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Atmospheric nitrogen inputs and losses along an urbanization gradient from Boston to Harvard Forest, MA

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Abstract Urbanization alters nitrogen (N) cycling, but the spatiotemporal distribution and impact of these alterations on ecosystems are not well-quantified. We measured atmospheric inorganic N inputs and soil leaching losses along an urbanization gradient from Boston, MA to Harvard Forest in Petersham, MA. Atmospheric N inputs at urban sites (12.3 ± 1.5 kg N ha^{-1} $year^{-1}$) were significantly greater than non-urban (5.7 ± 0.5 kg N ha^{-1} $year^{-1}$) sites with NH_4^+ (median value of 77 ± 4 %) contributing thrice as much as NO_3^-. Proximity to urban core correlated positively with NH_4^+ ($R^2 = 0.57, p = 0.02$) and total inorganic N inputs ($R^2 = 0.61$, $p = 0.01$); on-road CO_2 emissions correlated positively with NO_3^- inputs ($R^2 = 0.74$, $p = 0.003$). Inorganic N leaching rates correlated positively with atmospheric N input rates ($R^2 = 0.61, p = 0.01$), but did not differ significantly between urban and non-urban sites ($p > 0.05$). Our empirical measurements of atmospheric N inputs are greater for urban areas and less for rural areas compared to modeled regional estimates of N deposition. Five of the nine sites had NO_3^- leached that came almost entirely from nitrification, indicating that the NO_3^- in leachate came from biological processes rather than directly passing through the soil. A significant proportion (17–100 %) of NO_3^- leached from the other four sites came directly from the atmosphere. Surprisingly, the four sites where atmospheric sources made up the largest proportion of leachate NO_3^- also had relatively low N leaching rates, suggesting that atmospheric N inputs added to terrestrial ecosystems can move to multiple sinks and losses simultaneously, rather than being lost via leaching only after abiotic and biotic sinks have become saturated. This study improves our understanding of atmospheric N deposition and leaching in urban ecosystems, and highlights the need to incorporate urbanization effects in N deposition models.

Keywords Atmospheric inputs · Leaching · Nitrogen deposition · Nitrogen saturation · Stable isotopes · Urbanization gradient

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Introduction

Nitrogen (N) is often a limiting nutrient in temperate ecosystems (LeBauer and Treseder 2008); however, human activities have significantly altered N cycling

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within and around urban areas (Vitousek et al. 1997; Driscoll et al. 2003; Kaye et al. 2006). The geographical concentration of activities such as transportation (Fenn et al. 2003; Davidson et al. 2010), food and energy consumption (Galloway et al. 2003; Driscoll et al. 2003), land use change (Raciti et al. 2011a) and lawn management (Groffman and Pouyat 2009) make urban areas a major global source of reactive, gaseous forms of N (NO_x and NH_3; Vitousek et al. 1997). Intensification of anthropogenic activities and rapid increases in urban and agricultural areas have contributed to the exponential rise in reactive N emissions globally since industrialization (Galloway et al. 2003). By the year 2030, the world urban population is expected to increase to five billion people (UN 2012), with a 1.2 million km^2 increase in urban area extent (Seto et al. 2012).

The rapid increase in urban population and land area has raised concern about N pollution due to increases in impervious surface area and N in runoff (Elvidge et al. 2004), lawn area (Milesi et al. 2005) and associated N fertilizer inputs (Law et al. 2004), and local sources of N deposition from fossil fuel combustion within urbanizing watersheds (Bettez 2009; Davidson et al. 2010). Surprisingly, a number of studies have shown that urban watersheds can have a relatively high capacity for N retention, though they tend to have lower retention than paired non-urban forested areas (68 % compared to 82 % in Kaushal et al. 2011). Urban soils and vegetation, particularly in lawns, can be a substantial sink for atmospheric N deposition (Raciti et al. 2008), may accumulate N rapidly over time (Raciti et al. 2011a), and have a potentially high capacity for denitrification (Raciti et al. 2011b). However, rates of leaching losses tend to be greater in lawns and managed green spaces than forested areas (Groffman and Pouyat 2009; Kaushal et al. 2011). A considerable proportion of apparent N losses from urban watersheds may be due to leaking sewage infrastructure, but atmospheric N sources can be an important component of N losses during storm events (Kaushal et al. 2011).

With the exception of a few urban watersheds monitored over relatively short time intervals (e.g. Kaushal et al. 2011), it is not known what proportion of hydrologic N losses from urban watersheds come directly from atmospheric deposition and canopy throughfall versus nitrification in soils. It is possible that in urban areas, where atmospheric N inputs are likely to be greater, both plant and microbial demand for N could be reduced and therefore a greater proportion of N could be lost due to 'saturation' of biotic demand. In this case, the predominant source of NO_3^- leached would be directly from atmospheric deposition (and not biologically produced via nitrification), which could be a symptom that these sites have reached N saturation. It is important to understand sources of NO_3^- lost via leaching to make predictions of future fluxes of N from urban watersheds to downstream ecosystems. For example, if biotic sinks have become saturated due to elevated atmospheric N inputs, greater rates of N losses are likely to continue with continued elevated N deposition. Nitrogen from atmospheric deposition that exceeds biological demand or storage on soil exchange sites can leave terrestrial ecosystems through leaching into nearby waterways (Friedland et al. 1991; Dise and Wright 1995; Aber et al. 2003) or as gaseous emissions of N_2O, NO and N_2. However, if N is still being cycled through soil microbes and being produced via nitrification, that suggests that continued elevated rates of atmospheric N deposition may be buffered by biological sinks in soils.

Atmospheric N deposition often alters the canopy and soil chemistry of terrestrial ecosystems and influences the storage and cycling of carbon (C; Boggs et al. 2005; Fang et al. 2011a). Enhanced N deposition can result in increased rates of nitrification and mineralization in soil (Pouyat and Turechek 2001; Aber et al. 2003; Boggs et al. 2005), higher forest floor N concentrations and soil N content (Boggs et al. 2005; Fang et al. 2011a), and greater uptake of N by plants (Aber et al. 2003; McNeil et al. 2007). Some tree species that experience greater N availability from atmospheric deposition accumulate more N in their foliage and have greater rates of productivity (Thomas et al. 2009). However, stimulated rates of primary productivity can be offset by greater exposure to tropospheric ozone, which is produced in part due to elevated NO_x concentrations in the troposphere (Reich 1987).

Two national monitoring networks in the United States, the National Atmospheric Deposition Program (NADP) National Trends Network (NTN) and the Clean Air Status and Trends Network (CASTNET), provide continuous, long-term data on wet and dry N deposition, respectively. However, measurement stations in these monitoring networks are intentionally located away from urban areas and point sources of pollution in order to capture regional trends

(NADP 2012; CASTNET 2012). The US Environmental Protection Agency (EPA) monitors "criteria pollutants" including NO_x in urban areas, however, it only measures N emissions and not deposition (EPA 2011). Models have been used to spatially predict estimates of N deposition between established deposition collectors, but these models may under-estimate rates of N deposition in areas with local sources of N emissions and often do not account for heterogeneity of the landscape between collectors (Weathers et al. 2006). ClimCalc is one such spatially explicit model that uses measurements of wet and dry deposition in combination with estimates of precipitation volume and deposition velocities to predict rates of atmospheric deposition across the northeastern United States (Ollinger et al. 1993).

Although some studies have measured rates of N deposition within urban areas, many of these treat the landscape as an urban–rural dichotomy (e.g., Groffman et al. 2004; Templer and McCann 2010). In order to understand the effects of the gradual transformation between urban and rural areas, we took advantage of an urbanization gradient (similar to Lovett et al. 2000; Raciti et al. 2012) that begins in the city of Boston, MA. This enabled us to better capture N inputs, transformations and outputs across a gradient of human activity. In this study, we used measurements of inorganic N inputs and leachate from nine sites located along an urban-to-rural gradient in the Boston region to understand the dynamics of N fluxes across this spatially heterogeneous area. First, we quantified rates of inorganic N inputs from the atmosphere and N losses via leaching along the gradient. Second, we analyzed the relationships between inorganic N fluxes and metrics representing the intensity of urbanization. Finally, we examined the sources of NO_3^- in soil leachate by examining natural abundance stable isotopic composition of atmospheric N inputs and leachate. We hypothesized the following:

1. Inorganic N input rates are higher in urban areas than in non-urban areas of the Boston region and are positively correlated to measures of urbanization intensity such as proximity to urban core, impervious surface area (ISA) fraction, and on-road CO_2 emissions.
2. Rates of measured atmospheric N deposition within the urban area are under-estimated by regional scale models such as ClimCalc (Ollinger et al. 1993).
3. Urban areas have greater rates of N leaching losses than non-urban areas, which is attributable to enhanced direct losses of atmospheric N inputs primarily rather than to stimulated rates of nitrification.

Materials and methods

Study area and sampling design

This study took advantage of an urban-to-rural gradient that begins in Boston, MA and extends 100 km westward (Fig. 1). This region experiences a temperate climate with mean annual summer and winter temperatures of 23.3 and −1.5 °C, respectively, and mean annual precipitation of 105 cm $year^{-1}$ spread uniformly across the year (National Climatic Data Center 2009). The soils are mostly acidic with glacial origins (USDA NRCS 2009) and metamorphic bedrock is common (Hall et al. 2002). The dominant vegetation type in this region is mixed temperate forest mainly comprising oak (*Quercus spp.*), maple (*Acer spp.*), birch (*Betula spp.*), ash (*Fraxinus spp.*), pine (*Pinus spp.*), and eastern hemlock (*Tsuga Canadensis*; Forest Inventory and Analysis 2005). Since 1950, urbanization, particularly residential and commercial development, has reduced forest cover from 85 to 63 % of Massachusetts land cover (Forest Inventory and Analysis 2005).

We made use of two 100-km urban-to-rural transects established to examine the effects of urbanization on ecosystem C and N dynamics (see Raciti et al. 2012; Rao et al. 2013 for experimental details). The northern transect extends from Boston to Harvard Forest Long Term Ecological Research site (LTER) in Petersham, MA, and the southern transect extends from Boston to Mass Audubon's Broad Meadow Brook Wildlife Sanctuary in Worcester, MA (Fig. 1). We established nine study sites along these transects (Fig. 1; Table 1) for measuring atmospheric N inputs, leaching losses, natural abundance composition of NO_3^- in leachate, and C and N concentrations of vegetation foliage and soil. We delineated ~ 1 km^2 (990 m × 990 m) grid boxes around each site and defined an urban intensity class for each grid box based on two common urbanization measures: ISA fraction and population density (MassGIS 2010). The three urban classes

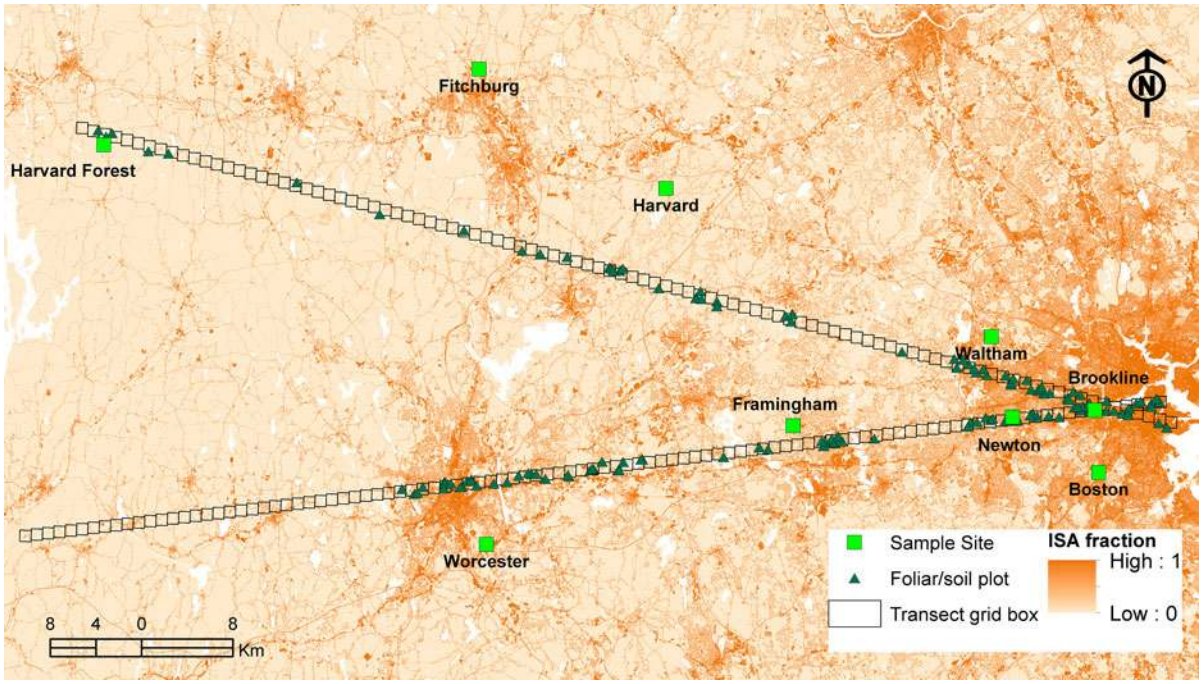

Fig. 1 Two sampling transects along an urbanization gradient from Boston, MA westward to Harvard Forest (to the north) and Worcester (to the south). Nine sampling sites for atmospheric N inputs and losses are indicated with *green squares*. Sampling sites for vegetation and soil chemistry (Raciti et al. 2012) are indicated with *green triangles*

include high population density urban (ISA $\geq$ 0.25 and population density $\geq$ 2500 persons km^{-2}), low population density urban (ISA $\geq$ 0.25 and population density $<$ 2500 persons km^{-2}), and non-urban (ISA $<$ 0.25 and population density $<$ 2500 persons km^{-2}); hereafter referred to as high-urban, low-urban, and non-urban, respectively. Of the nine sites, Waltham (WA) and Brookline (BR) were characterized as high-urban, Newton (NE) and Arnold Arboretum, Boston (BO) as low-urban, and Harvard (HA), Fitchburg (FI), Framingham (FR), Worcester (WO) and Harvard Forest (HF) as non-urban (Fig. 2; Table 1). We grouped the high- and low-urban classes into a single urban category for statistical analyses because of their small sample size ($n = 2$ for each class). We chose these site locations to span the gradient, to account for the heterogeneity of urban ecosystems in this region, and to minimize potential tampering and disturbance of the samplers.

Sample collection

We used mixed ion exchange resin (Simkin et al. 2004; Templer and McCann 2010) to measure rates of atmospheric N inputs to the forest floor from May to October 2011. We measured throughfall N beneath the canopy because it is a reasonable surrogate for total atmospheric deposition (wet, dry, and cloud; Lindberg and Lovett 1992). At each of the nine sites, we set up three throughfall collectors which were at least 1 m apart to capture as much of the canopy heterogeneity within each site as possible. Each collector consisted of a 20 cm diameter funnel attached to a 20 ml disposable chromatography column and set on top of a PVC pipe so that collectors were each 1.5 m aboveground. The 20 ml disposable chromatography columns were packed with Dowex Monosphere MR-3 UPW mixed ion exchange resin and had a 30 μm pore-size filter at the bottom of each resin column. Poly wool was placed at the neck of the funnel to prevent debris from entering the resin column. The funnel collected rainwater and canopy throughfall and channeled it through the resin column where charged N compounds (specifically NO_2^-, NO_3^- and NH_4^+) from the throughfall were adsorbed to the resin. To prevent saturation of the resin beads, we replaced the resin columns every 6 weeks during May–October 2011

Table 1 Description of the nine sites where we measured atmospheric N inputs and leaching losses

Site identifier (urban and land use class within 1 km^2)	McConnell land use history	Elevation (m), slope (°), aspect	Tree species	N inputs (kg N ha^{-1} $year^{-1}$)	N losses (μg N g $resin^{-1}$ $year^{-1}$)
Boston (low-urban; Low density residential)	Vegetated; participatory recreation (1971–present)	9 m, 6.7°, east	Dominated by tree of heaven (*Ailanthus altissima*), sumac (*Rhus coriaria*), cherry (*Prunus spp.*) and elm (*Ulmus spp.*) understory of stinging nettle (*Urtica dioica*), Japanese knotweed (*Fallopia japonica*) and vines.	14.8 ± 3.48	2335 ± 700.3
Brookline (high-urban; High density residential)	Residential, <¼ acre lots (1971–present)	18 m, 3.5°, northeast	Red maple (*Acer rubrum*) and Norway maple (*Acer platanoides*)	9.8 ± 1.49	278 ± 123.9
Fitchburg (non-urban; Low density residential)	Residential, ¼–½ acre lots 1999; deciduous forest 1971 and 1985	179 m, 2.0°, east	Dominated by *Acer rubrum* and red oak (*Quercus rubra*) with white pine (*Pinus strobus*) in understory	5.0 ± 0.53	1618 ± 640.2
Framingham (non-urban; Low density residential)	Residential, >½ acre lots (1971–present)	72 m, 1.7°, north	Large-crowned dogwood (*Cornus mas*) tree on raised planter	8.4 ± 1.18	2318 ± 965.3
Harvard (non-urban; deciduous forest)	Residential, >½ acre lots (1971–present)	98 m, 3.3°, east	Dominated by sugar maple (*Acer saccarum*), witch hazel (*Hamamelis spp.*), one large dead ash (*Fraxinus spp.*)	6.1 ± 0.54	856 ± 552.7
Harvard Forest (non-urban; mixed forest)	Urban open (1971–present); adjacent to large tracts of forest	334 m, 9.4°, southwest	Dominated by *Acer rubrum* and *Quercus rubra*	3.7 ± 0.65	8.0 ± 3.9
Newton (low-urban; Low density residential)	Residential, <¼ acre lots (1971–present)	41 m, 2.2°, east	*Quercus spp.* with grey birch (*Betula populifolia*) understory	8.8 ± 1.65	210 ± 188.6
Waltham (high-urban; Low density residential)	Residential, <¼ acre lots (1971–present)	58 m, 5.8°, south	*Quercus rubra*, *Fraxinus spp.* and *Acer platanoides* with *Prunus spp.* understory	17.3 ± 2.68	5468 ± 3635.5
Worcester (non-urban; deciduous forest)	Deciduous forest (1971–present)	144 m, 6.2°, east	Dominated by *Acer spp.*, some *Quercus spp.*, few clumps of paper birch (*Betula papyrifera*)	5.0 ± 0.31	424 ± 313.7

The urban and land use classes were defined for a neighborhood of 1 km^2 surrounding each site. McConnell land use history data reflects the site land use in 1971, 1985, and 1999

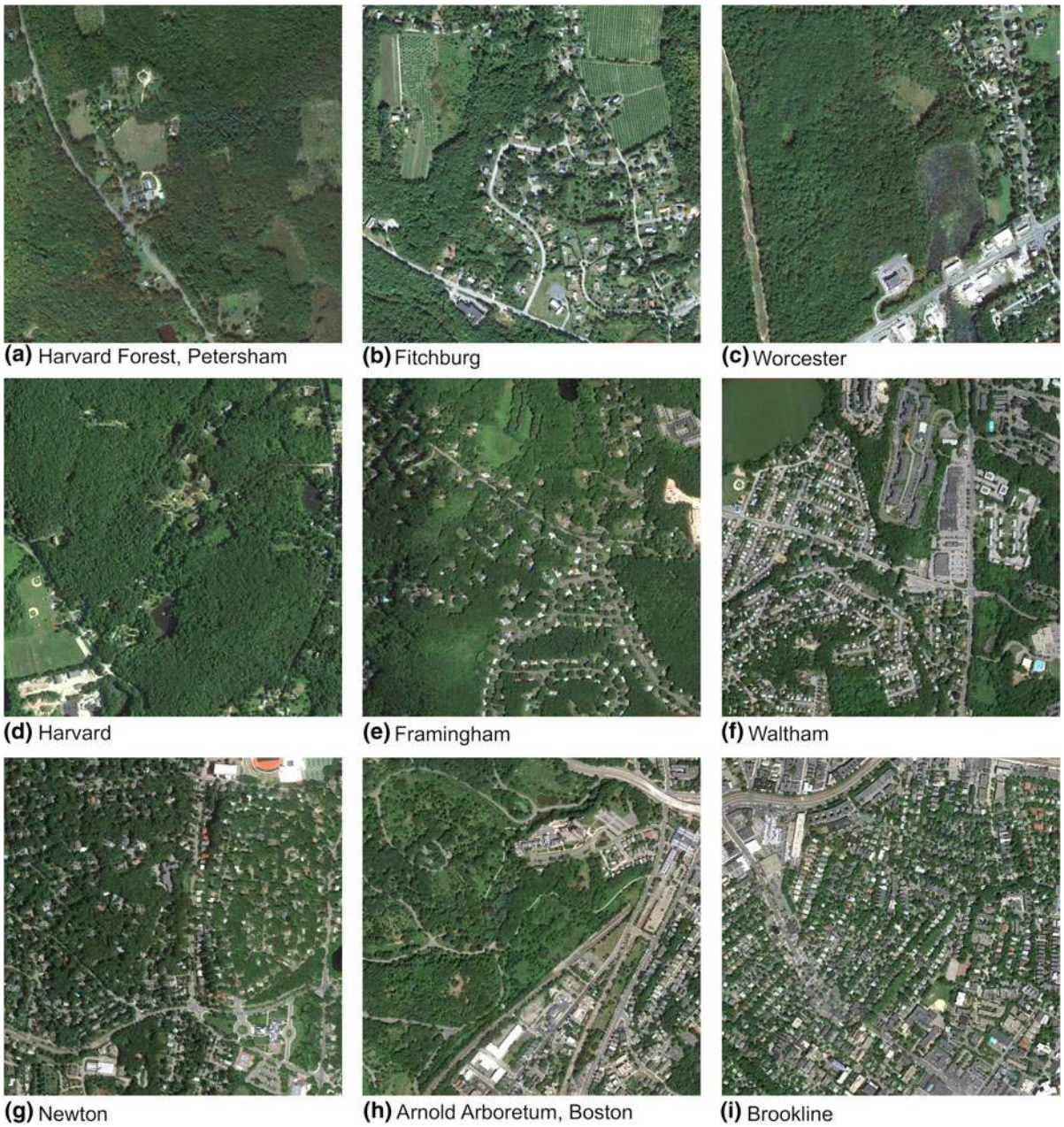

Fig. 2 The nine sample sites for atmospheric N inputs and loss measurements, arranged in increasing order of proximity to the urban core of Boston; (**a–i**). Each image shows 1 × 1 km area approximately centered on the sampling site

(Online Resource 1). Thus, for each of the four sampling periods, we prepared 30 resin columns ($n = 3$ for each of the nine sites and three for blanks).

We placed mixed ion exchange resin bags in the soil at a depth of 10–15 cm to estimate potential N losses in leachate below a majority of the rooting zone. The amount of inorganic N adsorbed in the resin is a reliable proxy for the mobility of the inorganic N ions in the leachate, and provides a relative index of inorganic N leaching from the soil (Giblin et al. 1994). These values of potential N losses in leachate will be

referred to as leaching hereafter. Within each of the nine sites, three resin bags total packed with 10 g of Dowex Monosphere MR-3 UPW mixed ion exchange resin were paired with each of the three throughfall collectors. The resin bags were left in the field between July and October 2011.

At each site, we collected two representative soil samples to a depth of 10 cm using a 5 cm diameter slide-hammer corer (AMS Equipment Corp., American Falls, Idaho). We collected one foliar sample for every dominant tree species present at each site (Table 1). Each foliar sample was composited from leaves collected from the lower and middle sunlit sections of the canopy using a 5 m tall pole pruner. For three sites, Boston, Brookline and Newton, we used foliar and soil data from field measurements made during the 2010 growing season (Rao et al. 2013). For the remaining six sites, we collected foliage and soil during the 2012 growing season. We assumed that the temporal variation between adjacent years is insignificant compared to the spatial variation among the nine sites. We dried (at 60 °C), homogenized and analyzed the soil and foliar samples for C and N concentrations by flash-combustion/oxidation using a Thermo Finnigan Flash EA 1112 elemental analyzer (0.06 % C and 0.01 % N detection limits; for detailed methodology, see Raciti et al. 2012; Rao et al. 2013).

Nitrogen fluxes as atmospheric deposition and leaching

Resin extraction was done within 24 h of collecting each batch of resin columns and resin bags from the nine sites. For resin extraction, we added 50 ml of 2 M KCl to the 10 g resin beads three times sequentially (a total of 150 ml) and filtered with Whatman #1 filter paper. NH_4^+, NO_3^- and NO_2^- concentrations were determined on a Lachat QuikChem 8000 flow injection analyzer. We used the salicylate method (E10-107-0602-A) for NH_4^+ concentrations in solution and the NO_3^- 8000 method (E10-107-04-1-C) for determining NO_3^- and NO_2^- (hereafter NO_3^-) concentrations in solution (see Templer and McCann 2010 for further details). We used an external calibration standard, Environmental Resource Associates catalog #505. Samples with concentrations higher than the detection limits were diluted with resin extract solution and re-analyzed on the Lachat QuikChem 8000 flow injection analyzer. We summed NH_4^+ and NO_3^- of each resin column and resin bag within each site during May–October 2011 to estimate total atmospheric N inputs and N leaching, respectively.

Partitioning sources of nitrate in leachate

The denitrifier method (Casciotti et al. 2002; Templer and Weathers 2011) was used to determine the natural abundance isotope composition of NO_3^- in atmospheric input and leachate of those samples that had sufficient NO_3^- concentrations (>0.1 mg N l^{-1}). The stable isotope composition of N and oxygen in nitrous oxide gas produced by the bacteria was measured on a SerCon Cryoprep trace gas concentration system interfaced to a PDZ Europa 20-20 isotope ratio mass spectrometer (SerCon Ltd., Cheshire, UK) at the University of California Davis Stable Isotope Facility. We used USGS standards #32, 34 and 35.

We estimated the relative contributions of atmospheric inputs and nitrification to soil leachate at each of the nine sites using the natural abundance isotope composition of NO_3^- in a two end-member mixing model (Pardo et al. 2004; Templer and McCann 2010). Natural abundance $\delta^{18}O$ values of NO_3^- differ significantly between NO_3^- of precipitation and NO_3^- produced microbially during the process of nitrification. Therefore, the $\delta^{18}O$ signature of NO_3^- in soil solution or stream water can be measured and, with a two end-member mixing model, the predominant source of NO_3^- being leached from a terrestrial ecosystem can be determined. The following equation was used to partition the sources of NO_3^- in the soil leachate between atmospheric inputs and nitrification:

$$\%\ NO_3^-\ \text{from atmospheric inputs} = \left(\frac{\delta^{18}O_{loss} - \delta^{18}O_{nitrification}}{\delta^{18}O_{input} - \delta^{18}O_{nitrification}}\right) \times 100$$

where $\delta^{18}O_{loss}$ is the value of $\delta^{18}O$ in soil leachate, $\delta^{18}O_{input}$ is the value of $\delta^{18}O$ in atmospheric inputs and is the published value of for nitrification (Kendall 1998; Pardo et al. 2004).

Spatial analyses

We used three spatial metrics to characterize the intensity of urbanization at each of the nine sites: proximity to urban core, ISA fraction, and on-road CO_2 emissions. We defined the urban core of Boston

as the intersection of our two transects in downtown Boston (42.3500 N 71.1038 W) and calculated the distance for each site from this geographical location. ISA fraction and land use data were extracted for the study area from Massachusetts statewide datasets derived from 2005 near-infrared ortho-imagery (0.5–1 m spatial resolution; MassGIS 2010). On-road CO_2 emissions were based on 2010 data from the Boston and Worcester Metropolitan Transportation Organizations as described in Brondfield et al. (2012). Following previous studies (Raciti et al. 2012; Rao et al. 2013), we estimated the urbanization metrics for the 1 km^2 area centered at each of the nine sites and used these data to regress linearly against the inorganic N flux data (see "Statistical analyses"). We also examined potential relationships between atmospheric N inputs and losses, and foliar and soil N concentrations at the nine sites.

We compared our field measurements with modeled estimates of atmospheric N deposition (ClimCalc; Ollinger et al. 1993) for the nine sites. The model spatially interpolates annual rates of wet and dry deposition of NH_4^+, NO_3^- and HNO_3 based on historic regional measurements of precipitation and its ion concentrations, and dry deposition of N compounds. These interpolated N deposition rates for the northeastern United States are modeled based on latitude, longitude and elevation (including slope and aspect) across space. The geographic coordinates of the nine field sites in our study were estimated using a Garmin Dakota GPS (Garmin International, Olathe, Kansas, USA). The elevation, slope and aspect of each site were determined from the 30 m Shuttle Radar Topography Mission (SRTM) Digital Elevation Model.

Statistical analyses

The R software package, version 2.12.2, was used for all statistical analyses (R Core Team 2011). The data for atmospheric N inputs and leaching were not normally distributed, therefore we used the nonparametric bootstrap method (Efron and Tibshirani 1993) to empirically estimate the 95 % confidence intervals (CI) of the urban and non-urban class means. We used linear regression to examine the relationships between urbanization metrics and atmospheric N inputs and leachate losses. We set an alpha value of 0.1 to determine the statistical significance of these relationships.

Results

Inorganic N fluxes along the urbanization gradient

Atmospheric N inputs

Site-specific total inorganic N inputs ranged from 3.71 ± 0.65 to 17.33 ± 2.68 kg N ha^{-1} $year^{-1}$ (Fig. 3), with NH_4^+ inputs (2.39 ± 0.48 to 15.20 ± 2.57 kg N ha^{-1} $year^{-1}$; lowest to highest mean site values) exceeding NO_3^- inputs (0.30 ± 0.11 to 3.46 ± 2.23 kg N ha^{-1} $year^{-1}$). NH_4^+ inputs, as a percent of total inorganic N inputs, varied from 65 % at Harvard site to 97 % at Waltham site with a median value of 77 ± 4 % across the two transects. With an annual rate of total inorganic N inputs of 14.79 ± 3.48 kg N ha^{-1} $year^{-1}$, the Boston site at the urban end experienced 3–4 times greater inputs compared to the Worcester (5.01 ± 0.31 kg N ha^{-1} $year^{-1}$) and Harvard Forest (3.71 ± 0.65 kg N ha^{-1} $year^{-1}$; Fig. 3) sites located at the less urban, outer ends of the two transects.

The four urban sites had significantly higher mean rates of atmospheric N inputs (9.74 ± 1.20, 2.52 ± 0.58, 12.26 ± 1.48 kg N ha^{-1} $year^{-1}$ for NH_4^+, NO_3^- and total inorganic N, respectively) than the five non-urban sites (4.51 ± 0.63, 1.19 ± 0.15, 5.70 ± 0.53 kg N ha^{-1} $year^{-1}$, Online Resource 2). All three urbanization metrics had positive relationships with atmospheric N inputs, but not all of these relationships were statistically significant (Fig. 3). Proximity to urban core was positively correlated with NH_4^+ inputs ($R^2 = 0.57$, $p = 0.02$) and total inorganic N inputs ($R^2 = 0.61$, $p = 0.01$; Fig. 3a). There was significant positive correlation between ISA fraction and NH_4^+ ($R^2 = 0.36$, $p = 0.09$), NO_3^- ($R^2 = 0.42$, $p = 0.06$) and total inorganic N inputs ($R^2 = 0.44$, $p = 0.05$; Fig. 3b). Modeled on-road CO_2 emissions were significantly positively related to NO_3^- inputs ($R^2 = 0.74$, $p = 0.003$) and total inorganic N inputs ($R^2 = 0.36$, $p = 0.09$), but there was only a trend for the positive relationship with NH_4^+ inputs ($R^2 = 0.23$, $p = 0.19$; Fig. 3c). Road density was positively, but not significantly correlated with NH_4^+, NO_3^- and total inorganic N inputs ($p = 0.16$, 0.10, and 0.11, respectively).

The measured values of NH_4^+, NO_3^- and total inorganic N inputs did not correlate well with the corresponding modeled values for N deposition from

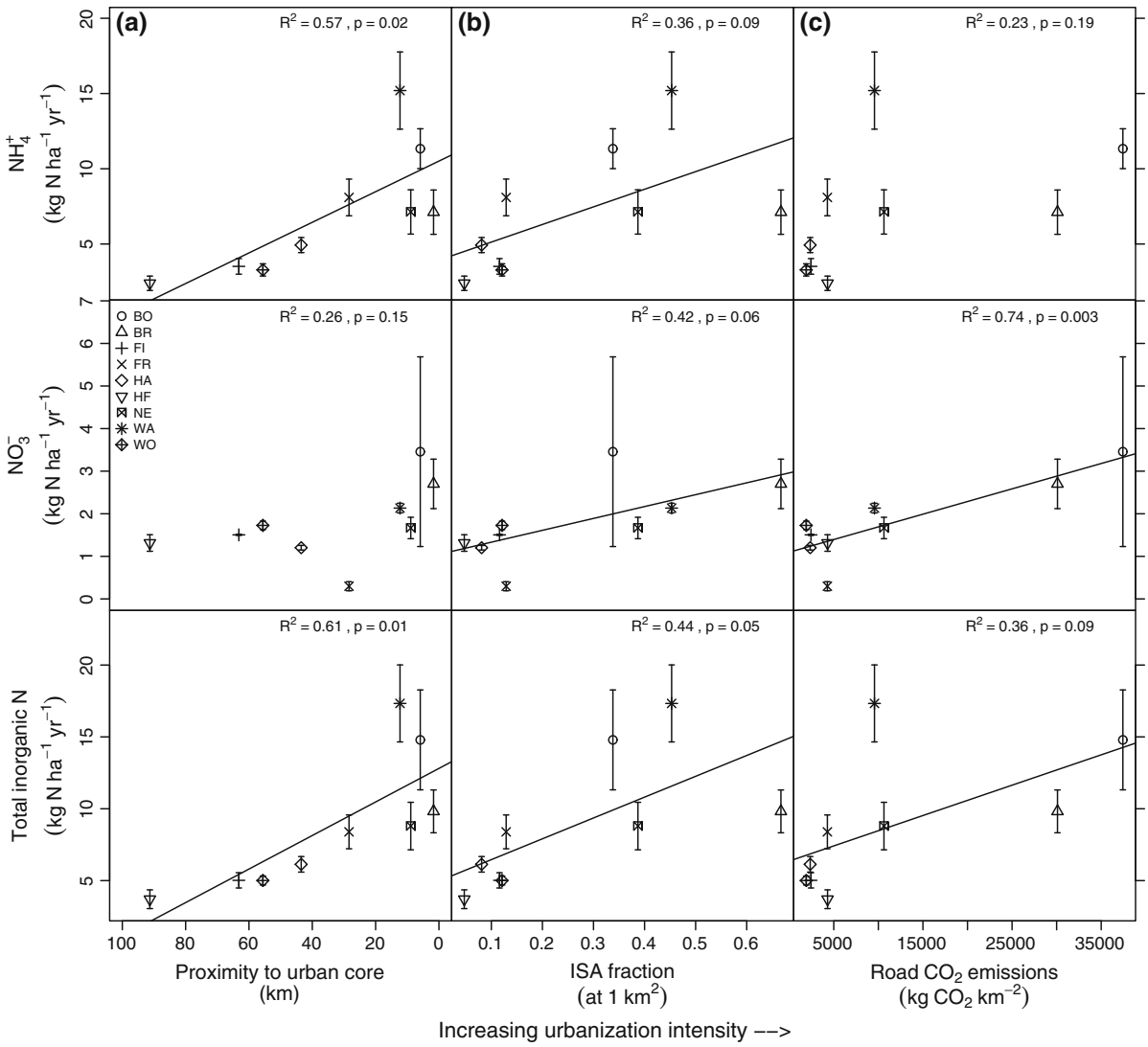

Fig. 3 NH_4^+, NO_3^- and total atmospheric inorganic N inputs as a function of increasing urbanization intensity, including **a** proximity to urban core of Boston, **b** the impervious surface area (ISA) fraction, and **c** road CO_2 emissions, based on the 1 km^2 area surrounding each location for measuring N inputs. **a** Shows the sites in increasing order of proximity to the urban core (distance along X-axis decreasing from 100 to 0 km). The urban sites (ISA fraction $\geq$ 0.25) include WA (Waltham), BR (Brookline), NE (Newton) and BO (Arnold Arboretum, Boston) and the non-urban sites (ISA $<$ 0.25) include HF (Harvard Forest), HA (Harvard), FI (Fitchburg), WO (Worcester) and FR (Framingham)

the ClimCalc model (Ollinger et al. 1993; Fig. 4). Our measured values for NO_3^- were lower and values for NH_4^+ were greater than those predicted by ClimCalc. Measured values for total inorganic N inputs were nearly twice the modeled values for urban areas, but were slightly lower than modeled values for non-urban areas. ClimCalc values for total inorganic N input rates ranged narrowly from 6.70 to 7.89 kg N ha^{-1} $year^{-1}$ across the nine sites, but we observed a much wider range (3.71 $\pm$ 0.65 to 17.33 $\pm$ 2.68 kg N ha^{-1} $year^{-1}$) in the field measurements (Fig. 4c). The difference between measured and modeled atmospheric inputs of NH_4^+ increased significantly with urbanization intensity (as measured by proximity to urban core and ISA fraction; Online Resource 3). In contrast, the difference between measured and modeled atmospheric inputs of NO_3^- decreased significantly with urbanization intensity (as measured

by ISA fraction and road CO_2 emissions; Online Resource 3).

Nitrogen leaching

The site-specific mean leaching rate for NH_4^+ and NO_3^- ranged from 2.01 ± 0.3 to 497.05 ± 252.32 (Fig. 5a) and from 4.50 ± 4.50 to 4970.85 ± 3383.14 μg N g resin^{-1} year^{-1} (Fig. 5b), respectively. NH_4^+ leaching was greater than NO_3^- at three sites (Brookline, Newton and Worcester) and varied from 56 to 98 % of total inorganic N leaching at these sites. At the remaining six sites, NO_3^- leaching was greater and varied from 71 to 97 % of total inorganic N leaching. Site-specific mean values of total inorganic N loss via leaching ranged from 7.99 ± 3.93 to 5467.9 ± 3635.46 μg N g resin^{-1} year^{-1} (Fig. 5c). Although, mean annual NH_4^+, NO_3^- and total inorganic N leaching rates were twofold greater at urban (290.54 ± 78.29, 1951.60 ± 1027.82, 2242.13 ± 1100.04 μg N g resin^{-1} year^{-1}, respectively) than at non-urban sites (187.05 ± 85.43, 858.02 ± 283.79, 1045.07 ± 314.22 μg N g resin^{-1} year^{-1}), the differences between these two classes were not statistically significant (Online Resource 2). With a total leaching rate of 2335.40 ± 700.32 μg N g resin^{-1} year^{-1}, the forest site at the urban end (Boston) experienced approximately 292 times greater inorganic N loss than the Harvard Forest site (7.99 ± 3.93 μg N g resin^{-1} year^{-1}) and 5.5 times greater than the Worcester site (424.08 ± 313.74 μg N g resin^{-1} year^{-1}) at the less urban, outer ends of the transects (Fig. 5c). Along the gradient, none of the three urbanization metrics correlated significantly with NH_4^+, NO_3^- or total inorganic N losses (see Fig. 5 for proximity to urban core), though there was a positive trend for each.

Total inorganic N inputs were positively correlated with total inorganic N losses across the sites ($R^2 = 0.61$, $p = 0.01$; Fig. 6a); however, NH_4^+ and NO_3^- inputs were not correlated with corresponding losses for each site ($p = 0.24$ and $p = 0.79$ for NH_4^+ and NO_3^-, respectively). Soil N ($R^2 = 0.48$, $p = 0.04$) and C ($R^2 = 0.57$, $p = 0.02$) were correlated positively and significantly with NH_4^+ leaching rates, and positively but insignificantly with NO_3^- ($p = 0.12$ and 0.30, respectively) and total inorganic N leaching rates ($p = 0.10$; Fig. 6b, and 0.23, respectively). Soil N and C concentrations showed positive but statistically insignificant correlations with NH_4^+, NO_3^- and total inorganic N inputs ($R^2 = 0.19$–0.39, $p = 0.07$–0.25). Foliage C and N concentrations of *Acer rubrum*, *Acer saccharum*, and *Quercus rubra* showed insignificant relationships with the corresponding site measurements of inorganic N input and leaching rates ($R^2 = 0.0001$–0.395, $p = 0.07$–0.98).

Natural abundance isotopes of the inorganic N fluxes

The site-specific mean $\delta^{15}N$ values of NO_3^- from atmospheric inputs ranged from −2.74 to −0.12 ‰, and was not statistically significantly different from the $\delta^{15}N$ values of NO_3^- from leachate which ranged

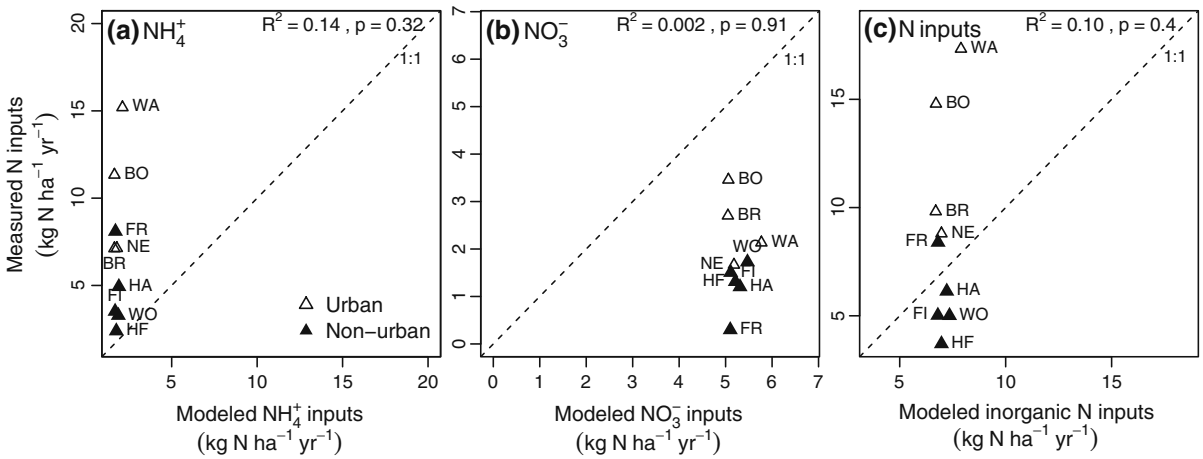

Fig. 4 Relationships between measured and modeled NH_4^+, NO_3^-, and total inorganic N inputs. The modeled values of atmospheric N deposition, from ClimCalc, are a function of geographical coordinates, elevation, slope and aspect. *Diagonal lines* indicate 1:1 relationship

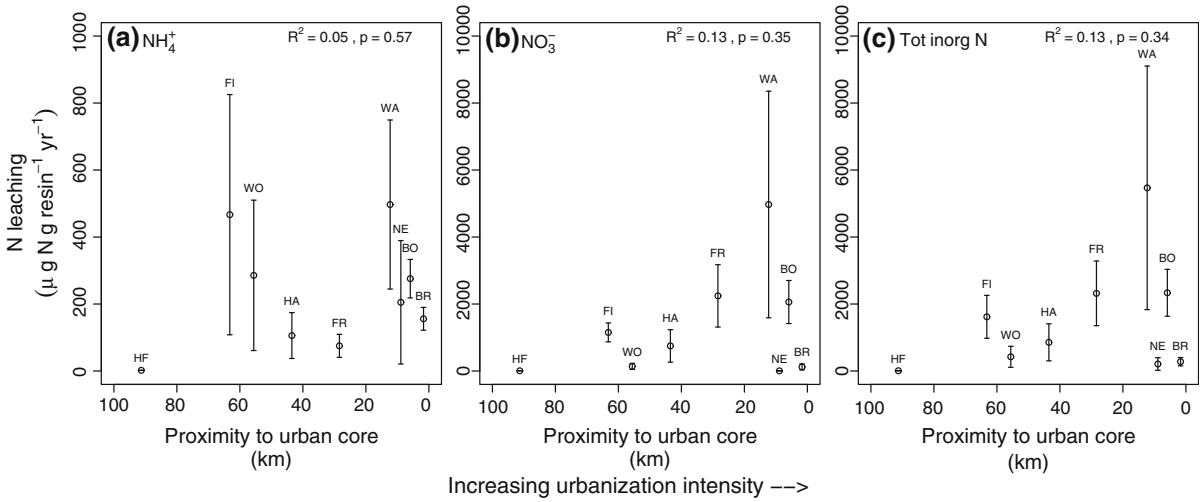

Fig. 5 **a** NH_4^+, **b** NO_3^-, and **c** total inorganic N leaching as a function of increasing urbanization intensity, including proximity to the urban core of Boston. Data are means with one standard error

from −7.47 to 2.19 ‰ ($p = 0.19$; Fig. 7). Mean $\delta^{15}N$ values of NO_3^- for both atmospheric inputs and leaching did not differ significantly among the urban versus non-urban sites ($p = 0.91$ for atmospheric inputs and $p = 0.995$ for leaching). Similarly, mean $\delta^{18}O$ values of NO_3^- for both atmospheric inputs and leaching did not differ significantly among the urban versus non-urban sites ($p = 0.22$ for atmospheric inputs and $p = 0.73$ for leaching). In contrast, the $\delta^{18}O$ values of NO_3^- from atmospheric inputs (57.42 to 69.19 ‰, lowest to highest mean site values) were greater than $\delta^{18}O$ values of NO_3^- from leachate (1.73 to 65.6 ‰; $p < 0.001$; Fig. 7). The leachate at five sites (both urban and non-urban) had a greater proportion of NO_3^- from nitrification (~80 to 100 %) than from the atmosphere (0 to 20 %; Fig. 8). However, a considerable proportion of NO_3^- in leachate at the urban sites of Newton (~100 %), Brookline (17–42 %) and non-urban sites at Worcester (68–77 %) and Harvard Forest (25–45 %) came from atmospheric inputs.

Discussion and conclusions

The process of urbanization alters both land cover and land use, resulting in significant changes in biogeochemical cycles (Kaye et al. 2006). Despite these clear changes, there is a paucity of data quantifying how N deposition varies along gradients of urbanization. In this study, we observed significantly higher total inorganic N inputs at urban sites (12.3 ± 1.5 kg N ha^{-1} $year^{-1}$) than non-urban (5.7 ± 0.5 kg N ha^{-1} $year^{-1}$) sites with NH_4^+ contributing thrice as much as NO_3^-. Our study shows that measures of urbanization intensity, such as proximity to urban core, ISA fraction, and on-road CO_2 emissions, are positive predictors of atmospheric N inputs. However, road density was not as strongly predictive of total atmospheric N inputs. The fact that NH_4^+ constituted nearly 75 % of total inorganic N inputs across the gradient suggests that future research in urban areas should take into account nearby N sources and transport of NH_3 emissions.

Our results also demonstrate that relationships between N leaching rates and landscape-scale factors, such as urbanization intensity and atmospheric N inputs are complex, and are strongly mediated by local site factors. Nitrogen leaching rates were not significantly related to urbanization intensity, but were significantly correlated with total inorganic N inputs. We did not find a direct relationship between urbanization intensity and sources of N lost via leaching; direct losses of N via leaching occurred without N being biologically processed in both urban and non-urban areas. These findings indicate that future studies may need to control for a greater range of local site factors along urbanization gradients to understand the relative importance of landscape- and site-scale factors in determining N leaching rates and N saturation status.

We also found that existing regional models of N deposition may underestimate total inorganic N inputs at urban sites and overestimate inputs at rural sites. The proportions of NH_4^+ and NO_3^- in total inorganic N inputs are spatially and temporally variable, and may differ among urban areas. Existing models for N deposition, including Climcalc, are empirically derived and based almost exclusively on rural, background observations of deposition, typically using basic climatic and/or geographic information (such as slope, aspect, and elevation) as model inputs. While these models have widespread utility within larger, regional modeling analyses, the urban bias has the potential to be significant within highly developed areas such as the Northeastern US. An expansion of the NADP and CASTNET monitoring programs to include developed sites within their sampling design would likely improve regional estimates throughout the United States and would empirically inform improved model development.

We are experiencing unprecedented urban population growth that is expected to impact the areal extent and character of the natural components of urban ecosystems (Grimm et al. 2008; Seto et al. 2012). This study improves our understanding of N cycling in urban ecosystems and highlights the complex relationships between urbanization intensity and inorganic N inputs and leaching. Our results demonstrate the need for additional measurements to quantify and understand process-level reactive N fluxes in and around urban areas.

Urbanization and atmospheric N inputs

The greater atmospheric N inputs to the urban sites are likely due to larger local sources of NO_3^- and NH_3 emissions from (1) fossil fuel combustion in vehicles, space and water heating systems, electric utilities, and industrial processes; (2) volatilization of residential and commercial lawn fertilizer; and (3) volatilization of wild and domesticated animal waste (Driscoll et al. 2003; Smith et al. 2007). Nitrogen inputs along the urbanization gradient correlated most strongly with proximity to urban core and on-road CO_2 emissions. Similar to other studies, we found that proximity to urban core covaried with N inputs. We also found that ISA fraction correlated well with total inorganic N inputs. Impervious surfaces are associated with fossil fuel emissions from vehicles moving on roads, parking lots and driveways (Bettez 2009; Davidson et al. 2010) and from other stationary sources of inorganic N emissions such as industries and power plants. Road

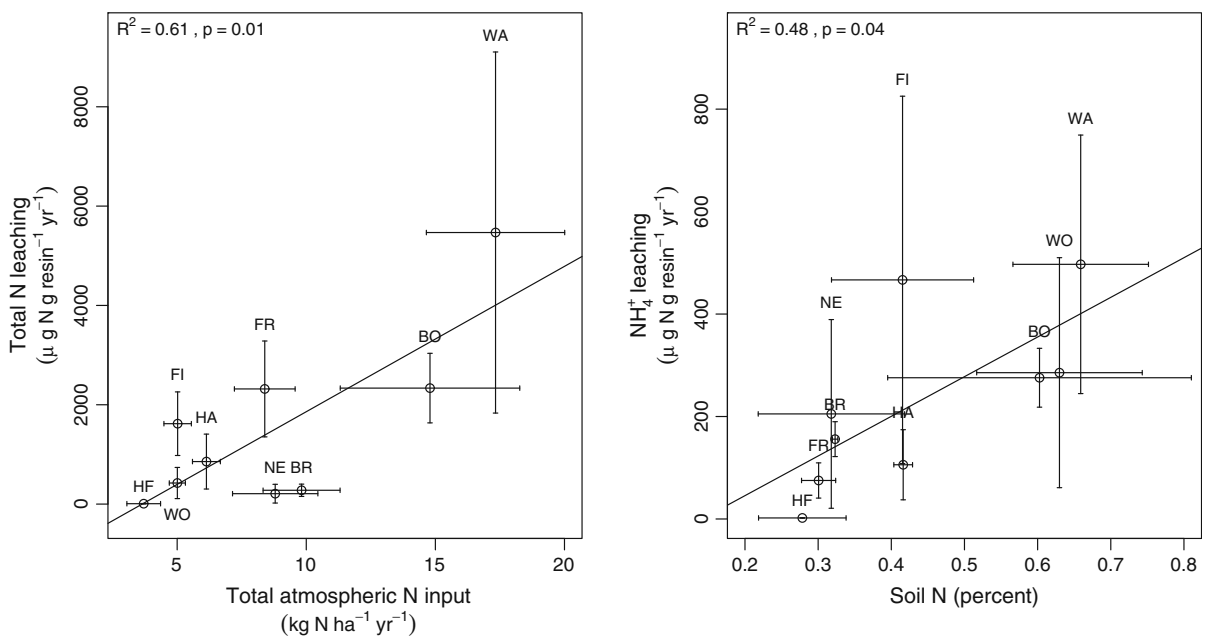

Fig. 6 Relationship between **a** total inorganic N inputs and leaching, and **b** soil percent N and total inorganic N leaching at the nine sample sites. Data are means with one standard error

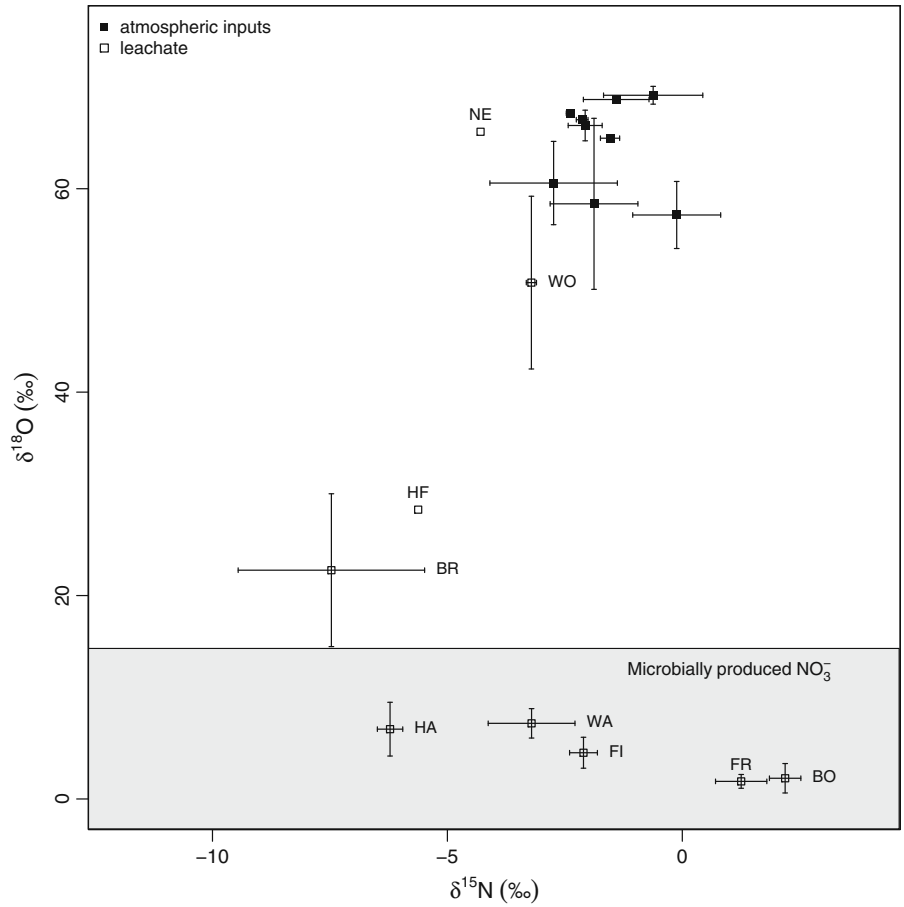

Fig. 7 Natural abundance stable isotope composition for nitrogen and oxygen in nitrate of atmospheric inputs and leachate. *The shaded area* represents the range of $\delta^{18}O$ and $\delta^{15}N$ values for microbially produced NO_3^- (from nitrification; Pardo et al. 2004)

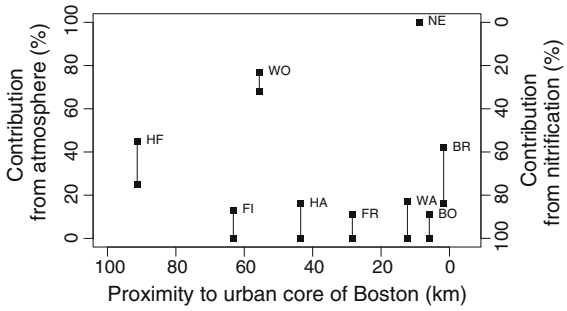

Fig. 8 Percent contribution of nitrate in leachate from atmospheric N input and nitrification. For each site, the minimum and maximum values are shown by the *filled squares*

density is also used frequently as a metric for urbanization intensity. Mobile sources, including on- and off-road vehicles, account for 56 % of NO_x emissions in the US (EPA 2005). However, we did not find a significant relationship between road density and inorganic N inputs. One potential explanation for the lack of relationship may be because road density alone does not capture variations in traffic volume and emissions. The modeled on-road CO_2 emissions values we used took into account not only road type and size, but also traffic volume, and proved to be significantly positively correlated with atmospheric NO_3^- inputs.

We found that the ClimCalc model did not capture the large variability observed in field measurements of NH_4^+, NO_3^- and total inorganic N inputs along the gradient. Moreover, the model predicted a higher proportion of NO_3^- than NH_4^+ inputs, which contrasted with our field measurements. The ClimCalc model estimates total inorganic N deposition rates for the northeastern United States based on NADP and CASTNET measurements made primarily at rural

locations, and does not account for local urban effects on N deposition. Also, these two networks measure deposition in open areas, whereas we measured throughfall beneath canopies. While some of the variation we observed may be due to within-canopy processing of N, it likely cannot explain the patterns we observed across the urbanization gradient. The results of our study strongly suggest the need for greater sampling of atmospheric N deposition in urban areas to capture local, urban inputs from gaseous emissions. The magnitude of the underestimation at the regional scale is difficult to assess with our limited number of urban monitoring sites, but within highly developed areas the bias is significant. Our results demonstrate that rates of total atmospheric inputs of inorganic N could be underestimated up to approximately 6 kg N ha^{-1} $year^{-1}$ in urban areas (Online Resource 3). Within Massachusetts, 38 % of the state is considered urban according to US census classifications (US Census Bureau 2013) and therefore estimates of atmospheric N deposition are likely biased downward in a large area of this region.

We observed a twofold increase in NH_4^+, NO_3^- and total inorganic N inputs from non-urban to urban sites, analogous to the results from a New York City (NYC) urbanization gradient (Lovett et al. 2000). Ammonium inputs comprised a greater proportion (77 ± 4 %) of the total inorganic N inputs than NO_3^- for both urban and non-urban sites in our study, similar to results of Holland et al. (2005), Fang et al. (2011b). In contrast, Lovett et al. (2000) found that in NYC, NO_3^- inputs (67–73 %) constituted a larger proportion of the total inorganic N inputs than NH_4^+ (27–33 %). This NO_3^- dominance is present across the United States, but not in Western Europe and China (Ollinger et al. 1993; Holland et al. 2005; Fang et al. 2011b). The difference in proportions of N forms in the atmospheric N inputs between NYC and our study are likely due to temporal changes in gaseous N emissions. The greater proportion of NH_4^+ in our measurements might have resulted from recent controls on NO_x emissions, which reduce NO_3^- deposition but not NH_4^+ (Pinder et al. 2011). The NYC gradient was measured in 1996, the 16 years between these studies likely contributes to the observed differences. Between 1981–82 and 2010–11, the ratio of atmospheric concentrations of NO_3^- to NH_4^+ at the two nearest NADP sites in MA (MA08 and MA13) decreased by half from 2.5:1 to 1.2:1.

Urbanization and nitrogen leaching

Although we found a positive trend, the lack of significant relationship between rates of N leaching and urbanization intensity (for all three metrics) was surprising. Compared to rates of atmospheric N inputs, N leaching rates in our study area had higher variability between sites. This variability may be attributed to site-specific variation in soil characteristics, plant and microbial activity, historical land-use, and disturbance patterns. Though all of the samplers were located under tree canopy and outside lawn areas, differences in the quantities or timing of fertilizer N amendments in the areas around these sites could have led to differences in soil N availability, and consequently N leaching (Petrovic 1990). Such local factors likely affected N leaching to a greater extent than urbanization.

Though not correlated with urbanization, N leaching rates were significantly positively related to total inorganic N input rates, a trend that has been observed in other forest ecosystems (Matson et al. 2002; Fang et al. 2011b). For example, of 41 ecosystem and soil variables examined, N inputs via throughfall and soil pH were the best predictors for N leaching rates for 65 forested catchments across Europe (Dise and Wright 1995). Similarly, Fang et al. (2011b) found a strong positive correlation between total inorganic N inputs and leaching losses in 50 broad-leaf forests across China. Our study demonstrates that the positive relationship between total inorganic N inputs and leaching found in forested ecosystems may also hold true for urban ecosystems wherein the retention is directly related to N deposition and availability. These results have implications for water and air quality of urban regions since NO_3^- leaching with H^+ or aluminum can cause acidification of stream water (Vitousek et al. 1997), which can lead to fish mortality (Murdoch and Stoddard 1992). Nitrogen leaching can also lead to eutrophication of estuaries and coastal areas (Howarth 1988).

The positive trend between soil N concentration and N leaching shows that higher soil N concentrations are associated with greater N leaching (Fig. 6b). Others have found a relationship between N deposition, soil N content, and leaching rates (e.g. Dise and Wright 1995). There is evidence for greater nitrification rates in soils with higher N concentrations (Pouyat and Turechek 2001; Boggs et al. 2005), which would be a plausible mechanism for this trend.

From resin bag measurements, we observed low NO_3^- leaching rates at two urban (Brookline and Newton) and two non-urban (Harvard Forest and Worcester) sites. However, stable isotopic composition of NO_3^- in leachate at the same four sites showed that a significant proportion of NO_3^- was coming directly from the atmosphere. These results suggest that even though these sites had a relatively low amount of N inputs, the N that came out of these stands passed directly via leaching without being biological processed. Nitrogen saturation has been traditionally defined as a temporal sequence of events whereby elevated rates of atmospheric N deposition first lead to saturation of abiotic sinks and biological demand, followed by increased N losses (Aber et al. 1989, 1998). As noted elsewhere (Lovett and Goodale 2011), our traditional view of N losses occurring only after all abiotic sinks and biological demand has been saturated needs to be reassessed. Across the northeastern US, some non-urban ecosystems experiencing increased N deposition above 8 kg ha^{-1} $year^{-1}$ have increased N losses, while some do not (Aber et al. 2003). Similar to Templer and McCann (2010), results of this study show that our traditional view of N saturation needs to be reassessed in urban ecosystems as well. Our results support the conceptual model of Lovett and Goodale (2011), which purports that atmospheric N inputs added to terrestrial ecosystems can move to multiple sinks and losses (i.e. soils, plant biomass, leaching, and gas loss) simultaneously. We conclude that atmospheric N inputs can pass directly through and be lost via leaching in both urban and non-urban ecosystems even if plant or microbial demand is not saturated.

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