

## Compound specific carbon and nitrogen isotope analysis of pesticides: Optimization of derivatization and combustion oven conditions

S. Reinnicke<sup>1</sup>, A. Bernstein<sup>1</sup>, M. Krummen<sup>2</sup>, D. Juchelka<sup>2</sup>, A. W. Hilkert<sup>2</sup>, M. Elsner<sup>1</sup>

<sup>1</sup>Helmholtz Zentrum München, German Research Center for Environmental Health (GmbH),  
Institute of Groundwater Ecology, Neuherberg, Germany

<sup>2</sup>Thermo Fisher Scientific, Bremen, Germany

Compound specific isotope analysis (CSIA) by gas chromatography-isotope ratio mass spectrometry (GC-IRMS) has become a promising tool in environmental and forensic studies. Our current research aims at developing this approach further to assess also natural transformation of pesticides. This study focuses on the development of robust and reproducible carbon and nitrogen compound specific isotope analysis for two frequently detected pesticides, bentazone and 2,6-dichlorobenzamid (dichlobenil) as well as for its metabolite 2,6-dichlorobenzamid (BAM). Bentazone is little volatile and therefore requires derivatization prior to measurement by GC-IRMS. Dichlobenil as well as its metabolite BAM are amenable to GC-IRMS analysis, but require optimization of the combustion process for measurement of nitrogen isotopes. We performed derivatization of bentazone with a temperature programmable injector. Solutions of bentazone and the derivatization agent trimethylsulfonium hydroxide (TMSH) were injected at 40°C, and the injector was heated to 250°C where derivatization took place. In the tested concentration range (4000 to 5000 ppm) accurate and precise  $\delta^{15}\text{N}$  values of  $-0.63 \pm 0.3\text{‰}$  were observed for the bentazone derivative when TMSH was used in a small excess. This value was in perfect agreement with results from elemental analyzer-IRMS ( $-0.62 \pm 0.03\text{‰}$ ). In contrast, carbon isotope values  $\delta^{13}\text{C}$  of the derivative became more positive with increasing excess of TMSH until, at an excess of 250 or more, constant and reproducible  $\delta^{13}\text{C}$  values ( $\text{SD} < 0.6\text{‰}$ ) were obtained for bentazone concentrations between 3 and 300 ppm. Due to the additional carbon atom introduced in the derivatization process, the measured  $\delta^{13}\text{C}$  value showed a systematic offset compared to values measured with EA-IRMS which can be corrected for by comparison with standards. For dichlobenil and BAM, accurate and reproducible  $\delta^{13}\text{C}$  values were obtained using a commercial CuO/NiO/Pt oven and combustion conditions recommended by the manufacturer Thermo Fisher Scientific. In contrast, for measurements of  $\delta^{15}\text{N}$  values combustion oven conditions proved critical. We present first results with a self-made oven, a conventional Thermo reactor, and with a new type of Thermo reactors sold in connection with the new GC-Isolink interface.