



Carbon and Nitrogen Isotope Analysis of Atrazine and Desethylatrazine at Sub- $\mu\text{g/L}$ Concentrations in Groundwater

Kathrin Schreglmann, Martina Hoeche, Sibylle Steinbeiss, Sandra Reinnicke, and Martin Elsner
Helmholtz Zentrum München, German Research Center for Environmental Health, Institute of Groundwater Ecology,
Neuherberg, Germany(kathrin.schreglmann@helmholtz-muenchen.de)

Environmental degradation of organic micropollutants is difficult to monitor due to their diffuse and ubiquitous input. Current approaches – concentrations measurements over time, or daughter-to-parent compound ratios – may fall short, because they do not consider dilution, compound-specific sorption characteristics or alternative degradation pathways. Compound specific isotope analysis (CSIA) offers an alternative approach based on evidence from isotope values. Until now, however, the relatively high limits for precise isotope analysis by gas chromatography - isotope ratio mass spectrometry (GC-IRMS) have impeded CSIA of sub $\mu\text{g/L}$ scale micropollutant concentrations in field samples.

We present the first measurements of C and N isotope ratios of the herbicide atrazine and its metabolite desethylatrazine at concentrations of 100 to 1000 ng/L in natural groundwater samples. Solid phase extraction and preparative HPLC were tested and validated for preconcentration and cleanup of groundwater samples of up to 10 liters without bias by isotope effects. Matrix interferences after solid phase extraction could be greatly reduced by a preparative HPLC cleanup step prior to GC-IRMS analysis. Sensitivity was increased by a factor of 6 to 8 by changing the injection method from large-volume-injection to cold-on-column injection on the GC-IRMS system. Carbon and nitrogen isotope values of field samples showed no obvious correlation with concentrations or desethylatrazine-to-atrazine ratios.

Contrary to expectations, however, $\delta^{13}\text{C}$ values of desethylatrazine were consistently less negative than those of atrazine from the same sites. Potentially, this line of evidence may contain information about further desethylatrazine degradation. In such a case the common practice of using desethylatrazine-to-atrazine ratios would underestimate natural atrazine degradation.