Advancing Non-Targeted LC-MS/MS Approaches for Aqueous Degradation Products of Pesticides and Polymers

by

Joules Provenzano

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ABSTRACT

Modern environmental chemistry increasingly recognizes that contaminant fate emerges from coupled transport and transformation of complex chemical mixtures rather than isolated compounds. This thesis develops and applies non-target liquid chromatography–tandem mass spectrometry (LC–MS/MS) methods and computational tools to detect transformation products for both pesticides and polymers in aqueous systems. Together, these studies aim to close critical data gaps for classes of chemicals that are poorly represented in existing standards and libraries.

The first study established an experimental and data-analysis platform for "pesticide degradomics," tracking the degradation of 12 widely used pesticides both individually and in a one-pot mixture under simulated solar irradiation. High-resolution LC–MS/MS, coupled with open-source feature detection, molecular networking, and formula annotation, was used to follow parent loss, library-matched products, and unknown features through time, yielding time-resolved "degradomes" for each condition. Pesticides degraded more rapidly in mixtures than in isolation, decay profiles frequently deviated from pseudo-first-order kinetics, and unique transformation products formed in both single-compound and mixture experiments. These results demonstrate that mixture effects and emergent pathways can substantially alter environmental fate relative to single-compound tests and illustrate how non-target workflows can capture these dynamics at scale.

The second study focused on improving detection of environmental polymer degradation products by generating and screening predicted MS/MS libraries. A virtual oligomer library and associated hydrolysis, photolysis, and biodegradation products were enumerated for a set of environmentally relevant polymers, and MS/MS spectra were predicted for both polymer-derived structures and non-polymer reference compounds. This generated oligomer and transformation product library (PolyDegLib) was then used to screen experimental datasets, enabling higher detection rates of polymer-derived features than existing approaches such as Kendrick mass defect analysis and mass remainder analysis. The work shows that predicted spectral libraries can substantially extend annotation coverage for polymers where authentic standards and reference spectra are scarce.

Taken together, the methods and case studies in this thesis advance non-target LC–MS/MS from single-compound testing toward mixture-aware, transformation-focused environmental fate analysis for both pesticides and polymers. The pesticide degradomics platform provides a route to characterization of mixture-dependent degradation behavior and product formation, while the polymer work demonstrates that predicted spectral libraries can recover degradation products in systems with limited reference data. More broadly, these contributions help establish experimental and computational foundations for mapping environmental “degradomes” and for integrating reaction and spectral prediction into future fate assessment and sustainable molecular design.

Thesis supervisor: Desirée L. Plata
Title: School of Engineering Distinguished Climate and Energy Professor
Associate Dean of Engineering

Thesis supervisor: Connor W. Coley
Title: Class of 1957 Career Development Professor of Chemical Engineering
Associate Professor of Chemical Engineering, Electrical Engineering and Computer Science