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Atmospheric nitrogen deposition in the Chesapeake Bay watershed: A history of change

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HIGHLIGHTS

- Atmospheric deposition is important nitrogen source to the Chesapeake Bay watershed and was dominant source from about 1960 to 2000.
- Implementation of Title IV of 1990 Clean Air Act Amendments has resulted in decreases of 60%–73% in wet and dry deposition of oxidized nitrogen and dry deposition of reduced nitrogen during 1995 to 2019.
- Despite these declines, atmospheric nitrogen deposition still contributes about 25% of the annual nitrogen load to the Chesapeake Bay watershed.
- A future projection based on planned implementation of Clean Air Act rules suggests atmospheric nitrogen deposition is likely to decline (from 2015) by an additional 21% by 2050.

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ABSTRACT

The Chesapeake Bay watershed has been the focus of pioneering studies of the role of atmospheric nitrogen (N) deposition as a nutrient source and driver of estuarine trophic status. Here, we review the history and evolution of scientific investigations of the role of atmospheric N deposition, examine trends from wet and dry deposition networks, and present century-long (1950–2050) atmospheric N deposition estimates. Early investigations demonstrated the importance of atmospheric deposition as an N source to the Bay, providing 25%–40% among all major N sources. These early studies led to the unprecedented inclusion of targeted decreases in atmospheric N deposition as part of the multi-stakeholder effort to reduce N loads to the Bay. Emissions of nitrogen oxides (NO_x) and deposition of wet nitrate, oxidized dry N, and dry ammonium (NH₄⁺) sharply and synchronously declined by 60%–73% during 1995–2019. These decreases largely resulted from implementation of Title IV of the 1990 Clean Air Act Amendments, which began in 1995. Wet NH₄⁺ deposition shows no significant trend during this period. The century-long atmospheric N deposition estimates indicate an increase in total atmospheric N deposition in the Chesapeake watershed from 1950 to a peak of ~15 kg N/ha/yr in 1979, trailed by a slight decline of <10% through the mid-1990s, and followed by a sharp decline of about 40% thereafter through 2019. An additional 21% decline in atmospheric N deposition is projected from 2015 to 2050. A comparison of the Potomac River and James River watersheds indicates higher atmospheric N deposition in the Potomac, likely resulting from greater emissions from higher proportions of agricultural and urban land in this basin. Atmospheric N deposition rose from 30% among all N sources to the Chesapeake Bay watershed in 1950 to a peak of 40% in 1973, and a decline to 28% by 2015. These data highlight the important role of atmospheric N deposition in the Chesapeake Bay watershed and present a potential opportunity for decreases in deposition to contribute to further reducing N loads and improving the trophic status of tidal waters.

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1. Introduction

Studies of atmospheric nitrogen (N) deposition in the Chesapeake Bay watershed have played a prominent role in the evolution of scientific thinking and analysis, modeling, and policy regarding the role of atmospheric deposition as an important source of N and a contributor to estuarine eutrophication. Research on this topic in the Bay watershed has influenced studies throughout the U.S. and internationally. Investigations have progressed from the first measurements demonstrating that precipitation included substantial concentrations of inorganic N to later acknowledgement that atmospheric N plays an important role in eutrophication of the Bay.

Recognition that precipitation in the U.S. includes substantial concentrations of various N chemical species dates from measurements of nitrate (NO_3^-) and ammonium (NH_4^+) first reported by Junge in the 1950s (Junge, 1958). Increased awareness of atmospheric N deposition was evident by the 1970s when acid rain became recognized as a widespread phenomenon across the eastern U.S., and early measurements indicated that nitric acid (HNO_3) contributed about 30% to total acidity (Likens et al., 1972). During the 1970s, the role of atmospheric N as a nutrient source to terrestrial ecosystems was also recognized (Swank and Henderson, 1976). Concurrently, evidence was mounting that N was an important contributor to primary production in coastal ecosystems, including the Chesapeake Bay (Ryther and Dunstan, 1971; Howarth and Marino, 2006).

Beyond the broad role of N as a driver of estuarine primary production and potential eutrophication, atmospheric deposition was first recognized as an important N source to coastal ecosystems in the 1980s (Paerl, 1985). In the Chesapeake Bay, a pioneering study concluded that N in precipitation provided 40% of the external load to the Rhode River Estuary (Correll and Ford, 1982). However, this and other early N investigations, although identifying the importance of atmospheric N deposition, likely underestimated its contribution by failing to account for dry deposition and by considering only direct deposition to the estuarine surface and not to the watershed (Tyler, 1988; Fisher and Oppenheimer, 1991). Inclusion of the atmospheric contribution from the watershed is critical to making accurate N budget estimates in the Chesapeake Bay because about 75% of the atmospheric N source emissions originate from outside of the immediate tidal bay waters (Castro and Driscoll, 2002; Howarth, 2007). The importance of the watershed stems from its large area, which is 14-fold greater than that of the tidal bay.

Fisher and Oppenheimer (1991) were among the first to provide quantitative estimates of the contribution of atmospheric deposition as one of many sources to the annual N load to the Chesapeake Bay. They concluded that annual atmospheric wet N deposition loads exceeded those of other sources such as fertilizer, manure, and point source discharges. They estimated that $25 \pm 5\%$ of the annual load originated from atmospheric oxidized N (NO_x), another 14% originated as atmospheric reduced N (NH_x) and argued that atmospheric sources are an important consideration in developing nutrient management strategies. These results were initially met with skepticism, but additional studies further refined these estimates, and confirmed their conclusions (Hinga et al., 1991; Castro and Driscoll, 2002). The Fisher and Oppenheimer (1991) study spurred similar work in other estuarine watersheds, many of which showed an even greater relative contribution of atmospheric N deposition to the total N load (Winchester et al., 1995; Howarth et al., 1996).

Reducing N and phosphorus loads to the Chesapeake Bay is the goal of Federal, State, and other stakeholder groups that participate in the Chesapeake Bay Program (CBP) which was initiated in 1987 to address the long-recognized issue of eutrophication and associated deleterious effects on aquatic biota (Boesch et al., 2001). When the CBP commenced, the importance of atmospheric N as a nutrient source was unrecognized. But following the publication of Fisher and Oppenheimer (1991) and subsequent investigations, the role of atmospheric N as a

major nutrient source to the Bay became widely known and eventually considered as an important component of nutrient management strategies (Krupnick et al., 1998).

The agreement to reduce N (and phosphorus) loads to the Chesapeake Bay is guided by the allocation of a Total Maximum Daily Load (TMDL), a process under the Clean Water Act that enables and guides the restoration of impaired water bodies (Birkeland, 2001). The Chesapeake Bay Watershed models, which simulate nutrient sources and transport, help establish N allocations in the watershed to guide nutrient reduction goals and strategies under the TMDL (Shenk and Linker, 2013). The 1992 version of these models first simulated atmospheric N deposition, and subsequent versions have included increasingly detailed N species and finer spatial resolution of the loads (Linker et al., 2000). Beginning with the 2010 TMDL allocations for the Bay watershed, atmospheric N load reductions were established for the first time, representing an unprecedented linking of provisions of the Clean Air Act and Clean Water Act to address nutrient-related restoration goals (Linker et al., 2013).

Given the precedent-setting scientific investigations into the role of atmospheric deposition as an N source to the Chesapeake Bay and application to policy, the objectives of this paper are to: (1) review and describe the history and evolution of knowledge and approaches used to estimate the relative importance of atmospheric N loads to the Bay, (2) describe trends in measured atmospheric N deposition from two monitoring networks and the policies responsible for those trends, and (3) describe a new data set that provides past estimates (from 1950) and future projections (to 2050) of atmospheric N deposition. Our goal is to make available these century-long data to inform modeling efforts (Shenk and Linker, 2013; Ator et al., 2019) by improving the ability of modelers to calibrate to historical data, informing historical reconstructions, and helping to guide discussions of future projections and policies.

2. Methods

Two approaches were applied in the analyses described here. The first, examines temporal patterns in atmospheric N deposition from wet and dry deposition network sites. The second, presents a new century-long atmospheric N deposition data set based on a measurement – model fusion approach. The first data set provides the most definitive representation of temporal patterns because of its basis on consistent and continuous measurements, but these data are limited by a lack of available data for some constituents known to be present in atmospheric N deposition, and therefore, can only be applied to evaluate temporal trends of select N chemical species over the past few decades. To provide a more comprehensive assessment of historic and projected future patterns, a second century-long data set (1950–2050) was compiled that included model simulations. This second data set was also compared with another data set that was recently developed to provide estimates of N loads in fertilizer, manure, and wastewater over the same century-long time frame. We also note that a glossary of terms applied to describe various forms of atmospheric N deposition in this paper is provided as Table S1 in the text supplement.

2.1. Measurement network sites - data compilation and analysis approach

Data on atmospheric wet deposition for this analysis were obtained from the National Atmospheric Deposition Program (NADP)/National Trends Network (<http://nadp.slh.wisc.edu/data/NTN/>, accessed 01/18/2021). Wet deposition of NO_3^- and NH_4^+ were calculated from analyses of weekly precipitation samples and precipitation volume. Dry deposition data were obtained from the Clean Air Status and Trends Network (CASTNET; <https://www.epa.gov/castnet>, accessed 01/18/2021). The data applied in this paper are termed the “Historical Deposition Data” and were preferred for this analysis because the data set extends back to the 1980s, necessary to evaluate long-term temporal trends. Dry deposition was calculated from measurements of HNO_3 , and

particulate NO_3^- and NH_4^+ by applying deposition velocity estimates and the Multilayer Model as described by Clarke et al. (1997). Data from these networks are important in exploring temporal patterns because they represent samples collected using consistent field and laboratory methods over many years. This is despite recognized limitations in the historic data set such as exclusion of N species known to be present in dry deposition, but not measured (Schwede and Lear, 2014).

An emphasis was placed on obtaining data from sites for this analysis that are located within the Chesapeake Bay watershed or in adjacent areas within the Chesapeake airshed that have been in continuous operation since at least 1990. The airshed is defined as the area from which the majority (70–80%) of the emissions are derived that result in deposition of a constituent such as NO_x to the Chesapeake Bay watershed (Dennis, 1997). Wet deposition sites included in this analysis are Wye, Maryland (MD13), Aurora Research Farm, New York (NY08), Penn State, Pennsylvania (PA15), Charlottesville, Virginia (VA00), Horton's Station, Virginia (VA13), Big Meadows, Virginia (VA28) and Parsons, West Virginia (WV18; Fig. 1, Table 1). The MD13, VA00, and VA28 sites are located within the Chesapeake Bay watershed, whereas the other four sites were outside the watershed but within the Chesapeake airshed. The sites NY08 and PA15 were included to better represent the northern part of the watershed, and the VA13 and WV18 sites were included to better represent the western part of the watershed. Dry deposition sites included Arendtsville, Pennsylvania (ARE128), Beltsville, Maryland

(BEL116) Connecticut Hill, New York (CTH110), Laurel Hill, Pennsylvania (LRL117), Parsons, West Virginia (PAR107), Prince Edward, Virginia (PED108), Penn State, Pennsylvania (PSU106), and Big Meadows, Virginia (SHN418; Fig. 1, Table 1). As with the wet deposition sites, some of the sites are within the Chesapeake Bay watershed (ARE128, BEL116, PED108, SHN418), whereas the others were outside the watershed but within the airshed.

Additionally, estimates of NO_x and NH_3 emissions data back to 1990 were obtained from the U.S. Environmental Protection Agency for comparison to patterns of wet and dry N deposition (<https://www.epa.gov/air-emissions-inventories/air-pollutant-emissions-trends-data>, accessed 01/18/2021). These data were compiled and summed for all states (and Washington D.C.) in which at least part of the landmass was located within the Chesapeake airshed for NO_x (DC, DE, IN, KY, MD, MI, NC, NJ, NY, OH, PA, SC, TN, VA, VT, WV) and NH_3 (DC, DE, IN, KY, MD, NC, NY, OH, PA, TN, VA, VT, WV) (Paerl et al., 2002). Data from states near the outermost edges of the Chesapeake airshed (MI, NJ, IN, SC, VT) were excluded from this analysis of reduced N because evidence indicates, that while NH_3 emissions have a longer transport distance in the atmosphere prior to deposition than once believed (Dennis et al., 2010), the atmospheric lifetime of NH_3 is typically about 15%–20% less than that of NO_x , though highly variable and dependent on a host of source and climatic factors (de Foy et al., 2015; Dammers et al., 2019).

Temporal trends in N deposition were identified by the Mann-Kendall test (Mann, 1945; Kendall, 1975), and correlation was identified by Pearson Product Moment analysis. A p-value <0.05 was considered significant and a value < 0.001 was considered highly significant. Relative change in deposition was described by calculating a mean value for 3-year periods at the beginning and end of each relevant time span discussed.

Emissions data for NH_3 , which includes agricultural activities, mobile sources, and wildfire, are considered to have high uncertainty and are subject to shifts caused by efforts to correct sources of bias in successive emissions inventories performed by the U.S. Environmental Protection Agency (Gilliland et al., 2006; Paulot et al., 2014). While NH_3 emissions estimates are considered relatively accurate on a nationwide basis, large discrepancies have been identified at regional scales (Paulot et al., 2014). Therefore, NH_3 emissions estimates are presented in this paper (in the text supplement) to provide a broad frame of reference, but trend and correlation analysis with deposition measures was not performed.

2.2. Atmospheric nitrogen deposition, 1950 to 2050

A watershed-wide, century-long data set of N species in wet and dry atmospheric deposition was developed for the Chesapeake Bay watershed by applying a measurement – model fusion approach (Hopple et al., 2020). An additional data set for total N loads in fertilizer, manure, and wastewater is applied here to provide context and comparison with atmospheric N estimates (Hopple et al., 2021). The atmospheric data set includes wet NO_3^- ($\text{NO}_{3\text{wet}}$), wet NH_4^+ ($\text{NH}_{4\text{wet}}$), dry NO_x (NO_{xdry}), and dry NH_x (NH_{xdry}) deposition. Wet and dry N deposition as described in the results represent the sum of $\text{NO}_{3\text{wet}}$ plus $\text{NH}_{4\text{wet}}$, and NO_{xdry} plus NH_{xdry} , respectively. Total N deposition is the sum of all four terms. Organic N deposition is not included in the data presented here because of a lack of available measurements and little knowledge of how to estimate or model net deposition to landscapes. The Community Multi-scale Air Quality (CMAQ) model, a 1-atm air simulation model of the North American continent, was applied to calculate monthly dry N deposition (Byun and Schere, 2006; Pleim and Ran, 2011; Linker and others, 2013). The CMAQ model provides estimates of oxidized dry N deposition that includes gaseous nitric oxide (NO) and nitrogen dioxide (NO_2), gaseous nitric acid (HNO_3), and particulate NO_3^- , a greater number of species than measured by the CASTNET dry oxidized N deposition. Deposition of NH_{xdry} includes gaseous NH_3 and particulate NH_4^+ , the gas phase an addition over the particulate NH_4^+ represented by

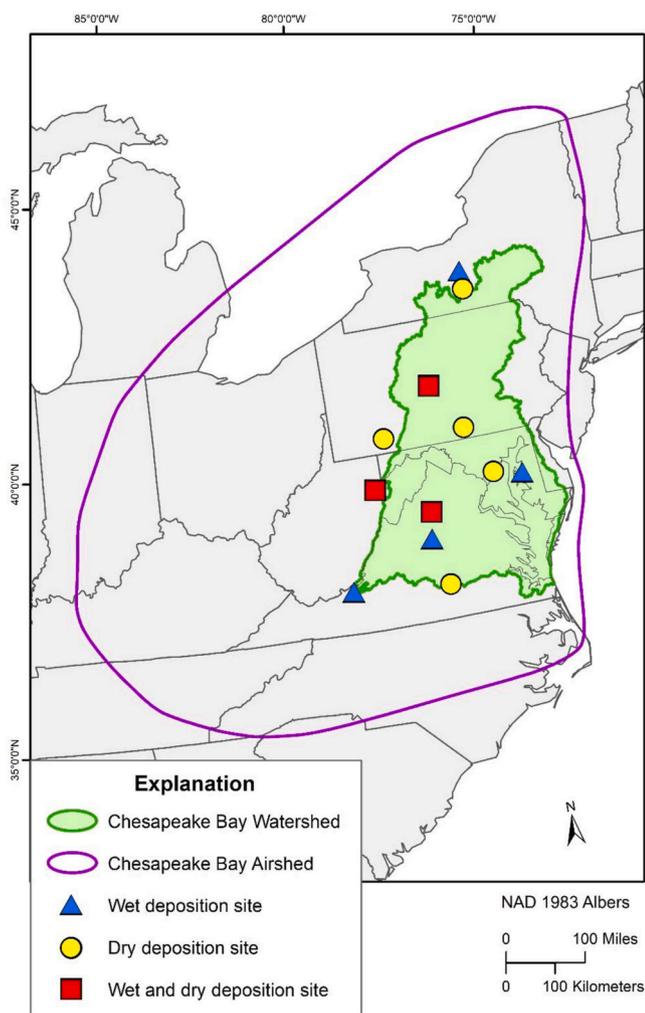


Fig. 1. Map showing the Chesapeake Bay watershed, the Chesapeake airshed, 7 sites that are part of the NADP/National Trends Network, and 8 sites that are part of CASTNET. Three of the wet and dry deposition sites are co-located and are distinguished on the map.

Table 1

Site identification and location information and start of record (all sites continue to present) for wet and dry atmospheric N deposition data used in this study. Wet atmospheric deposition data are from NADP (<http://nadp.slh.wisc.edu/data/NTN/>) and dry atmospheric deposition data are from CASTNET (<https://www.epa.gov/castnet>).

Site ID	Name	County	St.	Lat.	Long.	Elev. (m)	Start of Record
<i>Wet Deposition</i>							
MD13	Wye	Queen Anne's	MD	38.9131	-76.1525	6	3/8/1983
NY08	Aurora Res. Farm	Cayuga	NY	42.7339	-76.6597	249	4/17/1979
PA15 ^a	Penn State	Centre	PA	40.7883	-77.9458	393	6/7/1983
VA00	Charlottesville	Albemarle	VA	38.0402	-78.5427	172	10/2/1984
VA13	Horton's Station	Giles	VA	37.3294	-80.5579	916	7/25/1978
VA28 ^a	Big Meadows SNP	Madison	VA	38.5231	-78.4348	1072	5/12/1981
WV18 ^a	Parsons	Tucker	WV	39.0897	-79.6622	505	7/5/1978
<i>Dry Deposition</i>							
ARE128	Arendtsville	Adams	PA	39.9232	-77.3079	266	5/21/1988
BEL116	Beltsville	Prince George's	MD	39.0282	-76.8171	47	10/25/1988
CTH110	Conn. Hill	Tompkins	NY	42.4008	-76.6535	511	8/21/1987
LRL117	Laurel Hill	Somerset	PA	39.9883	-79.2516	609	12/11/1987
PAR107 ^a	Parson	Tucker	WV	39.0904	-79.6617	510	1/4/1988
PED108	Prince Edward	Prince Edward	VA	37.1652	-78.3071	149	10/29/1987
PSU106 ^a	Penn State	Centre	PA	40.7209	-77.9318	364	1/1/1987
SHN418 ^a	Big Meadows SNP	Madison	VA	38.5231	-78.4347	1073	5/17/1988

^a - indicates collocated wet and dry deposition sites.

CASTNET dry reduced N deposition. Thus, while CASTNET data are useful for examining temporal trends in some dry-deposited N species, the CMAQ model was applied because of its capability of simulating deposition of a more complete set of N species. Approaches for estimating atmospheric deposition differed among 3 periods of time, 1950 to 1983, 1984 to 2014, and 2015 to 2050.

Data for the period 1984 to 2014 are considered of the highest quality with the least uncertainty and were the foundation for making estimates of past deposition (1950–1983) and future projections (2015–2050). These data were developed by the Chesapeake Bay Program office (<https://www.chesapeakebay.net/>, accessed 01/18/2021) and are based on a measurement – model fusion approach as described by Linker et al. (2013). Wet deposition was estimated by a spatial regression model on an hourly time step whenever precipitation occurred in the watershed (Grimm and Lynch, 2005) based on data available from 45 NADP sites (<http://nadp.slh.wisc.edu/data/NTN/>). Predictive regression variables include aspects of land cover, seasonality, emissions, and meteorological data to make hourly estimates. All wet deposition values presented for 1950 to 2050 have been climate detrended by applying a mean precipitation amount to volume-weighted concentrations for each year to eliminate annual variation caused solely by variation in precipitation volume. Monthly estimates of dry deposition of NO_xdry, and NH_xdry were provided by CMAQ for the period of 2002–2012. A linear regression approach using NO₃wet was applied to provide estimates of NO_xdry for the entire 1984 to 2014 period to provide a consistent approach throughout. Constant NH_xdry was assumed during 1984–2001 when modeled values were unavailable using the 2002 to 2004 average values. Available CMAQ-derived NH_xdry estimates were applied for the years 2004–2014, using extrapolation for years when model-derived values were unavailable. Additional method details are described in the atmospheric N data release (Hopple et al., 2020).

Measurements and model simulations of atmospheric N deposition to the Chesapeake Bay watershed were uncommon before the first sites were established in 1978 as part of what later became NADP. Atmospheric N deposition during 1950–1983 was estimated from limited available wet deposition data, statistical relations identified in dry deposition data during recent decades, and temporal patterns in NO_x emissions. Estimates of atmospheric N deposition were based on spatial-gridded wet N deposition values reported for 9 years during 1950–1983 by Gronberg et al. (2014) along with U.S. NO_x emissions estimates reported by Nizich et al. (1996). Wet N deposition values for the Chesapeake Bay watershed were observed to increase proportionally with NO_x emissions based on 9 annual values, and a polynomial regression (p

< 0.0001 , $r^2 = 0.99$) was fit to these data to provide estimates of wet N deposition for years when values from Gronberg et al. (2014) were unavailable. Spatially gridded wet N deposition values were obtained by applying quadratic regression models ($p < 0.05$ for most landscape units) to provide annual values for the entire 1950 to 1983 period. These values were climate detrended by applying mean 1991 to 2000 precipitation amount (believed to represent long-term mean watershed precipitation amount) from the Parameter-elevation Relationships on Independent Slopes Model (PRISM) data set (<http://www.prism.oregonstate.edu/>, accessed 01/18/2021).

No measurements or model estimates are available for NO_xdry prior to the early 1980s. Therefore, estimates of NO_xdry for the period 1950 to 1983 are based on linear regression relations developed between NO₃wet and NO_xdry for each spatial landscape unit for the period 1984 to 2014. We assumed that the relations between wet and dry deposition observed during 1984–2014 applied similarly during the earlier period.

Values for NH₄wet and NH_xdry were estimated and are available in the atmospheric N data release (Hopple et al., 2020), but few measured values are available prior to the early 1980s, and data to form the basis of statistical relations are generally not available for this earlier period. This necessitated several simplifying assumptions that provide less confidence and high uncertainty in the estimates of reduced N species relative to those of oxidized N species, especially for the historical 1950 to 1983 period. Therefore, values for wet and dry reduced N deposition species are not presented in this paper. We do present total N deposition values to illustrate temporal and spatial patterns across the watershed and to provide comparisons to patterns of other N sources. However, we note that temporal patterns in total N deposition are largely driven by changes in NO_x emissions and resulting changes in NO₃wet and NO_xdry.

Future projections of atmospheric N deposition for 2015 to 2050 were obtained from the U.S. Environmental Protection Agency. These projections were developed using CMAQ model version 5.0.2 (Appel et al., 2013; Zhang et al., 2019). These model projections were guided by expected future emissions of NO_x and NH_x according to rules and regulations scheduled to be implemented under the Clean Air Act as of 2011. Modeled atmospheric N deposition concentration values were developed for 2017, 2025, 2030, and 2050. Linear interpolation was applied to estimate concentrations for the intervening years. Future deposition projections were climate detrended to maintain consistency with the historical data. The deposition values were derived by applying 2011 meteorological conditions, whereas future emissions changes are based on federal and state regulations and measures that represent the impact of current “on the books” regulations without implementation of the heavy-duty vehicle greenhouse gas Phase 2 rule (U.S. Environmental

Protection Agency, 2016).

Two major sources of uncertainty in these future projections are: (1) implementation of new clean air policies that were unknown when the future deposition projections were simulated, and (2) climate change. New clean air policies are commonly introduced by a new presidential administration. For example, the Affordable Clean Energy (ACE) rule was proposed by the Trump Administration in August 2018. Emissions of NO_x are expected to be 5% greater than if a pre-existing rule, the Clean Power Plan, were in place (Keyes et al., 2019). The ACE is currently being challenged in court and its implementation is uncertain. Climate change is expected to result in a warmer climate with greater precipitation in the Chesapeake Bay watershed than at present (Najjar et al., 2010). Campbell et al. (2019) simulated the effects of future climate change and concluded that atmospheric N deposition would increase by 4% relative to a neutral climate change scenario. Beyond these two factors, others such as future changes in land use and population density will affect atmospheric N deposition. Together, these factors highlight sources of uncertainty in future projections. In this analysis, we did not attempt to quantify the magnitude of this uncertainty, but rather acknowledge that the future projections have greater uncertainty than estimates for recent years, and additionally, that uncertainty increases as one extends further into the future.

The resulting century-long atmospheric N deposition estimates were compared to N load estimates for fertilizer, manure, and wastewater. These estimates were developed by a separate group of investigators and are available in a data release (Hopple et al., 2021). The methods applied to make these estimates are described briefly in the text supplement (S2), and more detailed descriptions are available in the metadata file available in Hopple et al. (2021).

3. Results and discussion

A review of studies that have made estimates of the role of atmospheric N deposition relative to other N sources to Chesapeake Bay watershed is first presented to provide context for the comparison of these sources that is presented later in this paper. Next, an evaluation of temporal and spatial patterns of wet and dry N deposition is presented and compared with emissions patterns in the Chesapeake airshed. Finally, century-long estimates of atmospheric N deposition based on a measurement – model fusion approach are presented and compared with estimates of other major N sources over the same 1950 to 2050

period.

3.1. Relative role of atmospheric deposition as a nitrogen source to the Chesapeake Bay

Since Fisher and Oppenheimer (1991) first provided estimates of the contribution of atmospheric deposition to N loads to the Chesapeake Bay, several studies have subsequently made estimates by applying a range of approaches and assumptions. These estimates have varied widely ranging from atmospheric deposition contributing <10% of the total N load to the Bay up to values > 60% (Table 2; Hinga et al., 1991; Jaworski et al., 1997; Alexander et al., 2001; Castro et al., 2001; Boyer et al., 2002; Castro and Driscoll, 2002; Castro et al., 2003; Ator et al., 2011; Birch et al., 2011; Linker et al., 2013; Ator et al., 2019). Caution is warranted when comparing these estimates, however, because of variation in factors such as the atmospheric N forms considered, assumed watershed retention rates, the estimated magnitudes of non-atmospheric N sources, whether direct deposition to the tidal Bay waters was included, and especially the years to which the analysis applies. Additionally, dry-deposited N forms and organic N are not well measured and not always included in analyses, further contributing to differences among atmospheric source estimates. The years selected for analysis are especially important because atmospheric N deposition has declined since the 1990s due to implementation of several rules under the Clean Air Act that have reduced emissions, primarily those of oxidized N species (Linker et al., 2013). Following publication of estimates of the substantive role of direct atmospheric N deposition to the surface of the Rhode River Estuary, a sub-estuary of the Chesapeake Bay (Correll and Ford, 1982), additional analyses of the role of atmospheric N deposition began to appear in the late 1980s in reports of environmental organizations, consultants, and conferences (not cited here, see Fisher and Oppenheimer, 1991). Following publication of the Fisher and Oppenheimer estimates (1991), some skepticism was expressed because the conventional wisdom at the time considered sources such as runoff from manure and fertilizer applied to agricultural lands and discharge from wastewater treatment plants to be the only substantial N sources (Hinga et al., 1991). But investigations in other regions such as the Baltic Sea and elsewhere in northern Europe also identified atmospheric deposition as an important N source (Ronner, 1985). The work of Hinga et al. (1991) applied an approach and set of assumptions independent of those employed by Fisher and Oppenheimer (1991) to test the robustness of

Table 2

Contribution of atmospheric N deposition relative to the sum of other N sources to the Chesapeake Bay watershed. Year(s) refers to period for atmospheric deposition estimates only as other N source estimates may have been based on different years. NA indicates uncertainty ranges were unavailable.

Citation	Year	Estimate (% of N load)	Uncertainty Range (% of N load)	Dry Dep Incl.	Org N Incl.	Comment
Fisher & Oppenheimer (1991)	1984	34	29–39 ^a	Yes	No	Equal source retention
	1984	39	34–44 ^a	Yes	No	Differential source retention
Hinga et al. (1991)	1986	31	12–59 ^b	Yes	No	
Jaworski et al. (1997)	1990–93	61 ^c	NA	Yes	Yes	Regression based on 17 sites
Alexander et al. (2001)	1980s–93	28	22–34	No	No	Steady-state model, dep. to Bay excluded
Castro et al. (2001)	1979–96 ^d	23	NA	Yes	No	Nitrate dep. only
Castro & Driscoll (2002)	1997	27	NA	Yes	Yes	
Boyer et al. (2002)	1991	25 ^c	NA	Yes	Yes	Net atmos. dep.
Castro et al. (2003)	1979–96 ^d	30	NA	Yes	Yes	
Ator et al. (2011)	2002	17	NA	No	No	Steady-state model, dep. to Bay excluded
Birch et al. (2011)	2008	24	NA	Yes	No	
Linker et al. (2013)	1985–2005	1985 = 32 2005 = 27	NA	Yes	Yes ^e	Modeled dep., dep. to Bay excluded
Ator et al. (2019)	1992, 2012	<10	NA	No	No	Steady-state models, dep. to Bay excluded

^a based on uncertainty for NO₃ only, no uncertainty provided for NH₄⁺.

^b based on total deposition for low range and high range numbers for each source.

^c basin area-weighted mean for Susquehanna, Potomac, Rappahannock, and James, does not include entire Chesapeake Bay watershed or the Bay itself.

^d years represent widest range among 10 NADP and 8 CASTNET sites used in analysis as described by Meyers et al. (2001).

^e wet deposition to fresh water and Bay surfaces only, no dry deposition.

their conclusions. They assembled independent data on N sources originating from agriculture and a more complex set of assumptions about retention on land and in rivers. Furthermore, they assumed that not all atmospheric N deposition was anthropogenic, allowing for a natural N deposition rate. Yet, despite yielding a wider range of uncertainty than Fisher and Oppenheimer (1991), Hinga et al. (1991) largely confirmed that about one-third of N transported to the Bay originated from atmospheric deposition (Table 2). Jaworski et al. (1997) later made what many considered implausibly high estimates that atmospheric N deposition was nearly two-thirds of the total N load to the Bay from four major tributaries (Table 2). Their approach of using a regression of atmospheric N deposition vs. river N runoff from watersheds with minimal human land use impact yielded atmospheric N loads that exceeded measured wet plus dry deposition reinforcing skepticism of their high estimates (Castro and Driscoll, 2002).

Later assessments of the role of atmospheric N deposition made new assumptions about sources to the watershed and landscape retention of N and generally concluded that about one-fourth of the N load to the Bay originated from atmospheric deposition (Castro et al., 2001; Castro and Driscoll, 2002; Boyer et al., 2002; Birch et al., 2011). Some studies added consideration of food and feed imports into the Chesapeake Bay watershed, that while not large (Castro and Driscoll, 2002; Boyer et al., 2002), lessened the relative role of atmospheric N deposition. Furthermore, NO_x emissions in the Chesapeake airshed and atmospheric N deposition at many measurement sites peaked in the 1980s and began to decline by the 1990s data periods considered by many of the more recent studies (Butler et al., 2005).

The steady-state SPATIALLY Referenced Regression on Watershed attributes (SPARROW) model has been applied in several instances to estimate the contribution of nutrient sources including atmospheric N deposition to the Chesapeake Bay. Alexander et al. (2001) provided an estimate that 28% of NO₃⁻ delivered to the Bay originated from atmospheric wet NO₃⁻ deposition by applying data from the 1980s and early 1990s. Later, Ator et al. (2011) estimated that 17% of the total N load delivered by tributaries to the Bay originated from atmospheric wet NO₃⁻ plus NH₄⁺ deposition for the year 2002 by which time atmospheric N deposition was substantially less than during the 1980s and 1990s. Ator et al. (2019), later compared N source estimates for 1992, 2002, and 2012 and concluded that although the load of atmospheric N deposition to the Bay had declined, only a slight change in the contribution of atmospheric N deposition was evident over 20 years, and values remained <10% of total N loads throughout the 20-year period.

One factor that tends to provide lower SPARROW-based estimates of the atmospheric N load delivered to the Bay relative to estimates originating from empirical approaches is that N is explicitly routed downstream in SPARROW, and the fraction of in-stream N retention is inversely related to stream depth (Alexander et al., 2000). This has the effect of retaining more N originating from atmospheric deposition than from other sources because of the greater role of atmospheric N deposition in upland headwater areas more distant from the Chesapeake Bay (Preston et al., 2011). In contrast, past empirical approaches that estimated the relative magnitudes of N sources to the Bay used land use-based export coefficients without explicit spatial landscape and hydrological representation (Fisher and Oppenheimer, 1991; Hinga et al., 1991; Castro and Driscoll, 2002; Castro et al., 2003). Retention of N through processes such as uptake and denitrification were represented as a simple loss fraction (Fisher and Oppenheimer, 1991) or were divided into terrestrial and in-stream retention that in some instances differed by land use type (Castro and Driscoll, 2002).

Another factor that lowers SPARROW-based estimates of the atmospheric N load is that atmospheric deposition is not explicitly included as a load term in urban and agricultural land but rather is implicitly part of the total N load originating from these land uses (Ator et al., 2019). Conversely, the entire N load originating from undeveloped land, which is largely forested in the Chesapeake Bay watershed, is assumed to be atmospheric N deposition. As a result, the contribution of atmospheric N

deposition to N loads in urban and agricultural land is not explicitly considered, though it is a recognized minor contributor in these settings.

Considering the widely varied estimates of the relative contribution of atmospheric deposition to total N export to the Chesapeake Bay, it is challenging based solely on a review of the literature to estimate the value in 2020, though it is likely less than the 25% cited in many earlier studies. Those cited here highlight wide ranging assumptions about the source magnitudes, transport, and retention applied in compiling past estimates, whether by an empirical or modeling approach. Undoubtedly, the export of atmospheric N deposition to the Bay has declined over the past 2 to 3 decades as NO_x emissions in the Chesapeake airshed have decreased (discussed in next section). Linker et al. (2013) applied the Chesapeake Bay Program models to estimate that atmospheric N deposition declined from about 32% to 27% of total N export to the Bay during 1985–2005. In contrast, the most recent estimates from the SPARROW model indicate that atmospheric N deposition declined during 1992–2012 but remained <10% of total N export to the Bay throughout the 20-year period (Ator et al., 2019). Furthermore, Ator et al. (2019) attribute most of the decline in total N export to the Bay during this period to a reduction of point source discharges, and only 13% of the decline is attributed to decreasing atmospheric N deposition. Another important point when comparing these values is that Ator et al. (2019) considered only atmospheric inorganic N deposition to the Bay watershed whereas Linker et al. (2013) included organic N in deposition estimates, and additionally considered direct atmospheric N to the tidal waters.

A contrasting view regarding the extent to which declining atmospheric N deposition has contributed to overall declines in watershed N export to the Chesapeake Bay is offered by Eshleman et al. (2013), who suggested based on water quality monitoring data from upland, largely forested parts of the Chesapeake Bay watershed, that stream N export has decreased by nearly half during 1986–2009 in 9 watersheds where atmospheric N deposition is assumed to be the dominant source. These atmospheric N deposition-driven declines in N export appear to be robust up to a spatial scale of the Potomac River just upstream of tidal extent, nearly one-fourth of the entire Chesapeake Bay watershed. This suggests a strong role for decreasing atmospheric N deposition even where a mix of land use sources are present, and furthermore, that the atmospheric deposition role is not strongly diminished at large basin scales (Eshleman and Sabo, 2016).

3.2. Spatial and temporal patterns of atmospheric nitrogen deposition from measurement networks

Fig. 2 provides a visual representation of the mean temporal patterns among the deposition types and emissions from the airshed states during 1990–2019. Slight declines are evident in NO_x emissions and wet NO₃⁻ deposition through the early-to mid-1990s, a regional pattern shown previously by others and likely resulting from a combination of rules implemented under the Clean Air Act of 1970 (Sickles and Shadwick, 2015; Lloret and Valiela, 2016). However, oxidized N emissions and deposition began to show sharp reductions after 1995 driven by Phase I of the Acid Rain Program that implemented Title IV of the Clean Air Act Amendments of 1990 (Burns et al., 2011). Therefore, trend analysis and patterns of change are described here using 1995 as a reference year. By the late 1990s, NO_x emissions and oxidized N deposition began to decline sharply, a pattern that continued through 2019. These decreases are highly synchronous with slight year-to-year deviations reflected by Pearson Product Moment correlation coefficients that range from 0.96 to 0.98 ($p < 0.0001$) among the 3 oxidized N measures. The 3-year mean percent change centered on 1995 and 2018 are -59.9%, -71.5%, and -72.5% for wet NO₃⁻ deposition, dry oxidized N deposition, and NO_x emissions, respectively (Table 3). These declines were highly consistent among sites for deposition and among states for emissions with the same direction of change and ranges of <15% among all measures. The trends for each of these metrics of oxidized N were highly significant ($p <$

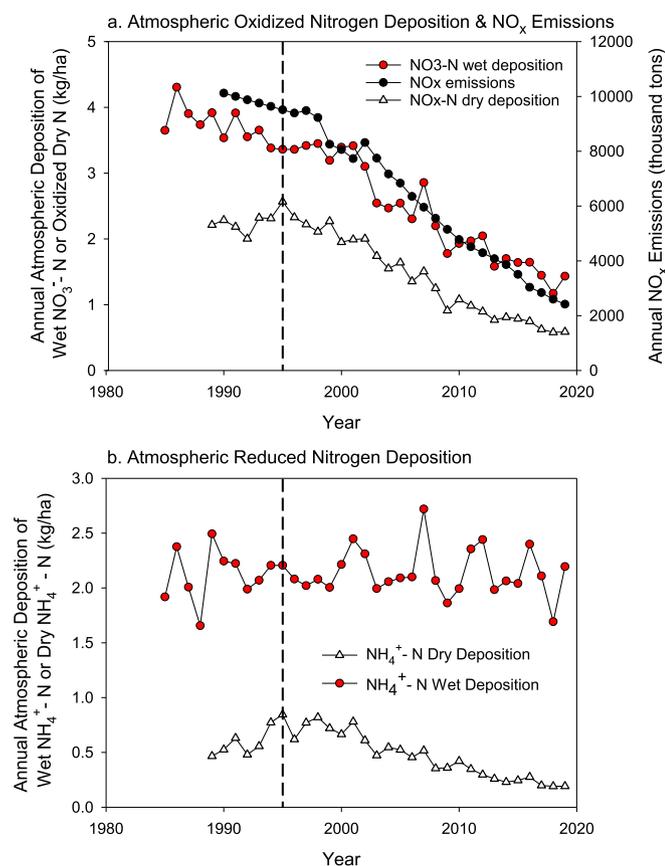


Fig. 2. Annual atmospheric wet and dry N deposition at selected sites and NO_x emissions in the Chesapeake Bay airshed. Wet deposition is the mean of 7 NADP/National Trends Network sites during 1985–2019, and dry deposition is the mean of 8 CASTNET sites. Emissions are total values for Chesapeake airshed states. a. annual mean wet NO₃⁻ deposition, annual mean oxidized dry N deposition, and annual NO_x emissions. b. annual mean wet NH₄⁺ deposition and annual mean NH₄⁺ dry deposition. Dashed vertical line indicates the year 1995.

Table 3

Sen slope and significance of Mann-Kendall trend test for oxidized N emissions and oxidized and reduced N deposition based on mean values for 7 NADP/National Trends Network wet deposition sites and 8 CASTNET dry deposition sites in the Chesapeake airshed. Percent change based on 3 year mean values centered on 1995 (1994–1996) and 2018 (2017–2019). Variation is the range in percent change among wet and dry deposition sites and among airshed states for emissions.

Constituent	Sen Slope (annual)	p-value	Percent Change	Percent Range
NO_x emissions	-314.3 (kilotons)	<0.0001	-72.5	-77.4 to -62.6
NO₃⁻ wet deposition	-0.096 (kg N/ha)	<0.0001	-59.9	-62.9 to -57.9
Oxidized dry N deposition	-0.084 (kg N/ha)	<0.0001	-71.5	-78.9 to -65.3
NH₄⁺ wet deposition	NS	0.71	+7.6	-18.6 to +23.2
NH₄⁺ dry deposition	-0.017 (kg N/ha)	<0.0001	-73.4	-77.8 to -68.9

0.0001) during 1995–2018 (Table 3). These temporal patterns in emissions and deposition of oxidized N are similar to those reported previously across the eastern U.S. (Sickles and Shadwick, 2015; Lloret and Valiela, 2016), indicating widespread geographic consistency of these downward trends.

In contrast to oxidized N patterns, those of wet and dry NH₄⁺

deposition show more varied and less persistent patterns (Fig. 2). No apparent trend was identified in wet NH₄⁺ deposition and dry NH₄⁺ deposition showed a pattern of decline that is visually and quantitatively similar to that of oxidized dry N deposition. These visual patterns are confirmed by Mann-Kendall trends that are not significant for wet NH₄⁺ deposition ($p = 0.71$) but highly significant for dry NH₄⁺ deposition ($p < 0.0001$) during 1995–2018 (Table 3). Observations of similarities and differences in temporal patterns among these two measures are largely confirmed by Pearson Product Moment correlation analysis that is not significant for wet and dry NH₄⁺ deposition ($p = 0.33$). Emissions of NH₃ that originate from the airshed and watershed appear to decrease during 1990–2019 (Fig. S1), but it is unclear whether these represent real changes in emissions patterns when considering the role of methods changes over time (Gilliland et al., 2006; Paulot et al., 2014). Because NH₃ emissions originate largely from agricultural activities and are commonly correlated with fertilizer use and farm animal numbers (Warner et al., 2016), estimates of the sum of total N from fertilizer and manure application in the Chesapeake watershed are shown as well for reference (Fig. S1). The apparent decrease in NH₃ emissions during 1995–2019, as reflected in the emission inventory data, were not accompanied by a parallel decline in agricultural N sources, which have remained relatively constant throughout this period. Additionally, there are other factors not reflected in emission estimates that may have countered any suggested declines by acting to increase NH₃ emissions and air concentrations. First, warming temperatures such as those identified in the Chesapeake watershed (Rice and Jastram, 2015) enhance emissions, and warming has been identified as an important secondary factor contributing to nationwide increases in NH₃ emissions over the U.S. in recent years (Warner et al., 2017). Second, decreasing atmospheric concentrations of NO_x and sulfur dioxide (SO₂) have resulted in a larger relative amount of NH_x remaining in the gas phase, thus contributing to increasing NH₃ concentrations independent of emissions. Given consideration of all these factors and the limitations of available data, we conclude that an assumption of little change in NH₃ emissions and atmospheric concentrations during 1995–2019 is reasonable and supported by other trend analyses that include the Chesapeake airshed (Butler et al., 2016). This conclusion is further supported by lack of a significant trend in wet NH₄⁺ deposition, which reflects atmospheric NH₃ concentrations.

There are several reasons that may explain in part why the patterns, trends, and correlations among oxidized and reduced N emissions and deposition differ. Foremost is that NO_x emissions originate largely from electricity generation and mobile sources, and trends and deposition measures have been driven strongly by Clean Air Act rules and regulations such as the Acid Rain Program and the NO_x State Implementation Plan (SIP) Call (McClenny et al., 2002). In contrast, NH₃ emissions originate largely from agricultural activities (vehicles and wildfire are secondary sources) and have not been well regulated by Clean Air Act requirements (van Grinsven et al., 2015). Divergence between temporal patterns of wet and dry NH₄⁺ deposition as observed among the sites examined here has also been observed more broadly across the eastern U.S., because particulate NH₄⁺ in dry deposition better reflects long-range atmospheric transport than does that of NH₄⁺ in wet deposition (Sickles and Shadwick, 2015; Rattigan et al., 2017). Particulate NH₄⁺ is linked to sulfate (SO₄²⁻) and NO₃ to balance particle charge, and these two anions act in part to limit particulate NH₄⁺ concentrations in the atmosphere. So, the apparent decrease in dry NH₄⁺ deposition shown in Fig. 2b may better reflect declining SO₂ and NO_x emissions over the past 3 decades rather than decreasing NH₃ emissions. The 73.4% decrease in NH₄⁺ dry deposition, is therefore, similar to the 72.5% decrease in NO_x emissions and 71.5% decrease in oxidized dry N deposition (Table 3). In contrast, wet NH₄⁺ deposition is affected by local scavenging of atmospheric NH₃ and is more closely linked with patterns in NH₃ emissions.

3.3. Atmospheric deposition patterns during 1950–2050

Fig. 3 shows the century-long patterns of total N deposition and wet and dry N deposition for the Chesapeake Bay watershed. The patterns of total N deposition and the individual wet and dry components show parallel patterns during 1950–2050. Relatively stable levels of reduced wet and dry N deposition were assumed in developing this data set. Therefore, the temporal dynamics in atmospheric N deposition are governed largely by patterns in NO_x emissions and oxidized N deposition. Both wet and dry N deposition estimates indicate a more than two-fold increase from 1950 until peak deposition in 1979. Estimated peak total N deposition in 1979 was 14.9 kg N/ha/yr. This deposition peak is broad but with a slight decline of <10% through 1995, when emissions reductions under the Title IV Clean Air Act Amendments began implementation. Rates of decline in N deposition steepened in the late 1990s parallel to observations at measurement sites discussed previously. For comparison to the observations, the century-long estimates indicate decreasing 3-year mean deposition of 40.2%, 38.9%, and 39.4% for wet N, dry N, and total N, respectively for the periods centered on 1995 and 2018. These 3-year mean decreases are less than relative decreases in wet NO_3^- , oxidized dry N, and dry NH_4^+ from the measurement networks, but greater than the decrease in wet NH_4^+ , which showed no persistent trend. When measured values are summed to be equivalent to wet, dry, and total N deposition as in the 1950–2050 data set, the relevant 3-year mean declines from 1995 to 2018 are 37.0%, 74.9%, and 49.8%, respectively. Modeled wet N deposition values decreased similarly to the measured mean values, whereas modeled dry N deposition values declined by about half relative to the measured mean values. A likely reason for this difference is that modeled values include net dry deposition of NH_3 as a bi-directional flux (Zhang et al., 2019; Pleim and Ran, 2011), whereas the dry N deposition data from CASTNET did not include NH_3 deposition, and represented dry NH_x deposition solely by particulate NH_4^+ . This is important because particulate NH_4^+ deposition patterns as represented by CASTNET data are closely linked, and therefore reflect temporal patterns of NO_3^- and SO_4^{2-} as governed by formation of $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 aerosols as discussed previously (Malm et al., 2004). In contrast, wet NH_4^+ deposition patterns are closely linked to patterns of NH_3 emissions and concentrations in the atmosphere. This explains why temporal patterns in dry deposition of NH_4^+ have diverged from those of wet NH_4^+ deposition and NH_3 emissions/concentrations as observed by others (Sickles and Shadwick, 2015; Saylor et al., 2015; Li et al., 2016; Rattigan et al., 2017).

The future projections of atmospheric N deposition show additional declines of 21% from 9.0 kg N/ha/yr in 2015 to 7.1 kg N/ha/yr in 2050,

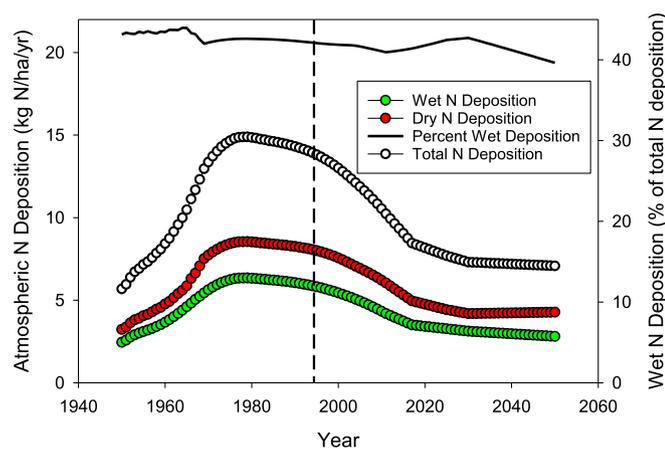


Fig. 3. Annual atmospheric N deposition estimates for the Chesapeake Bay watershed during 1950–2050. Total N deposition, wet and dry N deposition, and percent wet N deposition relative to total N deposition are depicted. Dashed vertical line indicates the year 1995.

based on clean air rules scheduled for future implementation as of 2011 (Fig. 3). Decreases in projected wet N deposition parallel those of total N deposition but dry deposition patterns are projected to differ, reaching a minimum value in 2030, and then increasing slightly to 2050. These divergent patterns between projected wet and dry N deposition, while slight, are driven largely by projected changes in future land use, which impacts localized dry deposition to a greater extent than wet deposition. The projections presented here are based on an assumed static climate. Highlighting the role of climate change, Campbell et al. (2019) applied a downscaled climate change scenario (RCP4.5), and a similar set of future N emissions and deposition data for the Chesapeake Bay watershed, and projected that future decreases in N deposition were lessened by about 4% when compared to a static climate. This climate change penalty was largely caused by the effects of increasing air temperature on the bi-directional flux of NH_3 , favoring greater airborne concentrations.

Atmospheric N deposition also shows wide spatial variation (Boyer et al., 2002; Ator et al., 2011; Campbell et al., 2019) not always well represented by analyses of NADP and CASTNET sites, which are located predominantly in rural and forested landscapes in the eastern U.S. These sites were generally located with an objective of representing the effects of regional changes in SO_2 and NO_x emissions from coal-fired power plants located primarily in the Ohio River Valley. However, other N emissions sources such as NH_3 from agricultural landscapes, and NO_x from mobile sources in urban areas are better represented in the CMAQ model-based results that are part of the century-long N deposition estimates presented here. To illustrate this point, we highlight the difference between atmospheric N deposition estimates for the Potomac River and James River watersheds, the 2nd and 3rd largest in the Chesapeake Bay watershed (Fig. 4). Both basins show the same general temporal patterns of increasing deposition from 1950 to the late 1970s, but the peak in the James is broad with declining deposition not evident until the late 1990s. This pattern most closely resembles those of oxidized N emissions and deposition across the Chesapeake Bay airshed and watershed, and largely reflects emissions patterns influenced by the Clean Air Act. In contrast, the Potomac River watershed has a more distinct unimodal peak with decreasing deposition evident during the 1980s through the late 1990s. The Potomac watershed consists of 34.6% agricultural land and 2.6% urban land, whereas the James watershed consists of 15.6% agricultural land and 1.4% urban land (Boyer et al., 2002). The patterns of N deposition in the Potomac are more greatly affected by localized NO_x and NH_3 emissions from agricultural and urban land.

We also note that the Potomac watershed is located to the east of a

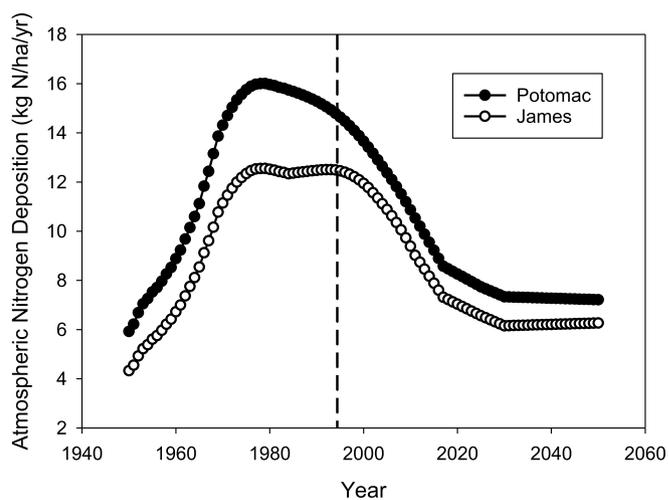


Fig. 4. Total atmospheric N deposition estimates for the Potomac River and James River watersheds during 1950–2050. Dashed vertical line indicates the year 1995.

region of high NO_x emissions from stationary sources in southwest Pennsylvania and eastern Ohio whereas similar areas with such high NO_x emissions are not as clearly evident directly to the west of the James watershed (Kim et al., 2006). So, higher NO_x emissions from power plants may also play a role in the higher rates of atmospheric N deposition in the Potomac than in the James watershed. Fig. 5a shows that fertilizer N loads declined across the Chesapeake watershed from 1980 through the mid-1990s, a pattern that would have more greatly influenced N deposition in the Potomac than in the James River watershed. Additionally, atmospheric N deposition is 2 to more than 3 kg N/ha/yr greater in the Potomac than the James watersheds throughout the century-long estimate period, another reflection of the persistently higher localized emissions from agricultural and urban lands. Differences in land use as well as broad multi-state stationary source emissions patterns affect the spatial and temporal patterns of atmospheric N deposition across the Chesapeake Bay watershed, patterns that are not always clear by examining available data from the NADP and CASTNET sites. This watershed comparison also highlights how future changes in agricultural and urban land use may affect atmospheric N deposition loads as well as impact those of other N sources.

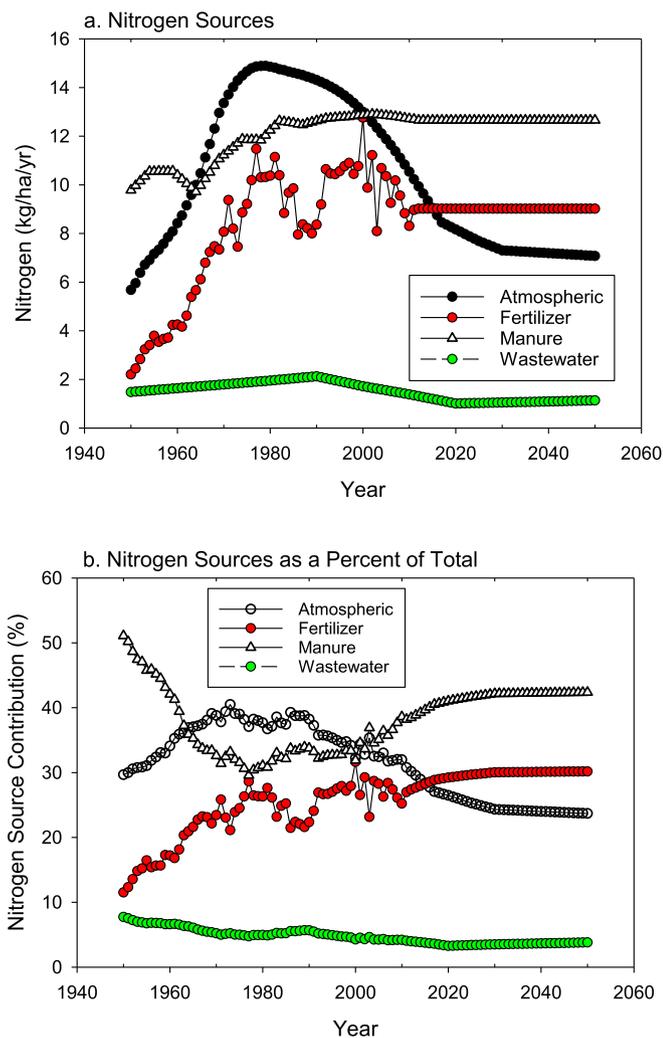


Fig. 5. Annual loads (or deposition) of major N sources to the Chesapeake Bay watershed during 1950–2050. Methods and assumptions for sources other than atmospheric deposition are described by Hopple et al. (2021). a. source loads, b. source loads as a percent of total loads.

3.4. Atmospheric deposition relative to other major nitrogen sources during 1950–2050

Total atmospheric N deposition has shown greater century-long temporal dynamics than estimates of the other major N sources, fertilizer, manure, and wastewater (Fig. 5a). Fertilizer N loads were estimated to have increased by about the same amount as atmospheric N deposition from 1950 to the late 1970s but have declined by less than atmospheric N during the past two decades. The fertilizer N estimates show greater interannual variation than the atmospheric N source and the other N sources from the late 1970s to recently. However, the atmospheric values reflect a large contribution from climate detrended wet deposition, which results in lower temporal variation than would be observed using the raw deposition values. Manure N load estimates also increased from 1950 to the early 1980s but have varied little since that time. Wastewater N load estimates reflect a slight increase from 1950 to 1990 and decline thereafter to present, but the magnitude of change is less than that of the other N sources.

Atmospheric N deposition to the Chesapeake watershed is estimated to have varied from about 30% among all N sources in 1950, reaching a peak of about 40% in 1973, and declining to about 28% by 2015 (Fig. 5b). Projected future changes in loads from these sources indicates an atmospheric N contribution of about 24% in 2050. Atmospheric N was the dominant source from 1960 to 2000 but has since declined to less than the relative contributions from manure and fertilizer, whose percent of total N have increased over the same time frame. Wastewater N was about 8% of the total N sources in 1950 but has since decreased to about 4% recently.

Despite the sharp declines since the 1990s in the role of atmospheric N deposition relative to the other N sources, its contribution to total N sources remains in the range of 25%–30%, similar to many past estimates shown in Table 2. However, when comparing these values to those discussed section 3a, two differences should be considered: (1) the values presented here apply to N sources to the landscape and do not account for transformation and retention during transit to the Bay, and (2) direct atmospheric N deposition to the Bay and other open water areas is not included in these estimates. Because atmospheric N deposition is disproportionately greater in upland parts of the watershed than other sources and transported to the Bay to a greater extent by small streams, in-stream N retention by processes such as denitrification and uptake is likely greater for atmospheric N than the other sources. This in part, is why estimates of N source contributions to the Chesapeake Bay by the SPARROW model are generally less than those of other approaches (Ator et al., 2011, 2019). Exclusion of atmospheric N directly to the Bay and open water in the estimates presented here, likely slightly lessens the atmospheric contribution relative to other sources, which are not deposited directly onto the water surface (wastewater point sources discharge directly into rivers but are viewed differently in this context).

4. Conclusions

A review of the history and evolution of scientific studies of the role of atmospheric N deposition in the Chesapeake Bay watershed highlights the importance of a 1980s study in the Rhode River estuary (Corell and Ford, 1982), and a later influential study (Fisher and Oppenheimer, 1991) that indicated more than one-third of N loads to the Bay originated from atmospheric deposition to the watershed and the Bay surface. Later studies largely confirmed the important role of atmospheric N deposition but differed in their quantitative estimates due to a variety of factors such as the chemical species considered, the extent of watershed retention, and the years considered in the analysis. As a result of these and other early studies, a formal target for reduction of atmospheric N deposition loads was established as part of the 2010 Chesapeake Bay TMDL, demonstrating an important linkage of elements of the Clean Air Act and Clean Water Act to address eutrophication of the Chesapeake Bay and other coastal waters.

An examination of trends in atmospheric N at 7 NADP/National Trends Network wet deposition sites, dry deposition at 8 CASTNET sites, and emissions from airshed states indicates sharp declines in most emissions and deposition measures, especially those that represent oxidized N. These decreases began in the mid-to late-1990s at all sites, a reflection of rules implemented as part of the 1990 Clean Air Act Amendments and range from 60% to 73% during 1995 through 2018. An exception is wet NH_4^+ deposition, which shows no clear pattern of change. Dry deposition of NH_4^+ declined by 73%, synchronously with wet NO_3^- and oxidized dry N deposition because patterns in this measure are governed by formation of NO_3^- and SO_4^{2-} aerosols that limit atmospheric transport and deposition.

A new century-long atmospheric deposition data set based on a measurement – modeling fusion approach and including the years 1950–2050 was introduced to provide a broad historical perspective and to assist future modeling efforts. These estimates indicate that N deposition increased sharply from 1950 to a peak value of about 15 kg N/ha/yr in 1979, followed by a slight decline of <10% through the mid-1990s, and a sharp decline thereafter of about 40% through 2019. This decline in total atmospheric N deposition is less than values of about 50% for total N deposition from measurement network sites in the Chesapeake airshed. This difference arises in part because the century-long estimates include deposition of NH_3 , which have changed little over time, whereas long-term measurements of this component are unavailable. Projected future estimates suggest a further 21% decrease of total atmospheric N deposition during 2015–2050, according to rules and regulations scheduled to be implemented under the Clean Air Act (as of 2011). Our projections did not include future changes in climate, land use, and human population, which could negate some of the decline expected from emissions projections alone.

Atmospheric N deposition exhibits spatial variation across the Chesapeake Bay watershed that is not always well demonstrated by measurement network sites, which are located mainly in rural areas and designed to reflect broad regional patterns. Recent development of a passive NH_3 monitoring network by NADP (<http://nadp.slh.wisc.edu/amon/>, accessed 01/18/2021) as well as recent improvements in remote sensing measurement capability, highlight great potential for improved measurements. Spatial variation in atmospheric N deposition evident across the Chesapeake Bay watershed is highlighted by greater total atmospheric N deposition in the Potomac River watershed than in the James River watershed. The Potomac watershed includes about twice the percentage of agricultural land and urban land as the James watershed. Localized sources of NH_3 and NO_x emissions from these land uses results in greater atmospheric N deposition in the Potomac watershed, highlighting the role of localized N emissions and deposition as a secondary factor in controlling atmospheric N deposition patterns. The review of historical studies along with the data presented here provide evidence of the seminal and influential role of the Chesapeake and its watershed as a “laboratory” for investigating the role of atmospheric N deposition, quantifying the important role of atmospheric deposition as a nutrient source, and highlighting the opportunity for future decreases in deposition to contribute to further reducing nutrient loads and improving trophic status in the Bay. Finally, we confirm the value of the extensive atmospheric monitoring sites and data available within the Chesapeake airshed in facilitating this analysis and providing insight to the effects of clean air and clean water policies.

CRedit authorship contribution statement

Douglas A. Burns: Formal analysis, Investigation, Visualization, Writing – original draft, Writing – review & editing. **Gopal Bhatt:** Methodology, Formal analysis, Validation. **Lewis C. Linker:** Conceptualization, Writing – review & editing, Supervision. **Jesse O. Bash:** Methodology, Writing – review & editing. **Paul D. Capel:** Conceptualization, Methodology, Writing – review & editing. **Gary W. Shenk:** Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.atmosenv.2021.118277>.

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