



## Modern methane and dissolved organic matter radiocarbon signatures suggest rapid transfer of organic carbon from a tropical forest to the underlying subterranean estuary ecosystem

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Biogeochemical processing of dissolved organic matter, including methane, along sharp salinity gradients in subterranean estuaries greatly alters the composition of submarine groundwater discharge into the marine environment. Along the margins of coastal carbonate (karst) platforms, which account for ~25% of all coastlines, subterranean estuaries extend kilometers inland within porous bedrock, flooding extensive cave networks. This environment harbors a poorly understood, but globally dispersed, anchialine fauna (invertebrates with subterranean adaptations) and characteristic microbial communities. In Mexico's Yucatan Peninsula, microbial processing of methane and dissolved organic carbon (DOC), originating from overlying tropical soils, is the critical link for shuttling organic matter to higher trophic levels of the food web within the coastal aquifer. To better understand carbon turnover during organic matter transformations in this habitat, we collected samples for stable and radiocarbon analyses targeting the biotic and abiotic components of the carbon cycle. In the freshwater, radiocarbon signatures of terrestrially originated DOC (pMC = 105.1; [DOC] = 517  $\mu$ M;  $\delta^{13}\text{C}$  = -27.8 ‰) and methane (pMC = 101.6; [CH<sub>4</sub>] = 6460 nM;  $\delta^{13}\text{C}$  = -71.5 ‰) correspond with modern <sup>14</sup>C ages, suggesting these sources of energy within the habitat are comprised of modern carbon fixed recently by photosynthesizing primary producers at the land surface. By contrast, DOC in the deeper saline groundwater is significantly lower in concentration (21  $\mu$ M), and substantially older (pMC = 47.3, equates to 6010  $\pm$  95 <sup>14</sup>C yrs). Similarly, dissolved inorganic carbon (DIC) in the freshwater is significantly younger (pMC = 86.5, equates to 1170  $\pm$  15 <sup>14</sup>C yrs) than in the deeper saline water (pMC = 58.4, equates to 4320  $\pm$  25 <sup>14</sup>C yrs). These findings demonstrate that important sources of nutrition for the food web are intimately linked to the overlying subaerial habitat, which suggests these ecosystems are highly vulnerable to nearby land use alterations. Furthermore, this study provides new insights into carbon turnover during the process of methane production/consumption, carbon exchange, and organic matter transformation before the emission of the dissolved constituents into coastal oceans from karst subterranean estuaries. Radiocarbon and stable isotopic analyses of the resident fauna will allow us to evaluate the ecological effects of the rapid top-down transfer mechanism for methane and DOC. Beyond better understanding the sources and fate of these carbon sources, our findings have the potential to support management and conservation efforts aimed at coastal groundwater ecosystems.