

## A new LC-MS/MS application provides molecular level insights into DOM photo-reactivity in tropical peatland canals of Indonesia

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Recent studies have shown that peatland-exported dissolved organic matter (DOM) undergoes rapid oxidation through photochemical mineralization to CO<sub>2</sub> in unshaded canals and streams. Changes in the chemical composition of DOM during sunlight exposure can strongly impact the downstream fate of organic carbon. However, little is known about the chemical transformation pathways that drive photochemical alteration of DOM in these environments. This poses a challenge that calls for the application of innovative analytical techniques and cheminformatics tools.

Many questions about compound reactivity and transformation pathways depend largely on chemical structure. High-resolution liquid chromatography tandem mass spectrometry (LC-MS/MS), which can track molecular level changes, provides information to complement optical measurements and Fourier-transform ion cyclotron resonance mass spectrometry. In this work, LC-MS/MS was used to study photochemical transformation pathways for DOM exported from peatlands in West Kalimantan, Indonesia, recently disturbed for agricultural purposes. Peat DOM exported to tropical canal waters was exposed to sunlight in controlled experiments, isolated using solid-phase extraction, and analyzed by LC-MS/MS with an Orbitrap mass spectrometer in positive and negative mode electrospray ionization. A cheminformatics workflow was used to process chromatographic data and assign over 1200 molecular formulas in each mode.

In this study, we found that tandem MS spectra enabled the annotation of suspected chemical structures with the aid of community-based library searches. Photo-exposure time and iron concentration were found to be the main drivers of chemical change in the low-pH, aromatic DOM-rich canal waters in

Indonesia. When low- and high-iron waters were compared, we found that iron played a key role in the extent of molecular diversity of DOM after light exposure, with a greater number of transformation pathways appearing to be activated in higher-iron waters. Given that dissolved Fe concentrations can vary 40-fold across Southeast Asian canals, these findings suggest that photochemical alteration of DOM may vary substantially across the landscape. We propose potential transformations that may shed light on the impact of photochemical alteration on CO<sub>2</sub> emissions and DOM lability.

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