands. Complementary analytical approaches may be combined to evaluate the transport and the degradation of chiral micropolluants in redox-dynamic environments such as wetlands.