

## High-resolution mapping of the carbonate system in mangrove porewaters

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Mangrove ecosystems sequester blue carbon at exceptionally high rates, primarily within sediments. However, the extent and variability of carbon stocks and fluxes remain insufficiently addressed. Organic matter degradation governs dissolved inorganic carbon (DIC) production, while the proton balance of diagenetic reactions determines the proportions of CO<sub>2</sub>, HCO<sub>3</sub><sup>-</sup>, and CO<sub>3</sub><sup>2-</sup>, influencing CO<sub>2</sub> flux and long-term carbon sequestration. Alkalinity, mainly controlled by HCO<sub>3</sub><sup>-</sup>, buffers pH fluctuations. Conventional techniques lack the spatial resolution to capture fine-scale geochemical gradients, where biologically driven perturbations and redox stratification create strong variability. This study introduces two-dimensional Diffusive Equilibrium in Thin-films (2D-DET) gels for high-resolution mapping of pH and alkalinity in mangrove porewaters. By combining in situ equilibration with colorimetric analysis, this approach provides sub-millimeter-scale insights into carbonate system dynamics. We applied this method to contrasting mangrove ecosystems along the Brazilian coast: Marapanim (MAR, Pará), a macrotidal coastal plain influenced by seasonal Amazonian rainfall, and Mamanguá (MAM, Rio de Janeiro), a sheltered bay with narrow shorelines and moderate tidal dynamics. Our results reveal substantial microscale and regional heterogeneity in pH and alkalinity. In MAM, sediments exhibit an acidic zone (pH ~5.5–6.0) transitioning to neutral conditions (pH ~7.5–8.0) towards the water column, with bioturbation enhancing mixing. Weaker hydrodynamics contribute to sharp pH gradients. Conversely, MAR shows a more uniform pH distribution (6.6–7.4), likely due to stronger diffusion and tidal mixing. Alkalinity differences further highlight ecosystem contrasts. MAR sediments exhibit lower values (~2.0–3.5 mM), suggesting limited sulfate reduction and HCO<sub>3</sub><sup>-</sup> production due to reduced vertical stratification. In

contrast, MAM sediments have higher alkalinity (~5.0–6.0 mM) potentially linked to organic alkalinity, given its sheltered setting limiting tidal energy and water exchange, and the marked presence of biofilms. This study underscores the utility of DET-2D gels in revealing microscale sedimentary dynamics. High-resolution methods are crucial for capturing the complexity of carbonate system heterogeneity across micro and regional scales. This work is part of project TROPECOS of the exploratory research program FairCarboN and received government funding managed by the Agence Nationale de la Recherche under the France 2030 program, reference ANR-22-PEXF-0012.