

Challenges in quantifying long-term air–water carbon dioxide flux using estuarine water quality data: Case study for Chesapeake Bay

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Estuaries play an uncertain but potentially important role in the global carbon cycle via CO₂ outgassing. The uncertainty mainly stems from the paucity of studies that document the full spatial and temporal variability of estuarine surface-water partial pressure of carbon dioxide ($p\text{CO}_2$). Here, we explore the potential of utilizing the abundance of pH data from historical water quality monitoring programs to fill the data void via a case study of the mainstem Chesapeake Bay (eastern United States). We calculate $p\text{CO}_2$ and the air–water CO₂ flux at monthly resolution from 1998 to 2018 from tidal fresh to polyhaline waters, paying special attention to the error estimation. The biggest error is due to the pH measurement error, and errors due to the gas transfer velocity, temporal sampling, the alkalinity mixing model, and the organic alkalinity estimation are 72, 27, 15, and 5%, respectively, of the error due to pH. Seasonal, interannual, and spatial variability in the air–water flux and surface $p\text{CO}_2$ is high, and a correlation analysis with oxygen reveals that this variability is driven largely by biological processes. Averaged over 1998–2018, the mainstem bay is a weak net source of CO₂ to the atmosphere of 1.2 (1.1, 1.3) mol m⁻² yr⁻¹ (best estimate and 95% confidence interval).