Decadal trajectories of land-sea couplings: Nitrogen loads and interception in New England watersheds, discharges to estuaries, and water quality effects

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Abstract

Couplings between coastal watersheds and estuaries were assessed in a series of sites across SE New England. Nitrogen loads to watersheds increased during 1985-1996, but decreased afterwards due to lowered atmospheric deposition. Within-watershed nitrogen interception was high and linked to forest cover. Loads to estuaries also increased pre-1996 and decreased after because of lowered atmospheric inputs. Concentrations of nitrogen compounds were higher in estuaries subject to larger nitrogen loads from land. Estuarine nutrients showed large scatter and decreased from less-saline to saltier reaches. Chlorophyll and oxygen

concentrations were less reliable indicators of coupling to watershed loads. Water quality variables were lagging indicators of changing nitrogen loads, with shifts in concentrations becoming detectable several years after the 1996 shift in total nitrogen loads. Lag delays will be of significance for assessment of the effectiveness of estuarine water quality management.

Keywords: Watershed, estuaries, nitrogen loads, water quality, nitrogen interception, lagging indicators

Highlights:

- Lower atmospheric N deposition decreased N loads to watersheds and estuaries
- Watersheds intercepted >80% of total N loads, an important ecological service
- Estuarine nutrients and chlorophyll were variable lagging indicators of N loads

1. Introduction

Coastal regions characteristically display powerful couplings between the adjoined land and estuarine ecosystems. The land-water couplings differ from one area to another, because of complexities and differences in land cover, geomorphology, hydrology, and topography of the watersheds, as well as hydrodynamic and habitat differences in the estuarine side. Local contrasts in such characteristics lead to differences in fluxes, losses, and exports of substances and materials. In addition, there are major regional or global-scale drivers that can exert strong influences on these rates and coupling processes, including the delivery of nitrogen (N) from watersheds into estuaries.

Discharges of N loads from land to estuaries are a major control on estuarine water quality and ecosystem function. Such discharges are substantial, widespread (Seitzinger et al., 2010), and have increased during recent decades (Bricker et al., 2008; Nixon and Buckley, 2002; Valiela, 2015, 2006). The increases in N loads, and the consequent eutrophication and lower water quality have prompted many monitoring efforts.

As many other coastal areas around the world, the estuaries in the Buzzards Bay region in SE New England have received increased N loads from land, associated with declining estuarine water quality as represented by decreases in seagrass cover (Costa, 1988; Costello and Kenworthy, 2011), and increases in macroalgal biomass (Valiela et al., 1999) and phytoplankton abundances (Rheuban et al., 2016). To assess decadal changes in water quality in estuaries of SE New England, the Buzzards Bay Coalition (BBC) has supported a water quality monitoring program that has sampled estuaries within Buzzards Bay since 1992 (Jakuba et al., 2021). The data from these sampling efforts documents decadal changes in water quality in a series of diverse estuaries that have been subjected to changed N loads from their watersheds (Rheuban et al., 2016; Williamson et al., 2017). Similar shifts have been reported for a number of other coupled watershed-estuary systems in the SE Massachusetts region (Benson et al., 2013; Carmichael et al., 2004; Tu, 2009; Valiela et al., 2021, 2016, 1997b, 1992).

In this region there have been two major changes that altered N loads. First, watersheds in the Buzzards Bay area have discharged increased N loads to estuaries, but the loads differ, because different watersheds followed different trajectories in the forest-to-urban transition, and so differ in land cover mosaics, with different proportions of forested, residential, agricultural and other land cover types (Williamson et al., 2017). Second, watersheds and estuaries of Buzzards Bay and elsewhere have been exposed to significant regional decreases in atmospheric deposition of N (Lloret and Valiela, 2016).

Williamson et al. (2017) found that in many Buzzards Bay watersheds, declines in N sourced from atmospheric deposition were offset by increases in housing development with onsite wastewater disposal, leading to no 30-year trend in total N loads. Similar results were observed in estuaries of Cape Cod by Valiela et al. (2016). Here, we delve deeper into the patterns in N loads to better understand if decadal, or even sub-decadal shifts are evident and if estuaries are responding to declining atmospheric deposition on shorter time scales.

Furthermore, these watersheds have received contrasting N inputs from the various human sources and changing atmospheric deposition, but the loads are not quantitatively transferred or discharged to receiving estuaries. In fact, a large fraction of the N delivered to the land is effectively intercepted within watersheds, before those inputs reach estuarine waters. Within-watershed interception is particularly significant in vegetated tracts, but the magnitude of this interception decreases as the land becomes progressively developed (Goodale et al., 2002; Lajtha et al., 1995; Seely et al., 1998; Sudduth et al., 2013; Valiela et al., 1997a, 1992). The degree to which N is intercepted within watersheds has considerable management and basic implications, since interception may protect water quality in receiving estuaries.

The existence of these marked changes in local vs regional sources of N to Buzzards Bay watersheds and estuaries, and the availability of the BBC monitoring record therefore allow an assessment of the importance of changes in atmospheric deposition, as well as defining the balance between increased wastewater and fertilizer contributions and lowered atmospheric deposition. Furthermore, most work on management of land-estuary couplings considers total N loads, but there are grounds to suspect that different forms of N (nitrate, ammonium, and dissolved organic N) might show different decadal trajectories, responses, and effects on water quality. The BBC monitoring data provide separate determinations of concentrations of the different N forms, and therefore allow assessing the role of each form as well as that of total N.

In this paper we first define the inputs to watersheds (as total N loads to watersheds, and separated by wastewater, fertilizer, and atmospheric deposition), within-watershed interception, and discharges to receiving estuaries in a series of coupled watershed-estuary systems in the SE coast of New England, and document decadal (1985-2013) trajectories of these variables. This task was made possible thanks to the availability of a validated and updated N loading model (NLM, Valiela et al., 1997a), and data on land use and atmospheric deposition from 1985-2013 (Williamson et al., 2017).

In a second phase of work, we tested the linkage of terrestrial discharges and water quality in the receiving estuaries, by defining 1) the role of local and regional drivers as they change across the decadal record; and 2) links of decadal changes in N loads to presumed indicators of water quality, including nitrate, ammonium, dissolved organic N (DON), total dissolved N (TDN), chlorophyll, and oxygen in the estuaries. To achieve these aims, we took advantage of multi-annual data (1992-2018) furnished by the BBC monitoring of nutrients, chlorophyll, and oxygen in estuaries in the SE New England region (Jakuba et al., 2021).

2. Materials and Methods

2.1. Estimating nitrogen inputs to watersheds and modeling nitrogen loads to estuaries

2.1.1. Estimating nitrogen inputs and interception within watersheds

To estimate annual N loads to each watershed and to each estuary, each year, we used the NLM model (Valiela et al., 1997a) that was validated (Valiela et al., 2000) and successfully applied in Barnegat Bay, NJ (Bowen et al., 2007b), 13 estuaries in New Zealand (Heggie and Savage, 2009), 74 estuaries in New England (Latimer and Charpentier, 2010), 12 coastal lagoons in MD, DE, VA (Giordano et al., 2011), Great South Bay, NY (Kinney and Valiela, 2011), Great Bay, NH (Wood and Trowbridge, 2014), 7 estuaries in Eastern Canada (McIver et al., 2015), and 28 estuaries in Buzzards Bay, MA (Williamson et al., 2017). NLM separately keeps track of N loads from wastewater, fertilizer, and atmospheric deposition unto watersheds, as well as losses—via sequestration or discharge as gases—during transit through watersheds. An additional asset of NLM are estimates of uncertainty for N loads obtained by error propagation methods (Collins et al., 2000), an unusual feature useful in comparisons of N loads.

NLM requires input data on land use, atmospheric deposition, number of homes using septic systems, point source discharges into the estuary, and land cover to estimate N loads (Valiela et al., 1997a). The necessary input data was obtained from Williamson et al. (2017), which used linear interpolations to generate a time series of land use, impervious surface coverage, and wastewater effluent loads in the study area that range from 1985 to 2013. The land use categories compiled by Williamson et al. (2017) included the areas of natural vegetation, lawns, golf courses, agriculture, impervious surfaces and freshwater ponds. Similarly, to create time series of atmospheric nitrogen deposition for each watershed, we used the data compiled by Williamson et al. (2017), who used a combined analysis of gridded total nitrogen deposition (wet and dry organic and inorganic nitrogen) and inorganic nitrogen deposition from the National Atmospheric Deposition Program (Lloret and Valiela, 2016; Schwede and Lear, 2014).

Watershed boundaries were obtained through the Buzzards Bay National Estuary Program. Although the cited Williamson et al. (2017) work compiled data for a larger area in Southeastern Massachusetts, this work focuses on a subset of eleven watershed-estuary systems located in the eastern and northern shores of the Buzzards Bay (Fig. 1). These eleven groundwater fed systems were selected not only because of their similar lithological and hydrological characteristics that differentiate them form the watersheds in the western side of Buzzards Bay (Simcox, 1992), but also because of the availability of the most updated and authoritative watershed delineations, developed and adopted in current regional plans (Cape Cod Commission, 2018). NLM simulations, following inputs of the appropriate land cover data, and other updated information provided calculation of total N inputs, partitioned into contributions by wastewater, fertilizer use, and atmospheric deposition to the watershed surface, as well as interceptions of these N inputs within the watersheds, for each of the selected systems, annually from 1985 to 2013.

2.1.2 Calculating nitrogen loads to estuaries

The selected Buzzards Bay estuaries are small, ranging from 0.3 to 5.5 km^2 in area, and relatively shallow, with an average depth of ~2 m. The estuarine area can be distinguished from the main Buzzards Bay by the existence of a well-defined inlet. We estimated N loads received by each estuary by adding estimated export from contributing watersheds, obtained by NLM, plus direct deposition of atmospheric N to the surface of each estuary. As done for contributing watersheds, direct atmospheric deposition onto the estuary surfaces was derived from the analysis of gridded nitrogen deposition from the National Atmospheric Deposition Program (Lloret and Valiela, 2016; Schwede and Lear, 2014). For our estimates, the estuary area included all area below the hightide mark, and contained not only bare sediment (as in Williamson et al. 2017) but also salt marsh habitats receiving the N, as done in many other previous studies (Carmichael et al., 2004; Valiela et al., 2021, 2016). The areal extent of fringing salt marsh habitats in the selected estuaries was obtained from Mcowen et al. (2017). Uncertainty in our calculations of N loads to the estuaries was estimated following Collins et al. (2000).

Two of the estuaries that we selected (WF and WR in Fig. 1) had an additional N source, discharges from a wastewater treatment plant (in all the other watersheds, wastewater was disposed via septic tanks). Treatment plant discharges from 1985 to 2013 were compiled and reconstructed by Williamson et al. (2017). These treatment plants collected wastewater from within and beyond the watersheds of the two estuaries, and then disposed of treated effluent directly into surface waters in the case of WR, or via filtration beds, and groundwater transport to the estuary in the case of WF.

2.1.3. Assessing net effects of decadal changes in contributions from wastewater, fertilizers and atmospheric deposition on estuary nitrogen loads

To evaluate the net effect of decadal increases in wastewater and fertilizer contributions vs the recent decreases in atmospheric deposition (Fig. 2), we separately calculated slopes of regressions of N loads to watersheds and to the estuaries (Figs. 3, 4, and 5) before and after 1996. That year was the statistically determined breakpoint in the sequence of data on regional atmospheric deposition marking the shift from variable, no-trend trajectory, to a decreasing trend (Lloret and Valiela, 2016) in regional atmospheric N deposition (Fig. 2).

2.2. Analyzing decadal trajectories on water quality indicators and their relationship to nitrogen loads

To test whether decadal changes in N load trajectories were reflected in changes in water quality, we compared changes in kg N per hectare of estuary^{-1} yr^{-1} to changes in measured concentrations of nitrate, ammonium, DON, chlorophyll, and oxygen, collected by the BBC water quality monitoring for each of the estuaries across the years of the sampling (Jakuba et al., 2021). These variables are frequently used as water quality indicators. The BBC stations in the selected estuaries were located at relatively similar shallow depths (2.2 ± 0.9 m, aver.±s.d.), facilitating our comparisons.

The analysis below is aimed at assessing the relative sensitivity of responses of the different indicators to changes in N loads. We fitted the data using a non-parametric locally estimated scatterplot smoothing (LOESS) regression. The fitted LOESS regressions were used to identify possible temporal changes in water quality trends. The analysis allowed us to define periods (i.e. segments of the distribution) where the trends in water quality indicators shifted significantly.

For our analyses we used all available observations for all the stations in the BBC network that were located within the limits of the selected estuaries. We used data collected in 64 sampling stations, accounting for a total of more than 7,000 observations for each of the studied variables. Sampling locations within each estuary were spaced to capture the major environmental gradients along the land-to-sea axis. The BBC data were mostly obtained during the summer, so conclusions are limited to the warm-weather season. Further details of the sampling and analytic procedures are given in Jakuba et al. (2021).

3. Results and discussion

3.1. Multidecadal changes in nitrogen inputs and interception within watersheds, and nitrogen loads to estuaries

3.1.1. Nitrogen loads to watersheds

The N loads delivered to the watersheds in this study varied across the decades, as did the contributions from the three major sources (Fig. 3). In general, total N loads increased up to about the end of the last century, then either decreased or remained variable but lacking in trend. The trajectories differed among watersheds, in part a result of different combination of contrasting land covers and type and magnitude of the major N sources (Table 2).

Contributions by septic system wastewater differed among the watersheds, but mostly increased across the decades, with a few year-to-year irregularities along the course of years (Fig. 3). From 1985 to 2013, delivery of N via septic system wastewater generally increased in most watersheds. The only exceptions where the BB and WR watersheds, where we found decreases of 10% and 7% of septic system wastewater. In the other watersheds septic N contributions increased by 15% to 68%.

N contributions by fertilizers to the watersheds increased by 8% to 139%, depending on the watershed, with a mean 20% increase. N loads from septic systems exceeded those of fertilizer in seven out of the nine watersheds without wastewater treatment plants (Fig. 3). The two exceptions were the BB and RB watersheds where cranberry bogs and other agriculture were more common, and where associated fertilizer contributions became more important.

N contributions by atmospheric deposition to the watershed surfaces varied from year to year (Fig. 3), with interannual changes that reflected the year-to-year pattern of trajectory of regional atmospheric deposition (Fig. 2). At decadal scales, atmospheric N deposition increased variably up to about 1996, and then ceased increasing or decreased post-1996 (Fig. 3), in parallel to regional trajectories (Fig. 2). The pre- and post-1996 N loads differed greatly among watersheds (Table 1 first column of numbers). On aggregate, for all the watersheds, mean pre-1996 loads increased by 9%, while post-1996 mean loads decreased by 10% (Table 2). The decreases in atmospheric N deposition were of sufficient magnitude to offset the parallel increases in contributions from septic system wastewater and fertilizers (Table 1).

3.1.2. Within-watershed interception of nitrogen

Throughout 1985-2013, interception of total N loads entering the eleven Buzzards Bay watersheds ranged between 80% and 87% (Table 1, last column of numbers), a narrow range in spite of differences in land use mosaics among the watersheds and areas of watersheds (Williamson et al., 2017). These estimates (Fig. 4) are within the range of published values of watershed N interception (Groffman et al., 2004; Jaworski et al., 1992; Lovett et al., 2000). Within-watershed N interception depends on land use mosaic on watersheds, including % forest cover (Fig. 4). Within-watershed N interception increased significantly in proportion to % forest cover, and in general was high (Fig. 4). There is one outlier point in Fig. 4 that was calculated for an urban watershed defined on the basis of an infrastructure map of drains through the area. This drain network assures fast transit and voids exposure to within-watershed loss processes. The resulting much lower N retention of this point highlights the importance of exposure during actual transit through watersheds to maintain high interception.

The range of within-watershed N interception documented in Fig. 4 is substantial, is remarkably consistent in a variety of different watersheds, and is in part linked to natural vegetation cover. These results point to the need to maintain forested tracts, because they provide an important long-term ecological service that has to a degree constrained eutrophication of down-gradient estuaries.

We note that only 16% of the N loads that managed to be discharged from watersheds to estuaries. That small amount is the source of eutrophication of these estuaries, which has attracted attention of agencies that are charged with maintenance of water quality, and have imposed regulations that require lowering N loads. There should be concern that further urbanization may decrease within-watershed interception—for example by decreasing area of forested tracts (Table 1, 8th column of numbers) and adding wastewater and fertilizer inputs, N sources that are less-well retained within watersheds (Table 1, 6th and 7th column of numbers). Such effects of urbanization likely will threaten the continuity of the high watershed interception we report here, and inevitably increase eutrophication of receiving estuaries. Research that further identifies mechanisms or land covers mainly responsible for N interception in coastal watersheds seems a high priority to establish coastal watershed land management policy.

3.1.3. Nitrogen loads to receiving estuaries

We estimated N loads to the estuaries by summing discharges from land to direct atmospheric deposition on estuary surfaces. Our loads differ from previous estimates by Williamson et al. (2017), since our estuary surface area definition includes the area of salt marsh habitats that are regularly inundated by tides, and therefore also receive the N.

Land-derived N loads to estuaries were significantly lower than N loads to watershed surfaces, an effect of the high degree of interception within watersheds (Table 1). A similar conclusion was reported in other local estuaries (Carmichael et al., 2004; Valiela et al., 2016; Williamson et al., 2017). We focus here on the mass balance inputs and losses via water transport. Other processes (N fixation, denitrification, retention etc.) are active within estuaries, and may increase or diminish N budgets, but lacking such data for the Buzzards Bay estuaries we focused on the water-borne mass flows.

Trajectories of total N loads to the different estuaries (Fig. 5) differed in magnitude and decadal trends. The among-estuary differences were generated by contrasting inputs from septic system wastewater, fertilizer, and atmospheric N deposition. Septic system wastewater contributions to estuaries increased by 15% across 1985-2013, as urbanization of the watersheds advanced, with some irregularities likely owing to changes in municipal regulations within the watersheds. Fertilizer use in the watersheds of all eleven estuaries added minor amounts of N, but their contribution increased by about 18% (mainly to use in turf and cranberry crops) in the period of study.

The one common N input to all the watershed-estuary systems was atmospheric deposition, a regional process (Fig. 2) that left an interannual imprint on the year-to-year changes in N loads to the estuaries (Fig. 5). To assess whether the decadal shift (pre- and post-1996) in atmospheric deposition (Fig. 2) was large enough to be detectable in the trajectory of N loads to the estuaries, we calculated the slopes of N load rates pre- and post-1996 for each estuary (Table 2). 8 out of the 9 estuaries without wastewater treatment plants showed increased N loads before 1996, with a weighted mean of 19.2% increase during 1985-1996 (Table 2). In contrast, 7 out of 9 estuaries received decreased N loads post-1996, with a weighted mean decrease of 12.1% (Table 2). The post-1996 decrease in atmospheric N deposition was sufficient to counter the increases from septic wastewater and fertilizers, with a net result of decadal decreases in N loads. We conjecture that, excluding the estuaries with N inputs from wastewater treatment plants, if increases in contributions of N from atmospheric deposition had remained at pre-1996 rates, by 2013 we could have seen N loads rising an additional 11%. Instead, we found decreases of about 12%. These net differences may or may not be large enough to suggest a regime change in N loads to the region's estuaries. Below we assess whether indicators of water quality that were measured in the BBC sampling reflected the changes in inputs of N.

The recent decrease in N loads, a result of air pollution regulations plus global-scale changes in airmass directions (Lloret and Valiela, 2016; Puntsag et al., 2016), provided some relief from the increasing N loads and resulting eutrophication in the region's estuaries. This may allow more time to evaluate the alternatives available for each estuary, and develop management strategies best suited for individual estuaries. The relative effects of local-scale, watershed-based controls by land covers and other local features, versus those of global-scale origin that our estimates have revealed is an issue that needs to be considered when making predictions for future management plans. Managers will need to include regional and global change issues as part of developing strategies to address local problems such as maintenance of estuarine water quality.

3.1.4. Nitrogen load trajectories in watershed-estuary systems with sewage treatment plant inputs

The decadal trajectories of N loads in two watershed-estuary systems with wastewater discharges from sewage treatment plants (WF and WR, Fig. 6) differed from those in the systems in Figs. 3 and 5. N loads to the WF watershed were relatively unchanged up to the early 1990s, and then increased sharply until early in this century (largely tracking N inputs from the Falmouth sewage treatment plant via filtration beds into the aquifer). The trend was halted when improvements in technology in the treatment plant prevented further increases. The discharges from the wastewater treatment plant overwhelmed other sources, including the increases in N loads from septic systems and fertilizers, and the decrease in atmospheric deposition (Fig. 6 top left). These patterns were even more pronounced in the estimated loads to the WF estuary, where the treatment plant discharges became even more dominant (Fig. 6 top right), suggesting considerably lower interception of N in the plume from the sewage treatment plant than for N from the other sources.

N load trajectories for WR were different still (Fig. 6 bottom panels). Contributions from septic systems and fertilizers increased slowly as in most of the watersheds. Fertilizer contributions were larger than those from septic systems, because cranberry cultivation in the WR watershed is widespread. Discharges from a sewage treatment plant occur directly into the WR estuary waters, and also decreased into the 21st century. These changes then allowed the decrease in atmospheric deposition to dominate the trajectory of total N loads to the receiving estuary (Fig. 6 bottom panels). The differences between WF and WR indicate that inputs from treatment plant plumes, whether directly to estuary waters or into the aquifer via infiltration beds, can completely alter decadal trajectories of N loads, and can be overwhelming, but that they can be effectively managed.

3.2. Multidecadal effects of changing nitrogen loads on water quality indicators

3.2.1. Links of nitrogen loads to nitrogen concentrations in estuaries

The N loads entering each estuary across the several decades fell within a relatively narrow range (Figs. 5 and 7). Up to this point we have presented data separately for individual watershed-estuary systems. To define the influence of the full range of N loading rates on concentrations of N in receiving estuaries, now we need to pool data on mean annual concentrations of N measured in the estuaries, collected each year of the monitoring survey, vs. the N loads to each estuary (Fig. 7). Larger N loads delivered to estuaries were significantly associated with larger concentrations of nitrate, ammonium, DON, and TDN (Fig. 7). Responses of nitrate and ammonium to higher N loads were accelerated (Fig. 7 top panels); that of DON (Fig. 7 bottom left) much less so. The decadal response of TDN to increased N loads (Fig. 7 bottom right), was similar to that of DON, owing to the influence of the large concentrations of DON.

The plots of Fig. 7 show considerable scatter. Some of that variation could be attributable to variables other than N loads (Bettez et al., 2015). We examined whether some of the variability could be attributed to the gradient in salinity from upper to lower reaches in these estuaries, and to effects of the recent decrease in atmospheric N deposition.

3.2.2. Effects of salinity

To assess possible effects of salinity on N concentrations, in Fig. 8 we re-plotted the pooled data of Fig. 7, sorting N concentration data into three salinity bins (<15, 15-25, >25). ANCOVAs, calculated after log transformation of the data to meet statistical assumptions, showed that, first, concentrations of nitrate, ammonium, and TDN (but not DON) increased as N load increased: larger external loads forced larger concentrations of these forms of N in estuary water.

Second, there were significant interactions of salinity and N loads (Fig. 8). Samples from upper reaches, with lower salinity, tended to significantly display larger concentrations of nitrate, and TDN, and the effect was larger in estuaries that received larger N loads from their watersheds. The interactive effects were smaller for ammonium and nil for DON. These contrasts suggest that the salinity links were not merely a feature of freshwater delivery rates. It is also important to note that, during the duration of this study, the area of Buzzards Bay did not experience changes in freshwater discharge that could have impacted nitrogen loads, as revealed by the lack of any significant trends in precipitation or salinity in these estuaries (Rheuban et al., 2016).

DON concentrations not only lacked evident responses to N loads or salinity but also ranged considerably higher than those of nitrate or ammonium (note change in scale in vertical axis, Fig. 8 bottom left), and were highly variable (Fig. 8 bottom left). DON is a dominant term in estuarine N pools, with minor responses to salinity or external N loadings, but may or may not be biologically active, since about 70% of DON may be refractory (Lusk and Toor, 2016; Neff et al., 2003; Seitzinger et al., 2002; Sun et al., 2017; Valiela, 2015; van Kessel et al., 2009). Since DON makes up a large fraction of TDN, the term usually used in regard to land derived N loads, investigation of responses of labile fractions of DON in estuaries seems a high priority.

TDN concentrations integrated the various features of its component parts. TDN concentrations responded to increased N loads across all reaches of the estuaries, but to a greater degree within fresher reaches of the estuaries, with attenuated responses at higher salinities (Fig. 8 bottom right). Mean TDN concentrations and their response to N loads differed significantly among the three salinity groups, as confirmed by the ANCOVA results.

3.2.3. Effects of lowered atmospheric nitrogen deposition

Concentrations of nitrate, ammonium, DON and TDN in the estuaries showed large variation within a sampling date, within and among estuaries, and across years. LOESS regression curves helped us identify shifts in the trajectory of changes in concentrations (Fig. 9). Up to the early 2000s, concentrations of nitrate and DON increased and those of ammonium remained variable but trendless (Fig. 9). More recently, concentrations of all the measured forms of N, while variable, decreased significantly. The change in trend occurred later for DON (2006) than in the case of nitrate and ammonium (2003 and 2001, respectively). TDN integrated all these shifts, increased up to 2005, and decreased in more recent years (Fig. 7 bottom right). The observed shifts in trajectories agree with the calculations in Table 1. Since N contributions from wastewater and fertilizers continued to increase during recent decades, we conjecture that the observed post-2000 decrease in concentrations are linked to lowered atmospheric N deposition.

The breakpoint we determined for the shift in atmospheric deposition was 1996 (Lloret and Valiela 2016, and Fig. 2). It might be of interest for management purposes to note that N concentration in the water lagged for some years after that date (Fig. 9). In these groundwater fed systems, the lagged response of estuarine N concentrations could be a result of legacies of N pollution in local aquifers and long groundwater residence times (Lindsey et al., 2003; Mullaney, 2007), as well as other within-estuary N processes and cycling in sediments and adjacent marshes (Bowen et al., 2007a; Fulweiler et al., 2010). These lagged responses suggest that managers need to expect that for any plan that lowers N loads by a 12-34% of N load to estuary (a magnitude comparable to the decrease created by the lowered atmospheric deposition), the responses in lowered N concentrations may become detectable some 4 to 10 years after the management plan is put in place.

3.2.4. Links of nitrogen loads to chlorophyll concentrations in estuary water

The concentrations of chlorophyll measured in the BBC monitoring were highly variable and did not respond to differences in N loads (Fig. 10 top). There was a significant and larger mean of chlorophyll concentrations measured in samples with lower salinities (Fig. 10 top). The salient feature of the chlorophyll data, however, was the large scatter, which suggests that warm-season chlorophyll concentrations might not be a highly reliable indicator of responses to changes in external N loads to estuaries.

Our analysis of decadal trends, as done for nutrient concentrations, showed that chlorophyll concentrations increased up to 2009, then decreased markedly in recent years (Fig. 10 bottom). This might be a response to the reduction in atmospheric N deposition reported in Fig. 2, and that appeared confirmed by the trajectory shifts in concentrations of DIN and TDN (Fig. 9). Chlorophyll may also be a lagging indicator of N supply and eutrophication.

3.2.5. Nitrogen loads and oxygen concentrations in estuary water

Oxygen concentrations were highly variable in the Buzzards Bay estuaries, along the N load gradient and across the years; the increase in scatter though the decades is likely an artifact of larger number of samples during recent years (Fig. 11 top and mid panels). The data scatter was large enough to overwhelm discernible effects of changing N loads across the decades of sampling or of salinity of the water sampled. This result implies that oxygen concentration is too labile or transient to be a reliable indicator of water quality, at least for these estuaries and with this sampling design and frequency. Only about 4% of oxygen concentration measurements in the Buzzards Bay estuaries were under the 4 mg L^{-1} threshold (Fig. 11 bottom panel) below which some damaging biological effects may be expected (Conley et al., 2009; Vaquer-Sunyer and Duarte, 2008). The level of eutrophication prompted by the N loads entering the Buzzards Bay estuaries during the decades of sampling by the BBC was mostly insufficient to create damaging hypoxic conditions. In these systems, discrete measurements of oxygen concentrations are probably not reliable indicators of incipient levels of eutrophication.

4. Conclusions

Our analyses have confirmed that the recent decrease in atmospheric nitrogen deposition over the New England region has been responsible for a measurable decrease in N loads to watersheds in the Buzzards Bay area. The watersheds of these estuaries carry out an important ecological service by intercepting a large fraction (>80%) of total N loads, and preventing larger inputs to estuaries. The importance of his service seems to be linked to the presence of extensive forested tracts in the landscape.

N loads to Buzzards Bay estuaries also decreased in response to lowered atmospheric inputs. Estuarine water quality improved in response to the decrease in N inputs, but the different indicators (nutrients, chlorophylls) showed a lagged response, with shifts in concentrations becoming detectable several years after the shift in total N loads. These lag delays will be of significance for assessment of the effectiveness of estuarine water quality management, since responses to decreased N loads may become detectable several years after plans are put in place.

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Author Contributions: JL and CV carried out modeling, calculations, and graphics; IV developed the plan of work, obtained the funding, and managed the course of the research; JR provided land use data and other needed model input information; RJ provided long-term water quality monitoring data; DH, KC, and EE contributed to data analyses. All authors participated in the writing and editing of the many versions of the manuscript.

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Table 1. N loads pre- and post-1996, and % losses within watersheds.

Period	Estuary	Average N load to watershed (kg N yr^{-1})	Change in N load to watershed (kg N yr^{-1})				Losses within watershed (% of inputs)			
			Septic	Fert.	Atm. dep.	WWTP	Septic	Fert.	Atm. dep.	Total
Pre-1996	Buttermilk Bay	81,147	-788[a]	+241	+172	-	74	89	88	84
	Great Sippewissett Marsh	7,952	+58	+30	+41	-	74	95	91	86
	Megansett Harbor	39,254	+159	+200	+197	-	73	94	90	86
	Phinneys Harbor	33,753	+128	+340	+124	-	74	91	90	85
	Pocasset Harbor	11,258	+24	+14	+27	-	74	93	91	84
	Pocasset River	25,187	+80	+48	+109	-	73	93	90	85
	Quissett Harbor	2,427	+8	+5	+4	-	74	95	91	85
	Red Brook Harbor	17,260	+40	+141	+97	-	72	87	91	87
	Wild Harbor	25,433	+179	+108	+111	-	74	94	90	85
	Wareham River Estuary	295,791	+166	+906	+725	-	73	86	88	80
	West Falmouth Harbor	17,364	+73	+71	+80	+371	73	94	91	84
	Mean for all estuaries						74	92	90	85
Post-1996	Buttermilk Bay	78,238	+143	-63	-427	-	74	89	88	84
	Great Sippewissett Marsh	8,267	+36	+15	-102	-	74	95	91	85
	Megansett Harbor	39,557	+97	+127	-447	-	74	93	90	85
	Phinneys Harbor	38,703	+241	+182	-260	-	74	90	90	84
	Pocasset Harbor	11,238	+20	+4	-64	-	74	93	90	84
	Pocasset River	24,682	+21	0	-237	-	73	93	90	84
	Quissett Harbor	2,571	+5	+12	-16	-	74	94	91	84
	Red Brook Harbor	16,799	+18	+25	-208	-	72	87	90	86
	Wild Harbor	29,802	-19	+302	-233	-	74	92	90	84
	Wareham River Estuary	280,345	-148	+35	-2,102	-	73	86	88	81
	West Falmouth Harbor	30,792	+70	+33	-184	+832	73	94	91	69
	Mean for all estuaries						73	91	90	83

[a]Decrease in Buttermilk Bay owing to an increase in the number of houses connected to sewer in the late 1980s and early 1990s and a subsequent decrease in septic system N.

Table 2. % N load changes to Buzzards Bay pre- and post-1996

Estuary	To watershed		To estuary	
	Pre-1996 N load change (%)	Post-1996 N load change (%)	Pre-1996 N load change (%)	Post-1996 N load change (%)
Buttermilk Bay	-5.2[a]	-6.9	-10.4[a]	-7.2
Great Sippewissett Marsh	+19.8	-9.1	+19.2	-11.1
Megansett Harbor	+17.7	-8.3	+16.3	-11.0
Phinneys Harbor	+22.7	+6.9	+20.2	+0.8
Pocasset Harbor	+6.7	-5.5	+8.5	-15.2
Pocasset River	+11.2	-12.6	+11.8	-7.8
Quissett Harbor	+8.3	+1.3	+8.4	-9.7
Red Brook River	+20.3	-13.8	+20.5	-12.1
Wild Harbor	+19.6	+2.8	+20.5	-0.5
Wareham River Estuary[b]	+7.1	-19.0	+6.4	-39.8
West Falmouth Harbor[c]	+45.0	+50.1	+84.9	+94.8
All estuaries	+9.1	-10.1	+22.9	-35.5

[a]Decrease in Buttermilk Bay owing to an increase in the number of houses connected to sewer in the late 1980s and early 1990s and a subsequent decrease in septic system N.
[b]Wareham River Estuary received direct discharges from a wastewater treatment plant that was upgraded to lower N discharges.
[c]West Falmouth Harbor received discharges from a wastewater treatment plant, whose inputs (via infiltration into the aquifer) increased greatly during last century, and remained stable after operational improvements in recent years.

Table legends*:*

Table 1. Averaged total N loads to watersheds, annual changes in N loads from septic system wastewater, fertilizer use, atmospheric deposition, and point sources and percent losses within watersheds from the various sources in the selected estuaries during the period of data collection, separately for pre- and post-1996 time intervals.

Table 2. % changes in N load to Buzzards Bay watersheds and estuaries, calculated for pre- and post-1996 years from data in Figs. 3, 4, and 5.

Figure legends*:*

Fig. 1. Location of the coupled watershed-estuary systems selected for this study: WR (Wareham River), BB (Buttermilk Bay), PhH (Phinneys Harbor), PR (Pocasset River), PH (Pocasset Harbor), RB (Red Brook Harbor), MH (Megansett Harbor), WH (Wild Harbor), WF (West Falmouth Harbor), GS (Great Sippewissett Marsh), and QH (Quissett Harbor).

Fig. 2. Trajectories of atmospheric nitrogen deposition for a) New England states (CT: Connecticut; ME: Maine; MA: Massachusetts; NH: New Hampshire; VT: Vermont) and b) Cape Cod region. Data compiled from the EPA NADP and CASTNET monitoring networks. Updated from Valiela et al. (2016).

Fig. 3. N loads to the watersheds of the estuaries in this study. Acronyms as in Fig. 1. Note that the scales for the vertical axes vary, with watersheds receiving lower loads in the upper row of panels, to those receiving larger loads in the lower row.

Fig. 4. % within-watershed N interception in the sites from this study, and from literature sources, plotted vs. the % of the watersheds that were forested. Data from watersheds with inputs from wastewater treatment facilities (WF and WR) were not included. Regression line includes all data except the outlier marked with an asterisk (see text).

Fig. 5. N loads to nine estuaries in this study that lack N inputs from wastewater treatment plants. Loads to estuaries are normalized per area of estuary. Acronyms as in Fig. 1. Note that the scales on the vertical axes differ in the three rows of panels.

Fig. 6. N loads to watersheds (left panels) and N loads to two estuaries normalized per area of estuary (right panels) that receive discharges from wastewater treatment plants. Acronyms as in Fig. 1.

Fig. 7. Mean annual concentrations of nitrate, ammonium, DON, and TDN, for each estuary, for every year (1992-2013), plotted versus the N loads to the estuary, normalized per area of estuary. Regression F values and their significance level indicated in each panel.

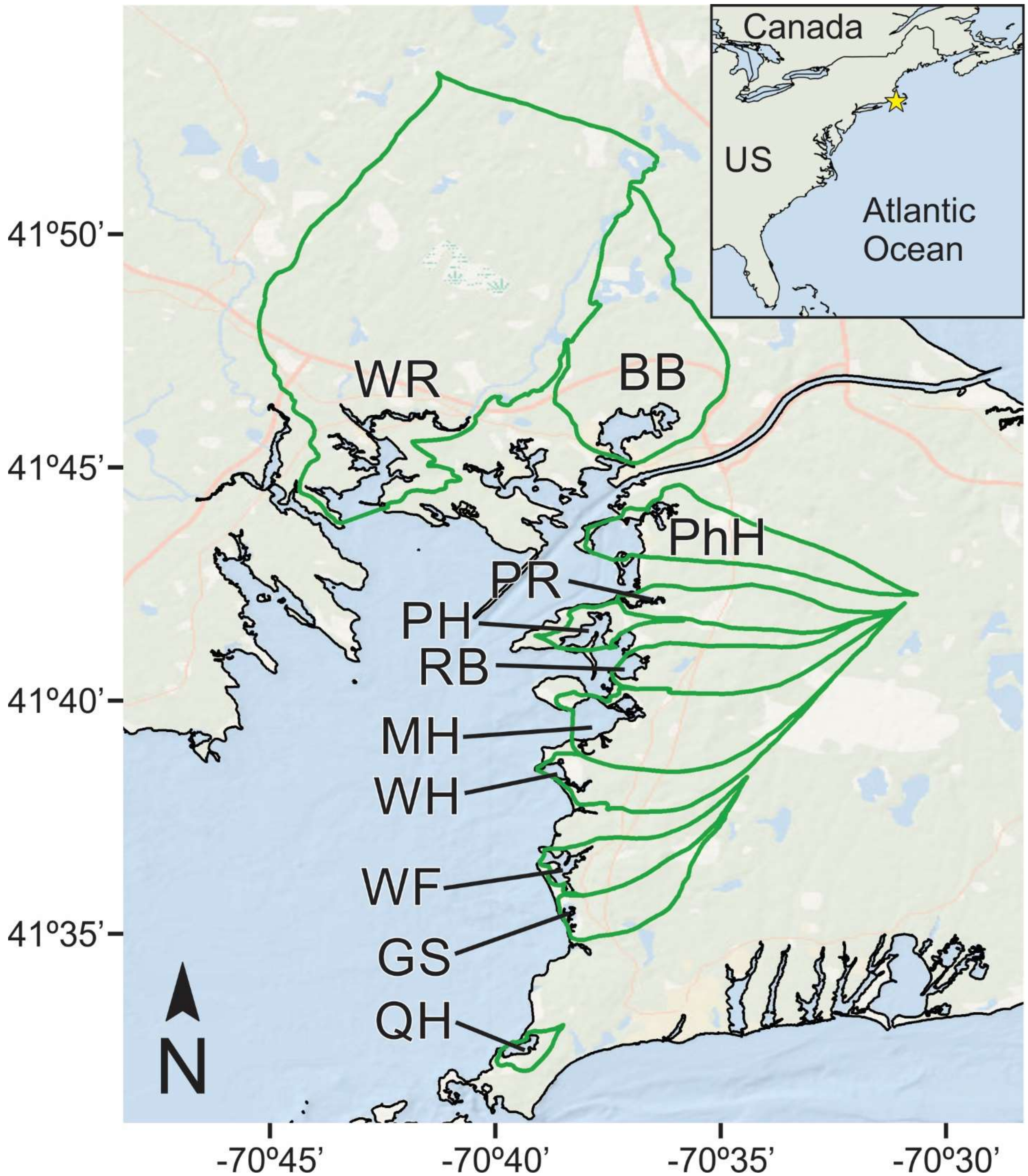
Fig. 8. Same data as in Fig. 6, but data averaged into salinity bins [<15 (black), 15-25 (grey), and >25 (white)]. F values for each salinity bin, and their significance level, indicated in each panel.

Fig. 9. Mean annual concentrations of nitrate, ammonium, DON, and TDN, for each estuary plotted versus the years of the sampling period (1992-2018). Black lines resulted from the adjustment of data to a LOESS regression model. Dashed lines correspond to the 2.5% and 97.5% confidence interval obtained by bootstrapping. Blue arrows and numbers indicate the year in which concentrations peaked indicating a shift in the trajectories of data.

Fig. 10. Mean annual concentrations of chlorophyll-*a*, for each estuary, averaged into salinity bins [<15 (black), 15-25 (grey), and >25 (white)], plotted versus the N loads to the estuaries (1992-2013) normalized per area of estuary (top), and versus the years of the sampling period (1992-2018) (bottom). Black lines in the bottom panel resulted from the adjustment of data to a

LOESS regression model. Dashed lines correspond to the 2.5% and 97.5% confidence interval obtained by bootstrapping. Blue arrow and number indicate the year in which concentrations peaked indicating a shift in the trajectories of data.

Fig. 11. Mean annual concentrations of oxygen, for each estuary, averaged into salinity bins [<15 (black), 15-25 (grey), and >25 (white)], plotted versus the N loads to the estuaries (1992-2013) normalized per area of estuary (top), and versus the years of the sampling period (1992-2018) (middle). Dashed red lines indicate the 4 mg L^{-1} threshold below which most marine biota is negatively affected. Bottom panel shows the percent of samples that fell below the threshold of 4 mg L^{-1}.


Canada
US
Atlantic
Ocean
WR
BB
PhH
PR
PH
RB
MH
WH
WF
GS
QH
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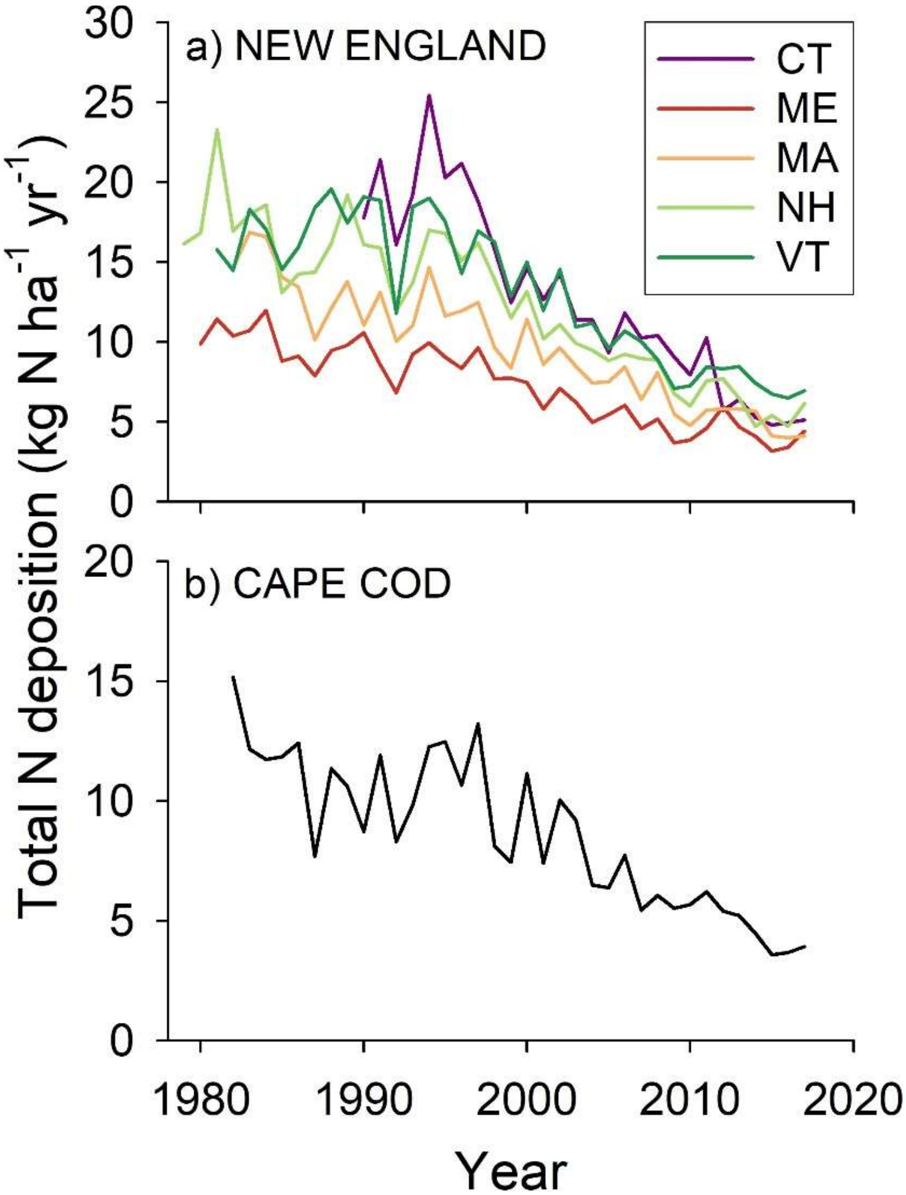
41º50'
41º45'
41º40'
41º35'
-70º45'
-70º40'
-70º35'
-70º30'

Fig. 1.



a) NEW ENGLAND
CT
ME
MA
NH
VT
b) CAPE COD
Total N deposition (kg N ha^{-1} yr^{-1})
30
25
20
15
10
5
0
1980
1990
2000
2010
2020
Year

Fig. 2.

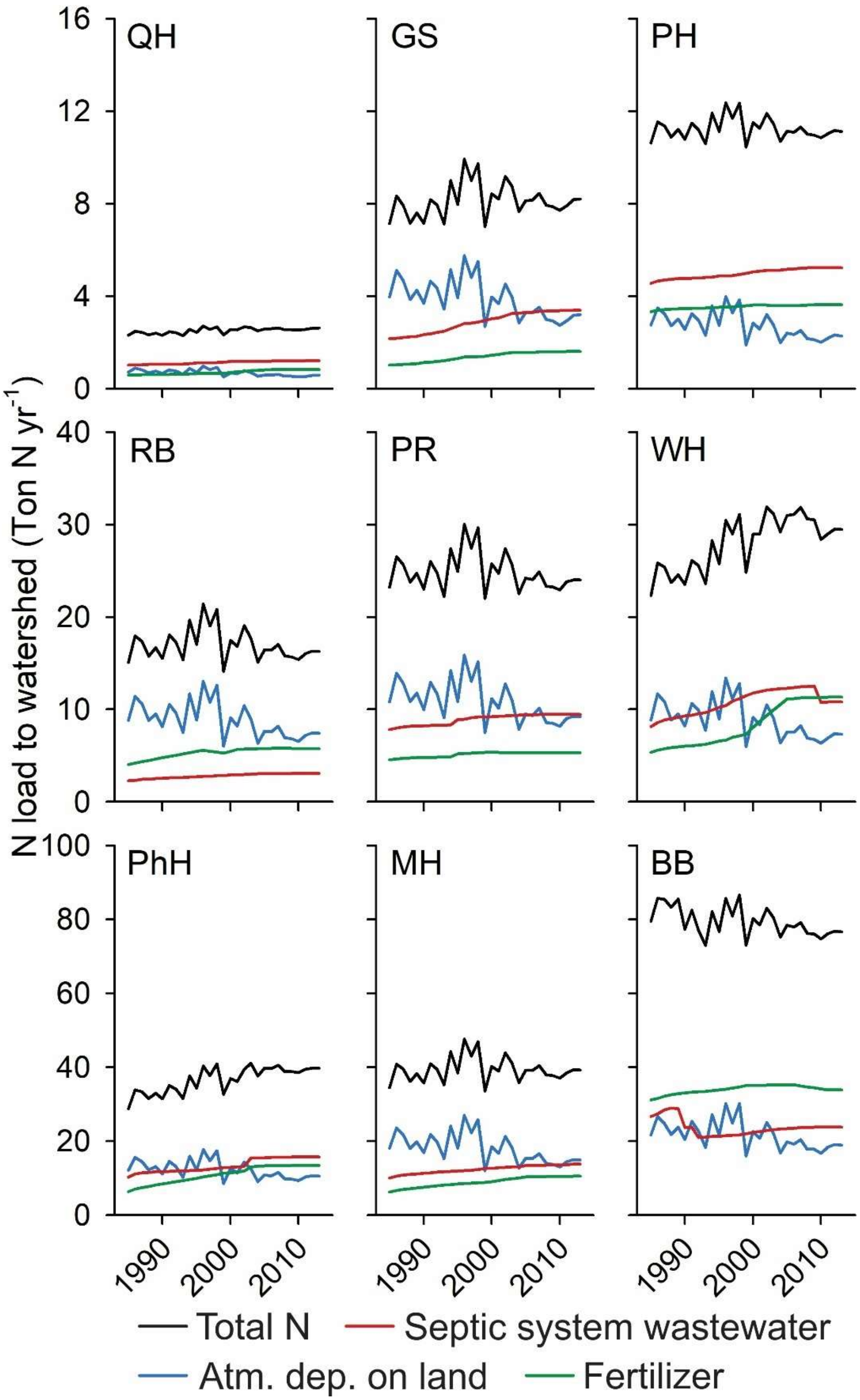
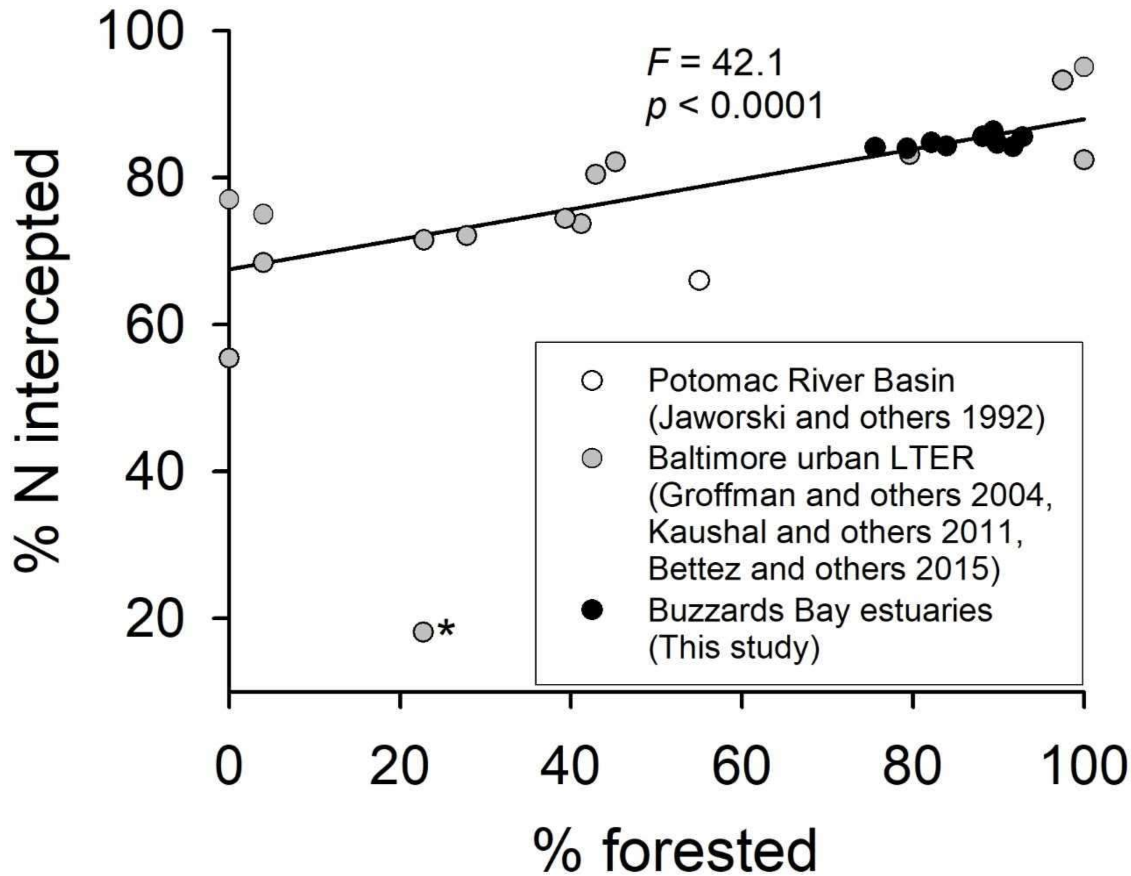
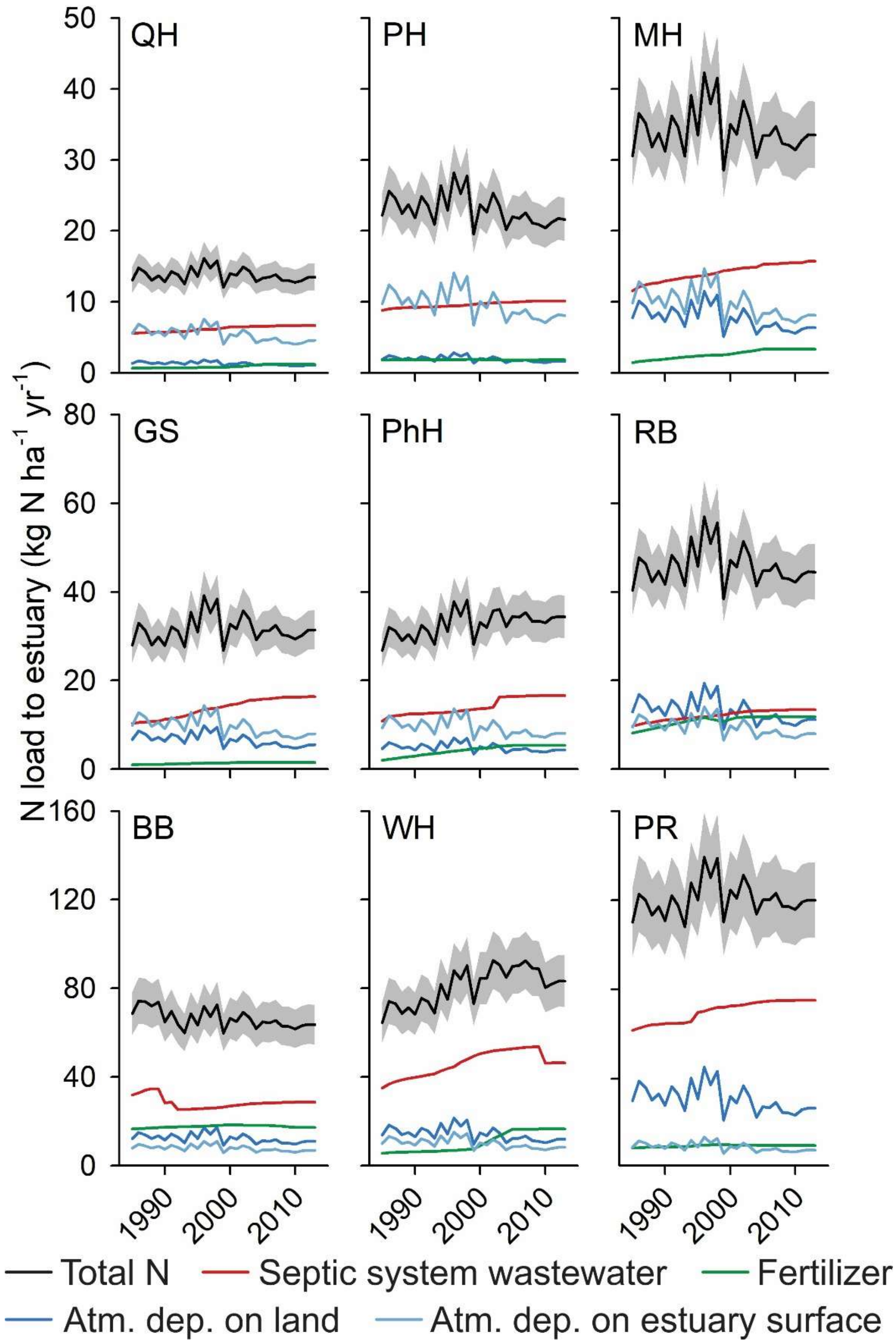

N load to watershed (Ton N yr-1)
QH
GS
PH
RB
PR
WH
PhH
MH
BB
1990
2000
2010
Total N
Septic system wastewater
Atm. dep. on land
Fertilizer

Fig. 3.



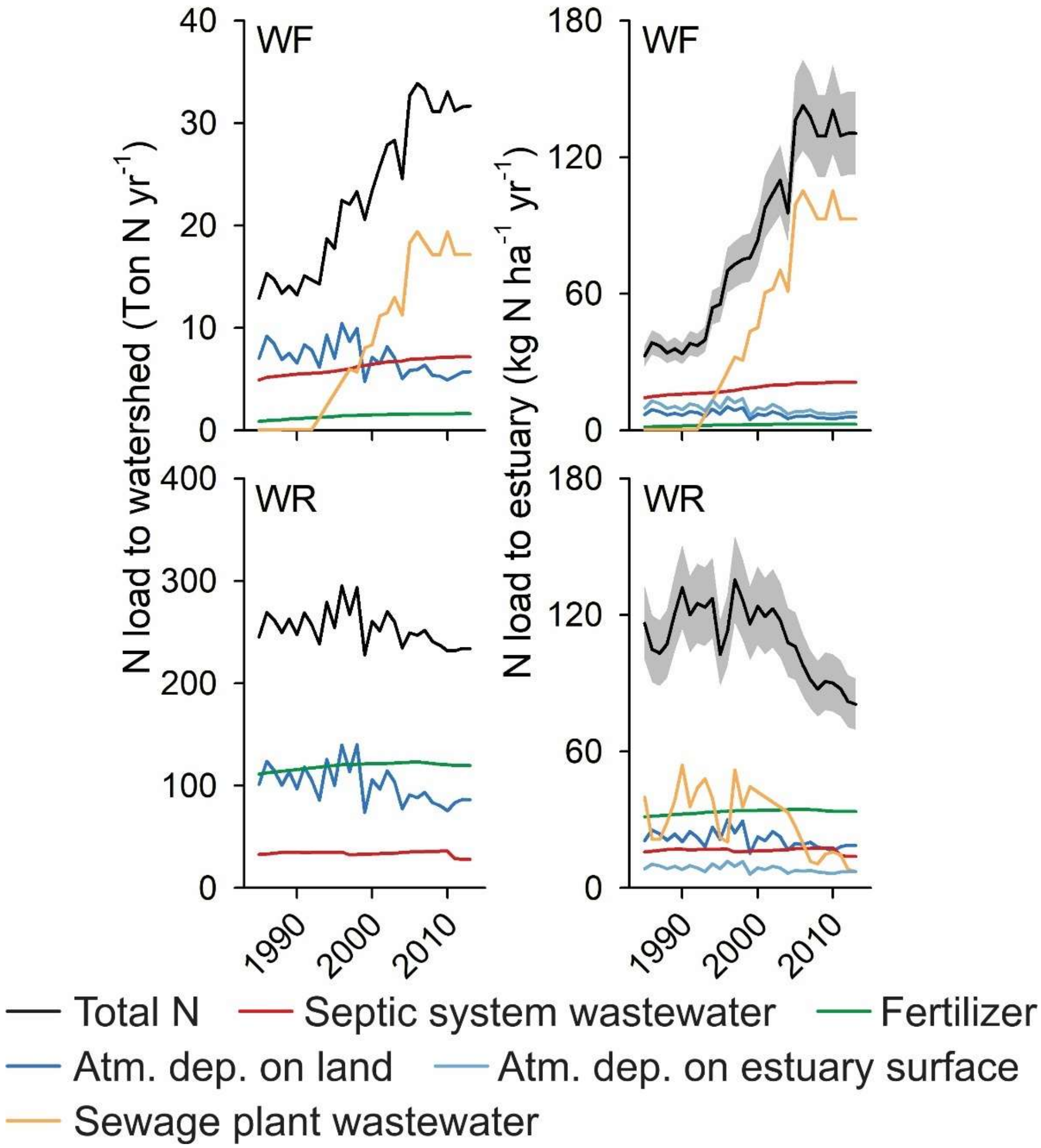
F = 42.1
p < 0.0001
% N intercepted
% forested
0
20
40
60
80
100
Potomac River Basin
(Jaworski and others 1992)
Baltimore urban LTER
(Groffman and others 2004,
Kaushal and others 2011,
Bettez and others 2015)
Buzzards Bay estuaries
(This study)
*

Fig. 4.



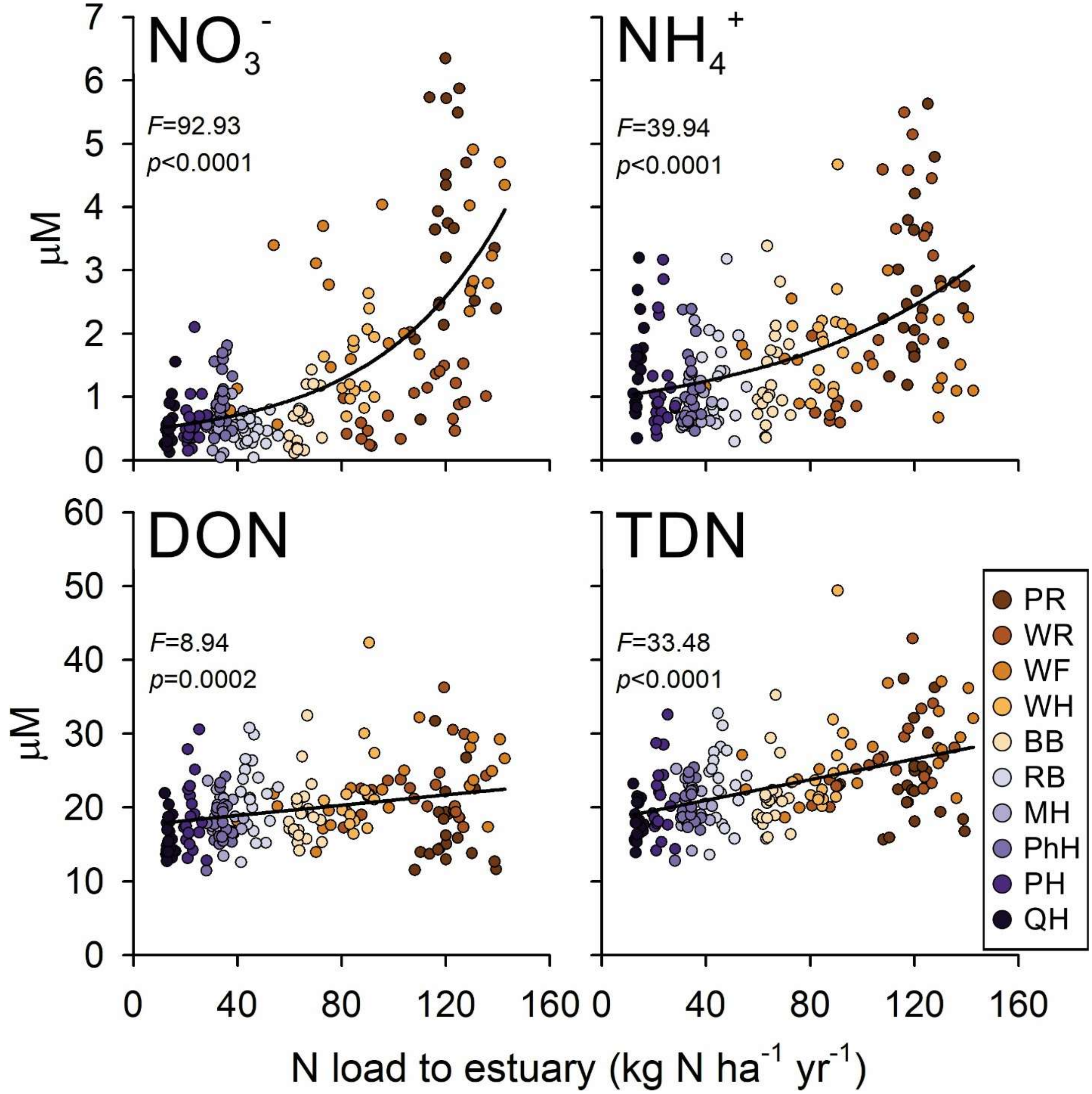
QH
PH
MH
GS
PhH
RB
BB
WH
PR
N load to estuary (kg N ha^{-1} yr^{-1})
50
40
30
20
10
0
80
60
40
20
0
160
120
80
40
0
1990
2000
2010
Total N
Septic system wastewater
Fertilizer
Atm. dep. on land
Atm. dep. on estuary surface

Fig. 5.



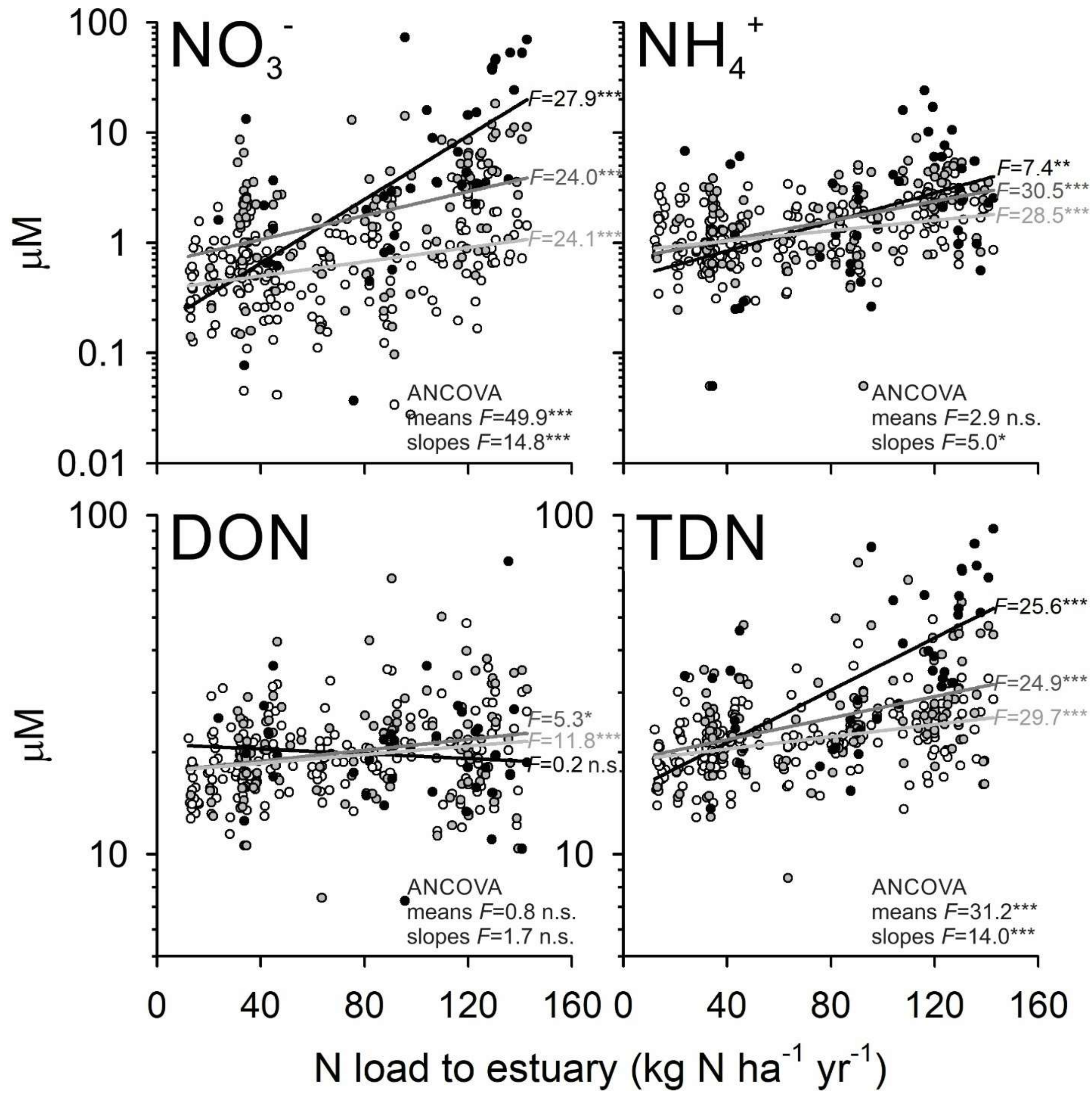
N load to watershed (Ton N yr-1)
N load to estuary (kg N ha-1 yr-1)
WF
WF
WR
WR
40
30
20
10
0
400
300
200
100
0
180
120
60
0
180
120
60
0
1990
2000
2010
1990
2000
2010
Total N
Septic system wastewater
Fertilizer
Atm. dep. on land
Atm. dep. on estuary surface
Sewage plant wastewater

Fig. 6.



NO3-
NH4+
DON
TDN
F=92.93
p<0.0001
F=39.94
p<0.0001
F=8.94
p=0.0002
F=33.48
p<0.0001
μM
μM
PR
WR
WF
WH
BB
RB
MH
PhH
PH
QH
N load to estuary (kg N ha-1 yr-1)

Fig. 7.



NO3-
NH4+
DON
TDN
F=27.9***
F=24.0***
F=24.1***
F=7.4**
F=30.5***
F=28.5***
F=5.3*
F=11.8***
F=0.2 n.s.
F=25.6***
F=24.9***
F=29.7***
ANCOVA
means F=49.9***
slopes F=14.8***
ANCOVA
means F=2.9 n.s.
slopes F=5.0*
ANCOVA
means F=0.8 n.s.
slopes F=1.7 n.s.
ANCOVA
means F=31.2***
slopes F=14.0***
µM
N load to estuary (kg N ha-1 yr-1)

Fig. 8.

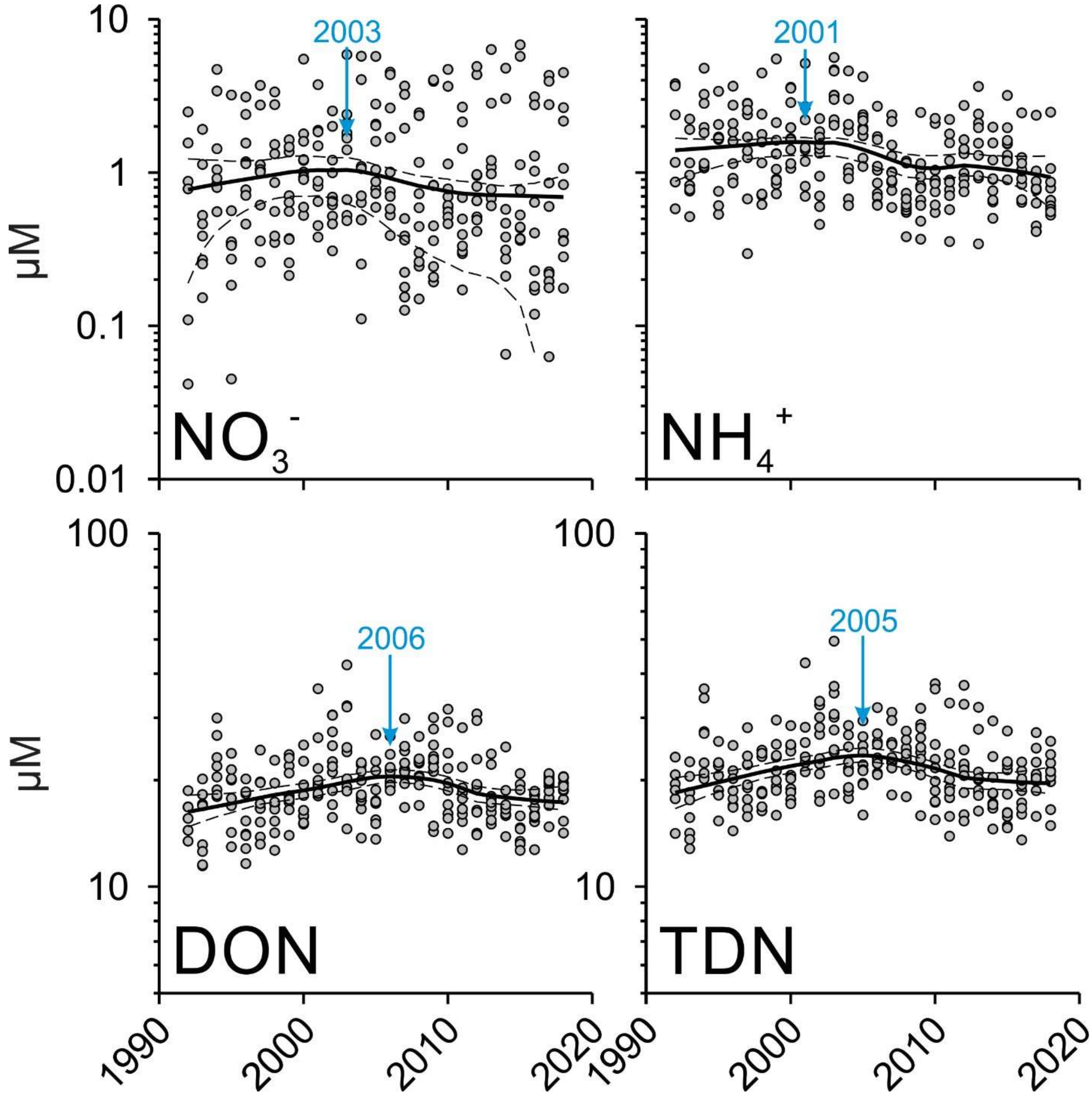

10
1
0.1
0.01
μM
2003
NO_3^-
2001
NH_4^+
100
10
μM
2006
DON
100
10
2005
TDN
1990
2000
2010
2020

Fig. 9.

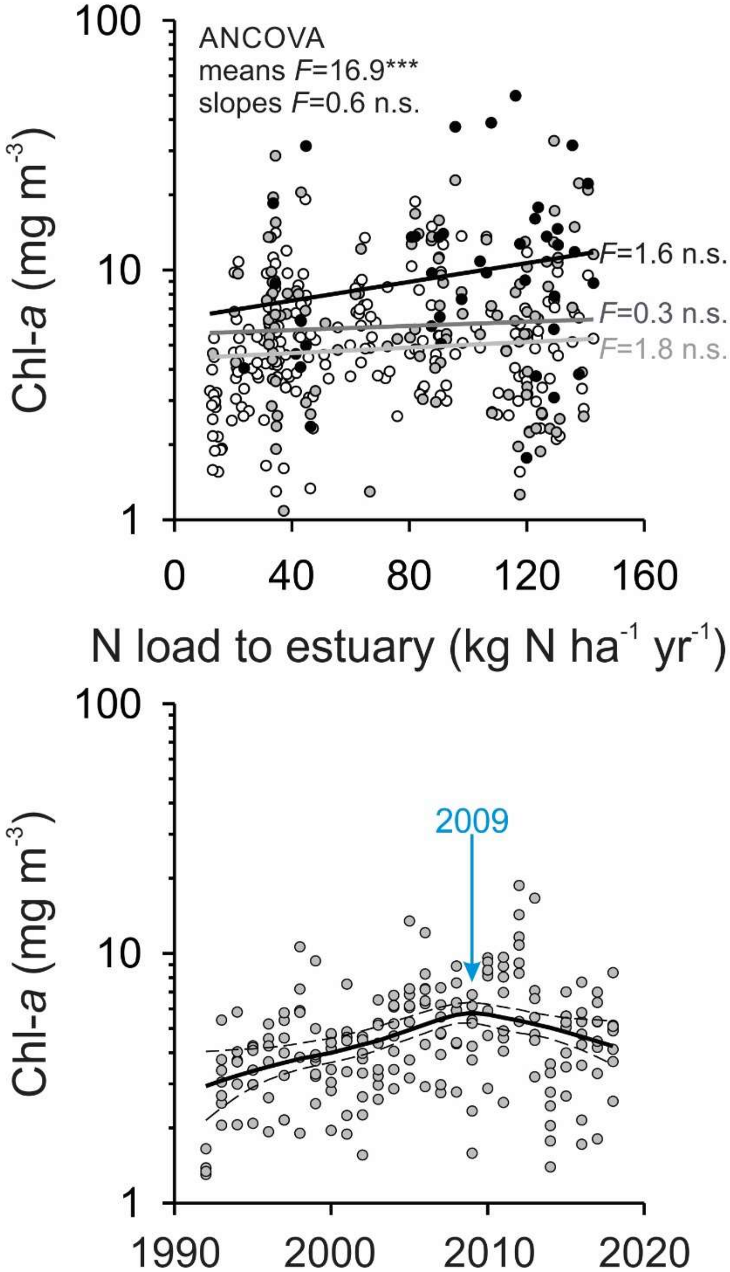
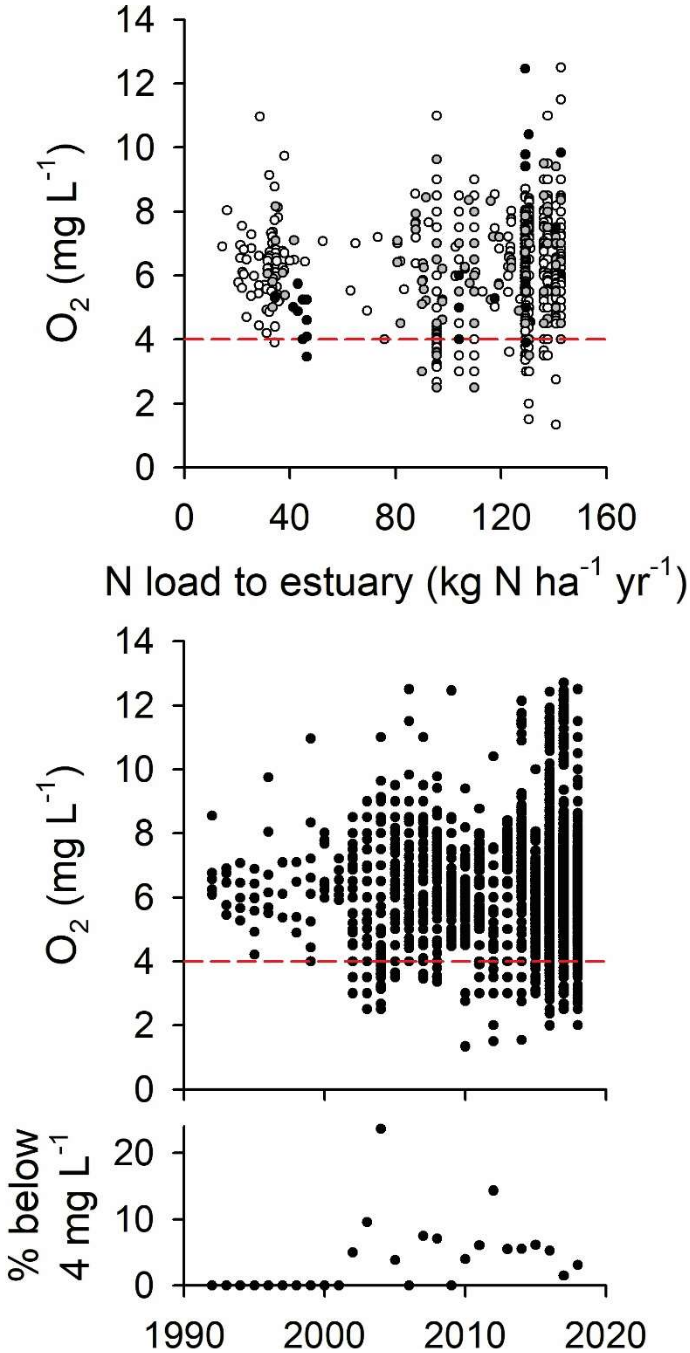

ANCOVA
means F=16.9***
slopes F=0.6 n.s.
F=1.6 n.s.
F=0.3 n.s.
F=1.8 n.s.
100
10
1
Chl-a (mg m-3)
0
40
80
120
160
N load to estuary (kg N ha-1 yr-1)
100
10
1
Chl-a (mg m-3)
2009
1990
2000
2010
2020

Fig. 10.



14
12
10
8
6
4
2
0
O2 (mg L-1)
0
40
80
120
160
N load to estuary (kg N ha-1 yr-1)
14
12
10
8
6
4
2
0
O2 (mg L-1)
20
10
0
% below 4 mg L-1
1990
2000
2010
2020

Fig. 11.