

Diurnal variation of oxygen and carbonate system parameters in Tampa Bay and Florida Bay

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Abstract

Oxygen and carbonate system parameters were measured, in situ, over diurnal cycles in Tampa Bay and Florida Bay, Florida. All system parameters showed distinct diurnal trends in Tampa Bay with an average range of diurnal variation of 39.1 $\mu\text{mol kg}^{-1}$ for total alkalinity, 165.1 $\mu\text{mol kg}^{-1}$ for total CO_2 , 0.22 for pH, 0.093 mmol L^{-1} for dissolved oxygen, and 218.1 μatm for pCO_2 . Average range of diurnal variation for system parameters in Tampa Bay was 73% to 93% of the seasonal range of variability for dissolved oxygen and pH. All system parameters measured in Florida Bay showed distinct variation over diurnal time-scales. However, clear diurnal trends were less evident. The average range of diurnal variability in Florida Bay was 62.8 $\mu\text{mol kg}^{-1}$ for total alkalinity, 130.4 $\mu\text{mol kg}^{-1}$ for total CO_2 , 0.13 for pH, 0.053 mmol L^{-1} for dissolved oxygen, and 139.8 μatm for pCO_2 . The average range of diurnal variation was 14% to 102% of the seasonal ranges for these parameters. Diurnal variability in system parameters was most influenced by primary productivity and respiration of benthic communities in Tampa Bay, and by precipitation and dissolution of calcium carbonate in Florida Bay. Our data indicate that use of seasonal data sets without careful consideration of diurnal variability may impart significant error in calculations of annual carbon and oxygen budgets. These observations reinforce the need for higher temporal resolution measurements of oxygen and carbon system parameters in coastal ecosystems.

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1. Introduction

Growing interest in the contribution of the coastal ocean to the global carbon budget has prompted numerous investigations on oxygen and carbon system

dynamics in estuaries and other coastal ecosystems. While the coastal ocean only represents approximately 7% of the total ocean area (Andersson and Mackenzie, 2004), carbon inventories may be higher in coastal waters than in the open ocean due to remineralization of organic carbon produced from high rates of primary production, and delivery of terrestrial organic material concentrated in a smaller volume of water (Ianson et al., 2003). Whether the coastal ocean represents a source or sink of atmospheric CO_2 and the magnitude of the

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coastal ocean's contribution to the global carbon budget have yet to be resolved (Borges and Frankignoulle, 2002). Significant progress has been made in understanding seasonal and interannual processes affecting oxygen and carbon system dynamics in temperate estuaries. Fewer studies have been undertaken in subtropical and tropical estuaries. Furthermore, the impact of diurnal variation of carbon and oxygen parameters on seasonal and annual carbon and oxygen budgets is not well understood.

Synthesis of data on input, burial, and oxidation of organic matter, and organic carbon metabolism is critical for developing coastal ocean carbon budgets (Smith and Hollibaugh, 1993). Many estuarine investigations estimate organic carbon metabolism and resulting CO₂ and O₂ gas fluxes from seasonal measurements of carbonate system parameters (including total alkalinity, TA; total carbon dioxide, TCO₂; the partial pressure of carbon dioxide, pCO₂; and pH), dissolved oxygen (DO), salinity, and temperature along transects that cross salinity gradients (e.g. Frankignoulle et al., 1996; Cai et al., 1999; Raymond and Bauer, 2000; Brasse et al., 2002). It is well known that TA, TCO₂, pCO₂ and pH are affected seasonally by temperature, evaporation, precipitation, freshwater runoff, biological fluxes (such as uptake and remineralization of organic carbon, and precipitation and dissolution of calcium carbonate), and mixing of water masses (Broecker and Peng, 1982; Brewer et al., 1975; Brewer and Goldman, 1976; Kempe and Pegler, 1991; Takahashi et al., 1991; Millero et al., 1998; Ianson et al., 2003). Relations among these parameters are used to determine the primary controls on carbonate system dynamics. For example, variation of TA and TCO₂ with salinity is generally linear when controlled by evaporation, precipitation, or runoff (e.g. Kempe and Pegler, 1991; Takahashi et al., 1991; Millero et al., 1998). Biological fluxes, surface exchange of TCO₂, and mixing of water masses with differing biological activity cause non-linear variations with salinity (Millero et al., 1998; Ianson et al., 2003).

Examples of large-scale, comprehensive investigations on estuarine carbon and oxygen dynamics determined from seasonal monitoring programs include select European estuaries such as the Scheldt (Frankignoulle et al., 1996; Vanderborght et al., 2002), the Elbe and German Bight (Brasse et al., 2002), the Ems, Rhine, Tamar, Thames, Gironde, Douro, and Sado estuaries (Frankignoulle et al., 1998), and outer estuary areas along the Belgian and southern Dutch coastal areas (Borges and Frankignoulle, 1999, 2002). These northern latitude estuaries located near highly industrialized areas receive elevated loads of detrital organic

material and, with the exception of the Elbe estuary (Brasse et al., 2002), are generally considered to be net heterotrophic ecosystems that emit carbon dioxide to the atmosphere (Frankignoulle et al., 1998). Seasonally varying salinity gradients, remineralization of high organic carbon loads from rivers, and primary production from seasonal phytoplankton blooms are considered to exert the primary control on carbonate system parameters in these European estuaries (Frankignoulle et al., 1998; Borges and Frankignoulle, 2002; Brasse et al., 1999, 2002).

The most comprehensive studies of U.S. river–estuary complexes have been undertaken in the temperate region of the southeastern United States along the coast of Georgia. Investigations have included the Savannah, Ogeechee, Altamaha, Satilla, and St. Mary's estuaries (Cai et al., 1999), and the York River estuary in Virginia (Raymond and Bauer, 2000). High rates of respiration in the intertidal marsh sediments surrounding Georgia estuaries, and transport of TCO₂ from marshes to the estuaries during tidal cycles are thought to be the primary controls on carbon and oxygen dynamics that create net system heterotrophy (Cai et al., 1999). Similarly, spatial and seasonal variations in pCO₂ and TCO₂ in the York River estuary are driven by high rates of respiration in the upper estuary and seasonal phytoplankton blooms (Raymond and Bauer, 2000).

With the exception of an investigation by Millero et al. (2001) on seasonal variation in carbonate system parameters in Florida Bay, very little information exists on carbon and oxygen dynamics in subtropical estuaries. Carbonate system parameters in Florida Bay are controlled seasonally by inflow of freshwater from surrounding mangrove wetlands, seasonal variation in primary productivity, and precipitation and dissolution of calcium carbonate (Millero et al., 2001). This type of study is instrumental in quantifying the impact of seasonal and interannual variability in the carbon dynamics of estuarine ecosystems.

It is well understood that diurnal variation in carbon and oxygen metabolism causes significant variation of carbonate and oxygen system parameters on diurnal time scales (Park et al., 1958; Smith and Key, 1975; Marsh and Smith, 1978; Barnes and Devereux, 1984). This has been well documented by studies of coral reef ecosystems that quantified diurnal variations in surface water chemistry, primary production, respiration, gas fluxes, and calcium carbonate precipitation (e.g. Smith, 1973; Barnes and Devereux, 1984; Gattuso et al., 1997). However, few estuarine studies, with the exception of that described by Borges and Frankignoulle (1999), have quantified diurnal variations in estuarine carbon

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