



Dual isotope plots reflect transformation pathways of pesticides: Potential to assess pesticide fate and elucidate transformation mechanisms

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The degradation of pesticides in deeper soil layers and groundwater is of growing interest, because they have repeatedly been found in drinking water supply wells and may pose a risk to future water resources. Current assessment schemes face a common problem, however: natural degradation often cannot be reliably assessed by concentration measurements alone, since mass balances are difficult to establish and transformation cannot be distinguished from sorption or dilution. Even detection of metabolites may only give an incomplete picture. When several transformation pathways occur, some metabolites may be degraded or form bound residues so that the associated pathways may be missed.

Our research shows that dual isotope plots derived from compound specific isotope analysis offer a novel approach to give additional, complementary insight into the natural degradation of pesticides. Detection of metabolites is not required, since the isotope fractionation can be fully observed in the pesticide itself.

Specifically, different initial biotransformation reactions of the phenylurea herbicide isoproturon (3-(4-isopropylphenyl)-1,1-dimethylurea) in pure culture experiments with bacterial and fungal strains showed strongly pathway-dependent isotope fractionation. When analyzing isotopic changes in different parts of the isoproturon molecule, hydroxylation of the isopropyl group by fungi was found to be associated with C and H isotope fractionation. In contrast, hydrolysis by *Arthrobacter globiformis* D47 caused strong C and N isotope fractionation, albeit in a different manner than abiotic hydrolysis so that isotope measurements can distinguish between both modes of transformation.

Likewise, we observed highly pathway-dependent C and N isotope fractionation of atrazine (1-chloro-3-ethylamino-5-isopropylamino-2,4,6-triazine). Desalkylation of atrazine by *Rhodococcus* sp. strain NI86/21 resulted in enrichment of both 13-C and 15-N in atrazine, whereas hydrolysis to hydroxyatrazine by *Chelatobacter heintzii*, *Pseudomonas* sp. ADP and *Arthrobacter aurescens* TC1 gave enrichment of 13-C, but depletion of 15-N. Comparison with abiotic reference experiments provided novel insight into the underlying enzymatic transformation mechanisms.

Our investigations show how characteristic isotope patterns may significantly add to the present understanding of the environmental fate of pesticides.