LETTER

Highly concentrated atmospheric inorganic nitrogen deposition in an urban, coastal region in the US

Emily E Joyce, Wendell W Walters, Emmie Le Roy, Sydney C Clark, Hayley Schiebel and Meredith G Hastings

1 Department of Earth, Environmental, and Planetary Sciences and Institute at Brown for Environment and Society, Brown University, Providence, RI 02912, United States of America
2 Department of Energy, Environmental, and Chemical Engineering, Washington University, St. Louis, MO 63130, United States of America
3 Center for Urban Ecology and Sustainability, Suffolk University, Boston, MA 02108, United States of America

E-mail: emily.joyce@brown.edu

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Abstract

Much of our understanding of atmospheric nitrogen deposition (AD) is based on important monitoring networks, such as the National Atmospheric Deposition Program (NADP) in the United States (US). However, it is likely that rural-based monitoring data are unrepresentative of reactive nitrogen concentrations found in urban areas. In this study, event-based precipitation was collected over one-year in Providence, RI - a mid-sized city situated at the head of Narragansett Bay, the largest estuary in the northeastern US. Significant concentration enhancements in inorganic nitrogen (i.e., ammonium and nitrate) were found for wet deposition in the urban area compared to nearby NADP rural and non-urban coastal monitoring sites. Moreover, the annual ratio of ammonium to nitrate was highest in urban precipitation (>1.0). From 164 precipitation events, the mean volume-weighted ammonium and nitrate concentrations were 32.9 μmol l⁻¹ and 28.4 μmol l⁻¹, respectively, with total inorganic nitrogen concentrations exceeding 100 μmol l⁻¹ in at least 30 events. AD data for Narragansett Bay is limited and outdated: our results suggest inorganic nitrogen is at least 2.5 times greater than currently estimated in policy decision-making related to improving water quality and ecosystem services. This underestimation is due to an increase (by as much as 6 times) in ammonium wet deposition since 1990, likely due to an increase in urban sources of precursor ammonia.

1. Introduction

Primary producers rely on sufficient nutrient levels in freshwater and estuarine ecosystems to photosynthesize and maintain the base of the food web. While nitrogen is often a limiting nutrient for photosynthesis, excess nitrogen can degrade estuarine water quality. Overgrowth of primary producers reduces light availability (which can cause a loss of sea grass) and decreases dissolved oxygen levels through bacterial respiration and decomposition (which can lead to death of biological organisms in hypoxic conditions) [1]. Thus, understanding the sources of excess nitrogen is key for effective nitrogen pollution management [2]. A potentially important component of excess nitrogen in coastal areas is atmospheric deposition (AD), which has implications for both air and water quality through direct (i.e., wet and dry deposition) and indirect (i.e., stormwater runoff) inputs. Our understanding of the contribution of nitrogen from AD is limited by a significant lack of observations conducted within urban areas [3–6]. The National Atmospheric Deposition Program (NADP) monitors precipitation chemistry in the United States (US) and provides a major foundation for our understanding and quantification of AD. The first NADP precipitation chemistry network began in 1978, and 263 sites now exist across the US. NADP samples are collected as bulk precipitation on a weekly basis...
using a standardized method at all locations [7]. NADP monitoring locations are specifically positioned to assess well-mixed background concentrations and tend to be located in rural areas [4]. However, recent work in Boston, MA found significant concentration gradients in nitrogen deposition between the city core and non-urban areas (100 km from city core), with up to two times more nitrogen deposition in the city [4]. This observation has generated significant interest in quantifying urban nitrogen deposition and several new urban NADP sites (defined as having a population density of at least 400 people km$^{-2}$) have been established. Strong concentration gradients in nitrogen deposition have also been predicted along coastlines such as Chesapeake Bay [8]. These sharp spatial gradients are apparent over a monthly time scale and enhanced with sea and bay breeze events, but are not represented in current air and deposition monitoring [8]. This makes it challenging to accurately estimate nitrogen concentrations and deposition, and its connection to anthropogenic activities.

Nitrogen wet AD in urban areas is primarily composed of its inorganic components including nitrate (NO$_3^-$) and ammonium (NH$_4^+$), with organic nitrogen making up an additional ~30% of total nitrogen AD [9]. Atmospheric NO$_3^-$ deposition is the result of wet scavenged nitric acid (HNO$_3$) and/or particulate NO$_3^-$ (p-NO$_3^-$), which are formed as secondary products in the atmosphere from NO$_x$ (NO + NO$_2$) emissions. NH$_4^+$ deposition is a sink of particulate NH$_4^+$ (p-NH$_4^+$) and gaseous ammonia (NH$_3$), collectively referred to as NH$_x$.

Both NO$_x$ and NH$_x$ have anthropogenic and natural sources. In the US, the main driver of NO$_x$ emissions is the combustion of fossil fuels in industry and energy use [10, 11], whereas the main driver of NH$_x$ is agriculture [12–14]. However, there are large spatial variabilities. For example, the main emission source of NH$_x$ in 440 counties across the US is now vehicle emissions [15]. Until recently, NO$_3^-$ was the dominant nitrogen component of precipitation and particulate matter across the US [4, 16–19]. Due to significant decreases in NO$_x$ emissions through air quality control policies (e.g., The Clean Air Act in 2000 set requirements for selective catalytic reduction on vehicle engines), NO$_3^-$ deposition has significantly decreased. Li et al (2016) identified that the largest decline in wet deposition of NO$_3^-$ has occurred in the Northeastern US [19]. NH$_4^+$ deposition has increased or remained steady across the US, and now dominates AD from lack of regulation of precursor NH$_3$ emissions [4, 16–19]. Moreover, reductions in sulfur dioxide (SO$_2$) and NO$_x$ emissions have decreased the amount of NH$_x$ partitioning to the particle phase (p-NH$_4^+$), and consequently increased the amount of NH$_x$ remaining in the gas phase (NH$_x$ (g)) [15, 18, 20]. Given the short depositional lifetime of NH$_x$ (g), this shift has important implications for deposition patterns [15, 18, 21, 22].

In the mid-latitudes, NO$_3^-$ has a typical atmospheric lifetime on the order of 1 day against conversion to HNO$_3$ (i.e. a more soluble form) [23, 24], meaning that much of the urban NO$_x$ can be transported downwind before being removed via wet deposition. Thus, wet deposition of NO$_3^-$ near a source is only important if HNO$_3$ deposition has significantly decreased. Li et al (2016) identified that the largest decline in wet deposition of NO$_3^-$ has occurred in the Northeastern US [19]. NH$_4^+$ deposition has increased or remained steady across the US, and now dominates AD from lack of regulation of precursor NH$_3$ emissions [4, 16–19]. Moreover, reductions in sulfur dioxide (SO$_2$) and NO$_x$ emissions have decreased the amount of NH$_x$ partitioning to the particle phase (p-NH$_4^+$), and consequently increased the amount of NH$_x$ remaining in the gas phase (NH$_x$ (g)) [15, 18, 20]. Given the short depositional lifetime of NH$_x$ (g), this shift has important implications for deposition patterns [15, 18, 21, 22].

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Providence, RI, US is a mid-sized city (population of 180,393 residents as of 2017 [26]) that surrounds the upper part of Narragansett Bay, New England’s largest estuary (figure 1). Narragansett Bay covers 381 km$^2$ and is adjacent to the city of Providence, major highways, large industrial plants, golf courses, wastewater treatment facilities (WWTF), a park and zoo, and a major airport. As a result, the Upper Bay (i.e., north of Prudence Island [27]) is heavily impacted by urban deposition and runoff because many of these sources are concentrated near the urban core. The Bay has had a history of excessive nutrient loading, resulting in eutrophication and anoxic/hypoxic conditions leading to fish kills, poor water visibility, and loss of sea grass and juvenile/eggs of aquatic organisms [28]. A major focus of nitrogen management has been the reduction of nitrogen in wastewater treatment effluent, which has led to an estimated 60% reduction in reactive nitrogen in Narragansett Bay from 2004 to 2017 [1, 3, 29]. Yet, the Bay still suffers from episodes of poor water quality, specifically after heavy rainfall [1, 29].

The influence of non-point sources (nitrogen AD and stormwater runoff) especially in the Upper Half of the Bay are based on limited, outdated data. In fact, the values used in policy frameworks today come from a study completed in 1990 [1]. Although NO$_3^-$ emissions in the US have been significantly reduced due to regulations, a major source of nitrogen pollution (in some cases accounting for 60%–70% or more) to US waterbodies is AD [8, 30–34]. Given the recent changes in nitrogen deposition and its potential impact on estuarine systems, updated AD data is needed. Here, the amount of AD and its speciated inorganic nitrogen forms (i.e., NO$_3^-$, NH$_4^+$) were quantified from event-based precipitation (i.e., a new sample for each rain event) in an effort to address whether concentration differences between urban and rural areas in Southern New England are significant and if appropriate concentrations are used in policy considerations.
2. Methods

2.1. Study site and sample collection
An automated precipitation collector (EigenBrodt model: NSA 181/KS-16) was installed on top of a 27 m tall building on Brown University’s campus (41.826 °N, −71.398 °E). The building is 16 km from T.F. Green International Airport; 4.8 km from the nearest golf course; and 1.6 km from downtown Providence, the nearest power plant, and the nearest highway. In 2017, Providence experienced annual mean high and low temperatures of 16 °C and 7 °C, respectively, and an annual mean precipitation of 120.5 cm.

AD was monitored by collecting event-based precipitation from January 2017-January 2018. This equipment allows for year-round observations by heating the collection chamber below 0 °C and venting at temperatures above 25 °C. The sampler is equipped with 16 collection slots, each of which holds a pre-cleaned 250 ml bottle. In event-based sampling, a separate sample is collected each time precipitation starts and stops. The collector operates by using a precipitation sensor (Model: RS 85) to sense precipitation, which causes the funnel cover to lift, swing to the side, and lower to prevent introducing aerodynamic interference to the sampling process. Precipitation passes through the funnel and directly into a sampling bottle via a silicon tube. When precipitation ceases, the precipitation sensor signals to close the funnel cover, and the system switches to a new bottle to prepare for the next event. If a collection bottle fills to 200 ml while it is still precipitating, then the collector will automatically switch to the next bottle. We define a separate precipitation event as whenever it stops precipitating for 5 min or longer before starting to precipitate again. The data logging system within the collector records the precipitation date, time, temperature, and bottle number (1–16). Samples were collected following each event; precipitation volumes were computed based on pre- and post-weighing of the sample bottles and samples were frozen at −20 °C until analysis. Field blanks were quantified to assess possible contamination from the collector and/or sample handling by filling a collection bottle with 200 ml of ultrapure Milli-Q water (18.2 MegaOhm (MΩ)) and placing it in the collector overnight to imitate actual field conditions. Blanks were collected and stored the following day using the same procedure as precipitation samples. All bottles and sampling materials were pre-cleaned - leaching with fresh Milli-Q water for three days.
2.2. Nutrient concentrations

Inorganic nitrogen concentrations (NH\textsubscript{4}\textsuperscript{+}, nitrite (NO\textsubscript{2}\textsuperscript{−}), NO\textsubscript{3}\textsuperscript{−}) for 296 samples were quantified via colorimetric methods (SMARTCHEM EPA Compliant Methods: 353.2 (Revision 2.0) for NO\textsubscript{3}; Method 354.1 for NO\textsubscript{2}; and Method 350.1 for NH\textsubscript{4}\textsuperscript{+}) using a discrete UV–vis analyzer (Westco SmartChem 200). Calibration curves for each set of samples were produced using five points over the range of 1 to 100 μmol l\textsuperscript{−1} for NH\textsubscript{4}\textsuperscript{+} and NO\textsubscript{3}, and 1 to 20 μmol l\textsuperscript{−1} for NO\textsubscript{2}. The detection limit for NO\textsubscript{2} and NO\textsubscript{3} was 0.5 μmol l\textsuperscript{−1}, and for NH\textsubscript{4}\textsuperscript{+} was 0.7 μmol l\textsuperscript{−1}. Based on repeated measures of standards and an in-house quality control sample, the standard deviation (1σ) for concentrations of NO\textsubscript{2} was 0.3 μmol l\textsuperscript{−1} and for NH\textsubscript{4}\textsuperscript{+} was 0.6 μmol l\textsuperscript{−1}, with a standard error of 0.04 μmol l\textsuperscript{−1} and 0.07 μmol l\textsuperscript{−1}, respectively. For large events that filled multiple bottles, an average concentration per event was calculated by multiplying each bottle’s concentration by its weight, summing these values for bottles in the same event, and dividing by the total precipitation amount collected in the event. Monthly and annual data that are reported as averages represent volume-weighted averages (e.g., for monthly averages each event’s concentration was multiplied by its weight, summed for all events in the month, and divided by the total precipitation for the month). For comparison purposes, data from the nearest NADP monitoring locations were used, including a large urban, coastal city (Boston, MA; 88.5 km from Providence), a rural site (Abington, CT; 54.7 km from Providence), and a non-urban coastal site (North Atlantic Coastal Lab (NACL), Truro, MA; 179 km from Providence; figure 1). The NADP locations and our study site represent varying levels of urbanization. Here, we define level of urbanization based upon density of urban sources and population density (according to the US Census and the World Population Review): Boston ~5,471 people km\textsuperscript{−2}, Providence ~3,785 people km\textsuperscript{−2}, Abington (village of Pomfret, CT) ~40 people km\textsuperscript{−2}, and NACL (located in Truro, MA) ~38 people km\textsuperscript{−2} [26, 35–37]. The differences in population density distinguishes an urban (defined as having a population density of at least 400 people km\textsuperscript{−2}) to rural gradient. National Trends Network (NTN) NADP precipitation samples were collected weekly on Tuesday mornings by site operators and sent to the Central Analytical Laboratory (CAL) at the Wisconsin State Laboratory of Hygiene (WSLH) to be analyzed for concentrations of important inorganic chemicals [7]. NADP concentration data is available online for download directly from the NADP website. For this study, NH\textsubscript{4}\textsuperscript{+} and NO\textsubscript{3}\textsuperscript{−} concentration data for Boston, Truro, and Abington were downloaded from the NADP website (http://nadp.slh.wisc.edu/NTN/) [7]. One-way Analysis of Variance (ANOVA) was used to evaluate statistical differences in wet deposition of inorganic nitrogen between seasons (i.e., Fall, Winter, Spring, Summer), as well as among different monitoring sites (i.e., Truro, MA; Abington, CT; Providence, RI; Boston, MA).

3. Results and discussion

3.1. Event-based providence data

A total of 296 samples were collected from January 2017 to January 2018 encompassing 164 distinct precipitation events. For 2017, precipitation was fairly evenly distributed throughout the year in Providence, RI, with the greatest amount of precipitation falling in April (16.54 cm) and May (16.99 cm; figure 2). The number of events per month varied considerably, with June having the greatest number of precipitation events (n = 22) and August having the least number of events (n = 6; figure 2). Over the 164 events, NO\textsubscript{3}\textsuperscript{−} concentrations ranged from 0.5–292.0 μmol l\textsuperscript{−1} and NH\textsubscript{4}\textsuperscript{+} concentrations ranged from 0.7–352.5 μmol l\textsuperscript{−1} (figure 3). Note that all field blanks had non-detectable NO\textsubscript{3} and NH\textsubscript{4}\textsuperscript{+}; all samples and blanks had non-detectable concentrations of NO\textsubscript{2}. The volume-weighted annual average concentrations were 28.4 μmol l\textsuperscript{−1} for NO\textsubscript{3} and 32.9 μmol l\textsuperscript{−1} for NH\textsubscript{4}\textsuperscript{+}. Many of the highest concentration events occurred during the warm season, April through October, especially in terms of NH\textsubscript{4}\textsuperscript{+} concentration (figure 3(a)). Overall, summer (June to August) had higher concentrations on average for both NH\textsubscript{4}\textsuperscript{+} and NO\textsubscript{3}, which was statistically significant (ANOVA) when compared to spring (p = 0.025 for NH\textsubscript{4}\textsuperscript{+}; p = 0.053 for NO\textsubscript{3}) and fall (p = 0.001 for NH\textsubscript{4}\textsuperscript{+}; p = 0.0001 for NO\textsubscript{3}), but not winter concentrations (p = 0.077 for NH\textsubscript{4}\textsuperscript{+}; p = 0.746 for NO\textsubscript{3}; figures 3(a), (b)). NH\textsubscript{3} emissions tend to increase as a function of temperature, so we would expect the wet deposition of NH\textsubscript{4}\textsuperscript{+} to also be higher with higher temperatures [19, 38]. The high concentrations of NO\textsubscript{3} could stem from fast NO\textsubscript{x} photochemistry (i.e., shorter NO\textsubscript{x} lifetime) and/or high amounts of NO\textsubscript{x} emissions from natural gas consumption. According to the US Energy Information Administration (EIA), natural gas consumption via electricity peaks in August in the region [39].

The event-based urban collections capture high variability in concentrations and show significant concentration enhancements compared to the rural and non-urban coastal NADP monitoring sites, especially during the warmer months. Thus, event-based impacts may be important to understanding the episodic nutrient loading to urban waterways, particularly during the growing season [32–34]. Moreover, the monthly NH\textsubscript{4}\textsuperscript{+} to NO\textsubscript{3} concentration ratio for Providence is high (>1) throughout the year, except in the coldest months.
and in August (figure 3(c)). In the case of August, however, the data was irregular with the fewest number of precipitation events (6 events) and a variable amount of rainwater amongst each of those events (0.13–1.3 cm; figure 2). Moreover, a wide range of concentrations were measured for both NO\textsubscript{3} \ (8.9–91.7 μmol l\textsuperscript{-1}) and NH\textsubscript{4} \ (2.7–102.9 μmol l\textsuperscript{-1}) within these few events, where high concentrations had a small volume and low concentrations had a large volume.

3.2. Comparison with nearby NADP monitoring sites

Comparing monthly volume-weighted average NH\textsubscript{4} and NO\textsubscript{3} concentrations for the year (January–December 2017) for the three nearest NADP sites (Boston, MA; Abington, CT; and Truro, MA) and Providence, RI reveals that urban areas have higher inorganic nitrogen concentrations in wet deposition (figure 4). Across the different seasons, the median and mean concentrations for each site followed this trend. NH\textsubscript{4} and NO\textsubscript{3} concentrations in wet deposition in urban, rural, and non-urban coastal areas are significantly different (ANOVA; p = 0.0002 for NH\textsubscript{4}, p = 0.047 for NO\textsubscript{3}) year-round. Given the rural to urban gradient, Providence falls as expected between Boston and Abington. This is also an indication that the event-based sampling difference compared to weekly NADP sampling does not have a significant influence on our results. Further, this result suggests that relying on well-mixed rural monitoring sites may lead to significant underestimates when quantifying deposition in urban areas. Finally, the observed differences amongst sites suggest the influence of an urban footprint on inorganic nitrogen deposition.

The NH\textsubscript{4} to NO\textsubscript{3} concentration ratio for locations that vary in urbanization gives insight into the importance of NH\textsubscript{4} and NO\textsubscript{3} emission sources in those areas. The annual average [NH\textsubscript{4}/[NO\textsubscript{3}]] ratio for the urban areas (Boston, Providence) was greater than that found in the rural and non-urban coastal sites (table 1). In other words, with increasing intensity of urban sources, [NH\textsubscript{4}] and [NO\textsubscript{3}] both increase with greater changes in [NH\textsubscript{4}]. According to the National Emissions Inventory (NEI), many of the same NO\textsubscript{3} and NH\textsubscript{4} emission sources are expected at each of the four locations, including vehicles, stationary fuel combustion, external combustion boilers, internal combustion engines, and biogenics [41]. The NEI suggests that the main driver for NH\textsubscript{4} emissions in Barnstable County (Truro, MA), Providence County (Providence, RI), and Suffolk County (Boston, MA) is fuel combustion via natural gas; although, the main driver for NH\textsubscript{4} emissions in Windham County (Abington, CT) is expected to be agriculture. For NO\textsubscript{3} emissions, the estimated primary source in Windham County, Providence County, and Suffolk County is fuel combustion via natural gas; while, in Barnstable County it is marine vessels. This greater NH\textsubscript{4} deposition in Providence and Boston suggests that different or additional sources are likely driving the trend. Additional tracers would be required to clearly tie our results to a specific emission source, however, recent work provides evidence that many urban and urban-affected regions now have higher NH\textsubscript{4} emissions from vehicles and could implicate the importance of urban NH\textsubscript{4} sources compared to NO\textsubscript{3} (HNO\textsubscript{3}, p-NO\textsubscript{3}, NO\textsubscript{2}) sources [15].

NH\textsubscript{4} is efficiently scavenged via precipitation compared to NO\textsubscript{3}, which is chemically converted to NO\textsubscript{3} before it is wet deposited. Thus, a greater relative portion of urban NH\textsubscript{4} compared to NO\textsubscript{3} would be removed via precipitation near sources [21]. This may help to explain the greater urban impact on NH\textsubscript{4} concentrations in wet
Figure 3. (a) NH$_4^+$ and (b) NO$_3^-$ concentrations volume-weighted by event ($n = 164$) as a function of time (January 2017–2018). The top and bottom of each box are the 25th and 75th percentiles of the samples, respectively; distances between the top and bottom are the interquartile ranges; median is drawn as a line in the middle of each box; whiskers represent the entire range of observations; observations beyond the whisker length are marked as outliers. Two outliers (one for NH$_4^+$ (352.5 μmol L$^{-1}$ or 4.9 mg L$^{-1}$ NH$_4$-N) and one for NO$_3^-$ (292.0 μmol L$^{-1}$ or 4.1 mg L$^{-1}$ NO$_3$-N)) are not displayed in the plots, and both are from an event in January 2018. Note that the units on the secondary y-axis are mg L$^{-1}$ of ammonium-nitrogen or nitrate-nitrogen. (c) The monthly mean NH$_4^+$ to NO$_3$ concentration ratio for event-based data. A dashed line is drawn at $y = 1$. One-way ANOVA was used to evaluate statistical differences between seasons (i.e., Fall, Winter, Spring, Summer).
Figure 4. Monthly volume-weighted average NH$_4^+$ (a) and NO$_3^-$ (b) concentrations for four monitoring locations in Southern New England (Providence, RI and three NADP sites (Truro, MA; Abington, CT; and Boston, MA)) for January-December 2017. See figure 3 caption for box and whisker details. Note that the secondary y-axis is in mg l$^{-1}$ of NH$_4$-N and NO$_3$-N. One-way ANOVA was used to evaluate statistical differences between monitoring locations (i.e., Truro, MA; Abington, CT; Providence, RI; Boston, MA).

| Location: | Truro, MA | Abington, CT | Providence, RI | Boston, MA |
|-----------|-----------|--------------|----------------|------------|
| Land Type: | Non-urban, Coastal | Rural | Mid-sized, Coastal City | Large, Coastal City |
| Population Density (people km$^{-2}$) | 38 | 40 | 3785 | 5471 |
| Annual Mean [NH$_4^+$] ($\mu$mol l$^{-1}$): | 5.5 | 8.4 | 12 | 16 |
| Annual Mean [NO$_3^-$] ($\mu$mol l$^{-1}$): | 5.7 | 7.8 | 11 | 10 |
| Annual Mean [NH$_4^+$]/[NO$_3^-$]: | 0.96 | 1.07 | 1.09 | 1.60 |

* Population densities values were retrieved from the US Census and the World Population Review [25, 34–36].
deposition than seen for NO$_3^-$.

Overall, the observed deposition relationships are likely a function of both emission sources and wet-scavenging mechanisms. Still, our results clearly indicate the importance of NH$_4^+$ wet deposition in urban regions. Moreover, the magnitude of the observed urban wet deposition is perhaps surprising for Southern New England since it be could be considered an NH$_4^+$-poor region compared to the midwestern U.S. [7].

3.3. Implications of high urban deposition

The Upper Half of Narragansett Bay has historically been greatly impacted by urban deposition and runoff [1, 42–44]. Despite significant reductions in effluent nitrogen from WWTF (~60%), water quality remains a concern for Narragansett Bay, specifically after precipitation events [1, 29, 45, 46]. Both intra- and interannual variability in chlorophyll concentrations have been found to be linked to precipitation in the Upper Bay, with higher chlorophyll abundance measured in wet years [1]. Moreover, a strong positive relationship ($r^2 = 0.61$) between summer precipitation amount (June to August) and the total number of summer days of hypoxia has been observed [29]. Prell et al (2016) have also shown that the area of hypoxia is related to the freshwater flux to the Bay [47]. These findings suggest that poor water quality is affected by precipitation amount, and Oviatt et al (2017) attribute this to a result of stratification induced by fresh water from precipitation [29]. However, stratification alone cannot explain the corresponding abundance of chlorophyll. Additionally, the importance of the influence of AD (direct and indirect via runoff) is based, in part, upon the assumption that the amount of nitrogen AD to Narragansett Bay should be lower today than in the 1980’s, following national decreasing trends in NO$_3^-$ deposition.

The State of Narragansett Bay and Its Watershed [1] estimates direct nitrogen AD for Narragansett Bay to be the same value as first measured 30 years ago - 924 × 10$^6$ lbs N yr$^{-1}$ with wet deposition of inorganic nitrogen accounting for 466 × 10$^6$ lbs N yr$^{-1}$ or 15.1 × 10$^6$ moles N yr$^{-1}$ [48, 49]. At that time (1989–1990), weekly precipitation samples were collected on Prudence Island, RI (figure 1) and were measured for NH$_4^+$ and NO$_3^-$ concentrations, following the NADP collection guidelines. These values were then summed and scaled up to represent the total direct wet deposition of inorganic nitrogen from the atmosphere onto Narragansett Bay, which totaled to 15.1 × 10$^6$ moles N yr$^{-1}$ (figure 5; please note collection and scaling details in supplement) [48, 49].

Much of the literature today emphasizes how NO$_3^-$ concentrations in wet deposition have decreased significantly in the last two decades due to NO$_x$ emission regulations [16–19]. Therefore, it has been considered reasonable to assume that overall nitrogen AD has decreased over this time and rely on older values to assess the contribution of direct AD nitrogen loading to the Bay [28]. In order to directly compare with the scaled values in the Nixon et al (1995) work, which are used by RI policymakers today, we scaled our findings to represent AD to the entire Bay, following the framework in Fraher (1991) [48, 49]. Based on this comparison, we found that NO$_3^-$ has indeed clearly decreased significantly over time. On the other hand, NH$_4^+$ has increased so much (as much as 6 times) that the amount of inorganic nitrogen entering Narragansett Bay via direct wet AD has increased by 2.5 times since 1990 (figure 5). This amount of inorganic nitrogen is also 2.5 times more than is currently considered in policy framing today [1].
According to the annual total nitrogen loading budget presented in *The State of Narragansett Bay and Its Watershed*, total direct AD (wet deposition + dry deposition) is currently assumed to contribute to only 8% of the nitrogen budget for Narragansett Bay [1]. Zhang et al (2018) report that total inorganic nitrogen deposition over the entire U.S is dominated by dry deposition, accounting for 58%–65% of the total [18]. This suggests that wet + dry deposition could be as much as 2.4 to 2.9 times higher than the wet only deposition measured in this study. Additionally, stormwater runoff is likely underestimated, as it includes both nitrogen AD and leaching nitrogen from the surrounding landscape. Recent studies from across the US have shown that the influence of indirect AD to waters during storm events is high in urban areas due to the increased delivery of atmospheric nitrogen via wash-off of dry deposition from impervious surfaces [32–34, 50–55]. Overall, it is clear that inorganic nitrogen AD is a much more important contributor to the nitrogen budget of Narragansett Bay than is reflected in current policy framing.

The shift in the dominate form of nitrogen deposition (i.e., shift from NO3 to NH4) may also exacerbate the impacts of nitrogen deposition, as NH4 is a preferred fixed form of nitrogen for biogenic activity [56–63]. On-road and power plant sectors have increased NH3 emissions significantly (91 and 70%, respectively) over the last two decades, largely as a byproduct of strict NOx control mechanisms [13, 15, 64, 65]. Because NH3 has a short lifetime, it is likely that urban areas with many vehicles and/or industrial stacks are influenced by high deposition of NH4. Furthermore, increases in urbanization in the future will likely continue to increase NH3 emissions. In sum, there are likely important tradeoffs between decreasing point sources (e.g., wastewater) and increasing direct and indirect AD for urban watersheds.

In this study, wet deposition was collected for a full year at only one location. Approximately two million people live within this watershed and most are concentrated on the northern end, contributing to a north to south productivity-hypoxia gradient in Narragansett Bay [44–46, 49, 66]. In the future, additional measurements in multiple locations would be useful to address heterogeneity in AD along the watershed and allow for better estimates of Bay-wide AD rates. Still, the much higher concentrations than expected, and the high variability in event-based precipitation, should be considered in assessing the causes of both eutrophication and hypoxic events. Moreover, recent studies worldwide have shown that urban watersheds are susceptible to increased delivery of atmospheric nitrogen during precipitation events, supporting the findings in this study [32–34, 50–55].

4. Conclusion

Understanding how nitrogen cycles through urban, coastal areas is important to quantify subsequent impacts on water quality in estuarine ecosystems. This understanding is challenged by a lack of long-term observations conducted in urban ecosystems. Our work presents an updated estimate for AD of nitrogen for Upper Narragansett Bay, and the first year-round event-based collection of nitrogen AD for Providence, RI. Reduction of nitrogen loading to estuaries is societally relevant and intersects directly with water quality policies, coastal ecosystem services, and human health. Many of the largest cities in the US are located along estuaries, and most Americans live within 100 km of the coast [2]. The majority of Narragansett Bay is currently surrounded by urban development, and predictions suggest that urbanization along the Bay will continue to increase in the future [67]. With increased urbanization, we expect higher amounts of nitrogen deposition, as well as an increase in the \([\text{NH}_4^+/\text{NO}_3^-]\) ratio. We also find evidence for a significant number of highly concentrated events (>50 μmol l⁻¹, for NO3 (n = 26) and/or NH4 (n = 33)), most often during the growing season. Urban sources of nitrogen to AD (and stormwater) need to be better considered, especially in water quality policy frameworks. Finally, additional work is clearly needed to better identify and quantify urban sources that contribute to inorganic nitrogen deposition.

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Data availability statement

The data that support the findings in this study are available in the supplemental information. The Supporting Information includes a table listing event-based sample information and concentration data for all 164 precipitation events and a section detailing the AD budget for Narragansett Bay (PDF).
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