



Source to sink characterization of dissolved organic matter in a tropical karst system

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Karst systems are widespread surface features present on all continents. They are characterized by complex hydrology with a multitude of possible flow regimes, from diffuse seepage through the host rock to fracture flow in larger conduits. As stalagmite proxy records are important indicators of past terrestrial climate conditions, detailed understanding of the biogeochemistry of cave systems and their relationships to the overlying karst network is crucial. Microbial communities that drive the carbon cycle in caves are nourished by dissolved organic matter (DOM) carried with water into the cave system. Water samples from the Yok Balum cave in Belize were collected for DOM analysis, including soil waters, drip waters and pool waters from inside the cave. Additionally, DOM extracts from a stalagmite from the same cave were analysed to examine DOM signatures and test their applicability for reconstruction of environmental conditions. Ultrahigh-resolution mass spectrometry (via the ESI-FT-ICR-MS technique) yielded detailed molecular fingerprints on DOM from these samples. Several thousand molecular formulae of DOM compounds were identified. In addition, radiocarbon analyses were performed on the DOM samples to gain information on karst turnover times. A principal component analysis of the molecular data revealed a clear gradient between soil waters and cave waters, as soil waters were enriched in highly unsaturated oxygen-rich compounds (typical for vascular plants), which were much less abundant in drip waters. Conversely, peptides, which can originate from bacterial processes, were present only in the drip waters. Our data clearly show connectivity between the cave and overlaying soils, and reworking of DOM by the cave bacterial community. Furthermore, we found molecular evidence for the selective removal of vascular plant-derived DOM in the caves, possibly due to abiotic interactions with minerals.