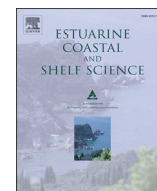




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## Invited feature

## Coastal ocean acidification: The other eutrophication problem

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## ABSTRACT

Increased nutrient loading into estuaries causes the accumulation of algal biomass and microbial degradation of this organic matter decreases oxygen levels and contributes towards hypoxia. A second, often overlooked consequence of microbial degradation of organic matter is the production of carbon dioxide (CO<sub>2</sub>) and a lowering of seawater pH. To assess the potential for acidification in eutrophic estuaries, the levels of dissolved oxygen (DO), pH, the partial pressure of carbon dioxide (pCO<sub>2</sub>), and the saturation state for aragonite ( $\Omega_{\text{aragonite}}$ ) were horizontally and vertically assessed during the onset, peak, and demise of low oxygen conditions in systems across the northeast US including Narragansett Bay (RI), Long Island Sound (CT–NY), Jamaica Bay (NY), and Hempstead Bay (NY). Low pH conditions (<7.4) were detected in all systems during summer and fall months concurrent with the decline in DO concentrations. While hypoxic waters and/or regions in close proximity to sewage discharge had extremely high levels of pCO<sub>2</sub>, (>3000  $\mu\text{atm}$ ), acidic pH (<7.0), and were undersaturated with regard to aragonite ( $\Omega_{\text{aragonite}} < 1$ ), even near-normoxic but eutrophic regions of these estuaries were often relatively acidified (pH < 7.7) during late summer and/or early fall. The close spatial and temporal correspondence between DO and pH and the occurrence of extremes in these conditions in regions with the most intense nutrient loading indicated that they were primarily driven by microbial respiration. Given that coastal acidification is promoted by nutrient-enhanced organic matter loading and reaches levels that have previously been shown to negatively impact the growth and survival of marine organisms, it may be considered an additional symptom of eutrophication that warrants managerial attention.

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## 1. Introduction

Coastal marine ecosystems are amongst the most ecologically and economically productive areas on the planet, providing more than US\$10 trillion in annual resources or ~40% of the global ecosystem goods and services (Costanza et al., 1997). Approximately 40% of the World population lives within 100 km of a coastline, making these regions subject to a suite of anthropogenic stressors including intense nutrient loading (de Jonge et al., 2002; Valiela, 2006). Excessive nutrient loading into coastal ecosystems promotes algal productivity and the subsequent microbial consumption of this organic matter reduces oxygen levels and can promote hypoxia (Cloern, 2001; Heisler et al., 2008). The rapid acceleration of nutrient loading to coastal zones in recent decades

has contributed to a significant expansion in hypoxic zones across the globe (Rabalais et al., 2002; Diaz and Rosenberg, 2008). Because these hypoxic zones can be lethal to aerobic marine organisms and have contributed toward declining yields of fisheries (Vaquer-Sunyer and Duarte, 2008; Levin et al., 2009), a prime motivation of coastal zone management has been to lower nutrient loads in order to reduce the intensity, extent, and duration of hypoxia (Scavia et al., 2004; Paerl, 2006; Scavia and Bricker, 2006).

A second, often overlooked consequence of microbial degradation of organic matter in coastal zones is the production of CO<sub>2</sub>, which enters the water and forms carbonic acid (H<sub>2</sub>CO<sub>3</sub>) dissociating into bicarbonate ions (HCO<sub>3</sub><sup>-</sup>), carbonate ions (CO<sub>3</sub><sup>2-</sup>) and hydrogen ions (H<sup>+</sup>) that cause acidification. Coastal ecosystems can also be acidified via atmospheric carbon dioxide fluxes (Miller et al., 2009; Feely et al., 2010), the introduction of acidic river water (Salisbury et al., 2008), and/or upwelling of CO<sub>2</sub> enriched deep water (Feely et al., 2008). Watershed geology, climate and acid deposition also have the potential to impact source water buffering

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capacities through their effects on mineral weathering and sea ice melting (Yamamoto-Kawai et al., 2009; Wang et al., 2013). Likely due to a combination of these processes, some recent investigations of coastal zones have detected seasonally low pH and/or elevated  $p\text{CO}_2$  conditions (Feely et al., 2010; Sunda and Cai, 2012; Duarte et al., 2013; Melzner et al., 2013), while others have documented that some coastal regions have experienced progressively declining pH levels in recent decades (Waldbusser et al., 2011).

Ocean acidification has garnered much attention among scientists, policy makers, and the public during the past decade. The term has generally been used to describe the ongoing decrease in surface ocean pH due to anthropogenic increases in atmospheric  $\text{CO}_2$  (Caldeira and Wickett, 2003). Since this acidification also decreases the availability of  $\text{CO}_3^{2-}$  it can have negative consequences for marine organisms, both pelagic and benthic, that produce structures made of calcium carbonate ( $\text{CaCO}_3$ ; Ries et al., 2009; Talmage and Gobler, 2009; Gazeau et al., 2013) and has sometimes been deemed ‘The other  $\text{CO}_2$  problem’ (Doney et al., 2009). A similar perspective could be adopted with respect to eutrophication processes, the literature on which generally emphasizes only nutrient-productivity-hypoxia relationships. Beyond calcifying organisms, information is mounting that acidification can also be damaging to some finfish (Munday et al., 2010), particularly during early life stages (Baumann et al., 2012; Frommel et al., 2012; Murray et al., 2014). While acidification in the open ocean is driven by external, atmospheric loading of  $\text{CO}_2$ , in coastal zones this process may be minor compared to internal loading processes, particularly within eutrophic regions where excessive nutrient loading and organic matter production have been associated with large hypoxic events.

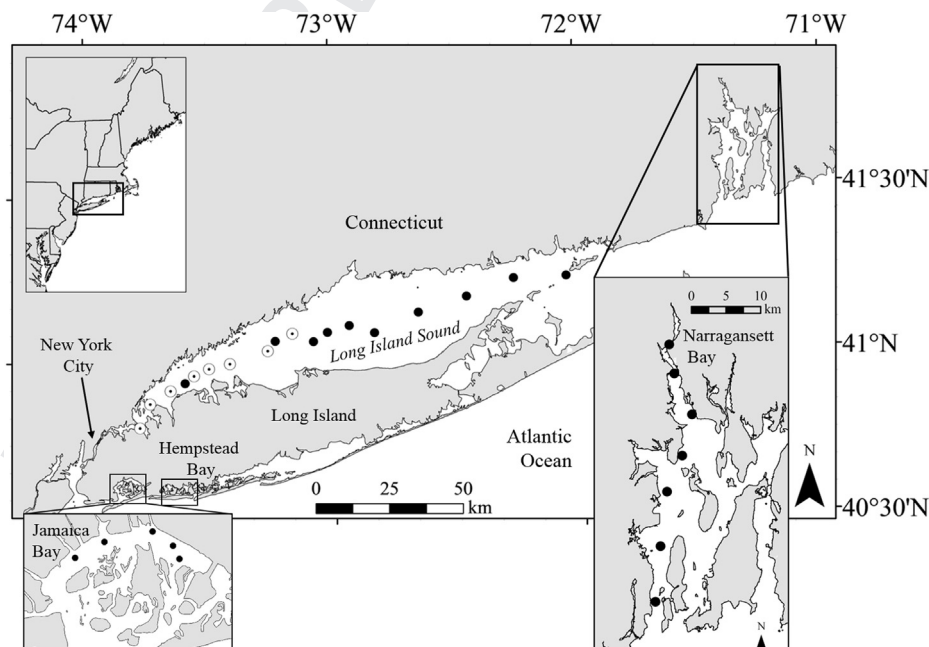
The goal of this study was to characterize the spatial and temporal dynamics of DO, pH,  $p\text{CO}_2$ , and  $Q_{\text{aragonite}}$  in the water columns of several representative, estuarine systems along the northern US Atlantic coast (Fig. 1). Multi-year monitoring datasets were assessed to define seasonal patterns in pH and DO while cruises were conducted to vertically and horizontally resolve spatial

patterns of acidification during the seasonal onset, peak, and decline of hypoxia in these estuaries. Given the excessive productivity and organic matter loading within eutrophic estuaries, we hypothesized that pH and DO would co-vary and reach extremes lower than those in the open ocean and most other coastal systems characterized to date. As a guide to possible impacts on ecosystem processes, we evaluated the saturation state of the water column with respect to common biogenic carbonate minerals, specifically aragonite.

## 2. Methods

This study characterized spatial and temporal patterns of DO, pH,  $p\text{CO}_2$ , and  $Q_{\text{aragonite}}$  in four, semi-enclosed estuarine systems across the Northeast US: Narragansett Bay (Rhode Island (RI), 41.63N, 71.37W), Long Island Sound (New York (NY)–Connecticut (CT), 41.11N, 72.86W), Jamaica Bay (NY, 40.61N, 73.84W), and Hempstead Bay (NY, 40.60N, 73.57W; Fig. 1). The Northeast US is the most heavily urbanized and populated region in the nation and contains some of the densest populations on the planet including the most populous US metropolis, New York City. Coastal waters in this region have also been shown to have a lower buffer capacity compared to the southeast and Gulf coasts of the US (Wang et al., 2013). We utilized three approaches for this study: 1) The analysis of monthly monitoring data across Long Island Sound; 2) Vertical measurements of water column conditions across Narragansett Bay, Long Island Sound, and Jamaica Bay; and 3) Continuous, horizontal mapping of conditions across Jamaica Bay and Hempstead Bay. All field work was performed during daylight.

Long Island Sound (LIS; Fig. 1) is the third largest estuary in the US, and its western end receives more than four billion liters of treated wastewater effluent daily from the nation's largest metropolis, New York City. The combination of excessive wastewater loads and sluggish circulation have contributed toward the annual occurrence of hypoxia within western LIS since the middle of the twentieth century (Parker and O'Reilly, 1991; O'Donnell et al.,



**Fig. 1.** Study sites. Long Island Sound CTDEEP sampling stations represented as black dots whereas small black dots surrounded by circles indicate CTDEEP sampling stations occupied for this study. Narragansett Bay in upper right box with black dots of inset indicating discrete sampling stations. Jamaica Bay and Hempstead Bay is small boxes at lower left, with black dots within inset depicting Jamaica Bay sampling stations. Upper left inset: Northeast US.

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