Cyanobacteria natural products chemistry: application of metabolomics to decipher cyanopeptide mixtures from blooms in Eastern Ontario and Western Quebec

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Cyanobacterial blooms have emerged as a major threat to freshwater ecosystems around the world. Eutrophication and climate change are recognized as the major drivers of bloom formation. Cyanobacteria natural products studies have largely focused on microcystins, which are regulated in most jurisdictions because they are potent hepatotoxins and possible human carcinogens. Despite this, the profiles of most metabolites released into waterways by blooms and the risks they pose to human and ecosystem health are unknown. Common bloom forming species produce diverse mixtures of other non-ribosomal peptides, polyketides and ribosomally synthesized and post-translationally modified peptides that have received minimal research attention. A major challenge for studying cyanobacteria metabolites, mainly cyanopeptides, is their immense structural diversity. To better understand cyanobacterial natural products chemistry, we use LC-MS based metabolomic approaches to decipher their cyanopeptide profiles. From cultures grown in the lab, we examined the strain-specific cyanopeptide profiles for several *Microcystis* and *Planktothrix* strains. Each strain generated unique cyanopeptide profiles. Most identified metabolites belong to non-microcystin cyanopeptide groups which are poorly characterized. Similar metabolomic approaches were applied to bloom events and sediment cores to determine the toxigenic potential of cyanobacterial populations in the region. The cyanopeptide profiles from each sampled watercourse were generally different; however, similar from year to year for most watercourses. Together, these data enabled the prioritization of strains producing common freshwater contaminants and the discovery of new natural products. Prioritized strains are cultivated in large amounts to enable natural product purifications, structural characterizations and biological activity assessments. The objective of these studies is to address the paucity of information on the environmental concentrations and biological activities of poorly studied cyanopeptides from common bloom forming cyanobacteria.