

Mechanism of degradation and degradation pathways of glyphosate

DEB P. JAISI^{1*}, HUI LI^{1*}, PRAJWAL PAUDEL¹² AND ADAM F. WALLACE³

¹Department of Plant and Soil Sciences, University of Delaware, Newark, DE USA (*jaisi@udel.edu; lihui@udel.edu)

²Department of Chemistry and Biochemistry, University of Delaware, Newark, DE USA

³Department of Geological Sciences, University of Delaware, Newark, DE USA

The organophosphonate N-(phosphonomethyl) glycine, commonly known as glyphosate, is a broad spectrum systemic herbicide. Widespread application of glyphosate primarily for weed control in agriculture and its presence detected in soils and environmental waters has elevated public concern that it may potentially harm animal and human populations and the environment. Here we present results from experimental studies aimed at determining the fate of glyphosate particularly the mechanism of glyphosate degradation and tracing glyphosate and its degradation products using an array of NMR, molecular simulation, and stable isotope methods. Our results show that the preference of C–P or C–N bond cleavage varies with changing glyphosate: Mn oxide ratio indicating sorption induced conformational change on mineral surface potentially plays a major role on the bond cleavage. Molecular simulation results revealed that the C–P bond cleavage was more facile and catalyzed more readily by hydroxyl radical. $\delta^{18}\text{O}_p$ values of orthophosphate produced from glyphosate degradation in ¹⁸O labeled oxygen and water indicated that C–P bond cleavage incorporates 19% (out of 25%, i.e., one out of four oxygen atoms in PO₄) O atoms from water. The mechanisms of C–P and C–N bond cleavage are presumed to be different and it is likely that C–P bond cleavage occurs through nucleophilic substitution while C–N bond cleavage is promoted by radical mediated reaction. Overall, our results highlight the distinction between C–P and C–N bond cleavage mechanisms and corresponding intermediate products and the isotope tracer to differentiate sources and products of glyphosate in the environment.