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Roads as nitrogen deposition hot spots

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Abstract

Mobile sources are the single largest source of nitrogen emissions to the atmosphere in the US. It is likely that a portion of mobile-source emissions are deposited adjacent to roads and thus not measured by traditional monitoring networks, which were designed to measure long-term and regional trends in deposition well away from emission sources. To estimate the magnitude of near-source nitrogen deposition, we measured concentrations of both dissolved inorganic nitrogen (DIN) and total (inorganic + organic) dissolved nitrogen (TDN) in throughfall (i.e., the nitrogen that comes through the forest canopy) along transects perpendicular to two moderately trafficked roads on Cape Cod in Falmouth MA, coupled with measurements of both DIN and TDN in bulk precipitation made in adjacent open fields at the same transect distances. We used the TDN throughfall data to estimate total nitrogen deposition, including dry gaseous nitrogen deposition in addition to wet deposition and dry particle deposition. There was no difference in TDN in the bulk collectors along the transects at either site; however TDN in the throughfall collectors was always higher closest to the road and decreased with distance. These patterns were driven primarily by differences in the inorganic N and not the organic N. Annual

throughfall deposition was 8.7 (±0.4) and 6.8 (±0.5) TDN - kg N ha^{-1} yr^{-1} at sites 10 m and 150 m away from the road respectively. We also characterized throughfall away from a non-road edge (power line right-of-way) to test whether the increased deposition observed near road edges was due to deposition near emission sources or due to a physical, edge effect causing higher deposition. The increased deposition we observed near roads was due to increases in inorganic N especially NH_4^+. This increased deposition was not the result of an edge effect; rather it is due to near source deposition of mobile source emissions. We scaled these results to the entire watershed and estimate that by not taking into account the effects of increased gaseous N deposition from mobile sources we are underestimating the amount of N deposition to the watershed by 13% - 25%.

Keywords: nitrogen deposition; roadside; forest edges; throughfall

Introduction

Nitrogen (N) availability limits primary production in most coastal ecosystems in the temperate zone (Howarth et al. 2011; Howarth 1988; Howarth & Marino 2006). Excess N can result in eutrophication, harmful or toxic algal blooms, loss of seagrass beds, and loss of biotic diversity (NRC 2000, Rabalais 2002). Excess N inputs now contribute strongly to the degradation of more than half of the estuaries in the US, especially those downstream of developed or agricultural basins (Bricker et al. 2008). The sources of this coastal nitrogen pollution include sewage, fertilizer runoff, wastes from animal agriculture, and atmospheric deposition of N that originates from fossil fuel combustion, and the relative importance of these inputs varies across regions and watersheds (Howarth 2008a, Hong et al. 2011, Howarth et al. 2012). While efforts to reduce this excess N in urbanized areas have often focused on reducing

inputs from sewage, a significant portion of the total N loading of estuaries (particularly in the northeastern US) may be due to N deposition, especially dry gaseous deposition that is not generally measured in monitoring networks (Howarth 2008a; Howarth 2008b). Much of this deposition is the result of N emissions from fossil fuel combustion (Howarth 2008a).

In the US, Mobile sources such as highway vehicles (cars and trucks) and off-highway vehicles (construction equipment, planes, boats, etc.) are the single largest source of emissions, accounting for 37% of the total amount of nitrogen emitted as NO_x N_2O, and NH_3 in the US (US USEPA 2011). They are the largest source of NO_x (3.8 TG ~ 56%), the second largest source of N_2O emissions (0.1 Tg ~12) after agriculture and soil management and although they are only a small part (0.1 Tg ~6.5%) of the NH_x emissions nationally, in urban areas they can be the largest source of NH_3 (Baum et al. 2000, USEPA 2011).

Although these emissions are the result of fossil fuel combustion, the primary source of the N is not the fuel but the N_2 in atmospheric air, which is 78% N_2 gas. Oxidized N gases are formed during combustion under the high temperature and pressure conditions in internal combustion engines, as N_2 and O_2 in atmospheric air are split into their atomic constituents N and O, which then re-combine to form NO and NO_2 (NO_x) (Abdel-Rahman 1998). Ammonia gas is formed in the catalytic converter when some of the NO, which is supposed to be converted back to N_2, is over-reduced to form NH_3 (Heeb et al. 2006).

The N emissions can be deposited on the landscape as dry deposition (gaseous NH_3, NO, NO_2, HONO, and HNO_3, or particulate NO_3^- and NH_4^+), or as wet deposition when dissolved in precipitation in the form of NO_3^- and NH_4^+. Although a great deal of research has been conducted on NH_3 deposition and its effects biota near areas of intensive animal husbandry (Krupa 2003), the relative magnitude of the contribution of gaseous N deposition resulting from

near-source emissions to total N deposition, as well as the resulting impact on local ecosystems and water quality are not well known (Howarth 2008b).

In the US, N deposition estimates are made using "wet deposition" (i.e., nitrogen in rainfall and snow) data collected by the National Atmospheric Deposition Program National Trends Network (NADP/NTN), which consists of 251 sites (NADP, 2009), and "dry deposition" (i.e., gas and particle concentrations in the air) data collected by the Clean Air Status Trends Network (CASTNET), which consists of 91 sites (US EPA 2010). For the dry gaseous deposition, CASTNET has focused just on HNO_3 and has not monitored the other gases. These networks were set up to monitor temporally integrated long-term trends and broad-scale regional patterns in precipitation chemistry and dry deposition, and so sampling sites were specifically located in areas uninfluenced by local pollution sources. The network sites were also purposefully located away from roads and urban areas (e.g., "sites should be located > 100 m away from a road and >10 km away from suburban/urban areas with a population of 10,000") (Bigelow et al. 2001). As a result, the current monitoring networks are likely missing or under-accounting for an important component of the N total deposition: gaseous compounds that are emitted and dry-deposited in close proximity to urban areas. Indeed, undercounting of N inputs from deposition has been documented in several continental scale input/output budgets (e.g., Howarth et al. 2002 and Holland et al. 2005) in which portions of the emissions are not accounted for in deposition measurements. While this under-accounting could be due to errors in estimation of emissions or export outside the US by advection prior to deposition (Howarth et al. 2002), it could also be due to a portion of the emissions being deposited in close proximity to where they were produced, and thus not measured by the current monitoring network (Howarth 2008a). The CMAQ model (which predicts the spatial patterning of all N deposition components

based on an emissions inventory and atmospheric transport, reaction, and deposition processes) suggests a high rate of dry gaseous deposition of N in areas of high population and vehicle density, such as the northeastern US and Sweden (Schwede et al. 2009, Hong et al. 2011, Howarth et al. 2012).

Nitrogen deposition from mobile source emissions can substantially increase the N delivery to ecosystems in proximity of roadways. In a study near a major highway in Germany Kirchner et al. (2005) found up to 3-fold higher NH_3 and NO_2 air concentrations and 2-fold higher N deposition at sites near the highway edge than at sites 500 meters away. DeCatanzaro (2009) found that the amount of N in coastal wetlands was positively correlated with the road density of their watersheds; and Davidson et al. (2010) found that even small residential roads accumulated N, and that there was a relationship between the antecedent dry period and the amount of N in road runoff. This increased N is likely due to direct deposition of gaseous N emissions from cars and trucks, although only a fraction of the total emissions from vehicles are deposited in the near vicinity of road. Marino et al. (ms. in prep) estimate that 10-25% of the NH_3 and 1% of the NO_x emissions from mobile sources are likely deposited within 50 m of the roadway sites used in this study.

Although deposition of N associated with roadways has been documented, the contribution of this near-source deposition to local N budgets and the impacts of this chronic N deposition on N cycling and export from roadside forests remain poorly known. In this study, we measured N throughfall along perpendicular transects away from 2 roads, and used the throughfall data to estimate total deposition, including that from dry gaseous deposition which we then used to refine estimates of total N deposition and leaching in the study area watershed. We also measured throughfall along a transect away from a non-roadside edge in order to

separately determine if elevated deposition was due to an edge effect (i.e., Weathers et al. 2001). In order to overcome problems associated with measuring total N deposition, we followed the approach of Lajtha et al. (1995) in estimating total N deposition from data on total N in throughfall, which is the material that falls through the canopy and includes N deposited on the canopy in both wet and dry deposition (as particles and as gases), plus the net exchange of material either taken up or leached by the canopy (Lajtha et al. 1995).

Methods

In this study we measured N inputs along two roadside edges and one non-road edge by placing precipitation collectors along transects in open fields to measure N in bulk precipitation and beneath forests to measure N in throughfall precipitation. The study was conducted in Falmouth, Massachusetts, on Cape Cod, at the Woods Hole Research Center (WHRC) (41°32'55"N, 70°38'35.00"W), and the Waquoit Bay National Estuarine Research Reserve (WBNERR) (41°35'50.00"N, 70°30'5.00"W) within the Waquoit Bay watershed (Figure 1). The forests at each site are ~ 100 year old aggrading secondary forests composed predominantly of *Quercus rubra* and *Quercus alba* (red and white oak) mixed with some mature *Pinus resinosa* (red pine) (Seely et al. 1998).

At the WHRC site, we had two 100-m long transects perpendicular to Woods Hole Road, which had an average annual daily traffic (AADT) volume of 8,800 vehicles day^{-1} (MHD 2008). The bulk transect was in an open field with collectors at 10, 50, and 100 meters at an angle 334° NNW away from the road and the throughfall transect was in an adjacent forest with collectors at 10, 50 and 100 meters at an angle of 322° NW away from the road. At the WBNERR site, we had two transects one bulk and one throughfall perpendicular to Waquoit Highway/ Falmouth

Road (Route 28), which had an estimated annual daily traffic volume of 18,800 vehicles day^{-1} (MHD 2008). The bulk transect was in an open field with collectors at 10, 50, and 100 m away from the road at an angle of 124° SE and the throughfall transect was in a nearby forest with collectors at 10, 50, 100, 150 and 300 m at an angle of 306° NW. We also had a throughfall transect (WB Edge) which was perpendicular to a power line right of way (i.e., non-road edge) that was more than 500 m away from the nearest road or traffic. The non-road transect had collectors at 10, 50, and 100 m at an angle of 180° S.

Collectors were 1 meter off the ground and consisted of a 2-L amber HDPE bottle attached to a 20 cm diameter polyethylene funnel with a polyester fiber filter plug to keep out coarse debris. We collected samples after each precipitation event (if it another precipitation event occurred prior to collecting samples both events were considered a single event) during the summer months at all three sites from 2004 - 2006 (13 Jul 04 – 15 Aug 04 (n = 5), 28 Jun 05 – 15 Sept 05 (n = 6) and 12 Jul – 6 Sept 06 (n = 9)) and at one of the road sites (WBNERR) for an entire year (12 Jul 06 – 6 Jul 07 n = 38). The exact number of collectors varied among sites and years but was between 2 and 4 at eat distance (Table 1). As soon as possible after each precipitation event (usually within 12 hours), we brought the collectors back to the laboratory, measured the total volume collected, and filtered subsamples for nutrient analysis using an ashed Whatman® GFF (nominal pore size of 0.7µm) glass fiber filter. We stored nutrient samples at -20°C until analysis for total nitrogen by In-Line UV/Persulfate digestion and oxidation (method number 10-107-04-3-P, range 0.02-10 mg N L^{-1} MDL 0.05 mg N L^{-1} Total (TDN); nitrate + nitrite (NO_3^-) by cadmium reduction (method number 10-107-04-1-L, range 0.02-2 mg N-NO_2+NO_3^{-1} L^{-1} MDL 0.002 mg N L^{-1}); and ammonium (NH_4^+) by sodium salicylate (method number 10-107-06-2-A, range 0.10 – 5.0 mg N-NH_3 L^{-1}, MDL 0.005 mg N L^{-1}) using a Lachat

QuikChem flow injection analyzer (Hach Company Loveland, CO, USA). Dissolved inorganic N (DIN) is composed of NO_3^- and NH_4^+.Total dissolved N is composed of dissolved organic N (DON) and DIN. We calculated TDN and DIN fluxes in precipitation (Bulk) and throughfall (TF) at each distance along the transects as follows:

1) Converting the concentration of each TF or Bulk sample to mass per unit area:

mg m^{-2} = total volume (l) * concentration (mg l^{-1}) / funnel area (m^2);

2) Summing the mass for all the events over each of the sampling periods (i.e., during each of the summers or from throughout an entire year from Jul 06 – Jul 07);

3) Dividing by the length of time of the sampling periods in order to get mg N m^{-2} day^{-1} for each collector; and

4) Averaging the collectors at each distance.

5) Annual fluxes were calculated for the collectors deployed from Jul 06 – Jul 07 by multiplying the average annual daily flux by 365 (i.e., the length of the sampling period) and converting mg N m^{-2} to kg ha^{-1} and corrected by 16% to account for canopy uptake (Lovett & Lindberg 1993). In this study, similarly to Lajtha et al. (1995) who also worked at this site and used TDN to measure deposition, we used 16% as an estimate of canopy uptake. This estimate of canopy uptake is from a study by Lovett and Lindbergh (1993) who found that when total N deposition (wet and dry) was plotted against throughfall total N (organic and inorganic) across a range of species at sixteen sites around the country the slope of the best-fit linear regression was 0.84 therefore 16% of the total wet and dry inputs were being removed by the canopy

We used the annual fluxes to calculate annual watershed N retention efficiency as (N inputs -N outputs)/N inputs (Lajtha et al. 1995). For inputs we used annual fluxes of total (DIN + DON) dissolved N (TDN) in throughfall and for outputs we calculated annual fluxes of N from

measurements of TDN leaching using zero-tension lysimeters. In August 2005, we installed four zero tension lysimeters below the rooting zone (~ 50 cm) at each distance (10, 50, 100, and 150 m) along the Waquoit Bay roadside transect. Each lysimeter consisted of a pair of 25 cm long, half-round pieces of 10.2 cm PVC with one end that was cut at 45 degrees to form a point and the other that was capped with a PVC end cap drilled and tapped to receive 0.6 cm diameter tubing that drained by gravity to a 1 liter HDPE bottle. Immediately following each precipitation event from Jul 06 – Jul 07, we collected the lysimeter samples, brought them back to the laboratory and processed them similarly to the precipitation samples and measured the same dissolved N species as for precipitation. Because lysimeters capture only a portion of the actual water flux in soils (Lajtha et al. 1999), the fluxes of N below the rooting zone were calculated using the annual volume-weighted average concentration in the lysimeter samples and the water flux estimates from a Thornthwaite-type monthly water-balance model (Dingman 1994), using precipitation and temperature data for the corresponding time period from the Waquoit Bay meteorological station (NOAA 2008).

In order to assess whether nitrate leaching was occurring along roads throughout the watershed we deployed ion exchange resin (IER) bags in plots at 10, 25, 50, and 100 meters along transects perpendicular to 17 different roads in the Waquoit Bay watershed. The resin bags were similar to those used by Lovett et al. (2004), and were prepared by placing ~10g of Sybron IONAC ASB-1P in nylon stocking, soaking in 10% HCl for 1 hour, rinsing with Deionized (DI) water, and soaking in 0.5 NaOH overnight. Bags were buried in the mineral soil just beneath the forest floor (~ 12-15 cm) using a pry bar to make a slit in the soil, inserting the resin bag, and closing the slit with gentle pressure. Resin bags were deployed in 2-3 groups of 5 (i.e., 10-15 bags at each distance) for 81 days from 11-Sept-07 until 1-Dec-07. At the end of each

deployment, bags were retrieved, rinsed with DI to remove soil, and extracted twice using 10 ml of 2 M KCl. The extracts were analyzed for NO_3^- nitrate + nitrite (NO_3^-) (Lachat QuikChem method number 10-107-04-1-L).

Statistics

All statistical analyses were performed using JMP 9.0.2 (SAS Institute 2010; Cary, North Carolina). Statistical significance was determined as $P < 0.05$ for all analyses. We used an analysis of variance (ANOVA) to test for differences in bulk deposition and throughfall among the road (WHRC, WBNERR) and non-road (WB edge) sites using data collected along the transects each summer from 2004 - 2006. We used an ANOVA to compare deposition, leaching, and retention at 10, 50, 100, and 150 m along the WBNERR roadside transect using measurements made from Jul 06 – Jul 07. Where the ANOVA's showed significant effects, we conducted post-hoc means comparisons using *Tukey's Honestly Significant Difference test* (HSD, $P < 0.05$). ANOVA results in the text and tables are followed by degrees of freedom (between-groups, within-groups), F ratio, and significance level. We evaluated the relationships between bulk and throughfall and distance from road and non-road edges with correlation and regression analysis.

Results

There were no significant differences between the two road sites (WHRC and WBNERR) and the non-road site (WB Edge) in the amount of bulk inputs of either TDN (Table 2). There was also no correlation between bulk inputs of either TDN or DIN with distance at either road

site: WHRC TDN (r^2 = .0241, p = 0.5380), DIN (r^2 = .0038, p = 0.8079); WBNERR TDN (r^2 = .0079, p = 0.9307), DIN (r^2 = .0264, p = 0.2584).

There were significant difference between the road (WBNERR and WHRC) and non-road sites (WB Edge) in throughfall TDN and DIN with the road sites both having significantly higher TDN and DIN (Table 2) than the non-road site (Table 3). Along the roadside transects both TDN and DIN in throughfall were correlated with distance from the road: TDN WHRC (r^2 = .2385, p = 0.0114), TDN WBNERR (r^2 = .3361, p = <.0001); DIN WHRC (r^2 = .3874, p = 0.0007), DIN WBNERR (r^2 = .4340, p = <.0001) while along the non-road site (WB Edge) neither TDN (r^2 = .0303, p = 0.4158) or DIN (r^2 = .0053, p = 0.7349) were correlated with distance from the edge. DON was not correlated with distance along any of the transects (WHRC, r^2 = .0068, p = 0.6892; WBNERR, r^2 = .0065, p = 0.6198, WB Edge, r^2 = .0842, p = 0.1689) sites.

Although the daily throughfall flux varied throughout the year at the WBNERR site (Figure 2), we saw similar patterns away from road and non-road edges each year with inputs decreasing with distance from roadside edges while remaining constant along non-road edges (Table 3). For example, along both roadside transects TDN in throughfall was elevated above bulk measurements along the entire length of the transects compared to the non-road transect in which it was equivalent or less than the TDN in the bulk measurements (Figure 3 A, B, C). Along both roadside transects throughfall DIN was higher than bulk DIN (i.e., net canopy flux) at the sites closest to the road compared to the non-road transect where throughfall DIN was less than bulk DIN (i.e., net canopy uptake) (Figure 4 A, B, C).

The composition or type of N measured in the throughfall also changed with distance from the road (Table 4). Near the roadside edges more than half (57%) of the TDN was DIN

(NH_4^+ and NO_3^-) but this decreased to less than half (40% and 47% for WBNERR and WHRC respectively) at the points farthest away from the road (Table 4). These changes were due mainly to changes in DIN, which decreased with distance from the roadside edges and not DON, which changed very little, with distance fro the edge. Also, the percent of TDN that was NH_4^+ decreased from 19.6% - 12.3% along the WBNERR transect. In contrast, along the non-road site the percent DIN declined only slightly from 54% - 52% and the percent NH_4^+ declined from 15% - 13% across the transect.

Along the WBNERR roadside transect the amount of deposition and leaching of TDN on an annual basis were both significantly higher at the site closest to the road (Table 5). Nitrate leaching (measured with ion exchange resins) along roadside transects throughout the watershed was also correlated with distance from the road ($r^2 = 0.133$, $p = 0.001$) (Figure 5).

We estimated the potential importance of roadside deposition within 10 meters and 50 meters of all roads within the entire 5,444 ha Waquoit Bay watershed by calculating area weighted deposition estimates to account for the increased deposition near roads. We calculated these roadside-corrected deposition estimates by using a GIS analysis to calculate the percentage of the watershed that is within 10 m and 50 m of a road (13.5% and 44.3% respectively) (T. Stone, personal Communication), and the annual deposition estimates from Waquoit Bay road transect (Table 5), to calculate average deposition within 10 and 50 meters of the roadway. We estimated that deposition across 0-10 m and 0-50 m away from the road was ~1.9x and ~1.6x the deposition we would have expected in an area uninfluenced by a road. To do this we calculated the average deposition from 0- 10 and 0-50 meters from the roadway by fitting a curve ($y= 10.64x^{-0.109}$, $r^2 = 0.6557$) to the deposition measurements collected along the roadside transect (Table 3) and compared it to the deposition in an area uninfluenced by a road (5.1 kg N ha^{-1} yr^{-1}

which we calculated by extrapolating summertime measurements of throughfall TDN from the 10-m WBNERR non-road edge site (Table 3) and correcting them by 16% to account for canopy uptake. While there are inherent problems with extrapolating average summertime daily throughfall inputs to annual estimates due to seasonal differences in leaf area (i.e., no leaves during half of the year, and so therefore probably less interception of nitrogen gases by the canopy) and traffic volumes (i.e., 0.75x-fold less traffic and therefore lower vehicle emissions during 9 months of the year than in the summer) this estimate seems reasonable considering that when we extrapolate the measurements made only in the summer months in 2006 (1.8 mg m^{-2} day^{-1}) for the 150 meter plot along the Waquoit Bay roadside and compare it to the measurements made over the course of an entire year for the same location (Table 5) they only differ by 1.2 %. Also, our extrapolated estimate of deposition is similar to measured wet-only DIN in precipitation (3.19 kg N ha yr-1) made over the same period at the nearest (NADP/NTN site MA01 (NADP 2013) (~ 50 km away) once it is adjusted for an estimate of dry deposition input using the IFS regression between wet-only DIN and total N inputs for low-elevation sites (total inputs = 2.09 x wet-only DIN, $r^2 = 0.91$ (Lovett & Lindberg 1993) (i.e., 2.09 x 3.19 = 6.67 kg N ha yr^{-1}). Thus, we estimate that the emissions deposited near roads results in an additional 3,500 kg N yr^{-1} (if the 10 m gradient is used) - 6,800 kg N yr^{-1} (if the 50 meter gradient is used) above our baseline estimate of 27,764 kg N yr^{-1}

Similarly, we can also estimate the impact of decreased N retention near roads for the watershed as a whole by calculating area-weighted leaching estimates for TDN using both 10 m and 50 m wide roadside margins and measurements from the zero tension lysimeters along the Waquoit Bay roadside transect (Table 5). By fitting a curve ($y = 48.827x^{0.0824}$, $r^2 = 0.7783$) to the leaching measurements, we estimate that the average N retention in the top 50 cm of the soil was

54% from 0-10 meters, 62% from 0-50 meters, and 71% from 50 - 150 meters. This resulted in an area weighted retention rate for the whole watershed of 69% (if the 10 m margin is used) and 67% (if the 50 m margin is used). This decrease in retention near the road results in an in additional 666 – 1,131 kg N yr^{-1} leaching beneath the rooting zone above the baseline leaching estimate of 8,010 kg N yr^{-1} which is an 8-14% increase in the amount of N leaching. More significantly, if in addition to the decreased retention near the road the increased deposition is also included, the area weighted retention rate for the watershed as a whole decreases from 71 % to 63% (if the 10 m margin is used) and 58% (if the 50 m margin is used) causing the amount of N that is leaching beneath the rooting zone to increase by 29 - 47% (10,295 – 11,736 kg N yr^{-1}) over the baseline estimate.

Discussion

Although the daily flux varied among years and sites we saw similar patterns away from road and non-road edges each year with inputs decreasing with distance from roadside edges while remaining constant along non-road edges. Our study is the first to explicitly compare throughfall gradients along both roadway and non-road edges. Our study is also the first to compare DIN and TDN in throughfall along gradients away from a road, providing further information that supports the idea that dry gaseous deposition of N is at least in part responsible for the elevated near-road deposition (Figures 3, 4), which show the differences between road and non – road edges and point to motor vehicles as the source of the increased N.

We found very different patterns in N inputs along the transects away from edges depending on the type of measurement (bulk vs. throughfall), the type of edge (road vs. non-road), and the type of N (DIN vs. TDN). At the non-road site the throughfall TDN was similar to

bulk TDN and did not change with distance from the edge (Figure 3 A). Conversely, at both road sites, the throughfall TDN was greater than the bulk TDN, and although it decreased with distance from the roads, it was still greater than the bulk TDN across the entire transect (Figure 3 B and C). Our finding of a gradient in throughfall TDN but not bulk TDN moving away from the roadways is consistent with the study of Kirchner et al. (2005) in Germany that found gradients in throughfall DIN but not bulk DIN. While TDN in throughfall was higher than the bulk measurements at all distances along the road sites, this was not true for DIN in throughfall (Figure 4 B and C). Along both road sites, the DIN in throughfall decreased with distance and was only higher than DIN in the bulk collectors at the site closest to the road (10 m).

Several lines of evidence suggest that the higher throughfall N that we observed near roads was due to input from vehicle emissions on the roads, and at least in part from gaseous deposition of N. First, we found significantly higher DIN in throughfall near roads than further away from roads, a pattern not observed at the non-road site. Second, we did not find significantly higher TDN in the bulk collectors near the roads; the bulk collectors would be expected to be far less likely to capture gaseous N inputs than the throughfall collectors. Third, we observed a decrease in the percentage of NH_4^+ in throughfall TDN samples with increasing distance from the roadside edge (Figure 6); this probably reflects increased deposition of ammonia gas onto the canopy near the road. Similar patterns of increased ammonia deposition near roads have been observed in Scotland (Cape et al. 2004) as well as at our research sites (Marino et al. ms. in prep).

The choice of sites and thus the orientation of the two road and non-road transects in nearly opposite directions was a purposeful aspect of the study design. While it was beyond the scope of this work to analyze the potential contribution of a gaseous marine N source to the

deposition measurements, similar results across both roadside transects despite their opposite orientations away from the prevailing NW (337.5°) wind direction in 2004, 2005, and 2006 (NOAA 2008) provided a control of sorts for this effect being due to marine source N. Similarly, the patterns in nitrate leaching observed along roads with different orientations throughout the watershed also point to roads as being the source of the additional N.

Our canopy throughfall fluxes ranged from 2.5 – 2.6 mg N m^{-2} day^{-1} for sites 10 meters away from the roads to 1.7 – 2.0 mg N m^{-2} day^{-1} for sites 100 meters from the roads (Table 3). At the non-road site, deposition was lower yet, 1.2 mg N m^{-2} day^{-1}, or about half of the near-road rate. In their study, Kirchner et al. (2005) reported a 2-fold drop in deposition along a transect of 50 m away from a four lane highway to 500 m away. These decreases in throughfall with distance away from roads but not along non-roads indicate that the increase is due to the proximity to the emission sources (i.e. motor vehicles) and not an edge effect as described by Weathers et al. (2001) and Kirchner et al. (2005).

Several investigators have capitalized on the fact that tree canopies, because of their large surface area, are excellent collectors and have used wash-off from canopies (i.e., throughfall) to estimate dry deposition (Lajtha et al. 1995; Lovett & Lindberg 1984). However, because throughfall is the result of many processes, including exchange of ions on leaf surfaces (Lovett et al. 1985), diffusion through the leaf cuticle and stomata (Sparks 2009), leaching of material from leaves (Stadler et al. 2001), and microbial conversions on leaves (Carlisle et al. 1966) throughfall is likely an underestimate of total deposition because some of the deposition is taken up by the canopy by stomatal uptake of gaseous NH_3, NO and NO_2 and leaf surface uptake (cuticular diffusion) of dry deposition (i.e., particulate and gaseous ammonium, and nitrate ions). Although, throughfall has been shown to be a good estimate of total (wet + dry) deposition (Butler &

Likens 1995) others have accounted for this canopy uptake by applying a correction factor (Lovett & Lindberg 1993). Lovett and Lindberg (1993), in their study investigating canopy interactions in forests in North America and Europe, found that although organic N was always released from the canopy, the amount released was, in all sites but one, exceeded by the amount of inorganic N that was consumed and that on average across a wide range of forest types throughfall measurements total N (organic and inorganic) underestimated total deposition of wet and dry) by ~ 16%. Therefore we follow Lajtha et al. (1995) in using TDN to estimate total N deposition, adjusting the throughfall measurements upward by 16%.

Our deposition estimate for areas away from the road (WBNERR non-road edge) was 5.1 kg N ha^{-1} yr^{-1}. This is substantially less than the estimate of 13.1 kg N ha^{-1} yr^{-1} made by Lajtha et al. (1995) in the same watershed and on the low end of the estimate of 5.2 - 9.6 Kg N ha^{-1} yr^{-1} for wet and dry deposition from the Community Multi-scale Air Quality (CMAQ) model run for the two 12 km x 12 km grid cells in our study area for time period of our study (2004 - 2006) (www.cmaq-model.org/).We suspect that our deposition rates are low compared to those of Lajtha et al. (1995) at least in part due to decreases in N emissions since 1990. NO_x emissions have been shown to be related to total (wet + dry) N deposition across the northeastern region (Butler et al. 2003), and between 1991 and 2004 NO_x emissions in the US as a whole have declined by ~24% and emissions in NY + CT + MA, which would have a greater impact on deposition on Cape Cod, have decreased by ~ 50% (USEPA 2005, Butler pers comm.). In addition to these decreases in NO_x emissions, over this same period of time NH_4^+ dry deposition also decreased. In a study that looked at changes in air quality and atmospheric deposition in the eastern United States (ME, NH, VT, MA, CT, RI, NY, PA, NJ, MD, and DE) between 1990 - 2004, Sickles et al. (2007) found that dry deposition of NH_4^+ decreased by 10%. Although, our

lower estimate of deposition also results in a lower baseline estimate of atmospheric inputs to the watershed (27,764 kg N yr^{-1}) compared to Valiela and Bowen's (2002) estimate of 64,400 kg N yr^{-1} which is based on deposition rate of 10-15 kg N ha^{-1} yr^{-1}, the additional 3,474 kg N yr^{-1} (if the 0-10 m margin is used) to 6,820 kg N yr^{-1} (if the 0-50 m margin is used) results in a relative increase of atmospheric inputs to the watershed of 13-25% compared inputs based on our deposition rate of 5.1 kg N ha^{-1} yr^{-1}).

Our results indicate that roads are hotspots of N deposition, which if not considered, can underestimate N deposition in urban areas and suburban areas with a high road density. Our estimates of the importance of roadside deposition in the entire Waquoit Bay watershed indicate that by not considering the effects of increased gaseous N deposition from mobile sources we are underestimating the amount of N deposition to the watershed by 13% (±2% at 95% confidence limits) if the 10 meter deposition gradient is used to 25% (±5% at 95% confidence limits) if the 50 meter gradient is used.

Although a portion of the N that is deposited within the watershed is exported to the estuary a portion is also retained due to either uptake by plants and microbes or lost due to denitrification. Our estimates of retention across our transect ranges from 58 - 73%, which is similar to the 62% that Lajtha et al. (1995) estimated for the Waquoit Bay watershed when they used throughfall to estimate N inputs. Although the differences that we measure in retention across our gradient are not significant we did measure higher deposition and leaching near the road compared the forest interior both of which are likely to have an impact especially in coastal watersheds with significant development and sandy, well drained soils such as those along the Atlantic coast where N retention is already lower and increased N has a direct impact on coastal eutrophication (Howarth 1988; Howarth & Marino 2006, Howarth et al. 2011).

Conclusions

Roads are overlooked as hotspots of N deposition in the landscape, and elevated N deposition near roads is largely the result of mobile source N emissions. In our study, deposition 10 m from roads was more than twice as great as deposition well away from areas uninfluenced by roads, and most of the elevated deposition occurred within the first 50 - 100 m from roads. Nonetheless, it is important to note that although NH_3 is a larger portion of the deposition due to its having a higher deposition velocity and that it has been increasing because of the introduction of catalytic converters, currently most of the emissions from mobile sources are not deposited near the roadway, particularly for NO_x emissions (Cape et al. 2004). Understanding the impact of mobile source emissions is especially important in urbanized and suburban areas like the northeastern US where vehicles account for over 50% of total NO_x emissions (Butler et al. 2005).

In the US, there are 6.3 million km of roads (Watts et al. 2007), which fill the landscape so fully that ~20% of the land area in the conterminous US is within 127 meters of a road (Riitters & Wickham 2003). While most of the emissions from all sources are deposited regionally and captured with the current monitoring networks (Holland et al. 2005; Howarth et al. 2002), in certain circumstances such as arid or semiarid sites, or areas where clouds or fog are important these networks underestimate deposition. We would add areas near roads to this list highlight that on a local scale, near roads and in urban and suburban areas, more work is needed to estimate transport distances for these gaseous N emissions (especially NH_3) and to assess their impacts. This is especially important when constructing ecosystem N budgets or designing policy to control N loading in N limited coastal areas.

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Table 1. The number of collectors at each distance, the length of the sampling period, and the number of events collected along each of the transects.

Site	Type	Distance (# samplers)	Sampling Period	Number of Events
WHRC	Bulk	10 (2), 50 (2), 100 (2)	13 Jul 04 – 15 Aug 04	5
WHRC	Throughfall	10 (4), 50 (2), 100 (4)	13 Jul 04 – 15 Aug 04	5
WBNERR	Bulk	10 (2), 50 (2), 100 (2)	13 Jul 04 – 15 Aug 04	5
WBNERR	Throughfall	10 (4), 50 (2), 100 (2), 150 (2)	13 Jul 04 – 15 Aug 04	5
WB Edge	Bulk	10 (2)	13 Jul 04 – 15 Aug 04	5
WB Edge	Throughfall	10 (2), 50 (2), 100 (2)	13 Jul 04 – 15 Aug 04	5
WHRC	Bulk	10 (2), 100 (2)	28 Jun 05 – 15 Sept 05	6
WHRC	Throughfall	10 (2), 100 (2)	28 Jun 05 – 15 Sept 05	6
WBNERR	Bulk	10 (2), 50 (2), 100 (2)	28 Jun 05 – 15 Sept 05	6
WBNERR	Throughfall	10 (2), 50 (2), 100 (2), 150 (2)	28 Jun 05 – 15 Sept 05	6
WB Edge	Bulk	10 (2)	28 Jun 05 – 15 Sept 05	6
WB Edge	Throughfall	10 (2), 50 (2), 100 (2)	28 Jun 05 – 15 Sept 05	6
WHRC	Bulk	10 (4), 100 (4)	12 Jul 06 – 6 Sept 06	9
WHRC	Throughfall	10 (4), 50 (2), 100 (4)	12 Jul 06 – 6 Sept 06	9
WBNERR	Bulk	10 (4), 50 (4), 100 (4)	12 Jul 06 – 6 Sept 06	9
WBNERR	Throughfall	10 (4), 50 (4), 100 (4), 150 (4), 300 (4)	12 Jul 06 – 6 Sept 06	9
WB Edge	Bulk	10 (4)	12 Jul 06 – 6 Sept 06	9
WB Edge	Throughfall	10 (4), 50 (4), 100 (4)	12 Jul 06 – 6 Sept 06	9
WBNERR	Bulk	10 (3), 50 (3), 100 (3)	12 Jul 06 – 6 Jul 07	38
WBNERR	Throughfall	10 (4), 50 (4), 100 (4), 150 (4)	12 Jul 06 – 6 Jul 07	38

Table 2. ANOVA results for comparisons of bulk and throughfall at the road (WHRC and WBNERR) and non –road (WB Edge) sites.

ANOVA results for bulk DIN x site (WHRC, WBNRR, WB Edge)

Source	*SS*	*df*	*MS*	*F*	*Sig.*
Between	0.25	3	0.12	0.88	0.422
Within	6.20	44	0.14		
Total	6.45	46			

ANOVA results for bulk TDN x site (WHRC, WBNRR, WB Edge)

Source	*SS*	*df*	*MS*	*F*	*Sig.*
Between	0.86	2	0.43	2.57	0.087
Within	7.38	44	0.17		
Total	8.24	46			

ANOVA results for throughfall DIN x site (WHRC, WBNRR, WB Edge)

Source	*SS*	*df*	*MS*	*F*	*Sig.*
Between	3.32	2	1.66	12.41	< .0001
Within	11.63	87	0.13		
Total	14.95	89			

ANOVA results for throughfall TDN x site (WHRC, WBNRR, WB Edge)

Source	*SS*	*df*	*MS*	*F*	*Sig.*
Between	14.92	2	7.46	31.81	< .0001
Within	20.40	87	0.24		
Total	35.32	89			

ANOVA results for throughfall DON x site (WHRC, WBNRR, WB Edge)

Source	*SS*	*df*	*MS*	*F*	*Sig.*
Between	4.16	2	2.08	19.88	< .0001
Within	9.11	87	0.11		
Total	13.27	89			

Table 3: Average daily throughfall TDN and DIN inputs (± Standard Error) for measurements made during summer months in 2004, 2005, and 2006 for plots along non-road and roadside transects.

Site	Distance	TDN (mg N m^{-2} day^{-1})	DIN (mg N m^{-2} day^{-1})
WBNERR non-road edge	10 m (n = 8)	1.2 (0.1)	0.7 (0.1)
	50 m (n = 8)	1.3 (0.1)	0.7 (0.1)
	100 m (n = 8)	1.3 (0.1)	0.7 (0.1)
WBNERR roadside edge	10 m (n = 10)	2.5 (0.1)	1.4 (0.1)
	50 m (n = 8)	1.9 (0.1)	1.1 (0.1)
	100 m (n = 8)	1.7 (0.1)	0.9 (0.1)
	150 m (n = 8)	1.8 (0.1)	0.8 (0.1)
	300 m (n = 6)	1.5 (0.1)	0.6 (0.1)
WHRC roadside edge	10 m (n = 10)	2.6 (0.2)	1.5 (0.2)
	50 m (n = 6)	2.5 (0.3)	1.1 (0.3)
	100 m (n = 10)	2.0 (0.1)	1.0 (0.1)
ANOVA		$F(2, 87) = 31.81$, $p = <.0001$	$F(2, 87) = 12.41$, $p = <.0001$

Table 4. Composition of the TDN inputs for measurements made during summer months in 2004, 2005, and 2006 for plots along non-road and roadside transects.

Site	Distance (m)	% DON	se	% NH_4^+	se	% NO_3^-	se
Bulk	10-100	20.3	1.6	33.0	0.8	46.7	1.3
WBNERR non-road edge	10	45.6	4.2	14.9	1.1	39.6	3.4
	50	48.0	5.0	16.2	0.8	35.8	4.8
	100	47.7	2.1	12.6	1.5	39.7	3.1
WBNERR roadside edge	10	42.9	1.9	19.6	1.3	37.5	2.2
	50	44.3	4.9	17.5	1.3	38.3	3.9
	100	47.2	5.5	14.4	1.4	38.4	4.6
	150	55.2	4.8	12.3	1.4	32.5	5.3
WHRC roadside edge	10	42.6	3.7	21.7	2.3	35.7	4.2
	50	51.1	6.2	15.8	1.7	33.1	5.2
	100	53.1	2.9	17.0	0.9	29.9	2.9

Table 5: Annual deposition and leaching of TDN and retention (± Standard Error, n = 4) along WBNERR roadside transect. Means of throughfall and leaching with different letters are significantly different *(Tukey's Honestly Significant Difference test* a = 0.05).

Distance (meters)	Deposition TDN - kg N ha^{-1} yr^{-1}	Leaching TDN - kg N ha^{-1} yr^{-1}	Retention
10	8.7 (0.4)^{A}	3.7 (0.5)^{A}	58% ^{A}
50	6.2 (0.2)^{B}	1.7 (0.2)^{B}	73% ^{A}
100	6.2 (0.1)^{B}	2.0 (0.2)^{B}	69% ^{A}
150	6.8 (0.5)^{B}	1.8 (0.5)^{B}	73% ^{A}
ANOVA	*F(3,12) = 13.02, p = 0.0004*	*F(3,12) = 6.30, p = 0.008*	*F(3,12) = 2.17, p = 0.1451*

Figure Legends

Figure 1: Map study area on Cape Cod in Massachusetts showing the road and non-road study sites and the Waquoit bay watershed.

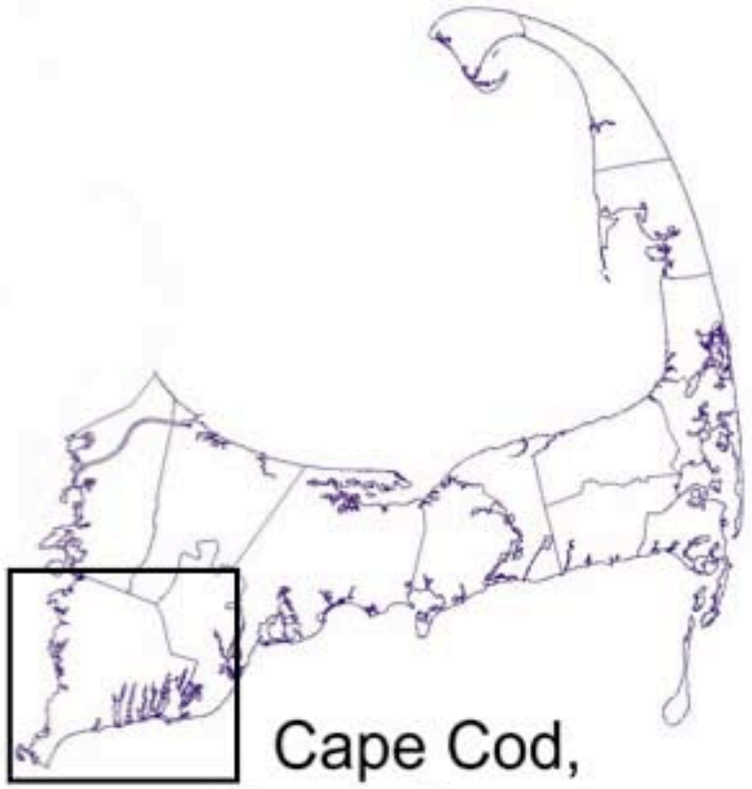
Figure 2: Total throughfall inputs (mg TDN - N m^{-2}) (±SE) for each event from Jul 2006 – Jul 2007 along WBNERR road site transect at 10 m (red), 50 m (yellow), 100 m (white), and 150 m (green).

Figure 3: Total throughfall inputs (mg TDN - N m^{-2} day^{-1}) (±SE) along transects at the non-road edge (A), the WBNERR road site (B), and the WHRC road site (C) with the average bulk input of TDN of all sites (1.3 mg N m^{-2} day^{-1} ± 0.1 SE) shown as a dashed line. Values are the average of samples taken in the summers of 2004, 2005, and 2006.

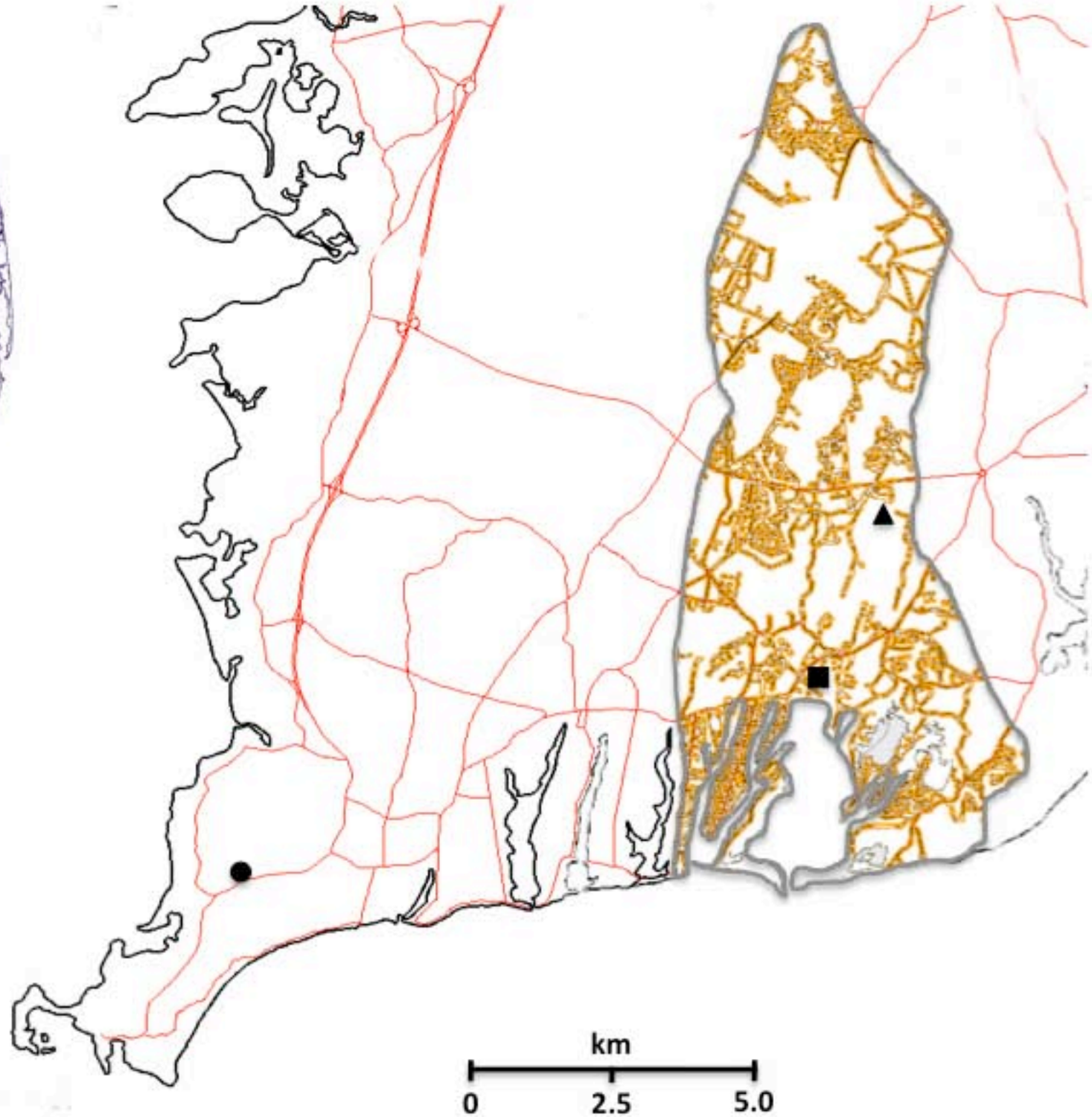
Figure 4: Inorganic throughfall inputs (mg DIN - N m^{-2} day^{-1}) (±SE) along transects at the non-road edge (A), the WBNERR road site (B), and the WHRC road site (C) with the average bulk input of DIN of all sites (1.1 mg N m^{-2} day^{-1} ± 0.1 SE) shown as a dashed line. Values are the average of samples taken in the summers of 2004, 2005, and 2006.

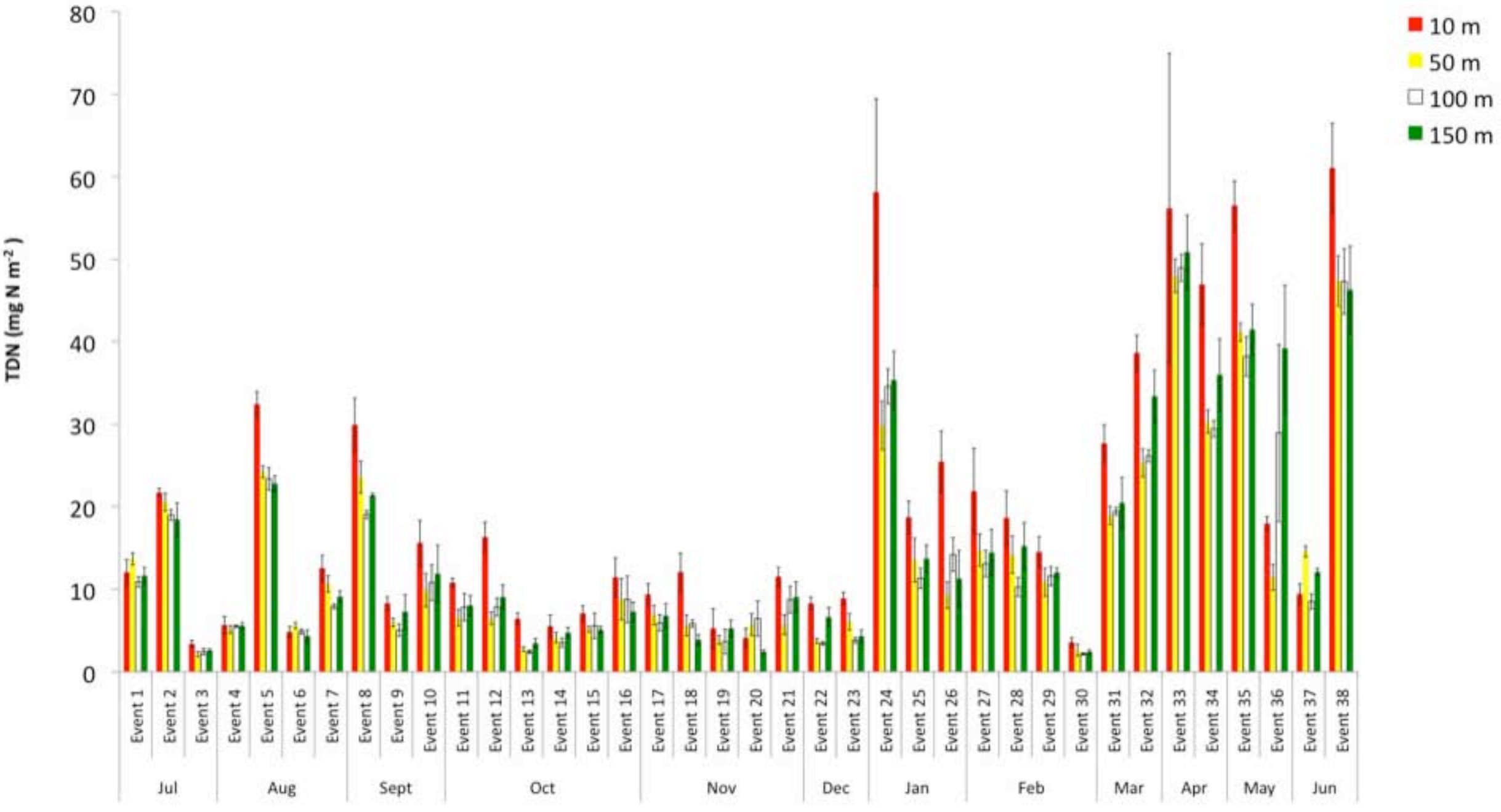
Figure 5: Graph of nitrate leaching (± SE, n = 17 at 10 m, 13 at 25 m, 11 at 50 m, and 8 at 100 m) along transects perpendicular to 17 different roads in the Waquoit Bay watershed measured with ion exchange resins (IER).

Figure 6: Graph of percent change of NH_4^+ in the throughfall TDN measurements made in plots along Waquoit Bay road transect from 2004-2006.



Cape Cod,
Massachusetts




TDN (mg N m-2)
80
70
60
50
40
30
20
10
0
10 m
50 m
100 m
150 m
Event 1
Event 2
Event 3
Event 4
Event 5
Event 6
Event 7
Event 8
Event 9
Event 10
Event 11
Event 12
Event 13
Event 14
Event 15
Event 16
Event 17
Event 18
Event 19
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Event 33
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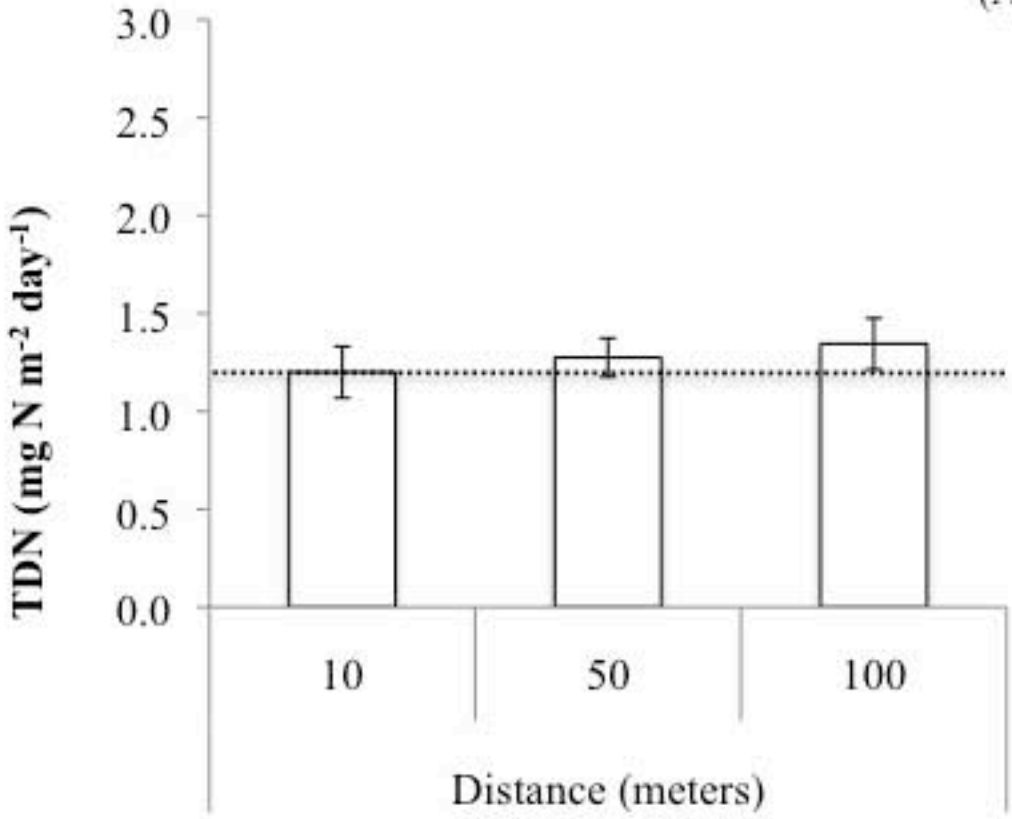
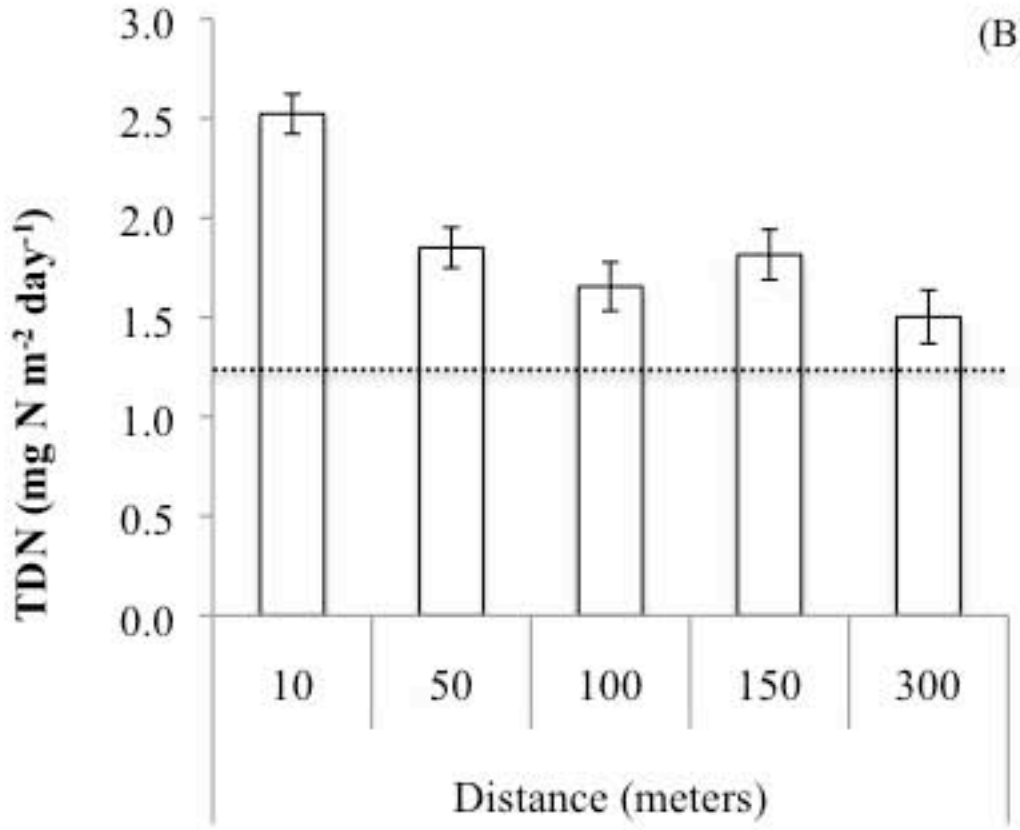
May
Jun

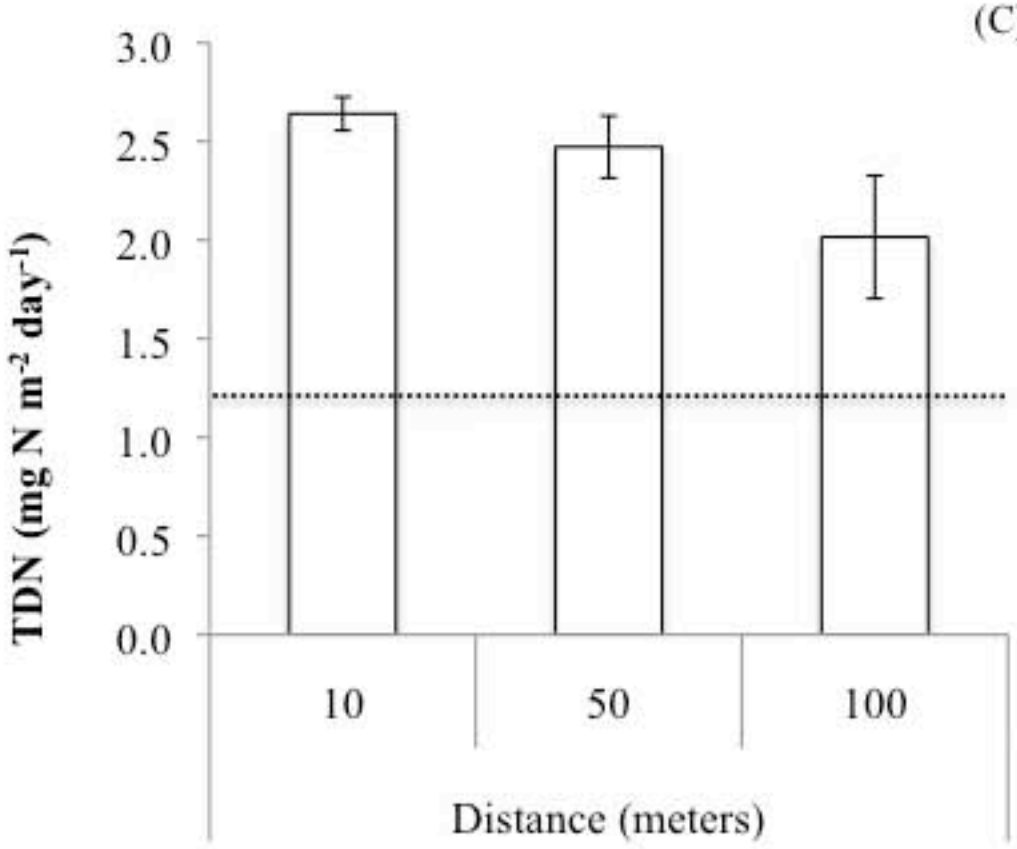
(A)


3.0
2.5
2.0
1.5
1.0
0.5
0.0
TDN (mg N m-2 day-1)
10
50
100
Distance (meters)

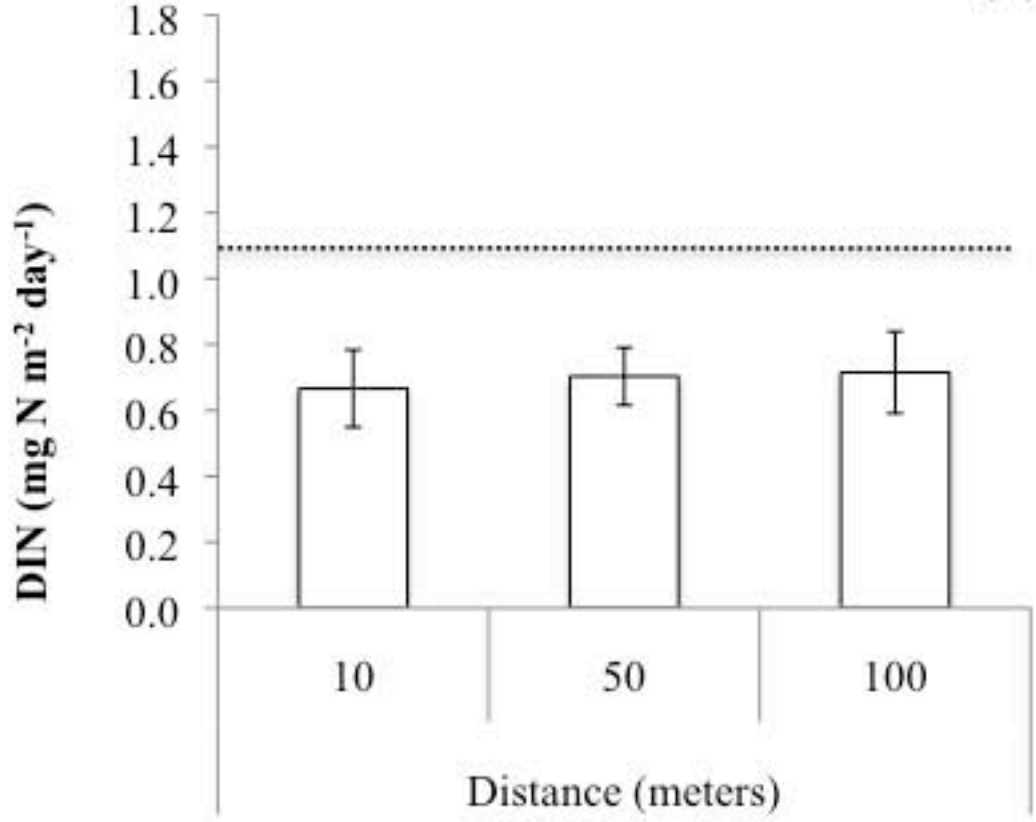
(B)


3.0
2.5
2.0
1.5
1.0
0.5
0.0
TDN (mg N m-2 day-1)
10
50
100
150
300
Distance (meters)

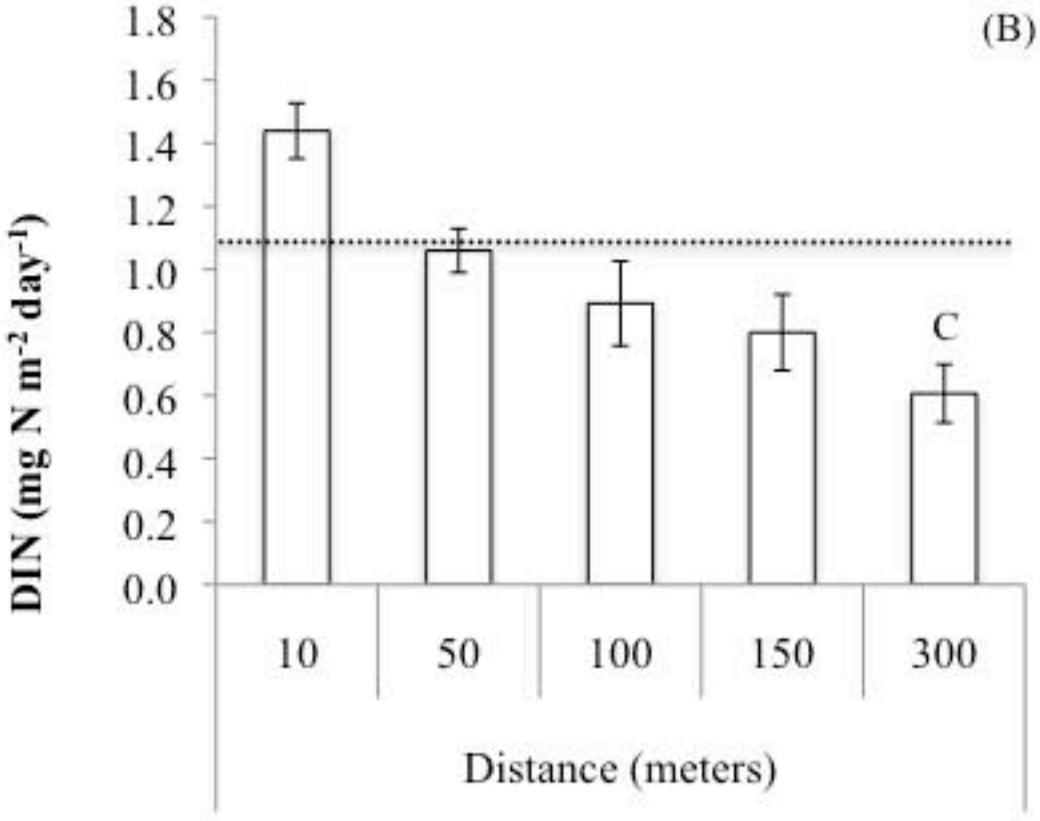
(C)


3.0
2.5
2.0
1.5
1.0
0.5
0.0
TDN (mg N m-2 day-1)
10
50
100
Distance (meters)

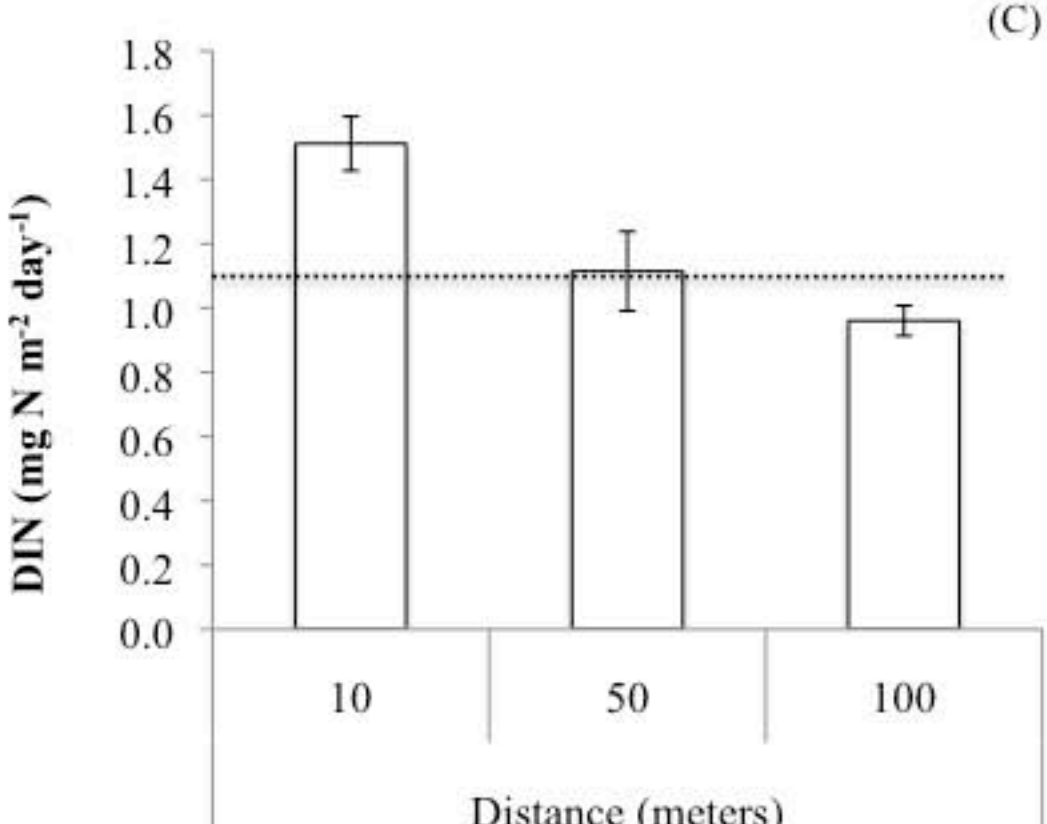
(A)

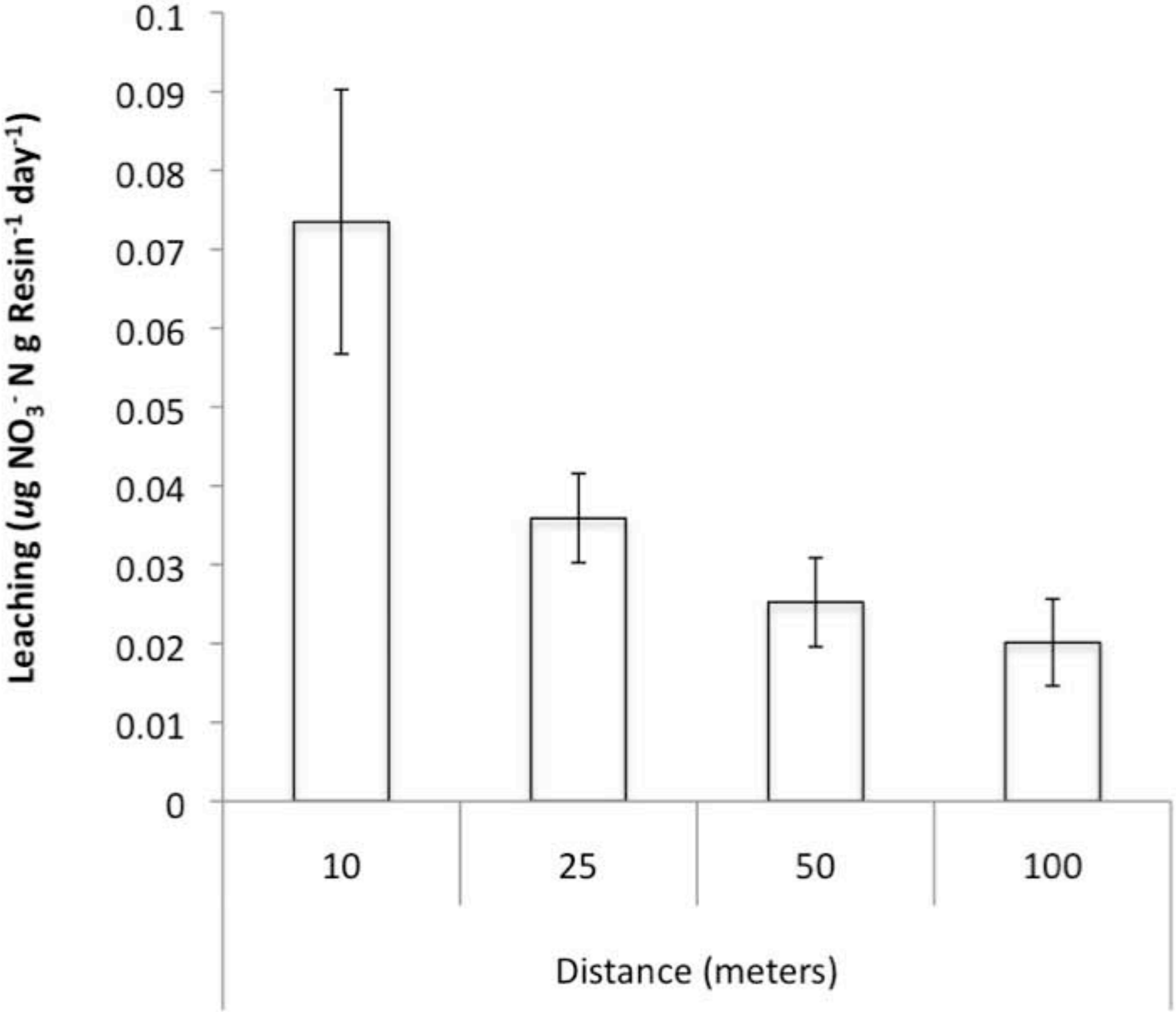

DIN (mg N m-2 day-1)
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
10
50
100
Distance (meters)

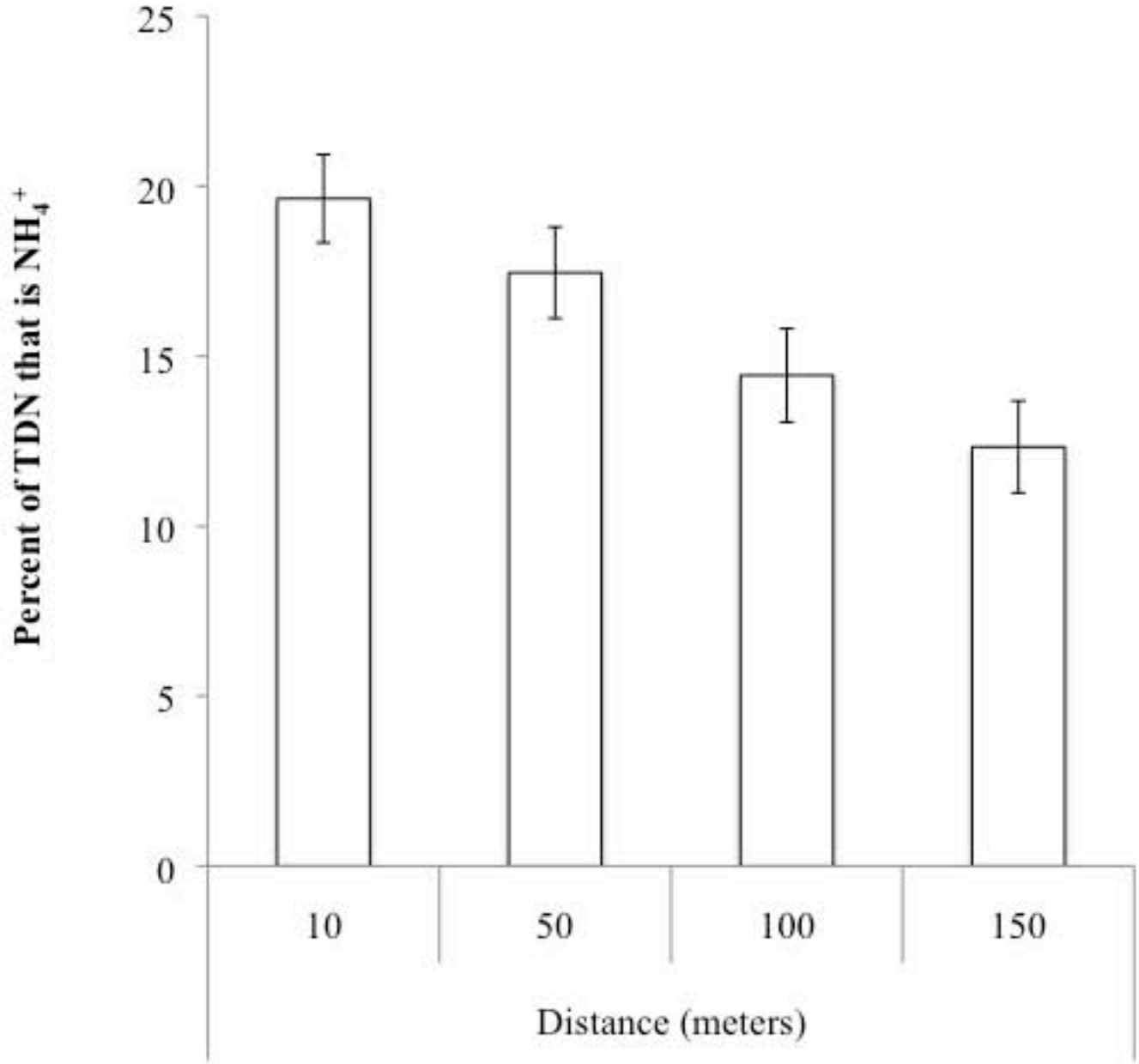
(B)


DIN (mg N m-2 day-1)
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
C
10
50
100
150
300
Distance (meters)

(C)


DIN (mg N m-2 day-1)
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
10
50
100
Distance (meters)


Leaching (ug NO3- N g Resin-1 day-1)
0.1
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
10
25
50
100
Distance (meters)


Percent of TDN that is NH_4^+
25
20
15
10
5
0
10
50
100
150
Distance (meters)