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Historical changes in atmospheric nitrogen deposition to Cape Cod, Massachusetts, USA

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Abstract

We reconstructed the historical trends in atmospheric deposition of nitrogen to Cape Cod, Massachusetts, from 1910 to 1995 by compiling data from literature sources, and adjusting the data for geographical and methodological differences. The reconstructed data suggest that $\text{NO}_3\text{-N}$ wet deposition to this region increased from a low of $0.9 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ in 1925 to a high of approximately $4 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ around 1980. The trend in $\text{NO}_3\text{-N}$ deposition has remained since the early 1980s at around $3.6 \text{ kg N ha}^{-1} \text{ yr}^{-1}$. In contrast, $\text{NH}_4\text{-N}$ wet deposition decreased from more than $4 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ in the mid 1920s to about $1.5 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ from the late-1940s until today. Emissions of $\text{NO}_x\text{-N}$ in the Cape Cod airshed increased at a rate of 2.1 kg N ha^{-1} per decade since 1910, a rate that is an order of magnitude higher than $\text{NO}_3\text{-N}$ deposition. Estimates of NH_3 emissions to the northeast United States and Canada have decreased slightly throughout the century, but the decrease in reconstructed N-NH_4^+ deposition rates does not parallel emissions estimates. The trend in reconstructed total nitrogen deposition suggests an overall increase through the century at a rate of $0.26 \text{ kg N ha}^{-1}$ per decade. This overall increase in deposition may expose coastal forests to rates of nitrogen addition that, if exceeded, could induce nitrogen saturation and increase nitrogen loads to adjoining estuaries. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Nitrogen is introduced to watersheds of coastal ecosystems by wastewater, fertilizer application, and atmospheric deposition (Lee and Olsen, 1985; Hinga et al., 1991; Valiela et al., 1992; Gabric and Bell, 1993). Nitrogen from these sources moves from watershed to estuary via surface and groundwater flow. Once in the estuary, nitrogen stimulates primary productivity and can lead to eutrophication of coastal waters (Ryther and Dunstan, 1971; Nixon, 1995; Valiela et al., 1997b). Increasing human activities in watersheds has increased delivery of anthropogenic nitrogen through wastewater disposal and fertilizer application (Valiela et al., 1992, 1997a; Cole et al., 1993; Galloway, 1998; Caraco and Cole, 1999).

Wastewater and fertilizer are local sources, originating within the watershed. Atmospheric deposition of nitrogen is an important third source of nitrogen, originating both within and outside the watershed, that may have increased sufficiently over recent decades to induce coastal eutrophication (Paerl, 1995; Paerl and Whitall, 1999). Modeled data suggest that pre-industrial deposition of atmospheric nitrogen was only 5% of modern rates in the northeastern United States (Nixon, 1997).

Nitrogen can be deposited directly to estuaries, or indirectly to watersheds (Correll and Ford, 1982; Paerl, 1995; Valiela et al., 1997a; Peierls and Pearl, 1997). Direct deposition on estuaries is a significant portion of the total nitrogen load to some estuaries (Correll and Ford, 1982; Fisher and Oppenheimer, 1991; Scudlark and Church, 1993) where it can directly stimulate primary production (Aguilar et al., 1999; Paerl et al., 1999). The additional contribution of deposition to the watershed, and subsequent travel to the estuaries through streams and

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groundwater is another important pathway for atmospheric nitrogen. The importance of indirect versus direct deposition depends on the ratio between the size of the watershed and the size of the water body, as well as the type of land use within the watershed.

Industrial and urban development in broad regions of continents may alter nitrogen emissions to the atmosphere, and this in turn may change the distribution and composition of nitrogen deposited on specific watersheds (Galloway et al., 1982; Jaworski et al., 1997). Nitrate, ammonium, and organic nitrogen in the atmosphere derive from different sources. Major sources of ammonium include volatilization from livestock waste, fertilizers, and natural soils. Nitrate in the atmosphere largely derives from the combustion of fossil fuels (Likens and Bormann, 1974; ApSimon et al., 1987; Schlesinger and Hartley, 1992; Dentener and Crutzen, 1994). Dissolved organic nitrogen in the atmosphere may be produced by reactions between nitrogen oxides and hydrocarbons, such as soot, produced by industrial emissions (Cornell et al., 1995; Valigura et al., 1996).

Nitrogen concentrations in rainwater have been measured since the 1850s, but most studies of atmospheric nitrogen deposition have focused on wet deposition of dissolved inorganic nitrogen (DIN: $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$); dissolved organic nitrogen (DON) or dry deposition of inorganic and organic nitrogen are seldom included. Measurements of wet inorganic nitrogen are likely to underestimate nitrogen loads because 45–75% of atmospheric DON may be labile (Seitzinger and Sanders, 1999), and DON can range from 11 to 90% of total nitrogen deposition globally (Timperley et al., 1985). Measurements of dry deposition are difficult, and data are rarely available. Instead researchers have appealed to the convention that dry and wet deposition are about equal (Hinga et al., 1991; Fisher and Oppenheimer, 1991; Valiela et al., 1997a), although this conversion may be too simplistic (Lovett and Lindberg, 1993).

Reconstructions of time courses of N deposition are impaired by the fragmentary nature of available data. The sparse historical data make it necessary to compare studies with different methods applied in different locations (Likens and Bormann, 1974; Brimblecombe and Stedman, 1982; Hansen and Hidy, 1982; Cogbill et al., 1984; Stensland et al., 1986). Fortunately, some useful comparisons have been performed to assess whether differences in methodology may affect estimates of nutrient concentrations found in precipitation (Galloway and Likens, 1976; Peden and Skowron, 1978).

In this paper we reconstruct the historical record of atmospheric nitrogen deposition in the northeast United States and eastern Canada to estimate long-term changes in deposition to the Cape Cod, Massachusetts area. This is part of a larger study on long-term changes created by

nitrogen-induced eutrophication of estuaries in the region (Valiela et al., 1992, 1997a, b). Here we compiled data collected at intermittent intervals from 1908 to 1997 from various sites across the northeast United States and the maritime provinces of Canada. We spliced these data together and normalized the geographic distribution to that of Cape Cod to estimate long-term changes in atmospheric deposition of $\text{NH}_4\text{-N}$, and $\text{NO}_3\text{-N}$. We estimated trends in $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ in wet deposition, and further adjusted the data to include deposition of DON, and also dry deposition. The reconstruction thus represents a double extrapolation, first from diverse geographic locations to a more localized sub-region, and then from wet deposition to total deposition, including dry and DON deposition. Finally, we compared trends in the reconstructed atmospheric deposition record with historical data on changes in anthropogenic emissions of nitrogen from 1910 to the present.

2. Methods

2.1. Data sources

Published data on wet atmospheric deposition from 1910 to the present are intermittent; there are few sites offering long-term records (Fig. 1). Early records are sparse, including only four published studies between 1900 and 1930 (1–4 in Fig. 1), and one between 1930 and 1950 (5 in Fig. 1). There was a 1-yr country-wide sampling network that measured atmospheric deposition in 1955–1956 (6 in Fig. 1); we included the five stations in the northeast from that study, but there were few other reports of atmospheric deposition during that time. Data from the Hubbard Brook Experimental Forest (8 in Fig. 1) in the mid-1960s increased awareness of the atmospheric pollution issue, which resulted in more comprehensive sampling networks, including the National Atmospheric Deposition Program (13 in Fig. 1), which is still operating today. We did not include data from the first multi-site sampling network established in the early 1960s (Gambell and Fisher, 1966; Pearson and Fisher, 1971; Peters et al., 1982) because those results may have been inconsistent in methods and analyses (Miles and Yost, 1982).

2.2. Examination of sources of variability in the available data

Secular variation in atmospheric deposition measurements may arise from real temporal differences, but may also be due to differences in sampling methodology and analysis, or to differences in the location of collection. Below we discuss how we addressed the potential variability from each of these sources in the calculation of our reconstructed deposition records.

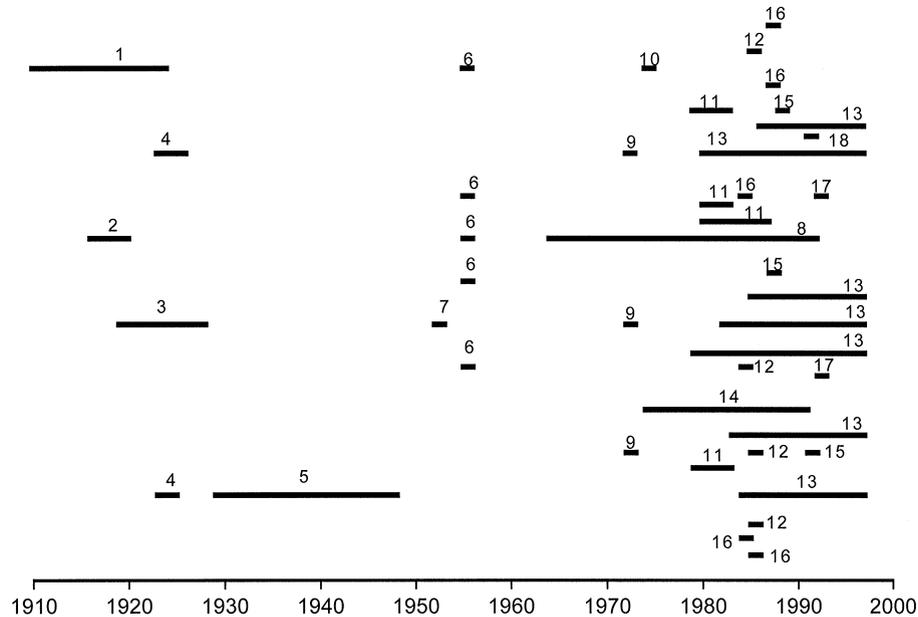


Fig. 1. Temporal distribution of atmospheric deposition studies used for this research in the northeastern United States and eastern Canada. The numbers above each line correspond to the reference and location for each study listed below. 1. Shutt and Hedley (1925), Canada; 2. Wilson (1921), NY; 3. Collison and Mensching (1932), NY; 4. Eriksson (1952), multiple sites; 5. Frink and Voigt (1977), CT; 6. Junge (1958), multiple sites; 7. Herman and Gorham (1957), Canada; 8. Hubbard Brook Experimental Forest (on-going), NH; 9. Cogbill and Likens (1974), multiple sites; 10. Valiela et al. (1978), MA; 11. Underwood et al. (1989), Canada; 12. Fisher and Oppenheimer (1991), multiple sites; 13. National Atmospheric Deposition Program/National Trends Network (on-going), multiple sites; 14. Correll and Ford (1982) plus Jordan et al. (1995), MD; 15. Lovett and Lindberg (1993), multiple sites; 16. Duce et al. (1991), multiple sites; 17. Hu et al. (1998), CT; 18. Lajtha et al. (1995), MA.

2.2.1. Methodological variability

Methods of collecting and processing wet atmospheric nitrogen deposition have changed over the course of the century. NADP/NTN collects weekly wet only deposition using wet deposition collectors exposed only during precipitation events (Stensland et al., 1986). Bulk deposition collectors, like those used at the Hubbard Brook Experimental Forest (Likens et al., 1984), are exposed both during and between storms, which adds a dryfall component to the measured concentration. To include data from both wet-only and bulk deposition collectors, we adjusted all of the bulk deposition data to wet deposition based on the ratio between co-located collectors maintained in Hubbard Brook, NH. The ratios of wet to bulk were 0.83 for $\text{NH}_4\text{-N}$ and 0.86 for $\text{NO}_3\text{-N}$ in all available years for which data overlapped. These ratios are similar to those reported by Hendry and Brezonik (1980) in Gainesville, FL ($\text{NH}_4\text{-N} = 0.80$, $\text{NO}_3\text{-N} = 0.82$), and those reported by Stensland et al. (1986) for their Area 1 (bulk : wet ratio = 1.1 for both $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$, compared to bulk : wet ratio of 1.16 for $\text{NO}_3\text{-N}$ and 1.21 for $\text{NH}_4\text{-N}$ in the Hubbard Brook data).

The collection container and pre-analysis processing of water samples could also affect concentrations of mea-

sured nitrogen. Historically, a variety of collectors have been used, including lead trays (Shutt and Hedley, 1925), copper gauges (Collison and Mensching, 1932), metal alloy gauges (Eriksson, 1952), and glass funnels (Peters et al., 1982). Most researchers today use acid-washed polyethylene containers. Differences in nitrogen concentrations in water collected by the different containers were small (Galloway and Likens, 1976; Cogbill et al., 1984).

The time that elapses between precipitation and sample collection and analysis can affect nitrogen concentrations as a result of microbial activity during storage. The addition of toluene or mercuric chloride was initially used to limit microbial transformations; filtration and cold storage before analysis also reduces biogenic reactions in the sample (Peden and Skowron, 1978). Butler and Likens (1998) showed that samples analyzed weekly resulted in no change in $\text{NO}_3\text{-N}$ concentrations over those analyzed daily, but biological activity decreased the concentrations of $\text{NH}_4\text{-N}$ by 14% between daily and weekly sampling. These results indicate that in early studies in which the duration of time between collection and analysis of water samples tended to be longer, measured $\text{NH}_4\text{-N}$ concentrations were lower than actual concentrations. Thus, values reported in early papers (Shutt and Hedley, 1925; Collison and

Mensingh, 1932, etc.) probably underestimate $\text{NH}_4\text{-N}$ concentrations.

2.2.2. Differences in analytical methods

Methods of analysis have changed over the century. Before the late 1960s the phenoldisulfonic acid method was used to determine $\text{NO}_3\text{-N}$ concentrations, and Nessler's reagent was used to determine concentrations of $\text{NH}_4\text{-N}$ (Shutt and Hedley, 1925; Collison and Mensching, 1934; Eriksson, 1952; Frink and Voigt, 1977). In the late 1960s and early 1970s indophenol blue became the preferred method for measuring $\text{NH}_4\text{-N}$ and cadmium reduction became the standard method for $\text{NO}_3\text{-N}$ analysis. Recently, the use of ion chromatography (EPA method 300.0) to measure $\text{NO}_3\text{-N}$ has become more common. Replicate samples have been used to compare differences among these methods and no consistent bias has been found (D. Buso, pers. comm.; Jordan et al., 1995).

2.2.3. Spatial variability

There is large variation in nitrogen deposition throughout the region from which we compiled data (Fig. 2). Ollinger et al. (1993) analyzed deposition records from the NADP/NTN network and found that within the northeast United States, $\text{NO}_3\text{-N}$ concentrations increased from east to west, and $\text{NH}_4\text{-N}$ concentrations increased from southeast to northwest. To clarify the relationship of location and year to concentrations of N in deposition, we included all data from sites shown in Fig. 2, and ran multiple linear regressions of $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ deposition against latitude, longitude, and year.

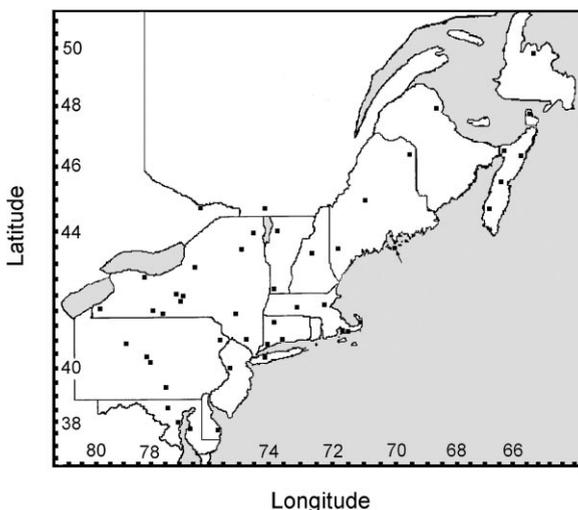


Fig. 2. Spatial distribution of sites of atmospheric deposition measurements in the northeastern United States and eastern Canada. Each black dot represents at least 1 yr of data collection at that location. Some locations were sampled for multiple years, frequently by different investigators.

Table 1

F statistics for multiple linear regression of nitrate and ammonium concentrations on latitude, longitude, and year

Independent variable	<i>F</i> statistic		
	Nitrate	Ammonium	
Latitude	0.3	NS	4.1 *
Longitude	124.3	**	124.3 **
Year	123.8	**	87.2 **

$\text{NO}_3\text{-N}$ concentrations were highly significantly related to both year and longitude, and $\text{NH}_4\text{-N}$ concentrations were significantly related to latitude, longitude, and year (Table 1).

These results show that indeed, there were clear differences in $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ concentrations in deposition across the years of our survey, and that the data compiled contained strong regional differences. For our reconstruction of long-term nitrogen deposition to Cape Cod we wanted to retain the inter-annual differences, but also needed to minimize or adjust for the geographical differences. To adjust the data from the different sites to our target area of Cape Cod, our approach was to regress the concentrations in relation to the latitude and longitude of Cape Cod. One obstacle to this approach was that the values of deposition collected across latitude and longitude were highly significantly related to each other ($F = 585.0^{**}$). Longitude was related to a larger proportion of the variation in concentration, so we opted to focus on removing the effect of longitude on $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ concentrations by adjusting all of the concentrations using the longitude of Cape Cod, and the regression equations in Fig. 3.

2.3. Calculation of dry deposition and deposition of DON

Mechanisms governing deposition of wet and dry $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ might differ. Measurements of both wet and dry nitrogen deposition from two national networks (Integrated Forest Studies and the National Dry Deposition Network) in the eastern United States indicate that dry deposition of $\text{NO}_3\text{-N}$ was 25–70% of total deposition, and $\text{NH}_4\text{-N}$ dry deposition was from 2 to 33% of the total (Lovett and Lindberg, 1993; Lovett, 1994). For our reconstruction of total deposition we converted wet deposition data to include dry deposition by using the mean percentage for each, 48% of total deposition for $\text{NO}_3\text{-N}$ and 18% of total deposition for $\text{NH}_4\text{-N}$. We verified the estimates of dry deposition for $\text{NO}_3\text{-N}$ with data from the Atmospheric Integrated Research Monitoring Network (AIRMoN; http://www.arl.noaa.gov/research/projects/airmon_dry.html) where annual estimates of HNO_3 dry deposition were generally within $1 \text{ kg ha}^{-1} \text{ yr}^{-1}$ of wet $\text{NO}_3\text{-N}$

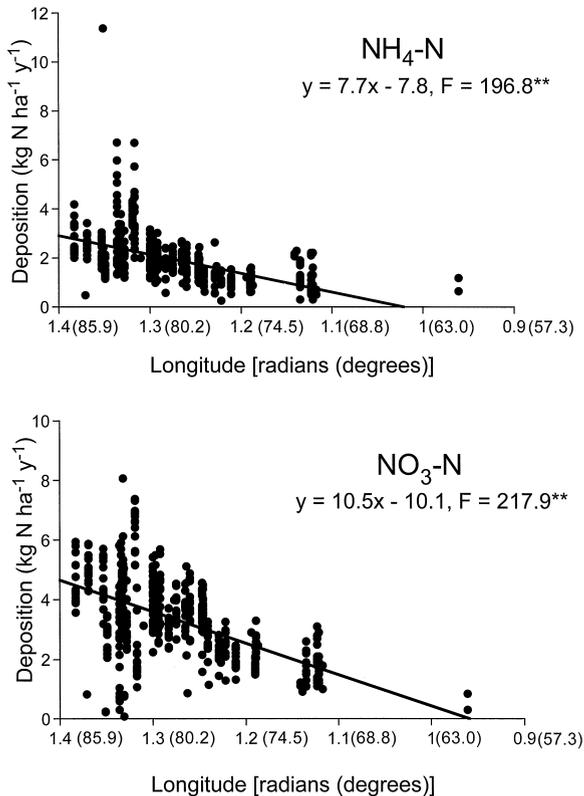


Fig. 3. Linear regressions of longitude in radians (and degrees) against ammonium deposition (top) and nitrate deposition (bottom). The west-to-east range of the data are from the Great Lakes area of western Pennsylvania and New York, to eastern Nova Scotia and Newfoundland. Both regressions are statistically significant at $p < 0.01$.

deposition data taken from the co-located National Atmospheric Deposition Program sites.

The paucity of historical data on DON in the atmosphere makes it difficult to describe multi-year changes. Reports of DON in rainwater today range from 21 to 84% of total deposition for a variety of locations worldwide (Cornell et al., 1995). Literature values of DON in wet deposition in the eastern United States (Table 2) are roughly 24% of total nitrogen deposition. As a best estimate we applied a factor of 24% to our wet and dry deposition data to account for DON. Since there was no other available data, we conservatively assumed that the amount of atmospheric DON remained constant throughout the century, and thus applied the 24% to our entire compilation.

2.4. Calculation of ammonia (NH₃-N) emissions

We compiled historical data on NH₃-N emissions to compare to the reconstructed record of deposition. We calculated NH₃-N emissions in the northeast United

Table 2

Dissolved organic nitrogen as a percent of total atmospheric deposition at various locations on the east coast of the United States. Data compiled by K.D. Kroeger

Reference	Location	DON as % AD
Valiela et al. (1978)	Cape Cod, Massachusetts	52
Jordan et al. (1995)	Chesapeake Bay	29
Cornell et al. (1995)	North Carolina	21
Scudlark et al. (1998)	Lewes, Delaware	20
Russell et al. (1998)	Lewes, Delaware	13
Peierls and Pearl (1997)	North Carolina	10
Mean		24

States from volatilization of animal excreta, fertilizer application, low-temperature coal combustion, naturally vegetated soils, biomass burning, and oceans (ApSimon et al., 1987; Warneck, 1988; Schlesinger and Hartley, 1992; Dentener and Crutzen, 1994) as follows:

Animal excreta: We compiled historical data from the National Agricultural Statistics Service on the number of cattle, sheep, hogs, and chickens in New England and New York (USDA, 1995), and multiplied these livestock numbers by published emissions factors (Table 3). We did not consider contributions of volatilization from faeces of wild animals in the northeast over the last century, nor did we include human waste as a contributor to NH₃-N emissions. We assumed that human waste received at least primary treatment, so that volatilization of NH₃-N to the atmosphere was diminished (Schlesinger and Hartley, 1992; Dentener and Crutzen, 1994).

Fertilizer application: To calculate the volatilization of NH₃-N from fertilizers we used mean national N fertilizer application rates (USDA, 1993, 1999), and multiplied these by the area of land dedicated to the cultivation of the major northeastern crops (hay, corn, wheat, oats and barley) obtained from USDA (1999). We then determined, from published values, the percentage of nitrogen in fertilizer that is volatilized, and applied that factor to the total fertilizer use per hectare (Table 3).

Coal combustion: Low-temperature coal combustion can be a large source of NH₃-N to the atmosphere (Dentener and Crutzen, 1994). We calculated NH₃-N emissions from coal based on consumption by residential and commercial properties only (EIA, 1996), making the assumption that all industrial uses of coal were burned at high temperatures, and emitted nitrogen as NO_x-N instead of NH₃-N. We used an emission factor of 1 g NH₃-N released per kg of coal burned (Table 3; Dentener and Crutzen, 1994).

Natural vegetation: Microbially mediated emissions of NH₃-N from naturally vegetated lands are dependant on the temperature, pH, and vegetative cover of the land, and are thus extremely variable, ranging from 0 to 100 kg N ha⁻¹ yr⁻¹ under different conditions (Bowden, 1986). We used the mean from a range of values to

Table 3

Emissions factors from various sources of ammonia as provided by different studies in the literature

NH ₃ source	Emissions (kg N yr ⁻¹ or % N released)	Reference
<i>Livestock</i>		
Cattle		
Dairy	33.3	Dentener and Crutzen (1994)
Non-dairy	10.0	Dentener and Crutzen (1994)
Cattle		
	19.3	ApSimon et al. (1987)
	15.5	Schlesinger and Hartley (1992)
	15.3	Warneck (1988)
Mean: 18.7		
Sheep		
	2.7	ApSimon et al. (1987)
	2.4	Schlesinger and Hartley (1992)
	4.4	Dentener and Crutzen (1994)
	4.9	Warneck (1988)
Mean: 3.6		
Swine		
	6.6	Warneck (1988)
	2.9	ApSimon et al. (1987)
	2.4	Schlesinger and Hartley (1992)
	12.0	Dentener and Crutzen (1994)
Mean: 6.0		
Poultry		
	0.23	ApSimon et al. (1987)
	0.21	Schlesinger and Hartley (1992)
	0.2	Dentener and Crutzen (1994)
	0.3	Warneck (1988)
Mean 2.3		
<i>Fert. appl.</i>		
Urea		
	15%*	Dentener and Crutzen (1994)
	20%	Schlesinger and Hartley (1992)
(NH ₄) ₂ SO ₄		
	8%	Dentener and Crutzen (1994)
	10%	Schlesinger and Hartley (1992)
NH ₄ NO ₃		
	2%	Dentener and Crutzen (1994)
	2.5%	Schlesinger and Hartley (1992)
Other		
	3%	Dentener and Crutzen (1994)
	3%	Schlesinger and Hartley (1992)
Mean 8%		
<i>Coal</i>		
	1 g kg ⁻¹	Dentener and Crutzen (1994)
<i>Nat. vegetation</i>		
	Mean (kg N ha ⁻¹)	Range (kg N ha ⁻¹)
	5.5	1–10
	1.6	0.51–2.7
	2.4	
	0.2	
Mean 2.8		

calculate the amount of NH₃-N emitted (Table 3), and we applied that average emission factor to all land not in agriculture. The area of non-agricultural land was calculated by subtracting the total land in crops from the total land area in the region. Although the area of urbanized land in the northeast has surely increased throughout this century, that area is still extremely small compared to the total area of natural vegetation, and so we did not remove urban areas from our calculation of emissions from naturally vegetated land.

“Other” sources: We assumed that NH₃-N from marine emissions were a minor contributor since dominant weather fronts in this region arrive largely from the west.

We assumed that biomass burning was a negligible source of NH₃-N emissions in this region. Although firewood was more commonly used for heating in earlier years of the century, only 4% of the nitrogen in biomass is released as NH₃ (Loebert et al., 1990). Globally, biomass burning accounts for a maximum of 12% of NH₃-N emissions, most of which occurs in the tropics (Schlesinger and Hartley, 1992).

2.5. Calculation of nitrogen oxide (NO_x-N) emissions

To determine the trend in emissions of nitrogen oxide (NO_x-N) to the northeastern United States, we used

annual nitrogen oxide emissions data (Gschwandtner et al., 1985 for 1900–1980; EPA, 1997 and Nizich, pers. comm. for 1980–1995). NO_x -N emissions can be transported from 400 to 1200 km before being deposited (Schwartz, 1989), so determining a regional budget for NO_3 -N deposition requires both a knowledge of NO_x -N sources, and an understanding of prevailing winds and climate variation. We estimated the airshed for Cape Cod based on output from the Regional Acid Deposition Model (RADM; R. Dennis, pers. comm.) to include the New England states, New York, Pennsylvania, New Jersey, Delaware, Maryland, District of Columbia, Virginia, West Virginia, and Ohio. The methodology used for the model is described in Dennis (1995).

We composited the published EPA NO_x -N source categories into industrial, vehicular, and other sources of NO_x -N. Industrial NO_x -N emissions include emissions from bituminous and anthracite coal used for industrial boilers, electric utilities, coke plants, and railroads, oil used for industrial, commercial, and electric utilities, and natural gas. Vehicular emissions include gasoline and diesel highway vehicles, off highway diesel, and marine vessels. Other emissions include emissions of NO_x -N from wild fires, domestic wood combustion, cement plants, smelters, and miscellaneous sources (Gschwandtner et al., 1985; EPA, 1997).

3. Results and discussion

3.1. Deposition trends

The reconstructed wet deposition data can be represented in various ways. The vertical lines in Fig. 4 show the standard deviation of the spliced, longitude-adjusted means for NO_3 -N and NH_4 -N; these error terms provide a frame of reference in which we can interpret the differences in mean year-to-year wet deposition (shown by the dashed line in Fig. 4 top and bottom). Some features of the changing year-to-year deposition trends do not seem significant in the context of the standard deviations of the mean. Other features, for example the increase in both NO_3 -N and NH_4 -N deposition between 1960 and the early 1970s, stand out as more convincing. The near-doubling of NO_3 -N concentrations during this time was described by Gene Likens and colleagues (Likens and Bormann, 1974, 1995; Likens et al., 1984), and helped to alert the public to the growing importance of acid deposition in the northeastern United States (Fig. 4, bottom).

In this paper, however, we are more interested in decadal-scale trends, and for that purpose we calculated 10-yr moving averages of the reconstructed deposition data (thick line in Fig. 4 top and bottom). This device provides a view of longer-scale trends. Wet deposition of NH_4 -N and NO_3 -N to the Massachusetts region underwent considerable change since the early 1900s. The

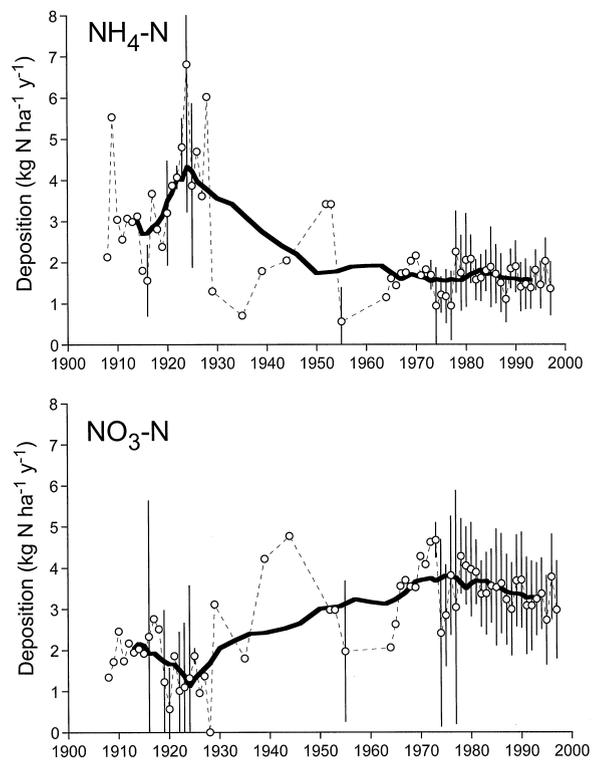


Fig. 4. Top: Estimated atmospheric wet deposition of ammonium ($\text{kg N ha}^{-1} \text{yr}^{-1}$) from 1910 to 1997 in the Cape Cod region. Bottom: estimated atmospheric wet deposition of nitrate ($\text{kg N ha}^{-1} \text{yr}^{-1}$) from 1910 to 1997 in the Cape Cod region. Open circles are the annual mean, with vertical lines representing standard deviations for those years that have more than one study; 30 of the data points represent only a single study; the rest represent the mean of from 2 to 32 data points, depending on the number of individual studies available for each year. The dashed line connects the yearly values, and the solid line shows the 10-yr moving average.

reconstructed data suggest that NH_4 -N deposition may have peaked in the mid-1920s, and then decreased until the late 1940s (Fig. 4, top). Deposition of NH_4 -N appears relatively uniform for the remainder of the century. NO_3 -N deposition was low up to the 1930s (Fig. 4, bottom), and increased steadily from the 1920s until the mid 1970s.

It is possible that the extremely high NH_4 -N values in the 1920s result from localized contamination at some sampling locations. Many of these early data were measured at agricultural experiment stations (Collison and Mensching, 1932; Shutt and Hedley, 1925), and their data could have been influenced by proximity to agricultural areas. Comparisons of early 20th century deposition data taken at Ithaca, NY and Geneva, NY, with data taken at the same locations in the mid-1950s and early 1970s (Likens and Bormann, 1974), indicate the same general

trend of increasing $\text{NO}_3\text{-N}$ and decreasing $\text{NH}_4\text{-N}$ deposition that we report in our reconstructed data. This suggests that the early data may reflect real differences in $\text{NH}_4\text{-N}$ deposition. To evaluate the importance of these early high $\text{NH}_4\text{-N}$ values in our overall trend, we selectively deleted the $\text{NH}_4\text{-N}$ data that were higher than $4 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ (which included all the high values obtained during the 1920s, Fig. 4, top) and recalculated total N deposition. There was no significant difference between the regression describing the rates of overall decrease across the century with and without the high $\text{NH}_4\text{-N}$ values (regression not shown), so we included all the data in our analyses.

The reconstructed values of wet $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ deposition, when extrapolated to total nitrogen deposition yield results that are quite variable (Fig. 5). In view of the magnitude of the standard deviations, the changes on the year-to-year scale are not compelling. The 10-yr moving average suggests tantalizing but to some extent unexplained trends. The most conservative conclusion might be that taking the entire record, there was a significant increase in total nitrogen deposition across the century. If we accept the regression as aptly describing the trend, we can calculate that total nitrogen deposition has increased at a rate of about $0.26 \text{ kg N ha}^{-1}$ per decade, amounting to a 23% increase in deposition of total N between 1910 and 1997 (Fig. 5). The increase in total N is driven by the 84% increase in wet $\text{NO}_3\text{-N}$ deposition this century (Fig. 4, bottom). The increase in $\text{NO}_3\text{-N}$ is enough to counter the decreasing $\text{NH}_4\text{-N}$ deposition trends (Fig. 5, top).

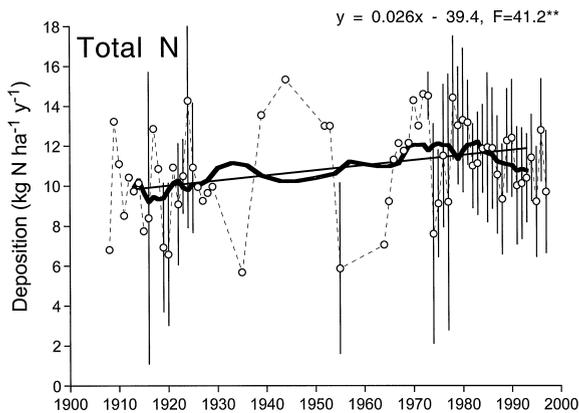


Fig. 5. Modeled total nitrogen deposition ($\text{kg N ha}^{-1} \text{ yr}^{-1}$) after adjustments for dry fallout (18% of wet NH_4^+ deposition and 48% of NO_3^- wet deposition) and dissolved organic nitrogen (24% of total atmospheric nitrogen deposition). Vertical lines represent standard deviations for those years that have more than one study; the dashed line connects yearly values, and the thick solid line shows the data plotted with a 10-yr moving average. The regression (thin solid line) for the entire data set shows secular increases at a rate of $0.26 \text{ kg N ha}^{-1}$ per decade.

3.2. Emissions trends

The sources of atmospheric nitrogen changed during the 20th century (Fig. 6). Ammonia emissions in the northeastern United States seem to have been dominated by emissions from livestock and natural vegetation throughout the century (Fig. 6, top), and have decreased slowly but significantly since 1910 (Table 4). This decrease is driven by the decline in the number of livestock in the northeast United States, with total livestock emissions decreasing from about $2 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ to a little less than $1.5 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ (Fig. 6, top). The northeast has undergone substantial reforestation since the mid-1800s (Foster, 1992), resulting in a slow increase in emissions from vegetated lands that slightly offset the decrease in emissions from agriculture. The area of cropland also declined during the century, but this decline seemed to be offset by volatilization from increased fertilizer use, so that the $\text{NH}_3\text{-N}$ emissions from crops were largely unchanged throughout the century. Minor contributions to the total $\text{NH}_3\text{-N}$ budget from residential and commercial coal combustion and the poultry industry were insufficient to alter the long-term trend.

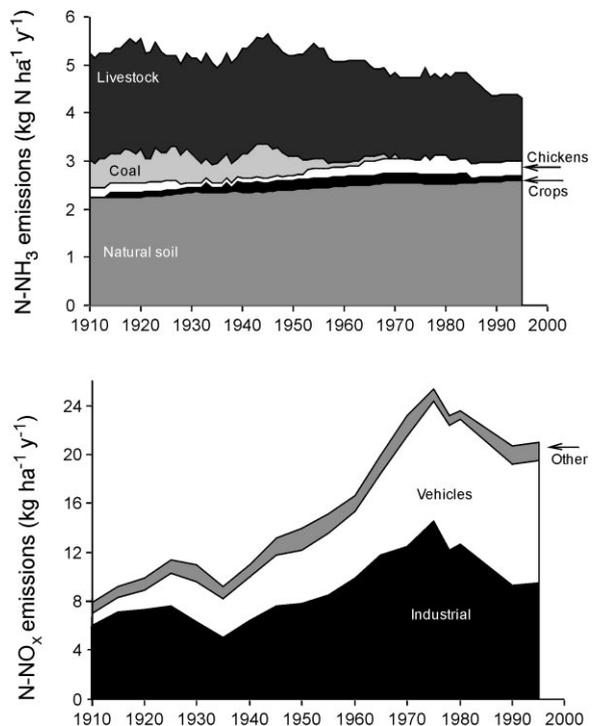


Fig. 6. Top: Historical change in $\text{NH}_3\text{-N}$ emissions ($\text{kg N ha}^{-1} \text{ yr}^{-1}$) sources from 1910 to 1995 in the Northeastern United States. Data were calculated as described in the text. Bottom: Historical change in the sources of NO_x emissions ($\text{kg N ha}^{-1} \text{ yr}^{-1}$) within the generalized Cape Cod airshed. Data are reported as total emissions by source, and are modified from Gschwandtner et al. (1985).

Table 4
Regression statistics for linear regressions

Test	Regression equation	df	F	P value
NH ₃ -N emissions vs. time (Fig. 7, top)	$-0.01 \times + 25.5, R^2 = 0.66$	60	167.6	**
NH ₄ -N deposition vs. time (Fig. 7, top)	$-0.025 \times + 52.4, R^2 = 0.36$	84	34.6	**
NO _x emissions vs. time (Fig. 7, top)	$0.21 \times - 395.6, R^2 = 0.90$	60	734.2	**
NO ₃ deposition vs. time (Fig. 7, top)	$0.025 \times - 45.6, R^2 = 0.47$	84	53.9	**
TDN vs. time (Fig. 5)	$0.026 \times - 39.4, R^2 = 0.44$	60	41.2	**

We verified our NH₃-N emissions estimates by comparison with other global surveys. Global data from Dentener and Crutzen (1994) resulted in estimates of mean emissions of 3.5 kg NH₃-N ha⁻¹ for the entire Earth, while Schlesinger and Hartley (1992) give a range from 3.9 to 10.1 kg NH₃-N ha⁻¹ with a best estimate of 5.9 kg NH₃-N ha⁻¹. Our calculation of about 4.5 kg NH₃-N ha⁻¹ emitted from the northeastern United States is certainly comparable to these other estimates.

Anthropogenic NO_x-N emissions in our airshed derive from industrial (electric utilities, commercial and residential furnaces, coke plants, and industrial boilers), vehicular (on- and off-road vehicles, railroads, and marine vessels), and ‘other’ (lightning, biomass burning from both wild fires and wood products, smelters, cement plants, and miscellaneous) sources. NO_x-N emissions have increased from just under 8 kg N ha⁻¹ yr⁻¹ in 1910 to over 20 kg N ha⁻¹ yr⁻¹ today. Industrial sources accounted for 76% of NO_x-N emissions at the beginning of the century, but the increase in vehicles since the 1920s reduced the industrial emissions to only 45% of the total emissions by the end of the century. Vehicular emissions increased from 12% of the total emissions in 1910 to 48% of all NO_x-N emissions recently. ‘Other’ emissions decreased in importance from 12% of total NO_x-N emissions at the beginning of the century to only 7% of the total today (Fig. 6, bottom).

3.3. Comparison of emissions and deposition

Ammonia emissions and NH₄-N wet deposition both decreased through the century (Table 4; Fig. 7, top), although not synchronously. This slow decrease may be a result of a shift from an agricultural-based landscape to a region that is now dominated by urban and suburban land uses. NH₃-N emissions and deposition are increasing in many other areas as a result of an intensification in animal husbandry such as is occurring in the southeastern United States (Paerl and Whitall, 1999) and Europe (Asman et al., 1988). In New England less than

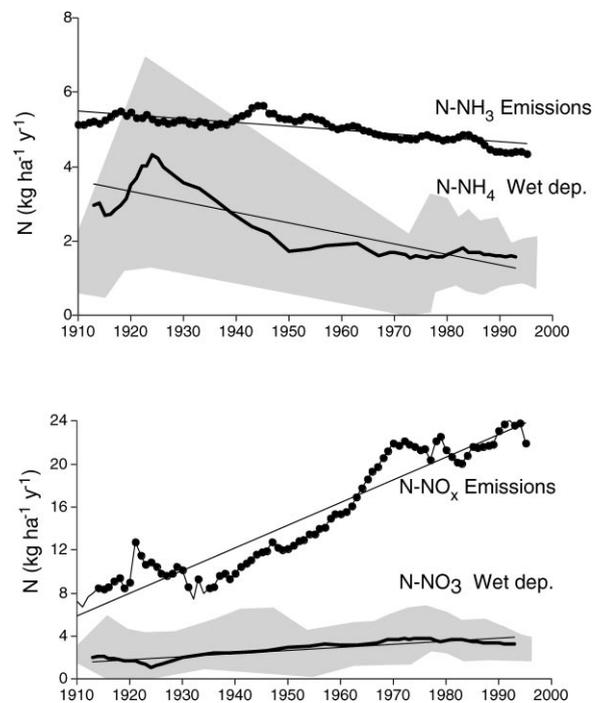


Fig. 7. Top: Estimated emissions of ammonia (kg N ha⁻¹ yr⁻¹) in the northeast, and estimated wet ammonium deposition (kg N ha⁻¹ yr⁻¹) to Cape Cod, Massachusetts from 1910 to the present. Bottom: National nitrate emissions (kg N ha⁻¹ yr⁻¹) and estimated wet nitrate deposition (kg N ha⁻¹ yr⁻¹) to the Massachusetts area. Emissions estimates are shown with filled circles. The dark solid lines represents the 10-yr moving average of the deposition data, and the shaded region around the moving average represents an envelope of the standard deviation around the deposition estimates (for regression statistics see Table 4).

25% of the land is used for agriculture, and the emissions and deposition of nitrogen reflect the relative importance of industrially derived NO₃-N in this region instead of the agriculturally derived NH₃-N.

Nitrogen oxide emissions and reconstructed $\text{NO}_3\text{-N}$ wet deposition both increased throughout the century (Table 4; Fig. 7, bottom); as with NH_x , the increases were not synchronous. Emissions of $\text{NO}_x\text{-N}$ increased at a rate of 2.1 kg N per decade, an order of magnitude higher than $\text{NO}_3\text{-N}$ deposition across the century (Fig. 7, bottom), suggesting major horizontal transport out of the region. Links between emissions and deposition have characteristically been difficult to define (Butler and Likens, 1991), because inter-annual variability in precipitation chemistry and meteorological patterns weaken the relationship between source and sink (Butler and Likens, 1991; Russell et al., 1998). Regional-scale horizontal transport and chemical transformations in the atmosphere may further obscure the link between emissions and nitrogen oxides and deposition of $\text{NO}_3\text{-N}$. Considering these complex interactions, the lack of similarity in the time courses is not surprising.

The total nitrogen deposition calculated for Cape Cod is similar to other areas around the region. Total DIN deposition to North Atlantic watersheds range from 1.5 kg N ha^{-1} in Northern Canada to 18.3 kg N ha^{-1} in northwest Europe (Prospero et al., 1996). The reconstructed 1990s nitrogen deposition of approximately 11 kg N $\text{ha}^{-1} \text{yr}^{-1}$ for Cape Cod is on the low side of inputs reported for other areas in the North Atlantic (Prospero et al., 1996). Atmospheric nitrogen deposition accounts for 12–64% of total anthropogenic inputs to the North Atlantic Ocean (Howarth et al., 1996), depending on the degree of development within the watershed. In the Waquoit Bay watershed atmospheric N accounts for 23% of the total N load in the most developed sub-watershed, and 58% of total N load in the least developed sub-watershed (Valiela et al., 1992, 1997a, b).

Increased nitrogen deposition this century raised awareness of the importance of nitrogen in both terrestrial and aquatic systems. In terrestrial forests increased nitrogen supply — by direct deposition or through increased nitrification in soils — may result in nitrogen leaching from forests soils and into adjoining aquatic systems (Aber et al., 1989; Nadelhoffer et al., 1995). Such increases in nitrogen throughput, referred to as nitrogen saturation, are increasingly common in temperate forests and are important in many ways. Nitrogen saturation changes the watershed-level role of forests from that of a nitrogen sink to a nitrogen source (Aber et al., 1989, 1995). Increases in acidic $\text{NO}_3\text{-N}$ deposition also results in base cation depletion in forest soils (particularly Ca^{2+} and Mg^{2+}), thus altering the acid–base balance in soils and surface waters (Likens et al., 1996). Leachate from N-saturated forests may also travel through vadose zones and aquifers, and flow into receiving lakes, ponds, and estuaries (Aber, 1992) where significant eutrophication can occur. Land-derived nitrogen enrichment can change the functioning of coastal ecosystems. For example, eelgrass meadows disappear as nitrogen loads

increase (Duarte, 1995). A compilation of data from East Coast estuaries indicates that 80% of estuarine eelgrass is lost in systems with nitrogen loads over 20 kg N $\text{ha}^{-1} \text{yr}^{-1}$ (Valiela et al., in press).

The rate of nitrogen release from forests depends in part on forest stand age, soil properties, and rate of nitrogen loading. In Cape Cod forests, however, retention of nitrogen seems unaffected by forest type and age, based on results from mixed plots ranging in age from 1 to 226 yr (Lajtha et al. 1995). Cape Cod soils are underlain by highly porous, unconsolidated sediments; the infiltration rates are high, and N retention by soils may be less efficient (Joslin et al., 1987). Leaching of $\text{NO}_3\text{-N}$ through the soil may therefore be faster than in other forests, regardless of the age of the forest stand. As a result any increase that occurs in total deposition will result in an increase in nitrogen loads to receiving waters.

At present, atmospheric N deposition adds nitrogen at a rate of about 11 kg N ha^{-1} to Cape Cod forests, according to our reconstruction. Symptoms of nitrogen saturation in Welsh forests began to be measurable in some systems as nitrogen inputs went beyond 10 kg N $\text{ha}^{-1} \text{yr}^{-1}$ (Emmett et al., 1993). Nitrogen additions > 25 kg N $\text{ha}^{-1} \text{yr}^{-1}$ resulted in substantial N leaching at all sites (Dise and Wright, 1995). Our reconstructed rates of N deposition (Fig. 5) increased secularly to above the lower limits of the range of 10–25 kg $\text{ha}^{-1} \text{yr}^{-1}$. Even ignoring their greater propensity for nitrogen losses, Cape Cod forests are presently poised at the lower limit of nitrogen saturation. The reconstructed deposition data suggest that, fortunately, the secular pattern of total atmospheric nitrogen deposition has not increased since the mid-1980s on Cape Cod, and may even be decreasing somewhat (cf. right side of Fig. 5), contrary to the whole-century trend. It thus seems important to maintain or intensify regulatory controls of emissions of $\text{NO}_x\text{-N}$ and $\text{NH}_3\text{-N}$ to prevent coastal forests from being subjected to deposition rates higher than their present levels of exposure. If coastal forests are exposed to higher rates of deposition, it is almost certain that increased nitrogen loading of receiving waters will ensue.

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