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# Abstract



Keywords: atmospheric deposition, wastewater, Cape Cod, eutrophication, macroalgae, *Zostera marina* 

#### 1. Introduction

The degree of eutrophication of estuarine ecosystems is largely determined by the magnitude of external nitrogen (N) loads (Howarth, 1988; Valiela, 2006). Atmospheric, fertilizer, and wastewater sources contribute to loads of N, the main production-limiting nutrient in estuaries (Valiela *et al.*, 1997). These inputs are likely to change across decades. In the case of New England watersheds, atmospheric deposition of N has decreased by approximately 50% since the year 2000 (Fig. 1a, and Lajtha & Jones, 2013; Vet *et al.*, 2014). Similar decreases in atmospheric delivery of N have also taken place on Cape Cod (Fig. 1b), the region that is the locale of the present study. The decreases in atmospheric deposition are linked to larger-scale national and global influences [reductions of emissions from sometimes distant regions under large air-sheds, 48 and shifting directions of air mass transport, governed by global-scale phenomena, Lloret & Valiela (under review)].

It turns out that the decadal trajectories of watershed land use in Cape Cod have also changed during these same decades, owing to trends in urbanization: forest cover decreased, impervious cover increased, and the number of buildings increased (Fig. 2a,b,c). On the whole, for Cape Cod and similar regions, local-scale processes that occur during increased urbanization increase delivery of wastewater and fertilizer N loads to estuaries and foster eutrophic conditions, as we have reported in a series of papers (Valiela *et al.*, 1992, 1997, 2000). More detailed trajectories in the number of buildings on Cape Cod watersheds have been reported (http://buzzardsbay.org/wastewater-timeline.html). Even though the number of newly constructed structures has tapered off owing to recent economic constraints (Fig. 3 black points), the number of septic tank wastewater plumes arriving at the edge of estuaries has continued to

rise (Fig. 3 hollow points). This is a result of lag time involved in travel of wastewater within aquifers, and distance from shore in the location of buildings, as wastewater plumes travel approximately 100 meters per year in the soil types found on Cape Cod (Valiela et al. 1997). 

There is considerable evidence that in Cape Cod, external N loads determine water quality and level of eutrophication of estuaries, and that there has been a decadal transition in recent years during which the two major sources of N loading, globally-driven atmospheric deposition and local-scale-driven wastewater inputs (Valiela *et al.*, 1997), have changed significantly. To discern the consequences of the realignment of sources and rates of N loads entering receiving estuaries, in this paper we carry out three lines of work. First, we model the relative effects of lower atmospheric and increased wastewater N sources on the resulting N loads discharged from watersheds to six estuaries within the Waquoit Bay estuarine system in Cape Cod. Second, to assess existing level of eutrophic conditions, during 2015 we measured N concentrations and biomass of macroalgae and seagrasses in three test estuaries subject to low, intermediate, and high N loading rates. Third, to evaluate whether the changes in atmospheric and wastewater N sources led to detectable long-term changes in water quality in the test estuaries, we compare data obtained from the 2015 sampling to data on the same indicator variables in previous studies conducted during the 1990s and early 2000s (McClelland *et al.*, 1997; Valiela *et al.*, 2001; Deegan *et al.*, 2002; Fox *et al.*, 2008; Olsen, 2008; Tomasky Holmes, 2008).

2. Methods

*2.1 Study Sites* 



run NLM were obtained from the Cape Cod Commission (CCC), which furnished the most recent available land cover data (2014) derived from MassGIS satellite imagery. Recent estimates of atmospheric deposition rates were compiled from NADP and EPA CASTNET data (Lloret & Valiela, under review).

In addition to these input categories, NLM uses numerical loss terms and transport constants estimated from extensive survey data and literature reviews. The model estimates have been validated and the associated uncertainties quantified (Valiela *et al.*, 1997a, 2000; Collins *et al.*, 2000). NLM has been successfully applied in Barnegat Bay, New Jersey (Bowen *et al.*, 2007), 74 estuaries in New England (Latimer & Charpentier, 2010), 12 Maryland, Delaware, and Virginia coastal lagoons (Giordano *et al.*, 2011), Great Bay, New Hampshire (Trowbridge *et al.*, 2014) and elsewhere. Latimer and Charpentier (2010) concluded that NLM, with greater simplicity and less demanding inputs, performed well in comparisons with other models, including SPARROW, the "gold standard" model used by USGS. We updated NLM, and added specific local information relevant for this study, using new local data (CCC, 2012; Horsley Witten, 2014) to account for changes in current fertilizer use practices and residential occupancy rates (Table 2). We also corrected the number of built structures reported in the CCC data compilation to consider only buildings that contributed wastewater. These updates to NLM were of modest magnitude. To obtain data layers that accurately represented land use in the watersheds of Waquoit Bay as of 2014, we verified the updated data by selected comparisons with remote-sensed data layers in the MassGIS 2014 orthoimagery, and modified the land cover data by digitizing any new features (cleared land, structures, paved surfaces, etc.). Land use input data consisted of total land area in each watershed, and area of each land cover category. The land use categories required for NLM in



right panels). Surface water was collected in acid-washed 1 L polypropylene bottles; 60 mL of each sample was immediately filtered through pre-ashed GF/F Whatman microfiber filters and frozen for nutrient analysis. Nitrate concentrations were determined using standard colorimetric assays in a Lachat QuikChem 8000 Auto Analyzer. Ammonium concentrations were determined 148 by spectrophotometry using a Varian Cary-50 UV-Visible Spectrophotometer. On each sampling date, benthic vegetation samples were collected using a 152x152 mm Eckman grab at the same nine stations in each estuary where water samples were collected,

rinsed through 1 mm sieves or mesh to remove excess mud, and then stored on ice until further

processing could be conducted in the lab. In the laboratory, samples were sorted by species, and dead biomass was separated out. All plant matter was then dried at 60° C to constant weight for at least 24 hours before being weighed.

## *2.4 Comparison of this study to previous results*

From earlier studies in Waquoit Bay, we had previously published measurements of modeled N loads (Valiela *et al.*, 1997a) as well as measured nutrient concentrations and macroalgal and eelgrass biomass during the growing season in the test estuaries (McClelland *et al.*, 1997; Valiela *et al.*, 2001; Deegan *et al.*, 2002; Fox *et al.*, 2008; Olsen, 2008; Tomasky Holmes, 2008). A model 2 major axis regression was used to compare 1990 and 2014 modeled total loads and modeled loads from each source. To ascertain whether there were detectable changes in eutrophic status of the test estuaries, we compared the older measured data with the sampling results obtained during 2015. We compared nutrients and macroalgal biomass in Childs River, Quashnet River, and Sage Lot Pond, through the span of years pre- and during 2015, with a two-way ANOVA, followed by Tukey's HSD *post hoc* tests to see whether there were significant differences among estuaries and years. 3. Results *3.1 N loads during 2014 and comparisons with 1990*  We used NLM to calculate total N loads to each of the six Waquoit Bay estuaries during

1990 and during 2014, and partitioned the contributions by wastewater, atmospheric deposition,

and fertilizer use (Fig. 5). In the largely suburban landscapes of Cape Cod, fertilizer inputs are

relatively small and derived almost entirely from residential lawns (Table 3 and Valiela *et al.*,

1997a); we therefore summed fertilizer and wastewater inputs in our results.

1990 and 2014 modeled total loads did not differ significantly, while modeled loads from each source showed strong and opposing changes over the course of the study period (Fig. 5, Table 3). The N loads contributed by atmospheric sources to Waquoit Bay estuaries during 2014 (Table 3) were 23-48% lower compared to estimates based on deposition data from 1990 (Fig. 5, Table 4). This is roughly consistent with the 50% decrease estimated by Lloret and Valiela (under review), with some variation due to interception within the watershed. In contrast, because of the increased urbanizing development that took place on the watersheds of Waquoit Bay from 1990 to 2014, the contributions of wastewater and fertilizer delivered from watersheds 186 to the six estuaries increased by about 80% during 2014 compared to wastewater and fertilizer N contributions during 1990 (Fig. 5, Table 4).

Total N loads estimated by NLM for 2014 ranged widely across the six Waquoit estuaries (Table 3); in spite of the lower atmospheric inputs, and larger wastewater and fertilizer inputs, there were no significant changes in the total N loads discharged from watersheds into the receiving estuaries (Fig. 5, Table 4). Given the variation present in the estimated N loads to the six estuaries, the regression fitted to points of 2014 total N loads vs. 1990 total N loads did not differ statistically from the 1:1 line of perfect fit (Fig. 5 and Table 4). Quite fortuitously, in this particular case, the changes in atmospheric deposition and in wastewater and fertilizer N loads that took place over the period of the study approximately cancelled each other.

### *3.2 Tests of the model results*

The lack of change in total N loads across the decades anticipated by the model results (Fig. 5) would suggest that indicators of water quality and eutrophication within the Waquoit Bay estuaries should not have undergone detectable changes across the decades. We assessed this conclusion by comparisons of the indicators known to be sensitive to shifts in N loads. 

3.2.1 *Concentrations of dissolved inorganic N*—Nitrate made up the dominant portion of DIN, with ammonium representing a small but consistent portion. A model 2 major axis regression showed that nitrate concentrations increased significantly as modeled N loads increased (*P*=0.015). Ammonium concentrations were not related to modeled N loads (*P*=0.58) (Fig. 6). We summed concentrations of nitrate and ammonium to report DIN, a proxy of the forms of N most likely to be of short-term biological significance as regulators of production and hence of level of eutrophication (Nixon, 1992). Concentrations of DIN in the three test estuaries 212 paralleled modeled N loads ( $P=0.02$ ) and showed significant variation among estuaries, with no significant differences between data taken during 1994-2004 and in 2015 (Table 1). 3.2.2 *Macroalgal and seagrass biomass*—These longer-lived producers are, in general, sensitive and reliable indicators of N supply regimes (Teichberg *et al.*, 2010; Cebrián *et al*. 2014). First, there were no significant contrasts in macroalgal biomass between samples taken during 1992-1998, and during 2015 (Table 1). This result is corroborated by the lack of slopes in the multi-year trajectories in macroalgal biomass (Fig. 7a). A 2-way ANOVA showed significant differences in biomass among estuaries (P<0.07), but no significant differences among years (P>0.82) (Table 5).

Second, there were quite marked and statistically significant differences in amount of macroalgal biomass found in the three Waquoit estuaries (Table 5, Fig. 7): the biomass of macroalgae was largest in Childs River, the estuary subject to the largest N loads per hectare of estuary, and lowest in Sage Lot Pond, the estuary with the lowest N load per hectare (Table 1, Fig. 7b). In spite of the recent shifts in deposition and land covers, the long-term differences in N loads emerging from these three watersheds have been maintained across decades, owing to the overwhelming influence of the rather contrasting land covers on the watersheds (Valiela *et al.*, 1992, 1997a).

Eelgrass (*Zostera marina*) was only present in Sage Lot Pond, the estuary subject to the lowest N loads (Table 1); this has long been the case (Valiela *et al*. 1992). In the other estuaries subject to larger N loads, growth of macroalgae is stimulated, and the macroalgae shade the meristem of eelgrass and prevent its growth (Hauxwell *et al.*, 1998, 2003; Fox *et al.*, 2008, 2012). Consistent with the model results of Fig. 5, there were no significant changes in the biomass of eelgrass within Sage Lot Pond between 1990 and 2015 (Table 1).

3.3 *Biomass-loading regressions* 

To obtain an idea of the relative effect of the reduction in atmospheric deposition, we can take advantage of the demonstrated sensitivity of macroalgal biomass to external N loads

(Teichberg *et al.*, 2010; Cebrián *et al.*, 2014). We calculated the increase in algal biomass that would have been likely if there had been no lowered atmospheric deposition, so that the only change in loading regimes would have been due to the increased wastewater additions evident in Fig. 5. We used a relationship derived in Cebrián *et al.* (2014), enhanced by addition of points from our own work, which showed that macroalgal biomass in many estuaries is variably but significantly related to N loads (Fig. 8a). We used the equation for this relationship to estimate, in approximate fashion, how much more macroalgal biomass would have likely have been present in the three Waquoit Bay estuaries under the influence of the added wastewater N. The macroalgal biomass would likely have increased by 2 to 99% in the test estuaries, depending on the original relative importance of deposition and wastewater at each site. These estimates, albeit rough, provide some notion of the significant water quality subsidy that the lowered atmospheric N deposition has furnished.

We used the relationship derived in Cebrián *et al.* (2014) in another way, to assess whether the model results yielded N loads that were in any way reasonable in regard to the growth of macroalgae within each of the three Waquoit Bay estuaries (Fig. 8b). The values of macroalgal biomass that would be expected on the basis of the NLM predictions of N loads, and the consequent biomass that could grow, based on the relationship of Fig. 8a, are remarkably similar to the values we obtained through sampling in 2015 (Fig. 8b). This result simultaneously suggests that the NLM estimates of N loads seemed reasonable, and that the response by N-sensitive macroalgae was also reasonably described.

4. Discussion

The finding that changes in N sources to the Waquoit estuaries have been of significant magnitude argues that management of estuarine water quality needs to consider some measure of time-dependency in the development of N loads, and derived measures such as TMDLs, rather than fixing them to a single, unchanged time-explicit baseline. The importance of shifting baselines in water quality indicator trajectories under changing conditions highlighted here corroborates the importance of shifting baselines already pointed out by Duarte et al. (2009). Given the magnitude of the shifts that we report here, and the conclusions by Duarte et al*.* (2009), protocols assuring adaptive management measures and applications seem best suited to guide actions in a time of rapid external changes. In the case of the Waquoit estuaries, the balancing of lower deposition and higher wastewater contributions occurred in part because of the ratio of open to developed land, which alters the relative contributions of atmospheric deposition and wastewater loading. In estuaries with differently sized or developed watersheds, similar shifts in external drivers may significantly alter the magnitudes of N loads and of their effects. To maintain desired water quality and ecosystem health, managers need to make use of loading estimators that account for 282 the influence of such external drivers.

It should also be mentioned that the scope and feasibility of potential management action is constrained by the spatial scale of the process driving the changes. Management of the large-286 scale drivers, such as climatic shifts affecting air mass tracks, could only be effected by concerted global-scale international action. Regulation of emissions to the atmosphere would need at least national-scale action. On the other hand, control of watershed-scale N loads is well-









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## **Tables**

Table 1. Mean values  $\pm$  standard errors for nutrients and producers sampled from May-October in each of three studied estuaries. Sage Lot Pond (SLP) experiences the lowest rates of N loading per hectare of estuary and lowest proportion of N from wastewater, Quashnet River (QR) is intermediate in both categories, and Childs River (CR) experiences high loading rates and high loads from wastewater. Lines across columns indicate no significant difference between years or among estuaries. Pre-2015 nutrient data represents pooled means from 1994-2004; macroalgae data from 1992-1998; and eelgrass data from 1992-1998.



Table 2. New and original values of default variables used in the update for NLM. To ensure an accurate count only of buildings with septic systems, we selected three random 16-hectare plots in each watershed (in areas not served by sewage treatment plants), and counted the number of residences and of other kinds of structures on each plot. The original NLM model also accounts for nitrogen in runoff in two separate categories: off roads and commercial surfaces, which drain directly through grates, and off roofs and driveways, where water flows over the edge and percolates through adjacent vegetation and soil. In our update we added areas designated as driveways to the road category, since driveways often drain into streets, and because they were digitized in the new land cover data as part of the roads data layer. 2014 data from CCC (2012) and Horsley Witten (2014).



Table 3. Results from updated NLM showing modeled nitrogen loads, partitioned by source, arriving to each estuary. All loads in kg N yr<sup>-1</sup>.



Table 4. Statistical analyses pertaining to Figure 5.



Table 5. *P* values obtained from Tukey HSD post-hoc tests comparing nutrient and macroalgae data among estuaries experiencing varied rates of N loading, and between 2015 and previous years within each estuary. DIN concentration and macroalgal biomass vary significantly among estuaries but have not changed significantly over time.

