Nitrogen isotope analysis to trace sources and degradation of glyphosate and its metabolite AMPA

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To assess sources and degradation of the herbicide glyphosate (N-phosphonomethyl) glycine) and its metabolite AMPA (aminomethylphosphonic acid) in the environment, concentration measurements alone are often inconclusive [1].To advance an alternative approach, we present compound-specific nitrogen isotope analysis (¹⁵N/¹⁴N) of glyphosate and its metabolite AMPA by derivatization-gas derivatization-gas chromatography/isotope ratio mass spectrometry (GC/IRMS). In the first step the N-H group was derivatized with isopropyl chloroformate (iso-PCF). In the second step, remaining acidic groups were methylated with trimethylsilyldiazomethane (TMSD) [2]. Accurate δ^{15} N values were obtained (deviation from elemental analyzer-IRMS): 0.23% ± 0.88% for glyphosate and $0.37\% \pm 0.70\%$ for AMPA with a limit of precise $\delta^{15}N$ measurements of 150 ng (glyphosate) and 250 ng (AMPA), respectively. Isotope values in commercial products ranged from +3.3% to -1.9% for $\delta^{15}N$ and from -24.6% to -33.7% for δ^{13} C (measured with liquid chromatography-IRMS) [3].Nitrogen isotope fractionation during abiotic degradation of glyphosate with manganese dioxide (MnO₂) were as high as ε_{N} = $-17\% \pm 0.5\%$ indicating that AMPA formation by C-N bond cleavage rather than sarcosine formation by C-P bond cleavage [4] was the dominant initial step. Dual element isotope plots illustrate the potential of combined carbon and nitrogen isotopes analysis to trace sources and environmental fate of glyphosate and AMPA [5].

[1] G. Imfeld, M. Lefrancq, E. Maillard, S. Payraudeau (2012) *Chemosphere*, 471-479 [2] H. Kataoka, S. Ryu, N Sakiyama, M. Makita (1996) J. Chromatogr A, 726, 253-258 [3] D. M. Kujawinski, J. B. Wolbert L. Zhang, M. A. Jochmann,(2013) *Ana Bioanal Chem*, 2869–2878 [4]K.A, Barret, M.B. McBride (2005) *Environ. Sci. Technol*, 9222-9228 [5] M. Elsner, M. A. Jochmann, T. B. Hofstetter, D. Hunkeler, A. Bernstein, T. C. Schmidt, A. Schimmelman (2012) *Anal Bioanal Chem* 2471-2491