



Compound Specific Carbon and Nitrogen Isotope Analysis of Pesticides: Optimization of Derivatization and Combustion Oven Conditions

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Pesticides are an important threat to groundwater. Determination of con-taminant concentrations alone is often not sufficient for an adequate as-sessment, since processes like dilution and sorption can lead to an appar-ent reduction but not to actual elimination by transformation into non-toxic compounds. On the other hand, measurement of changes in isotope ratios have been shown to be a powerful indicator of natural degradation reactions, due to the kinetic isotope effects associated with (bio)chemical transformations. In a novel approach, we therefore use compound specific isotope analysis (CSIA) to assess natural transformation of pesticides.

The goal of this study was to develop 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). All three substances re-quire special treatment, due to their chemical structure. Bentazone is little volatile and therefore requires derivatization prior to measurement by gas chromatography-isotope ratio mass spectrometry (GC-IRMS). Dichlobenil as well as its metabolite BAM are amenable to GC-IRMS analysis, but re-quire optimization of the combustion process for measurement of nitrogen isotopes.

We performed derivatization of bentazone with a temperature program-mable injector. Solutions of bentazone and the derivatization agent trimethylsulfonium hydroxide (TMSH) were injected at 40°C, and the in-jector 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 excess. This value was in perfect agreement with results from elemental analyzer-IRMS (EA-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 a TMSH excess of 250 or more, constant and re-producible $\delta^{13}\text{C}$ values ($\text{SD} < 0.6\text{‰}$) were obtained for bentazone con-centrations 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 ob-tained using a commercial CuO/NiO/Pt oven and combustion conditions recommended by the manufacturer Thermo Fisher Scientific (800°C or 940°C). For dichlobenil minimum amplitudes (m/z 44) of 250 mV and for BAM minimum amplitudes of 500 mV were required for precise and accu-rate data. 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 operating at either 940 or 980°C, and with a new type of Thermo reactors sold in connection with the new GC-Isolink interface.