LC-IRMS Persulfate Oxidation: A Case Study of Neonicotinoid-Related Structures

Kara Müller^{1*}, Claudia Huber², Wolfgang Eisenreich², Martin Elsner¹, & Natalia P. Ivleva¹

² Bavarian NMR Center, Structural Membrane Biochemistry, Technical University of Munich, Garching, Germany.

*Presenting Author Email: kara.mueller@tum.de

Biodegradable polymers are desired for many agricultural applications (e.g., mulch films), where they are directly used in the fields and are difficult to retrieve entirely after their use. While conventional techniques to analyze plastic biodegradation, such as monitoring CO₂ production, miss a direct link between the polymer and the degradation products, we established a stable isotope approach using Raman microspectroscopy – stable isotope Raman microspectroscopy (SIRM) – to trace deuterium from labeled plastics into microbial biomass (Müller et al., Raman Microspectroscopy to Trace the Incorporation of Deuterium from Labeled (Micro)Plastics into Microbial Cells, submitted 2024). Based on the vibrational fingerprint spectra, we observed deuterations of single microbial cells based on the red-shift of the C-H vibrations of lipids, proteins, and DNA into the Raman-silent region after degradation of deuterated polylactic acid (dPLA). Those C-D vibrations indicated a larger D-lipid to D-protein and D-DNA ratio compared to reference experiments with D₂O and glucose d12. These findings suggest that the depolymerization products of dPLA can be used as direct building blocks for lipids.

More information on fatty acid deuteration of bulk samples can be gained by derivatization to fatty acid methyl esters with subsequent analysis by gas chromatographymass spectrometry (FAME-GC-MS). In a feasibility study we currently compare both complementary techniques for two different bacteria strains deuterated with different substrates (D₂O in combination with glucose or lactate and glucose-d12). While SIRM provides information on the total deuteration of single cells and their lipid to protein and DNA ratios, FAME-GC-MS allows to separate deuterated from non-deuterated fatty acid methyl esters based on retention times and further identifies different isotopologues. The next step is using this approach to study the biodegradation of perdeuterated polylactic acid (dPLA).

¹ Institute of Water Chemistry (IWC), Chair of Analytical Chemistry and Water Chemistry, Technical University of Munich, Garching, Germany.