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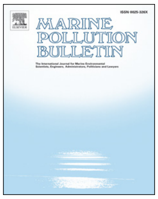

An empirical model using dissolved oxygen as an indicator for eutrophication at a regional scale

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ABSTRACT

Simple empirical models can sometimes capture salient patterns without sacrificing predictive capacity when compared to more complex models. Herein we examine dissolved oxygen as an indicator of eutrophication status for shallow estuaries. Dissolved oxygen was measured hourly in the upper estuary of 15 watersheds along a nutrient-loading and geographic gradient. Metrics describing hypoxia and supersaturation were devised and then analyzed using multivariate statistics. Results revealed independent responses for hypoxia and supersaturation with hypoxia-related metrics correlating strongly with water residence. A metric integrating hypoxia and supersaturation effectively discriminated between seagrass and algae-dominated habitats and was significantly correlated with both water residence and nitrate-N loading. Chlorophyll, measured bi-weekly, was not correlated with our predictor variables likely because it does not account for benthic production. Over 70% of the variability in hypoxia was explained by water residence and nitrate-N loading indicating that this model can be of use for managers.

1. Introduction

Nutrients are one of the most significant sources of influence on estuaries and coastal zones (Hemminga and Duarte, 2000; Larkum et al., 2006; Burkholder et al., 2007). Nutrient addition leads to the proliferation of micro- and macro-algal species (eutrophication) that are better able to increase their growth rate in response to nutrients than vascular flora such as seagrasses (Duarte, 1995; Hemminga and Duarte, 2000). Ultimately, algae displace seagrasses, the dominant vascular plant in shallow oligotrophic systems. Mild to moderate eutrophication leads to a habitat shift that has consequences for species specifically adapted to seagrass. In severe cases, decomposition of excess plant material culminates in anoxia that can result in mortality for fauna and an overall loss in diversity (Levin et al., 2009; Lamberth et al., 2010).

There is a well-established biological continuum from oligotrophic to eutrophic conditions in estuaries (Pearson and Rosenberg, 1978). However, identifying where a given estuary is on that continuum remains challenging, given the dynamic and spatially heterogeneous nature of this environment. Nutrient loading can be modeled, though it is not necessarily useful as an indicator of eutrophication as the effects of nutrients depend on plant growth which varies according to the characteristics of an estuary. Furthermore, the paradigm whereby a single nutrient limits productivity, e.g. nitrogen in saltwater, is certainly more complex in reality than in theory (Paerl et al., 2014).

While it is intuitive to measure plant productivity to assess eutrophication (Short et al., 2006), assessing plant biomass in eutrophic systems and over many estuaries at a regional scale is logistically intensive and prohibitively expensive. Chlorophyll *a* concentration in the water column is well established in the literature as a proxy for phytoplankton productivity in coastal systems (Meeuwig, 1999). However, blooms fluctuate significantly over time and with depth (Schein et al., 2012, 2013). Fluorescent probe-based chlorophyll loggers, that would be ideal for more frequent measurements, do not correlate well with traditional methods (Debertin et al., 2017), remain costly, and can be confounded in turbid estuarine environments (James, 2013). Furthermore, chlorophyll does not incorporate productivity from submerged aquatic vegetation, an important component of overall productivity in shallow estuaries.

Dissolved oxygen variability, i.e., the development of hypoxia and supersaturation of oxygen, is symptomatic of eutrophication and here we suggest that it may be the best available single indicator of trophic status in estuaries. Dissolved oxygen is a direct reflection of the balance between photosynthesis, respiration, and decomposition, i.e., it is

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metabolism-related (Kemp and Boynton, 1980). Furthermore, it has a direct effect on aquatic fauna through its impact on animal behaviour and survival (Miller et al., 2002; Landman et al., 2005; Vaquer-Sunyer and Duarte, 2008; Riedel et al., 2014). Recent improvements in optical sensor technology, i.e., increased data reliability stemming from insensitivity to biofouling and hydrogen sulfide, along with improvements to data storage and a reduction of cost, have eliminated impediments to the use of dissolved oxygen loggers in estuaries on a regional scale.

The hypothesis tested in this study is that dissolved oxygen provides sufficient information to differentiate between sites along a spectrum of eutrophication. The secondary hypothesis is that dissolved oxygen concentration can be predicted from nutrient loading and estuarine flushing in a manner that can be incorporated into simple models. This study examined 15 estuaries in the Southern Gulf of St. Lawrence, Canada that ranged from primarily forested watersheds to watersheds with intensive agriculture where estuaries are observed to undergo seasonal anoxia (Schein et al., 2012; Bugden et al., 2014; Coffin et al., 2017, 2018). The study utilized optical dissolved oxygen loggers installed in multiple estuaries to collect temporally detailed oxygen data. Key oxygen parameters were chosen from a suite of derived metrics and simple models using nitrogen loads and water residence were constructed.

2. Methods

2.1. Study area

In total 15 estuaries that empty into the Southern Gulf of St. Lawrence were selected across a nutrient loading and geographic gradient: 12 from Prince Edward Island (PEI), two from New Brunswick (NB) and one from Nova Scotia (NS; Fig. 1). Watersheds in the Southern Gulf of St. Lawrence are generally small, ranging from 31 to 386 km^2 in this study, and shallow, 1–5 m in depth, with sufficient light to support benthic production. Small watershed area translates to low freshwater input and well-mixed estuaries with a short transition zone between fresh and saltwater, i.e., the area of salinity 0–15 PSU typically extends only a few hundred meters. At nutrient impacted sites, the area immediately downstream of this transition zone is most susceptible to nutrient impact, can be inundated with macroalgae, primarily *Ulva lactuca* L. but also *U. intestinalis* L., *U. linza* L., and occasionally unidentified green filamentous algae, and is the area of interest for this study (Valiela, 1995; Valiela et al., 1997; Hemminga and Duarte, 2000; Burkholder et al., 2007). Estuaries here are lagoon-type with barrier islands or are coastal embayments (Glibert et al., 2010). Mean tidal amplitude and periodicity differ between sites (0.3–1.6 m), with some sites experiencing mesotidal, mixed semi-diurnal tides and others microtidal, diurnal tides (Pingree and Griffithis, 1980; Godin, 1987). For this study the estuary boundary was defined by salinity at the uppermost location (< 0.5 PSU) and geographical features for the outermost location, being where the estuary opens into a bay or into the Southern Gulf of St. Lawrence directly. In some estuaries, there was a barrier precluding saltwater incursion into fresh water that defined the upper extent of the estuary. For all estuaries, the total area from the uppermost to outermost boundaries was calculated using ArcGIS 10.3 (Table 1).

2.2. Nutrient loading

Nitrogen loading (total nitrogen and nitrate-N) data were obtained from two sources for watersheds in the region: primarily from Grizard (2013) and supplemented using data from Bugden et al. (2014). Nitrogen load calculations were based on nitrogen concentrations measured within the freshwater portion of streams immediately upstream of tidal influence. As hydrometric stations were only present on a subset of 6 streams, flow was modeled for all streams. Daily average flow rate from Environment Canada gauging stations in the region were log-transformed and found to be highly correlated to watershed area measured at the point of flow gauging (n = 8, $r^2 = 0.97$; S1). The equation of the line from the linear regression was then used to calculate the average daily flow rate for all 15 watersheds, whether they had hydrometric stations or not. The calculated nutrient load at the head of tide was pro-rated for the larger area of the watershed that included the upper estuary where the oxygen logger was located (see below), under the assumption that land use and nitrogen inputs for the remaining area of watershed not captured at the stream measurement station were proportional to those above (see Jiang et al., 2015). Using the mean nitrate-N and total nitrogen concentrations (mg/L) and flows (m^3/s), average annual nitrate-N and total nitrogen load were calculated (Table 1). The risk with this approach is that there may be a correlation between flow and nitrate-N concentration which could lead to an over- or underestimate of nutrient load. However, the approach used herein has been validated by Jiang et al. (2015) that found that nitrate concentration was approximately constant, irrespective of flow, for PEI watersheds over a 15 year period with a wide range of flows (see Fig. 2, therein).

2.3. Water residence

Water residence was calculated by dividing the overall estuarine volume at mean tide by the sum of freshwater and tidal volumes, i.e., a relatively coarse whole-estuary tidal prism model. Bathymetric data were acquired along transects spaced by approximately 200 m using an acoustic depth sounder with a 210 kHz transducer (Knudsen) for the entirety of each estuary; a Kriging interpolation was used to estimate areas that were not mapped explicitly (J. Hitchcock, University of Prince Edward Island, unpub. data). Estuarine volume was calculated from bathymetric data using ArcGIS 10.3. Water pressure data were collected every 10 min for at least 30 days using Onset Hobo Water Level Titanium® pressure loggers in each estuary with a barometric logger placed in air near the estuary as the reference. All pressure data were transformed into depth data and corrected for the average salinity for that area. Depth data were then used to create harmonic tidal models using the t_tides program under Matlab (Pawlowicz et al., 2002). For each estuary, these models were used to simulate tide over the period of dissolved oxygen logger deployment (see below). Mean tidal amplitude was derived by averaging the tidal amplitude of every tidal cycle that occurred over that period.

2.4. Dissolved oxygen monitoring and metrics

Onset Hobo® optical dissolved oxygen loggers (accuracy of: ± 0.2 mg/L from 0 to 8 mg/L and ± 0.5 mg/L from 8 to 20 mg/L and a resolution of 0.02 mg/L according to manufacturer) were deployed in the upper estuary near the boundary of the upstream 10% of the total area of the estuary, which corresponded to a salinity range of 15–25 PSU, and were set to record dissolved oxygen (mg/L) and temperature (°C) hourly. Dissolved oxygen loggers, henceforth loggers, were moored 0.5 m from the substrate, at a depth of 1–2.5 m, on a stainless steel pole that was embedded in concrete from May 21–November 30, 2013. Loggers were equipped with a copper-wound cap to reduce fouling but were downloaded and cleared of fouling, if present, every 2-weeks.

To analyze the oxygen time series data, hourly values were parsed into biologically relevant metrics to capture pre-defined oxygen events according to the duration, variability, frequency or timing of an event (see Table 2 for the list of metrics). Daigle et al. (2011) used similar statistical methodology for characterizing hydrological flow regimes with the benefit that using metrics eliminates serial autocorrelation. Although both hypoxic and supersaturated conditions are symptoms of eutrophication, the purpose of this study is to determine which metrics are best for discriminating between eutrophic and oligotrophic sites and not simply identifying eutrophic ones, hence the plethora of metrics and