This PhD dissertation, conducted within the HUMYCO project funded by the European Research Council (No. 946192), aims to enhance human biomonitoring, internal exposure assessment, and risk evaluation. Two human intervention trials were carried out to examine the toxicokinetics of tenuazonic acid (TeA) and citrinin (CIT). Analytical methods were developed and refined for quantifying these toxins in urine, feces, and capillary blood, using UPLC-MS/MS and VAMS Mitra<sup>®</sup> tips for sample collection. Chemometric filtering and suspect screening of the polar urinary metabolome, analyzed through UPLC-HRMS, were utilized to detect TeA metabolites and exposure biomarkers. Multi-compartmental toxicokinetic modeling, incorporating a hierarchical Bayesian population structure, was applied to derive the toxicokinetic parameters of TeA and CIT. Additionally, risk characterization was conducted using the internal Threshold of Toxicological Concern (iTTC) framework across various cohorts. The dissertation concludes with a summary of the key findings and discusses challenges in advancing human biomonitoring efforts.