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Abstract

Sea-air CO_2 fluxes over continental shelves vary substantially in time on both seasonal and sub-seasonal scales, driven primarily by variations in surface pCO_2 due to several oceanic mechanisms. Furthermore, coastal zones have not been appropriately considered in global estimates of sea-air CO_2 fluxes, despite their importance to ecology and to productivity. In this work, we aimed to improve our understanding of the role played by shelf waters in controlling sea-air CO_2 fluxes by investigating the southwestern Atlantic Ocean (21°–35°S) region, where physical, chemical and biological measurements were made on board the Brazilian R. V. *Cruzeiro do Sul* during late spring 2010 and early summer 2011. Features such as discharge from the La Plata River, intrusions of tropical waters on the outer shelf due to meandering and flow instabilities of the Brazil Current, and coastal upwelling in the Santa Marta Grande Cape and São Tomé Cape were detected by both *in situ* measurements and ocean colour and thermal satellite imagery. Overall, shelf waters in the study area were a source of CO_2 to the atmosphere, with an average of 1.2 mmol CO_2 m^{-2} day^{-1} for the late spring and 11.2 mmol CO_2 m^{-2} day^{-1} for the early summer cruises. The spatial variability in ocean pCO_2 was associated with surface ocean properties (temperature, salinity and chlorophyll-*a* concentration) in both the slope and shelf waters. Empirical algorithms for predicting temperature-normalized surface ocean pCO_2 as a function of surface ocean properties were shown to perform well in both shelf and slope waters, except (a) within cyclonic eddies produced by baroclinic instability of the Brazil