

IMPACTS OF CHRONIC LOW LEVEL NITROGEN DEPOSITION ALONG A
ROADSIDE DEPOSITION GRADIENT ON FOREST AND ESTUARINE N
LOADING

A Dissertation

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by

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Cornell University 2009

Despite large reductions in the emission rates of individual vehicles, mobile source NO_x emissions, which have increased by 33% since the Clean Air Act amendments of 1970, are the single largest source of nitrogen (N) emissions in the US. It is likely that a portion of these 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 precipitation chemistry and dry deposition. With this research, I address whether there is increased deposition near roadways. If so, is it due to near-source deposition of mobile source emissions or is it due to an edge effect? How much additional N is deposited, and how long is the gradient away from the roadway? What is the impact of this chronic N deposition on forest ecosystem processes such as decomposition and N retention, and what is the potential flux to downstream aquatic ecosystems? Near-source deposition of mobile source emissions results in the formation of deposition gradients away from roadways. These gradients are short, less than 150 meters, and steep, with most of the elevated deposition occurring within the first 10-50 meters. Deposition near the road (10 meters) is 1.5-2 x that of areas farther away (150 meters) from the road. This increased deposition was not due to an edge effect and is due to near-source deposition of mobile source emissions. This deposition has likely been occurring for decades, causing changes in

decomposition (-15%), leaching (~2x), forest floor C:N (-5.3 units), and pH (-0.41 units) in sites near the road compared with sites farther away.

BIOGRAPHICAL SKETCH

Neil Bettez was born and raised in West Warwick, Rhode Island. Because he couldn't imagine sitting at a desk, he enrolled in the Forestry Program at the University of New Hampshire. Although he enjoyed forestry, especially the applied aspect of it, after a single lecture on ecosystem ecology in a botany course he knew he wanted to be an ecosystems ecologist. He spent the following summer at Hubbard Brook in the Research Experience for Undergraduates (REU) program, after which he knew he wanted to do research. After graduating he wanted more experience, especially in aquatic ecology, so he sent letters to scientists, whose names he found in the membership directory of the American Society of Limnology and Oceanography, who were doing research that he was interested in and asked whether they knew of any jobs or could offer him any advice. Neil received many responses offering advice and encouragement, as well as a job offer. As an aside, many years later, as he looks over the names of the researchers who took the time to respond to his letter, he is struck that the majority of them came from scientists who were the leaders in their fields. While he is amazed and impressed that they took the time and effort to respond to his letter, he is not surprised that they are the leaders in their fields. The job Neil was offered was working for Parke Rublee at UNC Greensboro investigating microbial food webs in Arctic lakes. After a summer in the Arctic Neil was hooked; he then spent the next 12 summers (13 in all) at Toolik Lake, first as a graduate student, then as a research assistant on the Arctic LTER at the Ecosystems Center in Woods Hole. Although Neil loved the Ecosystems Center and the Arctic, he eventually decided to return to school and entered the PhD program at Cornell. By chance, his advisor, Robert Howarth, had just gotten a grant funded to investigate near-source atmospheric deposition from vehicle exhaust as a nitrogen source to coastal lagoons and asked whether he was interested in working on Cape Cod. Neil received an NSF Earth

Sciences Postdoctoral Research Fellowship to work with Peter Groffman at the Cary Institute of Ecosystem Studies investigating the contributions of mobile source emissions to watershed N budgets along an urban-to-rural gradient at the Baltimore LTER.

I dedicate this work to my parents, Dennis and Louise, for always valuing education and instilling in me a belief that I could accomplish anything I wanted in life; and to my brothers, Erik and Ryan, and their families (Nancy, Natalie, Michaela, Alexandra, Camden, Erin, Margaret, Liam, Brendan, Katherine), for their many trips to Ithaca and their willingness to help out in any way.

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I would like to thank my advisor, Robert Howarth, for giving me the opportunity to be part of a wonderful project and a member of a fantastic lab group. I owe thanks to the members of my committee, Gary Lovett, Christine Goodale, and Jed Sparks, as well as Roxanne Marino, Thomas Butler, and Eric Davidson, with whom I have had many helpful discussions during this study. I would also like to thank Katerina Bulygina, Wendy Kingerlee, and Kathleen Savage for technical assistance in the laboratory; Richard Wilson and Mohammed Pervaiz, for help in the field; and Tom Stone for all his work on the GIS. I could never have done it without all your help.

This work would not have been possible without funding from Woods Hole SeaGrant (grant NA06OAR4170021), small grants from the BEB IGERT (NSF IGERT grant DGE 0221658), an Edna Bailey Sussman Environmental Internship Award from Cornell University, and a Mellon Foundation award through Cornell University. I would also like to acknowledge the generosity of the Waquoit Bay and for Estuarine Research Reserve, for allowing us to use their research site; the Woods Hole Research Center, for allowing us the use of their property and analytical

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I would also like to thank my fellow students in the Biogeochemistry and Biocomplexity program at Cornell for their friendship and support throughout my time at Cornell. A special thanks to Julie and Dana, who have helped me more in the last year than they will ever know. Finally, I would like to thank Gretchen Gettel, a world-class researcher and friend. I never could have done it without you.

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CHAPTER 1:

THE ROLE OF MOBILE SOURCES EMISSIONS ON N BUDGETS: WHAT ECOLOGISTS NEED TO KNOW?

Anthropogenic activities are transforming the global nitrogen (N) cycle more rapidly than that of any other element (Vitousek et al. 1997). Although fertilizer use is the dominant driver of this change globally, in the United States, N emissions from fossil fuel combustion are significant drivers as well (Howarth et al. 2002a). In 2002, 8.5 Tg N were emitted from fossil fuel combustion in the US (US EPA 2005) compared to 11.0 Tg N applied as inorganic fertilizer (IFA 2008). However, while the majority of fertilizer application occurs in farms in the Mississippi drainage across the mid-west, the N emitted from the fossil fuel combustion is added to the landscape via dry and wet deposition (collectively “N deposition”) throughout the US especially in the northeastern US and other heavily populated areas where it is the largest source of N (Howarth et al. 2002a, Howarth et al. 2002b).

While the excess N due to overuse of fertilizer has been shown to be a significant cause of coastal eutrophication especially in the Gulf of Mexico (Howarth et al. 2000), the N emissions that are the result of from fossil fuel combustion in addition to having an impact air quality have serious environmental consequences when deposited onto the landscape. These emissions have been shown to contribute to the declining health of forests and lakes because of acid rain (Driscoll et al. 2003) and the eutrophication of coastal rivers and estuaries because of increased N loading (Howarth et al. 2000).

Although N (NO_x and NH_3) is emitted during all types of combustion, from electrical generation to forest fires, this paper focuses on emissions from mobile sources such as highway vehicles (cars and trucks) and off-highway vehicles

(construction equipment, planes, boats, etc.). Mobile sources are the single largest source of N emissions in the US, accounting for 46% of the total emissions of NH_3 and NO_x (Figure 1.1) (US EPA 2005). Over the last three decades, mobile sources have played an increasingly important component of the N emission inventories of the US with their percentage of total NO_x emissions increasing from 45-60%. This switch in the dominant source of NO_x emissions, from fuel combustion (Electrical, Industrial, other) to mobile sources over the last 30 years is due to emissions from mobile sources having increased by ~ 33%, while those from stationary sources have decreased by ~29% (Figure 1.2) (US EPA 2008a). This is clearly seen in the eastern US where although there have been relatively small overall changes in total NO_x emissions between 1991 and 2000, decreases in NO_x emissions from the non-vehicle sectors were offset by increases from the vehicle sector (Butler et al. 2003). This increase in mobile source emissions, which has occurred despite a decline in the emission rates of individual vehicles since the enactment of the Clean Air Act (CAA) amendments of 1970, is due to the number of miles driven each year having more than doubled in the last 30 years to more than 3 trillion miles driven annually (Figure 1.3) (FHWA 2008).

Efforts to monitor N deposition were initiated in the 1970's when emissions from stationary sources such as electric utilities and industry were the dominant source of atmospheric N and monitoring stations were established to capture regional trends in deposition from these stationary sources. However, with the increasing importance of mobile sources, especially in urban areas, the current monitoring network may miss a portion of the N deposition both because of where the sites are located and what they measure. Therefore, it is increasingly important to understand the significance of mobile source emissions when designing monitoring networks to measure N inputs and when attempting to implement effective policy in order to control the impact of increased N loading on terrestrial and aquatic systems. This paper summarizes how

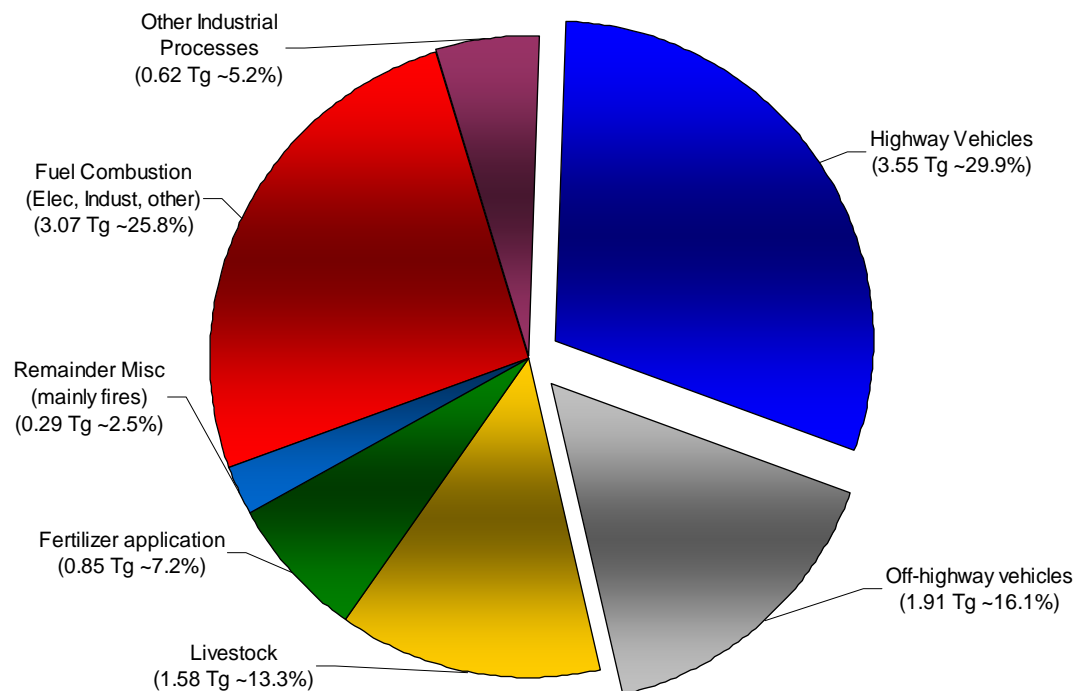


Figure 1.1. 2002 US N emissions (US EPA 2005). In 2002 mobile sources such as highway vehicles (trucks, cars) and off-highway vehicles (construction equipment, planes and boats) are the single largest source of nitrogen (NO_x –N and NH_3 –N) emissions in the US followed by fuel combustion 25.8%, emissions from livestock (13.3%), and fertilizer application (7.2%) (US EPA 2008).

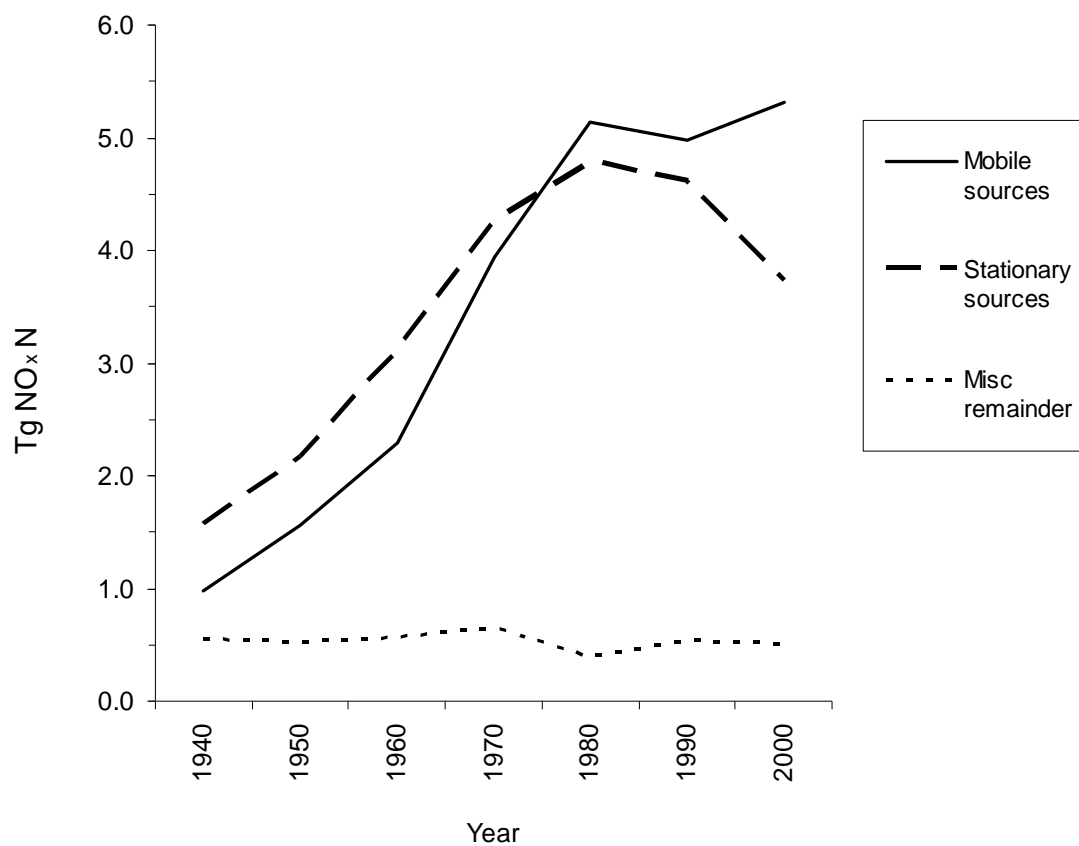


Figure 1.2. US emissions of NO_x –N from 1940 – 2000 from stationary sources (fuel combustion for electric utilities, industrial, and other) and mobile sources (highway vehicles and off highway vehicles) and miscellaneous remainder (other industrial procedures, petroleum and related industries, miscellaneous industries) (US EPA 2008).

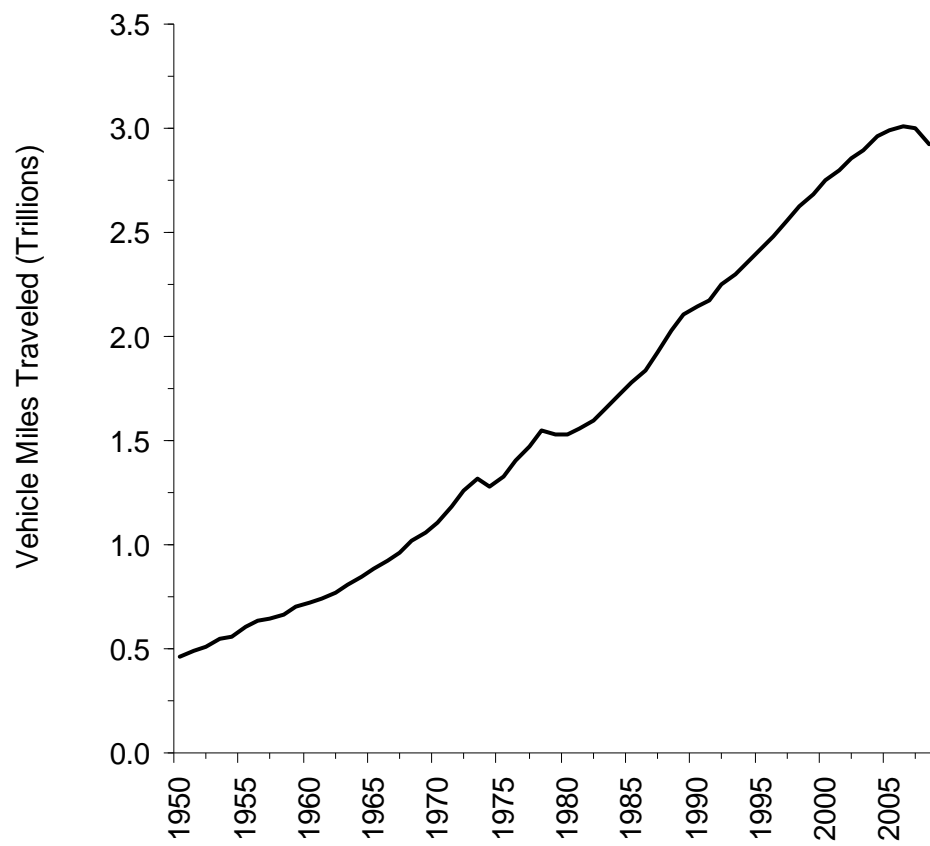


Figure 1.3. US Vehicle miles traveled (VMT) 1950- 2008 (FHWA 2008).

mobile source N emissions are formed and how changes in the way they have been controlled may have implications both for how these emissions are monitored and their environmental impact.

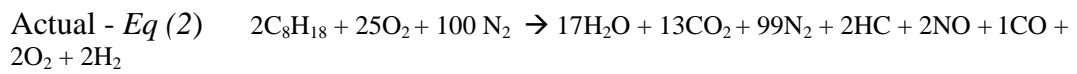
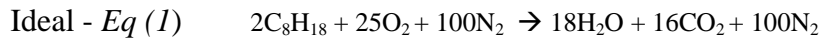
How Emissions Are Formed

Knowledge of the different forms of biologically reactive N that are formed and emitted by mobile sources is crucial to understanding their local and regional deposition trends. Mobile source emissions are the result of processes that occur during combustion as well as those that occur during the emission control process. During combustion in air (~78% N₂ and ~20% O₂), the carbon atoms within the hydrocarbon (HC) fuels are oxidized in the presence of oxygen to produce energy, CO₂, and H₂O (Figure 1.4, Eq 1). However, under the high temperature and pressure found in internal combustion engines, the N₂, which is normally an un-reactive form of N, is also oxidized, thus producing a reactive form of N (nitric oxide, NO) which is quickly oxidized to form nitrogen dioxide (NO₂). The two are collectively known as NO_x (Figure 1.4, Eq 2). Although pollutants such as CO, HC, and NO_x are only a small percentage (~1%) of the total emissions produced by automobiles, all three have serious impacts on human health and the environment and therefore have been the target of emission control efforts for several decades during which time standards have become progressively more stringent.

Mobile source emission standards for HC and CO were first established by the federal government in 1968, with an amendment to the CAA, titled the Motor Vehicle Pollution Control Act of 1965. Further reductions along with emission standards for NO_x were then mandated with successive amendments to the CAA in 1970, 1977, and 1990 (Table 1.1). The principal method for controlling emissions has been the catalytic converter, primarily the three-way catalytic converter which was introduced

in 1981 and has been mandatory for every vehicle sold in the US since 1983. Three-way converters use noble metals such as platinum, palladium, rhodium, and iridium to catalyze the oxidation of HC, and CO, to CO_2 and H_2O and reduction of NO_x to N_2 . The simultaneous removal of all three pollutants is only possible on modern vehicles because oxygen sensors and electronic fuel injection systems allow the air to fuel mixture to be continually adjusted, enabling engines to be operated under stoichiometrically ideal operating conditions of $\sim 14.6:1$ meaning that ~ 14.6 liters of air are used to combust 1 liter of fuel (Bhattacharyya and Das 1999). When vehicles are operated outside of this range, emissions of all three pollutants increase. Although vehicles sometimes operate outside of their stoichiometrically correct range due to mechanical problems (i.e., oxygen sensor feedback loop not working properly, engine timing problems), properly operating vehicles often operate outside of this range under everyday driving conditions such as stop-and-go traffic. For example, when vehicles are starting, accelerating, or decelerating there are intermittent changes in the air:fuel ratio. During deceleration, which causes lean air:fuel mixtures (i.e., more air in relation to fuel) more NO_x is output, because it is more difficult to reduce NO to N_2 in the presence of O_2 (Baum et al. 2000). Conversely, under fuel-rich conditions, which occur during acceleration and during start up, emissions of HC and CO increase because of incomplete combustion and because it is more difficult for oxidation to occur under the reducing conditions caused by fuel-rich mixtures. In addition to increases of HC and CO when vehicles are operated under rich air:fuel ratios, a secondary pollutant NH_3 , is formed in the catalytic converter due to NO reacting with excess H_2 (which is the result of either a water gas shift reaction of CO and H_2O or from steam reforming of hydrocarbons and H_2O (Baum et al. 2000, Heeb et al. 2006)).

Combustion



Emission Control

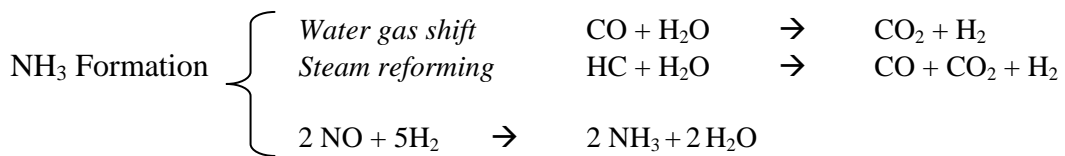
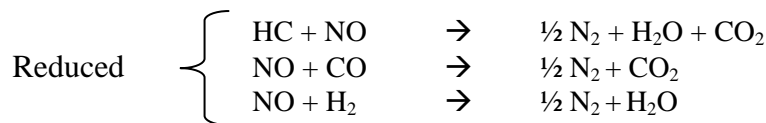
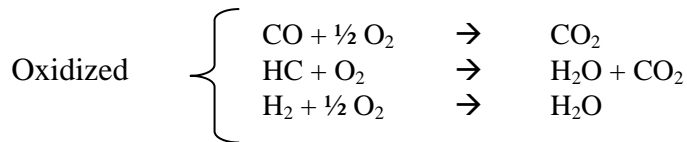


Figure 1.4. During combustion and subsequent emission control several forms of reactive N (NO and NH₃) are formed as a result of oxidation during the combustion process and over reduction in the catalytic converter.

Table 1.1. The CAA amendments of 1970 required that by 1976 manufacturers reduce the 1971 NO_x emissions from light duty vehicles (LDV), mainly passenger cars, and light duty trucks (LDT) pickup trucks and SUVs by 90%. The CAA amendments of 1977 subsequently extended the deadline until 1982 and decreased the reduction to 75% (i.e., emission standards were increased from 0.4 to 1.0 g/mi). In 1990, the Clean Air Act was again amended, with the goal of reducing NO_x emissions by 95 - 99% by 2004 compared with emissions of 1967 model-year vehicles for LDV and LDT respectively. Mandated emission reductions or Tiers were phased in over time with Tier 1 beginning in 1994 and Tier 2 beginning in 2004. Under Tier 2, instead of basing emissions on the weight of individual vehicles as it was previously done, standards were divided into “bins,” and manufacturers were allowed choose (with some weight limitations) among bins, as long as the average of all the vehicles sold each model year was below 0.07 g mi⁻¹ (Bin 5).

Legislation	Category	Model Year	NO _x (g mile ⁻¹)		NO _x N (mg km ⁻¹)	
			LDV	LDT	LDV	LDT
CAA of 1970		1973 – 1974	3	3	870	870
		1975 – 1976	3.1	3.1	899	899
		1977 – 1978	2	3.1	580	899
		1979 – 1980	2	2.3	580	667
CAA of 1977	Tier 0	1981 – 1987	1	2.3	290	667
		1988 – 1993	1	1.2	290	348
CAA of 1990	Tier 1	1994-2003	0.6	0.6	174	174
	Tier 2 - Bin 1	2004 -	0		0	
	Tier 2 - Bin 2	2004 -	0.02		5.8	
	Tier 2 - Bin 3	2004 -	0.03		8.7	
	Tier 2 - Bin 4	2004 -	0.04		11.6	
	Tier 2 - Bin 5	2004 -	0.07		20.3	
	Tier 2 - Bin 6	2004 -	0.01		2.9	
	Tier 2 - Bin 7	2004 -	0.15		43.5	
	Tier 2 - Bin 8	2004 -	0.2		58.0	

Overall, catalytic converters have been very effective. Compared with emissions of 1967 model-year vehicles, catalytic converters have decreased the per-mile-exhaust of regulated emissions of 2004 model-year vehicles by 95-99% (NRC 2004). However, these reduction estimates do not include NH₃ which, although not regulated, has been found in very high levels in the exhaust of gasoline-powered cars, especially in urban areas such as California’s southern coastal basin where mobile sources have been estimated to be adding twice as much ammonia to the air as

livestock (Baum et al. 2001). The few studies that have measured the amount of N being emitted as NH_3 find that, although emissions can vary depending on the type of vehicle and type of driving, the average emission factors range from 22-28 mg $\text{NH}_3 - \text{N km}^{-1}$ (Durbin et al. 2002, Emmenegger et al. 2004, Heeb et al. 2006, Heeb et al. 2008), which is equivalent to the current fleet average Tier 2 NO_x emissions (see Table 1.1 Bin 5). Although emissions have gone down considerably, a significant portion (~50%) of the current emissions are now occurring as NH_3 . Ammonia differs considerably from NO_x in its effect on the atmosphere and the environment once it is deposited.

Implications of Emissions

Emissions of NO_x and NH_3 have implications for both ecosystem and human health. When N is emitted as NO_x , it can be deposited as dry deposition, it can dissolve in water to form nitric acid (HNO_3 , a component of acid rain which is one of the main pollutants responsible for acidification and pollution in terrestrial and aquatic ecosystems), or in the presence of sunlight it can combine with volatile organic compounds (VOCs) to produce an array of photochemical products, including ozone which has human health effects. If the N is emitted as NH_3 , it can be deposited as dry deposition, or it can stimulate the formation of secondary particulate matter in the atmosphere which occurs when NH_3 reacts with nitric, sulfuric, or phosphoric acid to produce fine particle ammonium nitrate, ammonium sulfate, or ammonium phosphate, which are submicrometer airborne particles that are responsible for a smoglike haze and can have both environmental effects due to light scattering and cloud formation as well as health problems (Manahan 1993). In the atmosphere, NH_3 is a base and neutralizes the acidity of other aerosols. Once it is deposited, it ionizes to NH_4^+ and is either taken up by plants or nitrified (oxidized) by bacteria, both of which cause

acidification with detrimental effects on terrestrial and aquatic systems (Galloway et al. 1995). Although the different forms of N have different effects in the atmosphere depending on their reactant, they are eventually deposited (within hours to days) on the landscape either as wet deposition (NO_3^- and NH_4^+) or dry deposition (gaseous NH_3 and HNO_3 , and particulate NO_3^- and NH_4^+). The amount of dry deposition is a function of several factors including meteorological conditions (temperature, relative humidity), concentration, type of surface, atmospheric turbulence (Wesely and Hicks 2000) as well as the species of N which affects the deposition velocity (the rate of deposition) with $\text{HNO}_3 > \text{NH}_3 = \text{NO}_2 > \text{NO}$ (Hanson and Lindberg 1991). NO_2 can be absorbed in water droplets or oxidized in the gas phase by hydroxyl radicals to form nitrous acid (HONO) as well as nitric acid (HNO_3), which readily sticks to surfaces. This process occurs very rapidly and generally has a lifespan of less than 1 day in the atmosphere. NO_2 can also react with volatile organic carbon (VOC) to form Peroxyacyl nitrate (PAN), which dissociate slowly resulting in long range transport (Manahan 1993).

In the United States, N deposition is measured using several networks of sites: the Clean Air Status Trends Network (CAST/Net) which measures dry deposition at 91 sites (US EPA 2008b); the National Atmospheric Deposition Program National Trends Network (NADP/NTN) which measures wet deposition at 251 sites; and a subset of NADP, the Atmospheric Integrated Research Monitoring Network (NADP/AIRMoN) which measures both wet and dry deposition daily at 12 sites (NAPD 2009). These networks were designed to capture regional, not local deposition patterns. While most of the emissions are carried into the larger atmosphere and deposited broadly across the landscape and thus captured in these regional estimates, some emissions are deposited nearby “near-source deposition” and thus are unaccounted for in the current deposition estimates. This undercounting of deposition

has been documented in several continental scale input/output budgets in which emissions exceed deposition by 20-40% (e.g., Howarth et al. 2002a, Holland et al. 2005). One possible explanation for this mismatch is that none of these networks currently measure gaseous NH_3 . The NADP measures wet NO_3^- and NH_4^+ and CASTNet measures HNO_3 , and particulate NO_3^- and NH_4^+ . Although nearly all forms of NH_x deposition (NH_3 gas, and particulate NH_4^+) are due to NH_3 emissions, the species (gaseous or particulate) collected is related to the proximity of the collectors to the emission source; NH_3 has a high deposition velocity and is usually deposited as dry deposition near the source, while wet and particulate NH_4^+ are deposited farther away (Asman et al. 1998). These networks, which were set up to monitor long-term regional trends in precipitation chemistry and dry deposition, were specifically located in areas uninfluenced by local pollution sources (Bigelow et al. 2001) and thus are likely missing deposition that is deposited near its emission source (Howarth 2008b, Howarth 2008a).

Recently, the impact of near-source deposition on local N budgets has begun to receive more attention, with numerous studies finding gradients in N deposition away from urban areas (Lovett et al. 2000, Luo et al. 2003). In a study that measured throughfall along an urban to rural gradient, Lovett et al. (2000) found N deposition to be twice as high in New York City than in areas 150 km away from the urban center. Luo et al. (2003) compared deposition measurements from rural and urban sites and found that the land use characteristics surrounding the monitoring sites had profound effects, with significantly higher N concentration and dry deposition flux in urban areas compared to rural areas. Others have highlighted the role of near source deposition of mobile sources in particular. Chiwa et al. (2003) measured higher dry deposition fluxes of N on the urban-facing side of a mountain compared to its non-urban side, which they attributed to mobile sources. On a much finer scale, several

studies have found higher runoff of N from parking lots and roadways, with deposition onto roadways twice as high as deposition measured at nearby NADP sites (Davidson et al. Submitted). A number of studies have investigated gradients in NO_2 , NO , and NH_3 concentrations away from roadways (Roorda-Knape et al. 1998, Gilbert et al. 2003, Cape et al. 2004, Beckerman et al. 2008). These studies have found that the gradients are due to mobile source emissions and that they are relatively short (i.e., Roorda-Knape (1998) found NO_2 decreased to background levels between 100 and 150 meters from a major expressway; Beckerman et al. (2008) measured gradients of 100-500 meters; and although Gilbert et al. (2003) measured gradients up to 1300 meters in length, the majority of the decay occurred within the first 200 meters). Other studies have investigated the effect of these increased gas concentrations and measured gradients in ^{15}N in leaves and tree rings due to uptake of NO from car exhausts (Ammann et al. 1999, Saurer et al. 2004) while others have measured deposition gradients away from roadways that are the result of these mobile source emissions. For example, along heavily traveled freeways in Germany, Kirchner et al. (2005) measured short gradients away from roadways with up to 3x higher NH_3 and NO_2 concentrations and 2x higher N deposition at sites near the highway than at sites 500 meters away. Similar patterns were also found away from even moderately traveled ($\sim 10,200$ vehicles day^{-1}) roads on Cape Cod. Marino et al. (In Prep) found that 10-25% of the NH_3 and 1% of the NO_x emissions from mobile sources were deposited within 50 m of a roadway, and Bettez et al. (Chapter 3) found that the deposition at forest edges alongside roads was elevated over that in the forest interior as well as deposition along non-roadsides edges. These gradients were short, less than 150 meters, with most of the deposition occurring within the first 10-50 meters. This increased deposition (~ 2 x higher along roadside edges than in their interiors) resulted in changes to N cycling with areas that had been receiving higher deposition for

decades having lower forest floor C:N ratios, decreased litter decomposition, and increased N leaching.

There are more than 6.3 million km of roads within the conterminous US. This road network is so extensive that 20% of the land area is within 127 meters of a road (Watts et al. 2007) and it is difficult to be more than 35 km from a road (Riitters and Wickham 2003). While the effects of these roads are on wildlife, due to disruption of migration and noise (Forman 2003) and their influence on nearby terrestrial and aquatic systems, due to increased deposition and runoff of contaminants such as heavy metals and salt (Trombulak and Frissell 2000), are well documented, the impact of near source deposition from mobile sources has received less attention. Mobile sources, despite declines in emissions from individual vehicles, are contributing an increasing amount of N to the environment. Furthermore, as a result of changes in emission control technology (i.e., three way catalytic converters) there have been increases in NH_3 emissions which are not regulated and are more likely to be deposited nearby compared to NO emissions. These changes have implications not only for how emissions are regulated but for how I measure deposition and the impact of transportation and development.

REFERENCES

- Ammann, M., R. Siegwolf, F. Pichlmayer, M. Suter, M. Saurer, and C. Brunold. 1999. Estimating the uptake of traffic-derived NO₂ from N-15 abundance in Norway spruce needles. *Oecologia* **118**:124-131.
- Asman, W. A. H., M. A. Sutton, and J. K. Schjorring. 1998. Ammonia: emission, atmospheric transport and deposition. *New Phytologist* **139**:27-48.
- Baum, M. M., E. S. Kiyomiya, S. Kumar, and A. M. Lappas. 2000. Multicomponent remote sensing of vehicle exhaust by dispersive absorption spectroscopy. 1. Effect of fuel type and catalyst performance. *Environmental Science & Technology* **34**:2851-2858.
- Baum, M. M., E. S. Kiyomiya, S. Kumar, A. M. Lappas, V. A. Kapinus, and H. C. Lord. 2001. Multicomponent remote sensing of vehicle exhaust by dispersive absorption spectroscopy. 2. Direct on-road ammonia measurements. *Environmental Science & Technology* **35**:3735-3741.
- Beckerman, B., M. Jerrett, J. R. Brook, D. K. Verma, M. Arain, A., and M. M. Finkelstein. 2008. Correlation of nitrogen dioxide with other traffic pollutants near a major expressway. *Atmospheric Environment* **42**:275-290.
- Bettez, N. D. Chapter 3. Forest response to chronic low level N deposition along a roadside deposition gradient.
- Bhattacharyya, S., and R. K. Das. 1999. Catalytic control of automotive NO_x: A review. *International Journal of Energy Research* **23**:351-369.
- Bigelow, S. D., S. R. Dossett, and V. C. Bowersox. 2001. Instruction Manual NADP/NTN Site Selection and Installation. National Atmospheric Deposition Program, Champaign, Illinois 61820-7495.
- Butler, T. J., G. E. Likens, F. M. Vermeylen, and B. J. B. Stunder. 2003. The relation between NO_x emissions and precipitation NO₃⁻ in the eastern USA. *Atmospheric Environment* **37**:2093-2104.
- Cape, J. N., Y. S. Tang, N. van Dijk, L. Love, M. A. Sutton, and S. C. F. Palmer. 2004. Concentrations of ammonia and nitrogen dioxide at roadside verges, and their contribution to nitrogen deposition. *Environmental Pollution* **132**:469-478.
- Chiwa, M., N. Oshiro, T. Miyake, N. Nakatani, N. Kimura, T. Yuhara, N. Hashimoto, and H. Sakugawa. 2003. Dry deposition washoff and dew on the surfaces of pine foliage on the urban- and mountain-facing sides of Mt. Gokurakuji, western Japan. *Atmospheric Environment* **37**:327-337.

- Davidson, E. A., K. E. Savage, N. D. Bettez, R. M. Marino, and R. W. Howarth. Submitted. Nitrogen in Runoff from Residential Roads in a Coastal Area.
- Driscoll, C. T., D. Whitall, J. Aber, E. Boyer, M. Castro, C. Cronan, C. L. Goodale, P. Groffman, C. Hopkinson, K. Lambert, G. Lawrence, and S. Ollinger. 2003. Nitrogen pollution in the northeastern United States: Sources, effects, and management options. *Bioscience* **53**:357-374.
- Durbin, T. D., R. D. Wilson, J. M. Norbeck, J. W. Miller, T. Huai, and S. H. Rhee. 2002. Estimates of the emission rates of ammonia from light-duty vehicles using standard chassis dynamometer test cycles. *Atmospheric Environment* **36**:1475-1482.
- Emmenegger, L., J. Mohn, M. Sigrist, D. Marinov, U. Steinemann, F. Zumsteg, and M. Meier. 2004. Measurement of ammonia emissions using various techniques in a comparative tunnel study. *International Journal of Environment and Pollution* **22**:326-341.
- Federal Highway Administration. 2008. Traffic Volume Trends. U.S. Dept. of Transportation Federal Highway Administration, Washington, D.C.
- Forman, R. T. T. 2003. Road ecology: science and solutions. Island Press, Washington, DC.
- Galloway, J. N., W. H. Schlesinger, H. Levy, A. Michaels, and J. L. Schnoor. 1995. Nitrogen-Fixation - Anthropogenic Enhancement-Environmental Response. *Global Biogeochemical Cycles* **9**:235-252.
- Gilbert, N. L., S. Woodhouse, D. M. Stieb, and J. R. Brook. 2003. Ambient nitrogen dioxide and distance from a major highway. *Science of the Total Environment* **312**:43-46.
- Hanson, P. J., and S. E. Lindberg. 1991. Dry Deposition of Reactive Nitrogen-Compounds - a Review of Leaf, Canopy and Non-Foliar Measurements. *Atmospheric Environment Part a-General Topics* **25**:1615-1634.
- Heeb, N. V., A. M. Forss, S. Bruhlmann, R. Luscher, C. J. Saxer, and P. Hug. 2006. Three-way catalyst-induced formation of ammonia-velocity- and acceleration-dependent emission factors. *Atmospheric Environment* **40**:5986-5997.
- Heeb, N. V., C. J. Saxer, A.-M. Forss, and S. Brühlmann. 2008. Trends of NO-, NO₂-, and NH₃-emissions from gasoline-fueled Euro-3- to Euro-4-passenger cars. *Atmospheric Environment* **42**:2543-2554.
- Holland, E. A., B. H. Braswell, J. Sulzman, and J. F. Lamarque. 2005. Nitrogen deposition onto the United States and western Europe: Synthesis of observations and models. *Ecological Applications* **15**:38-57.

- Howarth, R. W. 2008a. Coastal nitrogen pollution: A review of sources and trends globally and regionally. *Harmful Algae* **in press**.
- Howarth, R. W. 2008b. Estimating atmospheric nitrogen deposition in the Northeastern United States: Relevance to Narragansett Bay. Pages 47-65 *in* A. Desbonnet and B. A. Costa-Pierce, editors. *Science for Ecosystem-based Management Narragansett Bay in the 21st Century*. Springer, New York.
- Howarth, R. W., D. M. Anderson, T. M. Church, H. Greening, C. S. Hopkins, W. C. Huber, N. Marcus, R. J. Naiman, K. Segerson, A. N. Sharpley, and W. J. Wiseman, editors. 2000. *Clean Coastal Waters: Understanding and Reducing the Effects of Nutrient Pollution*. National Academy Press, Washington, D.C.
- Howarth, R. W., E. W. Boyer, W. J. Pabich, and J. N. Galloway. 2002a. Nitrogen use in the United States from 1961-2000 and potential future trends. *Ambio* **31**:88-96.
- Howarth, R. W., A. Sharpley, and D. Walker. 2002b. Sources of nutrient pollution to coastal waters in the United States: Implications for achieving coastal water quality goals. *Estuaries* **25**:656-676.
- International Fertilizer Industry Association. 2008. Nitrogen, phosphate and potash statistics. *in* International Fertilizer Industry Association Data Bank. (<http://www.fertilizer.org/ifa/statistics/IFADATA/dataline.asp>).
- Kirchner, M., G. Jakobi, E. Felcht, M. Bernhardt, and A. Fischer. 2005. Elevated NH₃ and NO₂ air concentrations and nitrogen deposition rates in the vicinity of a highway in Southern Bavaria. *Atmospheric Environment* **39**:4531-4542.
- Lovett, G. M., M. M. Traynor, R. V. Pouyat, M. M. Carreiro, W. X. Zhu, and J. W. Baxter. 2000. Atmospheric deposition to oak forests along an urban-rural gradient. *Environmental Science & Technology* **34**:4294-4300.
- Luo, Y. Z., X. S. Yang, R. J. Carley, and C. Perkins. 2003. Effects of geographical location and land use on atmospheric deposition of nitrogen in the State of Connecticut. *Environmental Pollution* **124**:437-448.
- Manahan, S. E. 1993. *Fundamentals of environmental chemistry*. Lewis Publishers, Boca Raton.
- Marino, R., R. W. Howarth, N. D. Bettez, and E. A. Davidson. In Prep.
- National Atmospheric Deposition Program (NRSP-3). 2009. NADP Program Office, Illinois State Water Survey, 2204 Griffith Dr., Champaign, IL 61820.
- National Research Council. 2004. *Air Quality Management in the United States*. National Academy Press.

- Riitters, K. H., and J. D. Wickham. 2003. How far to the nearest road? *Frontiers in Ecology and the Environment* **1**:125-129.
- Roorda-Knappe, M. C., N. A. H. Janssen, J. J. de Hartog, P. H. N. van Vliet, H. Harssema, and B. Brunekreef. 1998. Air pollution from traffic in city districts near major motorways. *Atmospheric Environment* **32**:1921-1930.
- Saurer, M., P. Cherubini, M. Ammann, B. De Cinti, and R. Siegwolf. 2004. First detection of nitrogen from NO_x in tree rings: a N-15/N-14 study near a motorway. *Atmospheric Environment* **38**:2779-2787.
- Trombulak, S. C., and C. A. Frissell. 2000. Review of ecological effects of roads on terrestrial and aquatic communities. *Conservation Biology* **14**:18-30.
- United States Environmental Protection Agency. 2005. National Emissions Inventory Data. *in* National Emission Inventories for the US. <http://www.epa.gov/ttn/chief/net/2002inventory.html>.
- United States Environmental Protection Agency. 2008a. National Emissions Inventory (NEI) database. *in*. Environmental Protection Agency.
- United States Environmental Protection Agency. 2008b. US EPA CAST/Net site information. Pages site locations and links to active CAST/Net sites *in*.
- Vitousek, P. M., J. D. Aber, R. W. Howarth, G. E. Likens, P. A. Matson, D. W. Schindler, W. H. Schlesinger, and D. G. Tilman. 1997. Human alteration of the global nitrogen cycle: Sources and consequences. *Ecological Applications* **7**:737-750.
- Watts, R. D., R. W. Compton, J. H. McCammon, C. L. Rich, S. M. Wright, T. Owens, and D. S. Ouren. 2007. Roadless space of the conterminous United States. *Science* **316**:736-738.
- Wesely, M. L., and B. B. Hicks. 2000. A review of the current status of knowledge on dry deposition. *Atmospheric Environment* **34**:2261-2282.

CHAPTER 2:

NEAR-SOURCE DEPOSITION OF MOBILE SOURCE EMISSIONS: ROADS AS N DEPOSITION HOTSPOTS.

Introduction

Mobile source emissions are now the dominant source of oxidized forms of N (NO_x) in the US as a whole (Bradley & Jones 2002), and of ammonia (NH_3) in urban areas (Baum et al. 2001). The high temperature and pressure in internal combustion engines causes N_2 and O_2 to split into their atomic constituents resulting in the formation of nitric oxide (NO) (Abdel-Rahman 1998) while subsequent attempts to control these emissions result in the formation of NH_3 due to the over-reduction of NO by the catalytic converter (Heeb et al. 2006).

These gaseous emissions have several fates. They can affect ambient air quality: NO and NH_3 play roles in ozone formation and haze generation respectively. They can be deposited on the landscape both as dry deposition (gaseous NH_3 , NO, NO_2 , HONO, and HNO_3 , and particulate NO_3^- , and NH_4^+), or dissolved in precipitation and deposited as wet deposition in the form of NO_3^- , and NH_4^+ . These emissions and their subsequent deposition can significantly contribute to watershed nitrogen (N) inputs and subsequent N loading to coastal systems. On average for the entire US approximately 30% of coastal nitrogen pollution is estimated to come from N emissions from fossil fuel combustion (Howarth 2008a), while in the in the northeastern US deposition is the single largest source of nitrogen (N) to coastal waters (Howarth et al. 1996, Boyer et al. 2002). Excess N is a serious water-quality problem in most of the estuaries in the US, especially those downstream of developed coastal basins (Bricker et al. 1999, National Research Council 2000). This excess N is particularly harmful to estuarine ecosystems because it limits primary production, and

N surpluses result in harmful or toxic algal blooms, loss of sea grass beds, and in extreme cases, toxic effects on humans (Howarth 2000, Howarth et al. 2002a, Howarth et al. 2002b, Howarth 2008a, Howarth 2008b).

Accurate estimates of N deposition that include both wet and dry deposition are critical for a comprehensive understanding of the impacts of N deposition. 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, and “dry deposition” (i.e., gas and particle concentrations in the air) data collected by the Clean Air Status Trends Network (CAST/Net) that as of 2008 consists of 91 sites.

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 networks purposefully avoided urban areas (e.g., “sites should be located >10 km away from suburban/urban areas with a population of 10,000”) (Bigelow et al. 2001). As a result, the current monitoring networks miss a key component of the total deposition: that which is emitted and 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. 2002a and Holland et al. 2005) in which a portion of the emissions are not accounted for in deposition measurements. While this undercounting could be due to errors in estimation of emissions or export outside the US by advection prior to deposition (Howarth et al. 2002a), 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. For example, Elliot et al. (2007) used ^{15}N to track the contribution of different NO_x sources to deposition collected at NADP sites, and found

that despite mobile sources (mostly vehicle emissions) being the dominant NO_x source, the $\delta^{15}\text{N}$ values of the wet nitrate deposition were instead more strongly correlated with surrounding stationary source NO_x emissions.

Areas that are likely to receive higher deposition include forest edges. Much work has shown that forest edges act as nutrient concentrators, so that N in throughfall along forest edges is elevated over that found in their interiors (Weathers et al. 2001). This “edge effect” is the result of factors that occur along forest edges such as increased precipitation (Lovett and Reiners 1986), higher wind speed (Beier and Gundersen 1989), turbulence (De Ridder et al. 2004), and greater vegetation density (Weathers et al. 2001). Numerous other studies have found elevated N deposition at forest edges due to either an edge effect alone (Weathers et al. 2001) or as a consequence of nearby emission sources: agriculture (Draaijers et al. 1988, Pocewicz et al. 2007), industrial animal husbandry (Spangenberg and Kolling 2004), or industry (Lilleskov et al. 2001). Several of these studies have compared how differences in adjacent land use influences N dynamics along forest edges. They have found that regardless of adjacent land use type, edges show indications of increased N deposition compared to their interiors and that these edge effects typically extend 50-150 meters into the forest, but that the length of the gradient and type of changes seen in N cycling are related to the type of land use. For example, in a study that investigated throughfall fluxes away from two forest edges, one bordering a heath land and another adjacent to an agricultural area with large NH_3 emissions, Draaijers et al. (1988) found that the relative percent increase in throughfall N flux at the forest edge near an agricultural area was higher than it was at the forest edge adjacent to a heath land. While investigating the effects of current and historical land use, Pocewicz et al. (2007) found that while foliage and soil ^{15}N were higher and soil C:N were lower along forest edges adjacent to both currently and formerly fertilized areas they were

more strongly altered in areas adjacent to currently fertilized areas. Similarly, in a study of forest edges adjacent to both agricultural fields and animal agriculture operations, Spangenberg et al. (2004) found that while all sites showed increased N deposition, higher ammonia air concentrations, decreased C:N ratio, and increased soil solution nitrate concentrations, the effects from animal husbandry operations were larger than those of the agricultural fields. Finally, in a study investigating the effects of increased deposition downwind of an ammonia production facility in Alaska, Lilleskov et al. (2001) found increased foliar N and soil N availability, declines in species richness and reductions ectomycorrhizal fungi in zones of elevated N deposition.

In the same way that adjacent agriculture or industry can influence nearby N deposition; roads can also have an impact due to near-source deposition of emissions from cars and trucks. Recently, several studies have investigated the impact of motor vehicle emissions near roadways and found gradients of a few hundred meters or less with effects on ^{15}N in leaves (Ammann et al. 1999), ^{15}N in tree rings (Saurer et al. 2004) and N deposition (Kirchner et al. 2005, Marino et al. In Prep). These gradients, although short, can be significant with much higher concentration and deposition near the road than farther away. Kirchner et al. (2005), in a study along a transect away from a major highway in Germany, found up to 3x higher NH_3 and NO_2 concentrations and 2x higher N deposition at sites near the highway than at sites 500 meters away. Marino et al. (In Prep) found that 10-25% of the NH_3 and 1% of the NO_x emissions from mobile sources were deposited within 50 m of a roadway.

In this study, in order to determine if roads act as hot spots of N deposition in the landscape or if the increased deposition measured nearby was merely the result of an edge effect, I measured N deposition along transects away from 2 road side edges and 1 non-roadside edge. I also compared various nitrogen pools (foliar and forest

floor N) and fluxes (throughfall and nitrate leaching) along transects perpendicular to both sides of 3 road and 3 non-roadside forest edges. Then, in order to estimate the impact of near source deposition of vehicle emissions on the N budget of an N limited estuary, which has been the focus of N loading research for several decades, I scaled our results to the entire Waquoit Bay watershed.

Methods

My study sites were in Falmouth, Massachusetts, on Cape Cod at the Woods Hole Research Center (WHRC) (41°32'55"N, 70°38'35.00"W), the Waquoit Bay National Estuarine Research Reserve (WBNERR) (41°35'50.00"N, 70°30'5.00"W), and in several nearby forests (composed of similar species) along road and non-roadside edges. Soils consist of glacial outwash from the Wisconsinian glaciation and are generally classified as silty loam to coarse sand with low (<27%) clay and high (up to 90%) sand content (Fletcher 1993). The forests 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). Forest floors were ~12 cm thick. In 2006, the average annual precipitation, temperature, and wind speed, measured at the Waquoit Bay National Estuarine Research Reserve site, were 115 cm, 9.8 °C, and 0.76 m sec⁻¹ respectively. The wind direction from July 2006-July 2007 was predominantly from the south-south west to the north-west (NOAA 2008) (Figure 2.1).

Bulk and throughfall N inputs were monitored on an event basis during the summer months from 2003-2006 at two sites (WHRC and WBNERR) and for an entire year in 2006 at the WBNERR site using collectors placed along transects perpendicular to two roadways. Bulk precipitation and throughfall collectors were placed 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). Bulk collectors were placed at 10, 50, and 100 meters from the roadways in open fields. Throughfall collectors, which were identical in design but were used under the tree canopy rather than in open fields were placed at intervals along 10-300 meter transects away from the roadways in forests (Table 2.1). The WHRC site was along Woods Hole Road, which had annual daily traffic (ADT) volume estimated as 10,200 vehicles day⁻¹, and the WBNERR site was along Waquoit Highway/ Falmouth Road (Route 28), which had an estimated annual daily traffic volume of 18,800 vehicles day⁻¹ (MHD 2008) (Figure 2.1). Both throughfall transects ran in an ESE to WNW direction.

In 2004, 2005, and 2006, I also collected bulk and throughfall at a non-road edge site (Waquoit Edge) adjacent to a power line right of way ~1 km from the Waquoit Highway/Falmouth Road (Route 28) road site. I took bulk samples in the center of a clearing and throughfall measurements were taken at 10, 50, and 100 meters from the edge of the clearing along a north-south transect in a red oak forest.

Following each precipitation event in the sampling period, I brought back the bottles to the laboratory where I measured the volume collected in and filtered subsamples using an ashed Whatman® GFF (nominal pore size of 0.7µm) glass fiber filter. I stored nutrient samples at -20°C until analysis for total dissolved N, NO₃⁻, and NH₄⁺ on a Lachat quick chem. auto analyzer (Hach Company Loveland, CO, USA). I calculated nitrogen (TDN, NO₃⁻, NH₄⁺) fluxes in precipitation and throughfall by averaging the mean daily flux of either the bulk or throughfall measurements of all the collectors at each distance. I calculated this by: 1) converting the concentration of each sample to mass per unit area [$\text{mg m}^{-2} = (\text{bottle volume (liters)} * \text{concentration (mg liter}^{-1}) / \text{Funnel area (m}^2)]$; 2) summing the mass for all the events over the period of

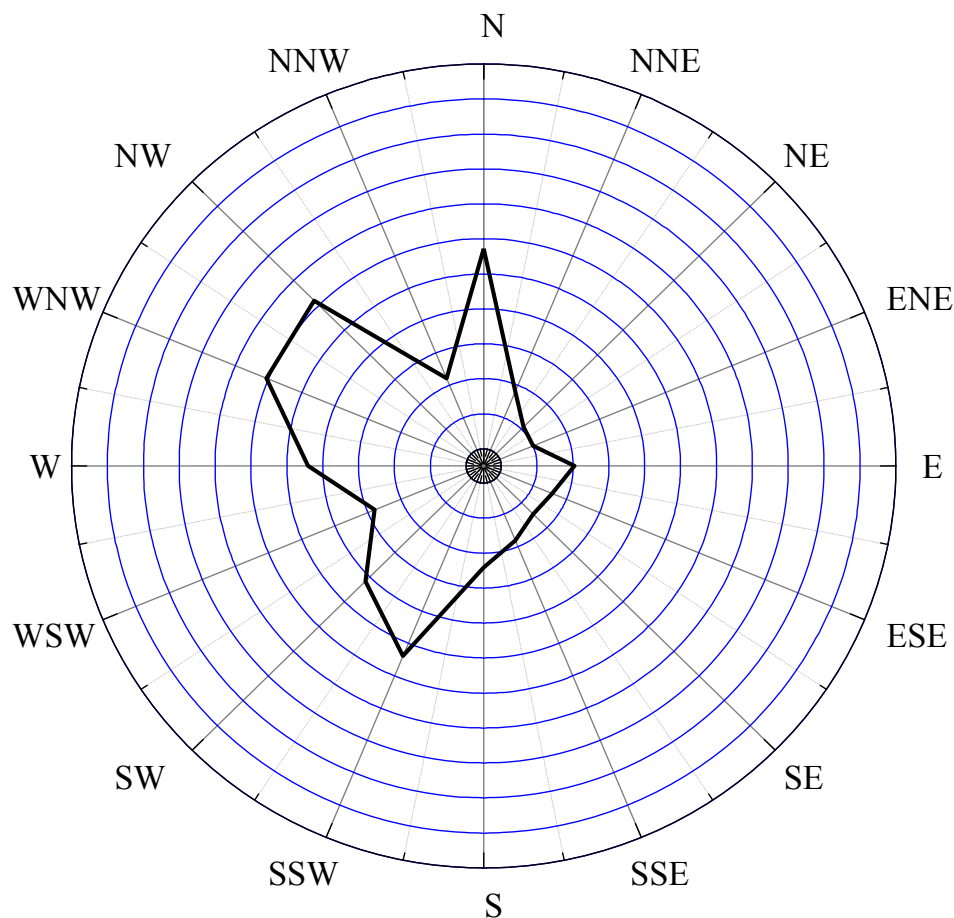


Figure 2.1. Wind rose plot depicting the distribution of the wind direction by compass direction for Waquoit Bay from July 2006-July 2007. The length of the rose petal is directly proportional to the frequency of time that the wind blows from a particular direction with each increment equal to 2%. For example in the figure above the wind was blowing from the east 4 % of the time.

Table 2.1. Bulk and throughfall N inputs (mg TDN - N m⁻² day⁻¹) (\pm SE) along roadside gradients at WHRC and WBNERR for 2003-2006. One-Way ANOVA and *Tukey's HSD Post Hoc* Test: ***P < 0.001, **P < 0.01, *P < 0.05.

Site	year	Bulk	10 m	50 m	100 m	150 m	300 m
WHRC	2003	1.35 (.12)	3.84 (.54)		3.07 (.29)		
	2004	1.45 (.11)	3.13 (.18)	3.44 (.17)	2.14 (.18)*		
	2005	1.13 (.25)	2.25 (.05)		1.50 (.21)		
	2006	1.69 (.07)	2.35 (.12)	1.99 (.05)*	2.14 (.05)		
WBNERR	2003	1.53 (.05)	3.03 (.29)		2.58 (.40)		
	2004	1.54 (.04)	2.83 (.10)	2.07 (.25)**	2.00 (.07)**	2.22 (.28)	
	2005	0.77 (.06)	2.29 (.10)	1.35 (.03)***	1.12 (.09)***	1.36 (.01)***	1.37 (.05)**
	2006	1.28 (.17)	2.34 (.12)	1.99 (.06)	1.75 (.04)**	1.84 (.09)*	1.57 (.12)***

interest; 3) dividing by the length of time in order to get $\text{mg m}^2 \text{ day}^{-1}$ for each collector; 4) averaging the collectors at each distance.

In 2007, I conducted a study comparing road and non-road edges in order to test if the increased N in throughfall near roadways was due merely to an edge effect. The study consisted of three road and three non-road sites within a 3 mile radius, in similarly vegetated forests (Figure 2.2). The three roads were: Waquoit Highway/Falmouth Road (Route 28) (the previously mentioned WBNERR site), State Road 28 (Route 28), with an ADT of 13,300 vehicles day^{-1} , and Gifford Street, with an ADT of 10,300 vehicles day^{-1} (MHD 2008). Non-road sites were located 400 to 700 m away from roads and were in the Crooked Pond Reservation (town of Falmouth Land Trust), and the Frances A. Crane Wildlife Management Area, northern section (MA Department fisheries and Wildlife) along either power line right-of-ways or a fire access road that is closed to vehicle traffic. Along each road and non-road edge, I established two transects (1 to the east and 1 to the west). Along each transect at 10, 25, 50, and 100 m distances from the edges I set up 3 plots beneath red oak trees. In each plot I collected leaf and forest floor samples and assessed nitrate leaching using ion exchange resins. I collected leaf samples from 3 different areas of the mid canopy in a single red oak tree using a 6m long pole pruner. I then dried the leaves @ 70°C and ground them using a Cyclone mill (UDY Corporation, Fort Collins, CO, USA). Beneath each tree, after clearing away the O_i horizon (the litter that is still largely intact and recognizable as litter) I collected 3 forest floor ($\text{O}_e + \text{O}_a$) samples within 0.5 m^2 using a 5.7 cm diameter bulb corer. I composited the three samples, passed them through a 4.75 mm sieve, dried them @ 70°C , and ground them using an 8000D MIXER/MILL (SPEX CertiPrep., Metuchen, NJ). I then analyzed the leaf and forest floor samples for C, N, $\delta^{15}\text{N}$, $\delta^{13}\text{C}$ at the UC Davis Stable Isotope facility. The $\delta^{15}\text{N}$ values are expressed as parts per thousand differences from a standard: Where R_{sample}

and R_{standard} are the $^{15}\text{N}/^{14}\text{N}$ ratios of the samples and the standards respectively (Peterson and Fry 1987).

$$\delta^{15}\text{N} = (R_{\text{sample}}/R_{\text{standard}} - 1) * 1000 \text{ [‰]}$$

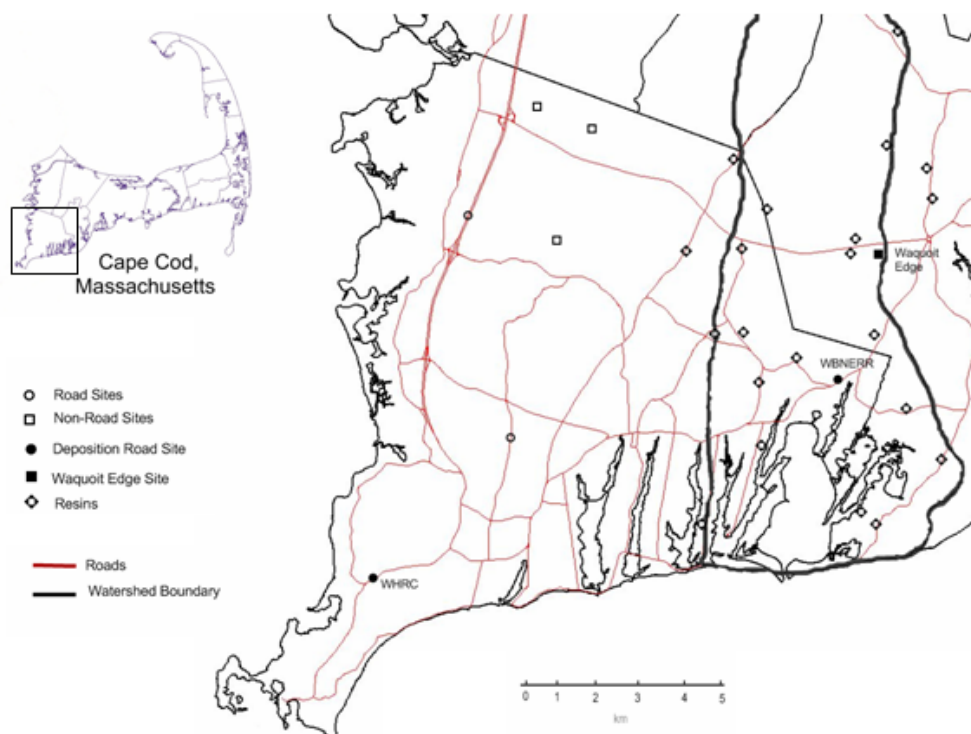


Figure 2.2. Road and non-road study sites in Falmouth on Cape Cod, Massachusetts.

Near each set of forest floor samples, as relative indicators of NO_3^- leaching, I deployed a set of ion exchange resin (IER) bags which consisted of 5 individual bags joined with mason's line. The resin bags were similar to those used by Lovett et al. (2004) and were prepared by: placing ~10g of Sybron IONAC ASB-1P (Sybron Chemicals, Birmingham, NJ) in a nylon stocking; cleaning the resins by soaking in 10% HCL for 1 hour; rinsing with Deionized (DI) water; and charging by soaking in 0.5 NaOH overnight. I buried the bags 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. I deployed the resin bags for 21 days, then

retrieved, rinsed with DI to remove soil, and extracted twice using 10 mls of 2 M KCl. I analyzed the extracts for NO_3^- on a Lachat auto-analyzer using the cadmium reduction method.

Scaling

I estimated the impact of mobile source emissions on deposition and leaching to a local watershed N budget by extrapolating deposition and leaching measurements made along our transect to the entire Waquoit Bay watershed. In order to estimate the area of the watershed that was impacted by near source deposition, I calculated the area within the watershed that was within 10, 20, and 50 meters of a roadway by euclidian allocation using a GIS created with data from the Massachusetts office of Geographic and Environmental Information (Mass GIS) and road centerline data from the US Census Bureau (T. Stone, *personal Communication*). Because the GIS data is based on road centerlines while our transects are from road edge, I used an average lane width of 2.75 meters to correct road buffer distances (i.e., distances used to calculate distances away from roads were 12.75, 22.75, and 52.75. This is the minimum recommended lane width for local roads (AASHTO 2001) and thus a conservative estimate, because larger busier roads are wider and would thus increase the percent area affected.

In order to assess whether leaching was occurring along roads throughout the watershed I deployed 550 resins bags along transects perpendicular to 17 different roads in the watershed. I deployed resin bags in groups of 5 with 2-3 groups per plot at 10, 25, 50, and 100 meter intervals along transects away from roads throughout the watershed. I deployed resin bags for 81 days from 11-Sept-07 until 1-Dec-07. At the end of the deployment I collected and processed resins as previously mentioned.

I used StatPlus Professional (Analystsoft, Vancouver, BC Canada) for statistical analysis. In the roadside deposition studies, I used a One-Way ANOVA and *Tukey's HSD Post Hoc* Test for pair-wise comparisons between distances. In the road and non-road study a 3-Way ANOVA testing the effects of sampling site type (road or non-road), transect direction (east or west), and distance (10, 25, 50, and 100 m) was performed on foliage %N, C:N, $\delta^{15}\text{N}$; forest floor C:N ratios and $\delta^{15}\text{N}$, and ion exchange nitrate concentrations.

Results

N deposition along roads

There were no significant differences in inputs of TDN bulk collectors with distance from roadways for either site (WHRC, WBNERR) in any of the years measured (2003 - 2006). Therefore, I averaged the estimates of TDN inputs via precipitation made using the bulk collectors at each site during each collection period (Table 2.1). Throughfall inputs of TDN were elevated near the roadway (10 meters) and decreased with increasing distance from the road for both sites (Table 2.1). Pair-wise comparisons of N inputs between sites near the road (10 meters) and farther away (> 10 meters) indicate that at the WHRC site, inputs at 10 meters are significantly elevated over sites farther away in 1 out of 4 years while at the WBNERR site the 10 meters sites are significantly elevated over all distances in 3 out of 4 years. At the Waquoit bay site in 2006, the year with the highest number of rainfall events, TDN at the 10 meter site was significantly elevated over all other distances (Figure 2.3)

However, while the results were not always significant in both sites in all years the TDN deposition in throughfall was consistently higher at 10 meters than at 100 meters at both sites (WBNERR and WHRC) and in all years (2003 - 2006). Although the amount of TDN in throughfall was significantly higher at 10 meters than at 100

meters from the road in only half of our estimates, 3/4 of the non-significant results were from the WHRC site which has a lower average daily traffic count than the WBNERR site. It is possible because of the small number of collectors (2-4) at each distance and events (5-9) during each collection period that the results are not always significantly different. On average, for both sites and all years, the deposition near the roadside edge (10 meters) was ~ 1.4 x higher than it was 100 meters away in the forest interior.

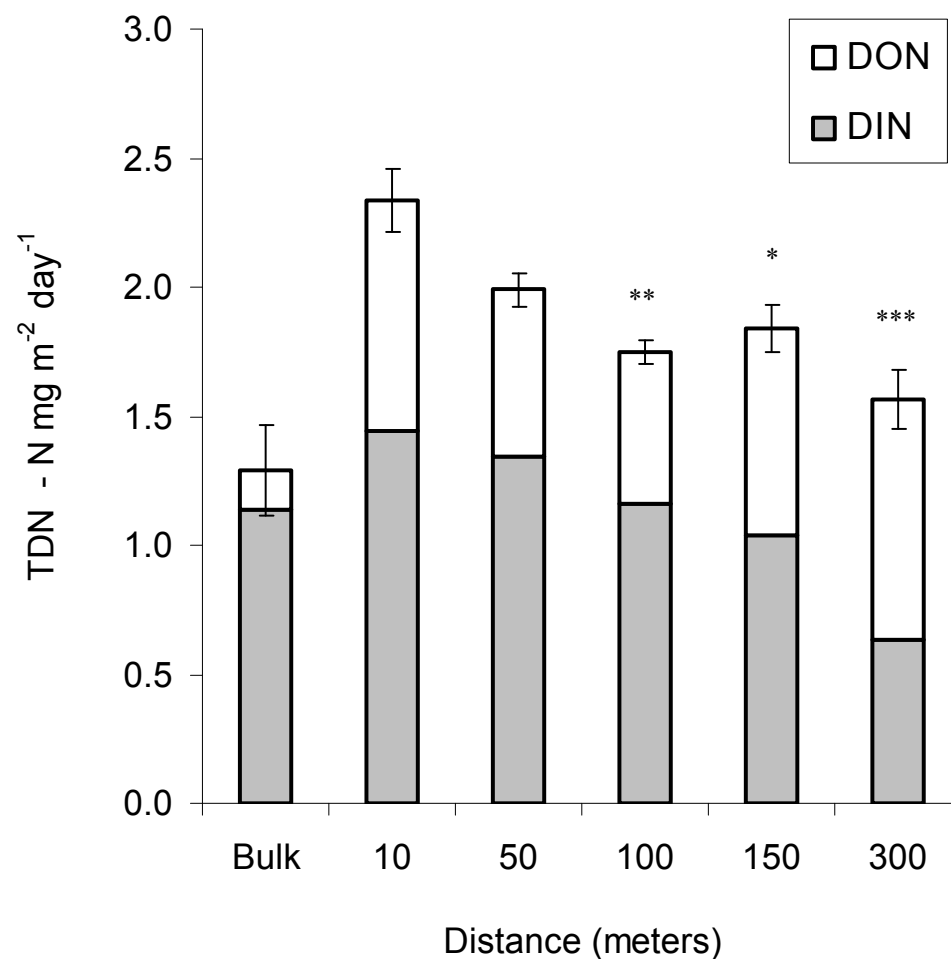


Figure 2.3. Throughfall across transect away from Road at Waquoit Bay site for TDN. Graphs are average mean daily flux of 9 events from 12 July 2006 - 6 September 2006 (\pm S.E., $n=4$). One-Way ANOVA and *Tukey's HSD Post Hoc* Test: *** $P < 0.001$, ** $P < 0.01$, * $P < 0.05$. $P = .007, .008, .0071, .001$ for 50, 100, 150, and 300 meters respectively.

I found no significant differences in inputs of total dissolved nitrogen (DIN) via precipitation among bulk collectors with distance from roadways for either site (WHRC, WBNERR) in any of the years measured (2003 - 2006). Therefore, I averaged the estimates of DIN inputs via precipitation made using the bulk collectors at each site during each collection period (Table 2.2). The amount of DIN collected at our sites is comparable to other measurements made at our site, as well as those made by the nearby by the NADP. For the period of Jul 2006 – Jul 2007, our estimate of bulk DIN (NO_3^- and NH_4^+) deposition was $3.77 (\text{SE} \pm 0.14) \text{ kg N ha}^{-1} \text{ yr}^{-1}$ (Chapter 3) this is similar to deposition estimates made at the nearest NADP site for 2006 ($3.02 \text{ kg N ha}^{-1} \text{ yr}^{-1}$) (NADP 2009) as well as those of Lajtha et al. (1995) ($4.2 \text{ kg N ha}^{-1} \text{ yr}^{-1}$) and Seeley et al. (1998) ($2.8 \text{ kg N ha}^{-1} \text{ yr}^{-1}$).

Table 2.2. Bulk and throughfall N inputs ($\text{mg DIN} - \text{N m}^{-2} \text{ day}^{-1}$) ($\pm \text{SE}$) for along roadside gradients at WHRC and WBNERR for 2003-2006. One-Way ANOVA and Tukey's HSD Post Hoc Test: ***P < 0.001, **P < 0.01, *P < 0.05.

Site	year	Bulk	10 m	50 m	100 m	150 m	300 m
WHRC	2003	.96 (.02)	1.90 (.34)		1.07 (.11)		
	2004	1.15 (.09)	1.70 (.20)	1.01 (0.04)	.91 (.1)*		
	2005	.59 (.02)	.96 (.05)		.55 (0.04)*		
	2006	1.41 (.06)	1.60 (.14)	1.17 (.05)*	1.21 (.06)*		
WBNERR	2003	1.10 (.04)	1.24 (.17)		.79 (.11)		
	2004	1.17 (.03)	1.56 (.10)	1.05 (.06)*	.83 (.05)**	.61 (.05)**	
	2005	.57 (.06)	1.18 (.14)	.50 (.02)**	.41 (.02)**	.52 (.02)**	.55 (.05)**
	2006	1.14 (.15)	1.45 (.08)	1.34 (.07)	1.16 (.06)*	1.04 (.04)**	.64 (.04)***

Distance from the roadway had a significant effect on throughfall DIN inputs. Throughfall inputs of DIN were highest near the roadway (10 meters) and significantly decreased with increasing distance from the road for both sites in all years (Table 2.2). At the Waquoit bay site in 2006, the year with the highest number of rainfall events, DIN at the 10 meter site was significantly elevated over all other distances (Figure 2.4). On average, for both sites and all years, the deposition near the

edge (10 meters) was ~ 1.9 x higher than it was 100 meters away from the road in the forest interior.

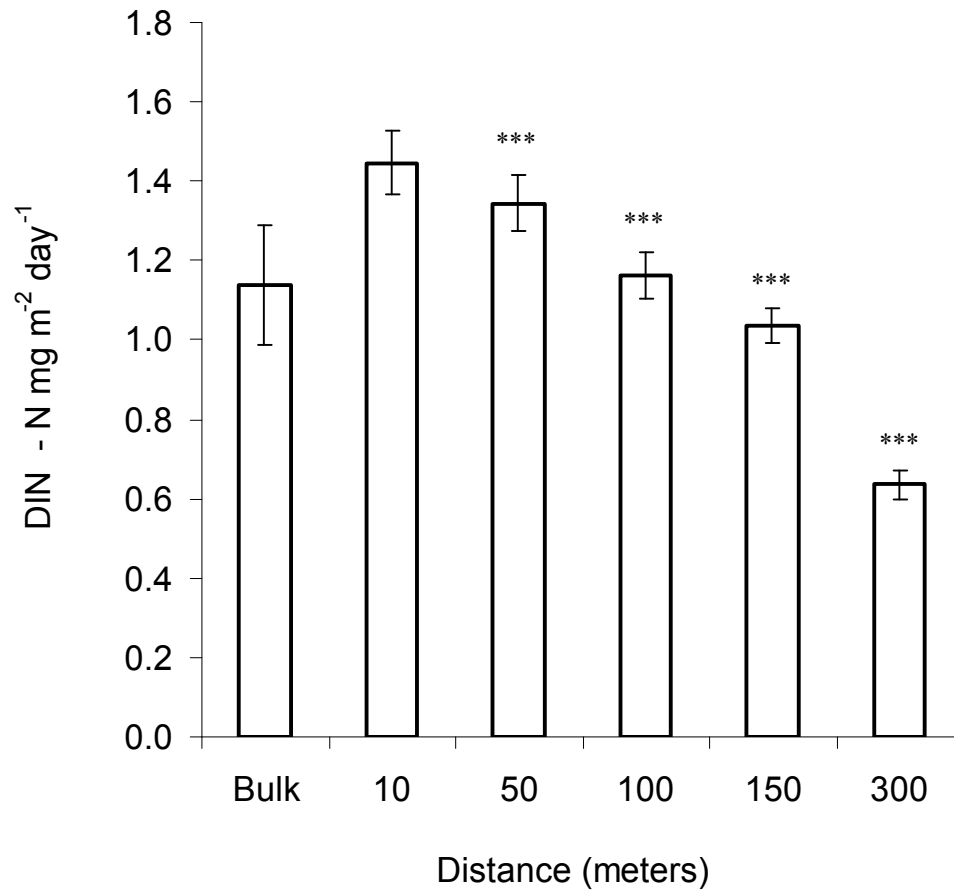


Figure 2.4. Throughfall across transect away from Road at Waquoit Bay site for DIN. Graphs are average mean daily flux of 9 events from 12 July 2006 - 6 September 2006 (\pm S.E., $n=4$). One-Way ANOVA and *Tukey's HSD Post Hoc* Test: *** $P < 0.001$, ** $P < 0.01$, * $P < 0.05$. $P = .007, .008, .0071, .001$ for 50, 100, 150, and 300 meters respectively.

An important aspect of quantifying the contribution of motor vehicle emissions of NO_x (NO and NO_2) and NH_3 to nearby deposition is measuring the amount of dry deposition. While measuring wet deposition is straightforward, because of low and uncertain deposition velocities measuring dry deposition is more difficult leading investigators to test different methods. Dry deposition can be inferred based on nitrogen content of atmospheric gases and particulates, along with their computed

deposition rates. It can be measured using either proxy collectors such as Petri plates (Lindberg and Lovett 1985); wash-off from either artificial trees (Dambrine et al. 1998, Stachurski and Zimka 2000), or live tree canopies (i.e., throughfall). This last method of using live trees has been used by several researchers (Lovett and Lindberg 1993, Butler and Likens 1995) who have found measurements of throughfall + stemflow to correlate well with estimates of total (wet + dry) deposition which are based on measurements of wet deposition and inferred estimates of dry deposition.

One problem with using throughfall as an estimate of dry deposition, however, is that it is not just a measure of the amount of dry deposition that is washed off the leaf, but the result of several different processes such as foliar uptake and leaching. In a review of how canopy interactions such as foliar leaching and uptake influence throughfall (Parker 1983) notes that nitrogen is tightly conserved in the canopy and most studies showed foliar uptake of NH_4^+ and NO_3^- . Canopy uptake or retention is the result of either cation exchange of ions on leaf surfaces (Lovett et al. 1985) or diffusion through the leaf cuticle and stomata (Sparks 2009), with the different forms of N entering through different pathways. For instance, nitric acid vapor, ammonium, and nitrate ions that accumulate on leaf surfaces from gaseous and particulate deposition (i.e., dry deposition) are transported into the leaf through cuticular diffusion (i.e., leaf surface uptake) while gaseous NH_3 , NO and NO_2 are taken up via the stomata (Draaijers et al. 1996). Although the gaseous forms (NH_3 , NO and NO_2) have different intermediate steps (i.e. nitrous (HONO , HNO_2) and nitric acid (HNO_3) must be reduced by nitrate reductase and nitrite reductase) all are eventually incorporated into plant proteins via glutamine synthetase. (Sparks 2009).

While several different methods have been used to measure the amount of canopy N uptake (i.e., by difference Lindberg et al. 1986, Lovett and Lindberg 1993), or tracing the fate of ^{15}N -labeled NH_4^+ (Garten and Hanson 1990) and ^{15}N -labeled

HNO₃ (Padgett et al. 2009)) the different methods have yielded comparable estimates. Using above and below canopy fluxes, Lindberg et al. (1986) found that canopy uptake decreased the flux of atmospheric NO₃⁻, and NH₄⁺ by 50-70 % and Lovett et al. (1993) found that canopies retained 10-90%, with a mean of ~50%. Similarly Padgett et al. (2009) using ¹⁵N-labeled HNO₃ estimated that as much as 60% of deposited nitrogen may be retained in the canopy and Garten and Hanson (1990) found that 58-84% of ¹⁵N-labeled NH₄⁺ was retained in the canopy.

In addition to removing DIN, canopies also leach DON. Several studies such as Carlisle et al. (1966) and Stadler et al. (2001) have investigated the source of this DON and suggested it is either the result of epiphytic microorganisms utilizing DIN that is adsorbed to the leaf surfaces or of DON leaching out of leaves. In their study, Lovett and Lindberg (1993) did not find any correlation between canopy uptake of inorganic N and canopy leaching of organic N across their sites as would be expected if microbial transformations were responsible. Conversely, in a study designed to assess the fate of ¹⁵N-labeled NO₃⁻ and NH₄⁺ applied as a mist to the forest canopy, Gaige et al. (2007) measured rapid incorporation of the labeled N into DON which they attributed to microbial N cycling rather than assimilation and re-release by trees.

In their study investigating canopy interactions in forests in North America and Europe, Lovett and Lindberg (1993) 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. Several studies have investigated canopy leaching in addition to foliar uptake and attempted to quantify both the amounts as well as the forms of N involved in each process by measuring the different N species above and below the canopy. A uniform result among all the studies was a net increase in organic N in throughfall samples compared to precipitation samples (Currie et al. 1996, Lovett and Lindberg 1993, Baker and Attiwill 1987, Friedland et

al. 1991, Goller et al. 2006, Jones et al. 2008, Schwendenmann and Veldkamp 2005). Whereas, a difference among the studies was in the percent of TDN due to DON which decreased with increasing N inputs. For example in a study by Goller et al. (2006) designed to investigate if organic N species contribute more to element cycles in areas without anthropogenic inputs, DON accounted for 45-60% of the TDN (in rainfall and throughfall), while in areas that receive higher N inputs such as subalpine spruce-fir forest in the Adirondacks it is 31% (Friedland et al. 1991), and in the N addition plots at the Harvard Forest in Massachusetts it is 32-39% (Currie et al. 1996), and in an N saturated pine plantation in northern Wales it accounted for only ~11% (Jones et al. 2008).

Thus, using N in net throughfall (throughfall – bulk deposition) to estimate dry deposition of motor vehicle emissions may be a conservative estimate because it is likely to miss any of the NH_3 , and NO_x that is retained in the canopy (Lovett and Lindberg 1984) and any N that is volatilized prior to being washed off (Raivonen et al. 2006). In order to overcome these losses a number of studies have chosen to use TDN which includes DON as well as DIN in their deposition estimates (Valiela et al. 1997, Lajtha et al. 1995). For example Valiela et al. (1997), Lajtha et al. (1995), and Butler and Likens (1995) included organic N in their estimates of deposition to compensate for foliar uptake of DIN and Neiryneck et al. (2008) used canopy flux of DON in order to explain the mismatch between throughfall flux of DIN and total deposition measurements. However, this may cause an overestimate of N deposition because some portion of the DON in throughfall is likely leached from the canopy as opposed to conversion of atmospherically deposited DIN. In this study in order to get a range of estimates for deposition I calculated deposition using both DIN, which is an underestimate and TDN, which may be either an underestimate or an overestimate depending on the relative balance of DON leaching vs. DIN uptake by the canopy. To

calculate deposition I measured inputs of DIN and TDN in throughfall for all precipitation events from Jul 06 - Jul 07 in plots at 10, 50, 100, and 150 meters from the roadway at our Waquoit Bay site. I corrected the DIN inputs to account for canopy uptake using the net-throughfall (throughfall - bulk) measurements of DIN made at our non-road site (Figure 2.5). The average canopy uptake across the transect was $0.16 \text{ mg DIN m}^{-2} \text{ day}^{-1}$ ($\pm \text{S.E. } 0.05$). Assuming this canopy uptake occurs from May-Nov when foliage is present, the throughfall inputs along the transect need to be adjusted upward by 8%. The TDN inputs were corrected for canopy uptake by 16% based on the Integrated Forest Study (IFS) regression of net canopy uptake and throughfall total N (Lovett and Lindberg 1993). In order to estimate deposition for areas along the deposition gradient (i.e from one plot to the next along the gradient) a simple model was developed by fitting a curve to the corrected deposition estimates using the least squares method along with the Solver function in Microsoft Excel (John 1998) (Figure 2.6). The resulting equations were then used to calculate deposition over the desired distance (i.e., 0-10, 0-50, and > 50 meters) (Table 2.3). Using these two methods gives a range of estimates for deposition across the gradient (Table 2.3) with the largest differences between the two occurring in the areas closest to the road. Across the gradient, the deposition near the road (0-10 meters) is $1.6 - 1.9 \times$ the deposition for distances > 50 meters from the road using the DIN and TDN estimates respectively. Comparing the two estimates, the deposition estimates made using the DIN are 53-63% of those made using TDN (with the lower values near the road).

I then used these TDN deposition estimates along with outputs measured with lysimeters (which are discussed at length in Bettez et al. (Chapter 3) to calculate forest retention rates in plots along the 150 meter Waquoit Road transect. In order to calculate average retention along the entire transect, a curve was fit (similarly to the deposition estimates) to the retention estimates made in the plots along the 150 meter

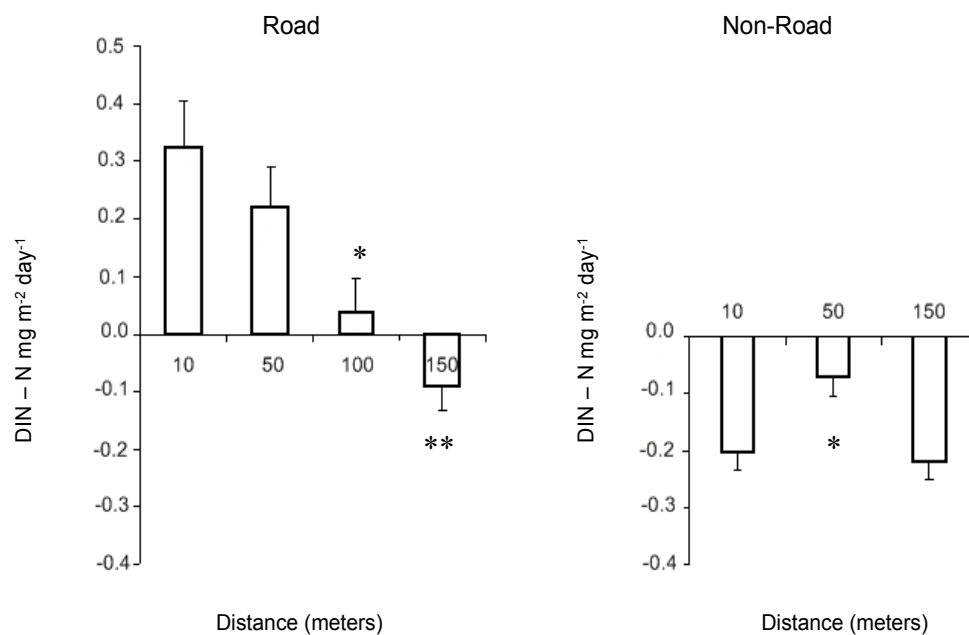


Figure 2.5. Net through-fall (TF-Bulk) for DIN at Waquoit Bay Road and non-road side sites. Net canopy flux of DIN decreases with distance from road with sites >100 meters showing net canopy uptake compared to all sites along non-road site showing net canopy uptake (\pm S.E., $n=4$). One-Way ANOVA and *Tukey's HSD Post Hoc* Test: *** $P < 0.001$, ** $P < 0.01$, * $P < 0.05$. $P = .NS$, .029, .0016, NS, .039, NS for 50, 100, and 150 meters respectively along road and non-road transects.

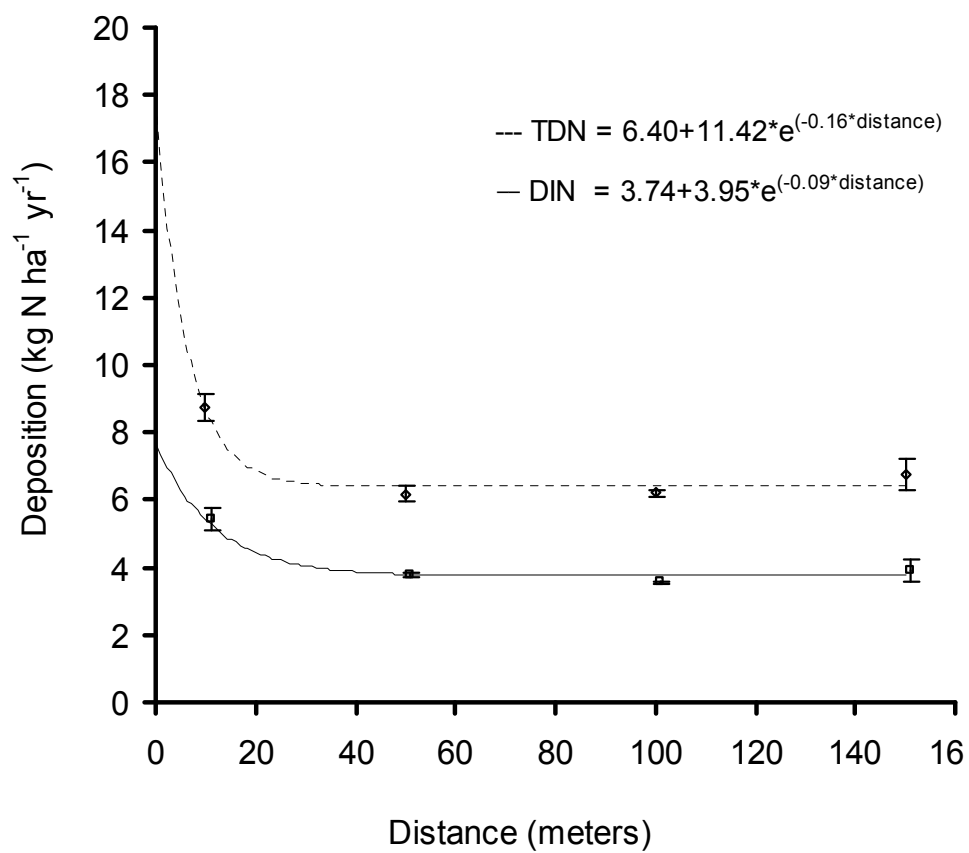


Figure 2.6. Modeled TDN and DIN deposition within 150 meters of roadways estimated by fitting a curve to deposition measurements made at the WBNERR roadside site.

Table 2.3. Average N deposition and forest retention rates with distance from roadside edge.

Distance	Deposition DIN kg ha ⁻¹ yr ⁻¹	Deposition TDN kg ha ⁻¹ yr ⁻¹	Retention Rate
0 - 10 meters	6.4	12.2	36 %
0 - 50 meters	4.7	7.9	62 %
> 50 meters	4.0	6.4	71 %

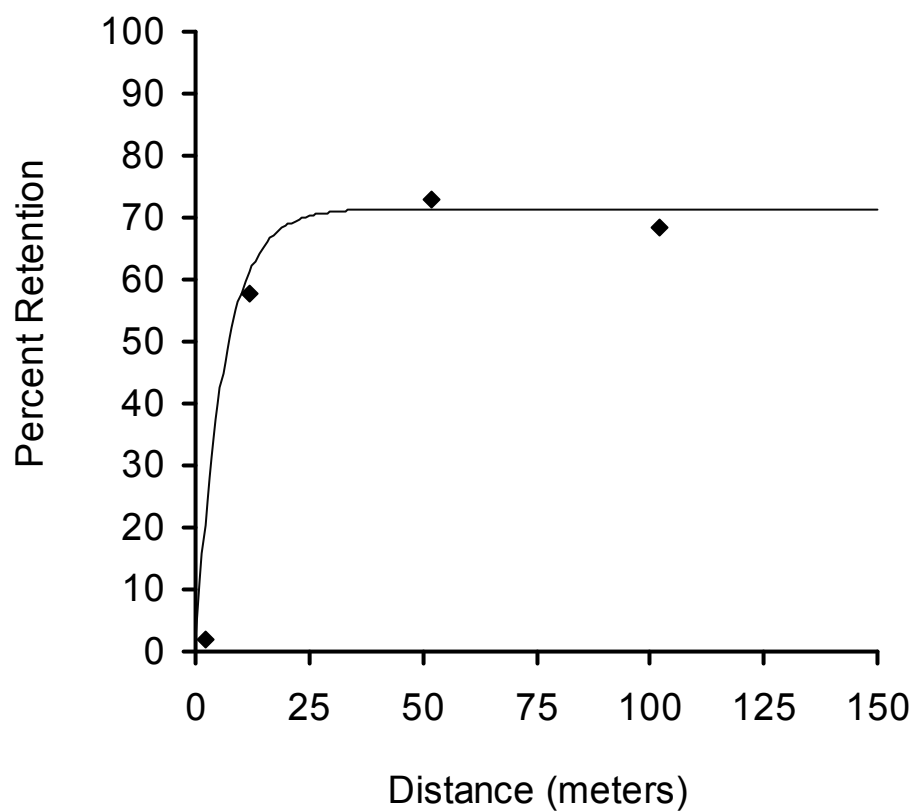


Figure 2.7. Modeled N retention within 150 meters of roadways estimated by fitting a curve to deposition measurements made at the WBNERR roadside site.

transect (Figure 2.7) and the resulting equation was used to calculate retention over the desired distance (Table 2.3).

Road and non-road edges

Throughfall deposition along roadside transects differed significantly from non-roadside transects, there were significant differences. While there were no significant differences in bulk TDN or DIN inputs among the different sites (WHRC, WBNERR, WBNERR Edge) in any year (2004 - 2006), when sites at closest to the edge of either road or non-road edges were compared road sites always had significantly higher throughfall deposition than non-road sites for both TDN and DIN. In fact, the furthest points on either road transect (100-300 meters) all had higher deposition than the closest non-road edge site. When net-throughfall (throughfall-bulk) for DIN was compared between the WBNERR road and non-road sites, there were significant differences between the two in net-throughfall along the transect, with net canopy flux (the amount of N washed off the canopy minus any canopy uptake) of DIN decreasing with increasing distance from the roadway and eventually becoming negative (i.e., canopy uptake) between 100 and 125 meters (Figure 2.5). Along the roadside transect, the net canopy flux of $0.32 \text{ mg DIN m}^2 \text{ day}^{-1}$ at 10 meters is significantly higher than at 100 and 150 meters. At the non-roadside site there is net canopy uptake along the entire transect with an average net uptake of $0.16 \text{ mg m}^2 \text{ day}^{-1}$ and while the 50 m site is significantly different from the 10 meter site the 100 meter site is not.

When data for parameters of N deposition (foliar and forest floor C:N and $\delta^{15}\text{N}$, IER leaching) along other road and non-road sites were compared, no significant differences were found between east and west transects at individual sites or among the 3 sites within each road and non-road edge type. Therefore, data from the east and

west transects for each of the 3 sites in each type were combined (Table 2.4).

Although foliar C:N and $\delta^{15}\text{N}$ values along road sites usually tended to be lower than non-road sites (Figure 2.8 A, C), the difference between types were not significant (Table 2.4). There were significant differences between transect types for forest floor $\delta^{15}\text{N}$ and C:N (Table 2.5) with significantly lower C:N and $\delta^{15}\text{N}$ values for transects near roads than non-roads (Figure 2.8 B, D). No significant differences with distance from the forest edge for either road or non-road transect type were found for C:N and $\delta^{15}\text{N}$ ratios in either foliar and forest floor samples (Table 2.4).

Table 2.4. Average deposition indices for three road and non-road transects (\pm S.E., n=6).

Site	Distance	Foliar C:N	Foliar ^{15}N	Forest Floor C:N	Forest Floor $\delta^{15}\text{N}$	Enrichment factor	IER NO_3^- mg liter day^{-1}
Road	10	24.72 (.61)	-2.42 (.32)	25.36 (1.7)	0.88 (.25)	-3.30 (.38)	0.24 (.05)
	25	23.84 (.60)	-3.08 (.45)	24.02 (1.1)	0.49 (.09)	-3.57 (.52)	0.07 (.007)
	50	25.00 (1.0)	-2.86 (.33)	25.83 (2.15)	0.70 (.32)	-3.56 (.62)	0.07 (.01)
	100	24.19 (1.0)	-3.24 (.42)	27.12 (2.15)	0.51 (.34)	-3.75 (.64)	0.068 (.008)
Non-road	10	24.31 (.98)	-2.88 (.32)	28.87 (1.3)	0.88 (.15)	-3.76 (.19)	0.066 (.007)
	25	24.87 (.72)	-3.04 (.18)	28.76 (.93)	1.38 (.29)	-4.43 (.30)	0.099 (.02)
	50	25.94 (1.2)	-2.71 (.30)	28.14 (1.2)	1.36 (.13)	-4.07 (.28)	0.065 (.005)
	100	25.03 (.43)	-3.00 (.22)	27.12 (.79)	1.01 (.26)	-4.02 (.28)	0.0817 (.012)

More nitrate ($\sim 1.4\text{x}$) was collected on ion exchange resins deployed along roads than along non-roads with the most nitrate collected at the site closest to the roadway (Figure 2.8 E). These differences were significant between the types of transects (Table 2.4), with more nitrate collected along roadside than non-roadside transects. Also more nitrate was collected on resins at 10 meters than at other sites (25, 50, and 100 meters) along the transects (Table 2.4).

In order to test if increased leaching was occurring along roads throughout the watershed, resin bags were buried beneath the forest floor along transects adjacent to roads throughout the watershed. While resin bags do not provide a quantitative

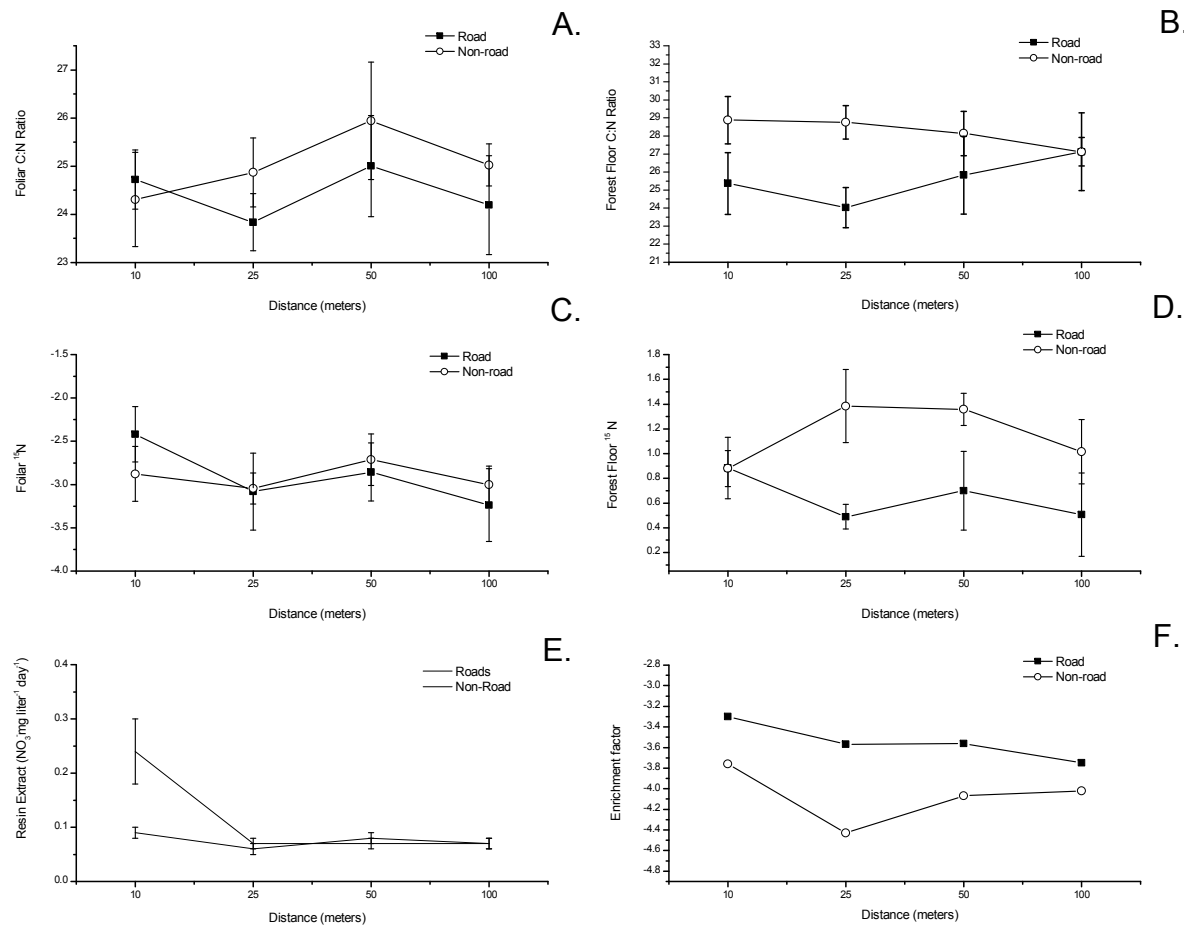


Figure 2.8. Graph of foliar C:N ratio (A), foliar $\delta^{15}\text{N}$ (C), forest floor organic layer C:N (B), forest floor $\delta^{15}\text{N}$ (D), Nitrate extracted from ion exchange resins (E), and enrichment factor ($\delta^{15}\text{N}_{\text{foliage}} - \delta^{15}\text{N}_{\text{forest floor}}$) (F) along transects away from road (closed circles) and non-road (open circles (\pm S.E., $n = 6$)).

measurement of N leaching, they are commonly used evaluate relative N loss (Binkley and Matson 1983). There were no significant differences in the amount of nitrate collected on the ion exchange resins with soil type (coarse, sandy), or average daily traffic when tested with an ANOVA. There were statistically significant differences between differences between resins at 10 meters and those at 50 meters determined using an ANOVA with the amount of nitrate collected on resins at 10 meters significantly greater than that collected on resins at 50 meters ($P = .0425$) and at 100 meters ($P = .0436$) determined using Tukey Kramer multiple comparison test (Figure 2.9). These results indicate that higher N leaching is likely occurring in areas within 10 meters of roads throughout the watershed.

Table 2.5. Results of 3-Way ANOVA on data type (road or non-road), direction (east or west), and distance (10, 25, 50, and 100 m).

	Foliage		Forest Floor		Enrichment	Resin
	^{15}N	C:N	^{15}N	C:N	Factor	NO_3^-
Direction	0.3300	0.2203	0.4626	0.5330	0.2443	0.1184
Type	0.9366	0.4007	0.0068***	0.0360*	0.104 †	0.0173
Distance	0.4941	0.6301	0.7153	0.9888	0.7227	0.0001
Direction x Type	0.8967	0.6078	0.1842	0.7135	0.4861	0.1567
Direction x Distance	0.9653	0.6817	0.4178	0.9213	0.9118	0.1037
Type x Distance	0.7606	0.8413	0.3423	0.5305	0.9531	0.0002
Direction x Type x Distance	0.9471	0.5503	0.3574	0.9809	0.6374	0.0006

Discussion

I measured elevated N inputs along roadside edges compared to non-road edges and found that N inputs decreased with distance from the roadside edge. I did not find any significant differences either with orientation at individual sites, or among sites within transect type, leading us to believe that these depositional gradients consistently form along roads. This increased deposition was reflected in several indices of increased N loading such as lower forest floor C:N values, higher forest floor $\delta^{15}\text{N}$, and increased nitrate leaching.

Foliar and forest floor $\delta^{15}\text{N}$ abundance and forest floor C:N ratios can be indicative of N enrichment in both whole ecosystem N addition experiments (Emmett et al. 1998b, Gundersen et al. 1998) and across regional gradients of N deposition (McNulty et al. 1991, Dise et al. 1998b, Pardo et al. 2006). In our study, I found significant differences between road and non-road edges for some (forest floor C:N, forest floor $\delta^{15}\text{N}$, and nitrate leaching) but not all (foliar $\delta^{15}\text{N}$) indices of N deposition. While foliar $\delta^{15}\text{N}$ abundance values were highest at the 10 meter road site, I did not find a significant difference between road and non-road sites for foliar $\delta^{15}\text{N}$ abundance. One possible reason for the lack of significance in foliar $\delta^{15}\text{N}$ values could be the result of differences in soil and plant $\delta^{15}\text{N}$ values due to land use history (Emmett et al. 1998b). In order to overcome these issues and make comparisons among road and non-road transects, I used a $\delta^{15}\text{N}$ enrichment factor which is the difference between $\delta^{15}\text{N}$ abundance in forest floor and $\delta^{15}\text{N}$ abundance in foliage (Emmett et al. 1998b). Emmett et al. (1998b) used the enrichment factor to identify the degree to which N deposition influenced different sites along a nitrogen deposition gradient from 10 kg N $\text{ha}^{-1} \text{yr}^{-1}$ in southern Sweden to 60 kg N $\text{ha}^{-1} \text{yr}^{-1}$ in the Netherlands. As deposition increases, the difference between the foliage and forest floor $\delta^{15}\text{N}$ values decreases either because the foliage becomes enriched or the forest floor becomes depleted, resulting in a decrease in the enrichment factor. These changes are the result of the lighter isotope (^{14}N) being favored during various transformations associated with N enrichment and loss (Nadelhoffer et al. 1995). For example, during nitrification, lighter NH_4^+ is preferentially nitrified leaving behind heavier NH_4^+ which is taken up by vegetation thus making it heavier, while during denitrification there is a greater loss of lighter N as N_2 leaving behind heavy NO_3^- . When the enrichment factor is calculated for our sites, the difference between road and non-road sites is statistically significant (Table 2.4) with the roadside sites having a higher enrichment factor than

the non-road sites (Figure 2.8 F). While the difference in enrichment factors between the road and non-road sites in our study was much smaller at 0.45 than the difference in enrichment factor of 6 found by Emmett et al. (1998b), the estimated difference in deposition between our road and non-road sites was also much smaller than the 50 kg ha⁻¹ yr⁻¹ difference between their high and low sites. Furthermore, although neither transect type had statistically significant differences with distance from their edges, possibly because of small sample size or small differences in deposition across their gradients, both showed patterns consistent with what would be predicted, with higher enrichment factors near their edges.

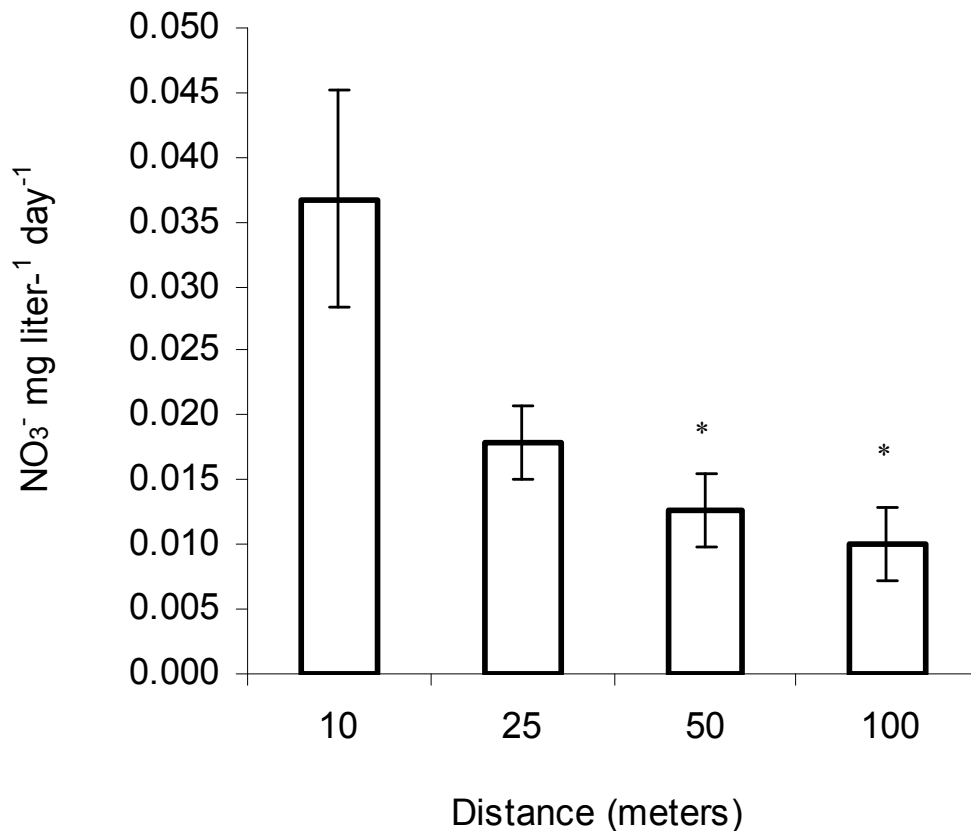


Figure 2.9. Average nitrate leaching away from roadways in the Waquoit Bay Watershed measured with ion exchange resins roadway (\pm SE, n = 12). ANOVA with Tukey Kramer multiple comparison test: ***P < 0.001, **P < 0.01, *P < 0.05, †P < 0.10.

The difference between road and non-road sites for forest floor C:N ratios is small but ecologically significant. Gundersen et al. (1998) identified a negative relationship between C:N ratio and nitrate leaching in whole-ecosystem N addition experiments, with the increased leaching resulting from the onset of nitrification at forest floor C:N ratios around 24:1 to 27:1. Therefore it is possible to use the forest floor C:N ratio as an indicator of the likelihood of NO_3^- leaching with the risk of leaching increasing from low to moderate to high as the C:N drops from >30:1 to between 30:1 - 25:1 and to < 25:1 (Gundersen et al. 1998). The forest floor C:N ratio for the 10 m roadside sites is 25:1 compared to 28.8:1 for the 10 m non-road sites, indicating an increased likelihood of nitrate leaching. This was also confirmed by our resin bag data, with 2.4x more nitrate collected on ion exchange resins at the 10 m roadside site compared to the 10 meter non-roadside site.

Scaling

Valiela et al. (2002, 1997) have constructed a detailed model that estimates the N inputs to the Waquoit Bay watershed from atmospheric deposition, sewage, and fertilizer, and then calculates N loading to the estuary from each of these sources. According to their model the 2 primary sources of N to the watershed are atmospheric deposition (56%) and sewage (27%). However, because they assume that 89% of the N from atmospheric deposition is retained in the watershed (which is somewhat higher than the 50% estimated by Lajtha et al. (1995)), atmospheric deposition only contributes 30% to estuarine overall loading while wastewater contributes 48% according to their model estimates (Valiela et al. 1997). Here, I use NLOAD (Valiela 2009), a web-based modeling tool based on Valiela et al. (1997), to investigate how including the additional N from mobile source emissions influences the relative contribution of each of these sources to watershed and estuarine N inputs.

Data for model parameters were obtained from 2001 aerial photos by Valiela and Bowen (2002). I used the same data for model input parameters (number of buildings; watershed area; area of wetlands; area of cranberry bogs; area of other agriculture; area of golf courses; area of parks and athletic fields; impervious surfaces; area of freshwater ponds, and buildings within 200 m of shore) as Valiela and Bowen (2002). With the exception of deposition and forest N retention, the remaining model defaults were left unchanged. Similar to Valiela et al. (1997) and Valiela and Bowen (2002), I use TDN for N deposition estimates. The average values of N deposition and forest N retention were calculated for areas within 0-10 meters, 0-20 meters, 0-50 meters, and > 50 meters from the roadside edge (Table 2.3) were calculated using modeled estimates (Figure 2.6, 2.7).

In order to estimate how increases in deposition and leaching would affect watershed and estuarine N inputs, the model was run twice, once using deposition and retention estimates for areas uninfluenced by roads in which values from areas > 50 meters away from the road were used and once using area weighted deposition and retention rates that reflected the influence of increased deposition and decreased leaching found near roads. The area weighted deposition and leaching rates were calculated using the percent of the watershed that is within 10, 20, and 50 meters of its 307 km of roads which were 13.5 %, 22.5 %, and 44.3 % respectively of the total watershed area (T. Stone, *personal Communication*) (Figure 2.10). For example the average deposition of the 10 meters closest to the road is 1.9 x the average deposition beyond 50 meters from the roadway. Similarly, the deposition over the first 20 and 50 meters was 1.55 x and 1.24 x the average deposition of 50-150 meters from the roadway. Using these ratios along with the percentage of the watershed that is within 10, 20, and 50 meters of a roadway, it is possible to calculate the amount of additional N deposition near roads that is added to a watershed (e.g., if 10 % of the watershed

receives 2 x the deposition and 90% receives the normal amount of deposition, the total deposition to the watershed increases by 10%). When calculated using area corrected deposition and leaching numbers, I estimate that the N inputs from atmospheric deposition increase by 12.3%, 12.5%, or 10.5% and N leaching increases by 6.7%, 6.8%, and 5.7% depending on if the 10, 20, or 50 meter buffers are used. Because the largest changes in deposition and retention occurred within the first 10-20 meters of the roadway and changes in area weighted deposition and leaching were similar irrespective of buffer area, the model was run using 0-10 meter values.

Using the model I estimate the N load to the watershed and estuary from atmospheric deposition to be much lower than that of Valiela (Table 2.6). This is likely because our estimate of deposition is much lower ($6.4 \text{ kg ha}^{-1} \text{ yr}^{-1}$) than Valiela's ($\sim 15 \text{ kg ha}^{-1} \text{ yr}^{-1}$) (Valiela et al. 1997, Valiela and Bowen 2002) who estimated deposition using data from Lajtha et al. (1995). Lajtha et al. (1995) estimated deposition to be $13.1 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ for their watershed N budget by adjusting throughfall TN measurements ($11.3 \text{ kg ha}^{-1} \text{ yr}^{-1}$) by 16% to account for canopy uptake. For my estimate of deposition, in order to be conservative, I use modeled deposition for areas > 50 meters from the roadway. The difference between our estimates is mainly due to differences in the DON because our estimates of DIN deposition are quite similar: $3.7 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ in Lajtha et al. (1995) compared to my estimate of $4.0 \text{ kg N ha}^{-1} \text{ yr}^{-1}$.

Despite increased deposition and leaching near roads, when these results are scaled to an entire watershed they only result in $\sim 2.6\%$ increase in N inputs to the watershed and N loading to the estuary (Table 2.6). Under both scenarios of the NLOAD model, deposition, wastewater and septic, and fertilizer each contribute roughly equivalent amounts of N to the watershed with wastewater and septic contributing slightly more than the other two. However, the contribution of

atmospheric N and the impact of mobile sources would likely increase as road density and traffic increase or as N retention decreases with time.

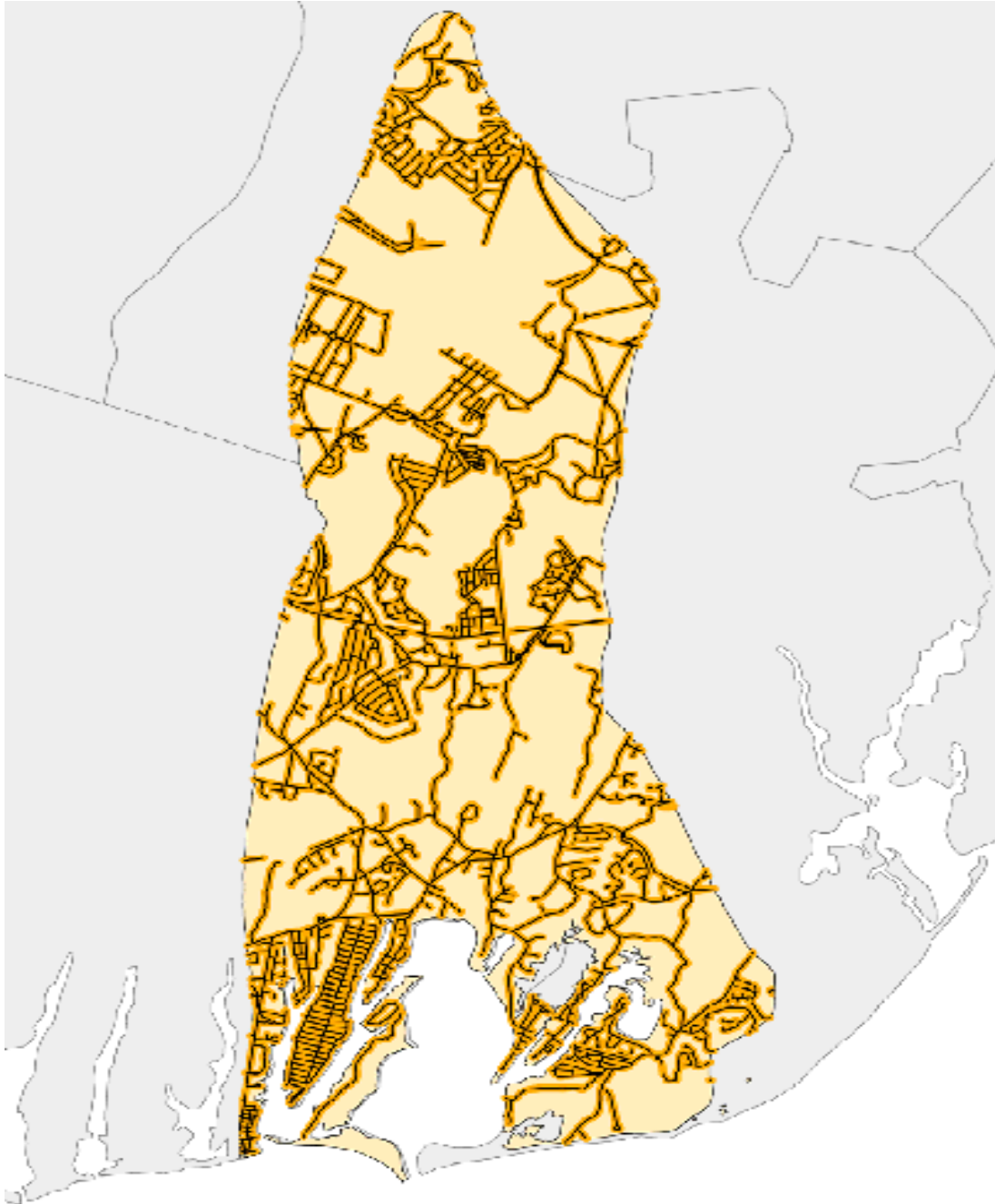


Figure 2.10. Waquoit Bay Watershed with area within 10m in black and 50 m in orange.

Table 2.6. Watershed and estuarine N loading from Valiela et al. 1997, and calculated using my data with and without near source deposition of mobile source emissions taken in account.

	Valiela et al. 1997		Without Mobile sources		With mobile sources	
	N load to watershed	N load to Estuary	N load to watershed	N load to Estuary	N load to watershed	N load to Estuary
Deposition	56%	30%	31%	15%	34%	18%
Wastewater and septic	27%	48%	37%	59%	36%	57%
Fertilizer	14%	15%	32%	26%	31%	25%
Total	100%	100%	100%	100%	100%	100%

Conclusions

This study compared deposition, foliar and forest floor C:N and $\delta^{15}\text{N}$, and nitrate leaching measurements along transects perpendicular to road and non-road forest edges. Along roads, plots near the forest edge showed higher deposition than those in the interior, while along non-roadsides edges plots near the edge did not show enhanced deposition over those in the forest interior. There were significant differences between the road and non-road transects for multiple other indices of N deposition such as $\delta^{15}\text{N}$ enrichment factor, forest floor C:N ratio, and nitrate leaching. Plots within 10 meters of roads had a higher enrichment factor compared to plots along the non-roadsides transect indicating increased N loading along roads. This is reflected in lower forest floor C:N ratios in plots near roads ($\text{C:N @ 10 m} = 25 \pm 1.7$) compared plots near non-road edges ($\text{C:N @ 10 m} = 28.8 \pm 1.3$) and increased NO_3^- leaching ($\sim 2.4\times$) as measured with ion exchange resins. However, beyond 10 meters there were no significant differences with distance along either the road or the non-road transects indicating that if there is an edge effect, because deposition is relatively low even with the increased deposition from vehicle emissions, compared to other areas where edge effects have been studied, it was not large enough to be seen in our study.

Near source deposition of mobile source emissions resulted in a 10-12% increase in atmospheric inputs to the Waquoit Bay watershed which resulted in a ~2.6% increase in the contribution of atmospheric N inputs to total watershed and estuarine inputs (Table 2.6). Although this increase is small, with continued chronic N inputs, decreases in retention will increase causing the contribution of atmospheric inputs to increase.

Roads are overlooked as hotspots of N deposition in the landscape. A portion of mobile source emissions are deposited nearby and have an impact on various pools and fluxes of N. Our data suggest that most of the near source deposition from traffic occurs within the first 100-150 meters. Forested areas immediately adjacent (within 10-50 m) of roadways see 1.5 - 2 times more deposition (due primarily to dry deposition) than sites more than 150 m from roadways, which see deposition rates similar to regional estimates. Deposition is likely even higher in pine strands which have been shown to have a higher edge effect (Wuyts et al. 2008). However, while these gradients are short they should not be disregarded. The roads in our study averaged less than 20,000 vehicles a day compared to highways which can have 5-10 times as many vehicles. When our results are extrapolated to the entire watershed, I estimate that deposition estimates could be underestimated by 10-12% and leaching by ~5.7-6.8%. Although this research was done in coastal area where development is high, road density throughout the remainder of the US is high as well. 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 and Wickham 2003). While most of the emissions from mobile sources are deposited regionally and captured with the current monitoring networks, more work is needed on their local contribution. This is especially important when constructing ecosystem N budgets or policy designed to control N loading in coastal areas that are N limited.

REFERENCES

- Abdel-Rahman, A. A. 1998. On the emissions from internal-combustion engines:.
International Journal of Energy Research **22**:483-513.
- American Association of State Highway and Transportation Officials. 2001. A policy
on geometric design of highways and streets, 2001, 4th edition. American
Association of State Highway and Transportation Officials, Washington, D.C.
- Ammann, M., R. Siegwolf, F. Pichlmayer, M. Suter, M. Saurer, and C. Brunold. 1999.
Estimating the uptake of traffic-derived NO₂ from N-15 abundance in Norway
spruce needles. *Oecologia* **118**:124-131.
- Baker, T. G., and P. M. Attiwill. 1987. Fluxes of Elements in Rain Passing through
Forest Canopies in Southeastern Australia. *Biogeochemistry* **4**:27-39.
- Baum, M. M., E. S. Kiyomiya, S. Kumar, A. M. Lappas, V. A. Kapinus, and H. C.
Lord. 2001. Multicomponent remote sensing of vehicle exhaust by dispersive
absorption spectroscopy. 2. Direct on-road ammonia measurements.
Environmental Science & Technology **35**:3735-3741.
- Beier, C., and P. Gundersen. 1989. Atmospheric Deposition to the Edge of a Spruce
Forest in Denmark. *Environmental Pollution* **60**:257-271.
- Bettez, N. D. Chapter 3. Forest response to chronic low level N deposition along a
roadside deposition gradient.
- Bigelow, S. D., S. R. Dossett, and V. C. Bowersox. 2001. Instruction Manual
NADP/NTN Site Selection and Installation. National Atmospheric Deposition
Program, Champaign, Illinois 61820-7495.
- Binkley, D., and P. Matson. 1983. Ion-Exchange Resin Bag Method for Assessing
Forest Soil-Nitrogen Availability. *Soil Science Society of America Journal*
47:1050-1052.
- Boyer, E., W., C. Goodale, L., N. Jaworski, A., and R. Howarth, W. 2002.
Anthropogenic nitrogen sources and relationships to riverine nitrogen export in
the northeastern U.S.A. *Biogeochemistry* **58**:137-169.
- Bricker, S. B., C. G. Clement, D. E. Pirhalla, S. P. Orlando, and D. R. G. Farlow.
1999. National Estuarine eutrophication assessment: Effect of Nutrient
enrichment in the Nation's Estuaries. NOAA, National Ocean Service, Special
Projects Office and National Centers for the Coastal Ocean Service, Silver
Springs, MD.

- Butler, T. J., and G. E. Likens. 1995. A Direct Comparison of Throughfall Plus Stemflow to Estimates of Dry and Total Deposition for Sulfur and Nitrogen. *Atmospheric Environment* **29**:1253-1265.
- Carlisle, A., A. H. F. Brown, and E. J. White. 1966. The Organic Matter and Nutrient Elements in the Precipitation Beneath a Sessile Oak (*Quercus Petraea*) Canopy. *The Journal of Ecology* **54**:87-98.
- Currie, W. S., J. D. Aber, W. H. McDowell, R. D. Boone, and A. H. Magill. 1996. Vertical transport of dissolved organic C and N under long-term N amendments in pine and hardwood forests. *Biogeochemistry* **35**:471-505.
- Dambrine, E., B. Pollier, M. Bonneau, and N. Ignatova. 1998. Use of artificial trees to assess dry deposition in spruce stands. *Atmospheric Environment* **32**:1817-1824.
- De Ridder, K., B. Neiryneck, and C. Mensink. 2004. Parameterising forest edge deposition using effective roughness length. *Agricultural and Forest Meteorology* **123**:1-11.
- Dise, N. B., E. Matzner, and P. Gundersen. 1998. Synthesis of nitrogen pools and fluxes from European forest ecosystems. *Water Air and Soil Pollution* **105**:143-154.
- Draaijers, G. P. J., J. W. Erisman, T. Spranger, and G. P. Wyers. 1996. The application of throughfall measurements for atmospheric deposition monitoring. *Atmospheric Environment* **30**:3349-3361.
- Draaijers, G. P. J., W. Ivens, and W. Bleuten. 1988. Atmospheric Deposition in Forest Edges Measured by Monitoring Canopy Throughfall. *Water Air and Soil Pollution* **42**:129-136.
- Elliott, E. M., C. Kendall, S. D. Wankel, D. A. Burns, E. W. Boyer, K. Harlin, D. J. Bain, and T. J. Butler. 2007. Nitrogen isotopes as indicators of NO_x source contributions to atmospheric nitrate deposition across the Midwestern and northeastern United States. *Environmental Science & Technology* **41**:7661-7667.
- Emmett, B. A., O. J. Kjonaas, P. Gundersen, C. Koopmans, A. Tietema, and D. Sleep. 1998. Natural abundance of N-15 in forests across a nitrogen deposition gradient. *Forest Ecology and Management* **101**:9-18.
- Fletcher, P. C. 1993. Soil Survey of Barnstable County, Massachusetts. The Massachusetts Agricultural Experiment Station. United States Service Soil Conservation Service, Washington, D.C.

- Friedland, A. J., E. K. Miller, J. J. Battles, and J. F. Thorne. 1991. Nitrogen Deposition, Distribution and Cycling in a Sub-Alpine Spruce-Fir Forest in the Adirondacks, New-York, USA. *Biogeochemistry* **14**:31-55.
- Gaige, E., D. B. Dail, D. Y. Hollinger, E. A. Davidson, I. J. Fernandez, H. Sievering, A. White, and W. Halteman. 2007. Changes in canopy processes following whole-forest canopy nitrogen fertilization of a mature spruce-hemlock forest. *Ecosystems* **10**:1133-1147.
- Garten, C. T., and P. J. Hanson. 1990. Foliar Retention of N-15-Nitrate and N-15-Ammonium by Red Maple (*Acer-Rubrum*) and White Oak (*Quercus-Alba*) Leaves from Simulated Rain. *Environmental and Experimental Botany* **30**:333-342.
- Goller, R., W. Wilcke, K. Fleischbein, C. Valarezo, and W. Zech. 2006. Dissolved nitrogen, phosphorus, and sulfur forms in the ecosystem fluxes of a montane forest in ecuador. *Biogeochemistry* **77**:57-89.
- Gundersen, P., I. Callesen, and W. de Vries. 1998. Nitrate leaching in forest ecosystems is related to forest floor C/N ratios. *Environmental Pollution* **102**:403-407.
- Heeb, N. V., A. M. Forss, S. Bruhlmann, R. Luscher, C. J. Saxer, and P. Hug. 2006. Three-way catalyst-induced formation of ammonia-velocity- and acceleration-dependent emission factors. *Atmospheric Environment* **40**:5986-5997.
- Holland, E. A., B. H. Braswell, J. Sulzman, and J. F. Lamarque. 2005. Nitrogen deposition onto the United States and western Europe: Synthesis of observations and models. *Ecological Applications* **15**:38-57.
- Howarth, R. W. 2000. Nutrient Over-Enrichment of Coastal Waters in the United States: Steps Toward a Solution. Pew Oceans Commission.
- Howarth, R. W. 2008a. Coastal nitrogen pollution: A review of sources and trends globally and regionally. *Harmful Algae* **8**:14-20.
- Howarth, R. W. 2008b. Estimating atmospheric nitrogen deposition in the Northeastern United States: Relevance to Narragansett Bay. Pages 47-65 in A. Desbonnet and B. A. Costa-Pierce, editors. *Science for Ecosystem-based Management Narragansett Bay in the 21st Century*. Springer, New York.
- Howarth, R. W., G. Billen, D. Swaney, A. Townsend, N. Jaworski, K. Lajtha, J. A. Downing, R. Elmgren, N. Caraco, T. Jordan, F. Berendse, J. Freney, V. Kudeyarov, P. Murdoch, and Z. L. Zhu. 1996. Regional nitrogen budgets and riverine N&P fluxes for the drainages to the North Atlantic Ocean: Natural and human influences. *Biogeochemistry* **35**:75-139.

- Howarth, R. W., E. W. Boyer, W. J. Pabich, and J. N. Galloway. 2002a. Nitrogen use in the United States from 1961-2000 and potential future trends. *Ambio* **31**:88-96.
- Howarth, R. W., A. Sharpley, and D. Walker. 2002b. Sources of nutrient pollution to coastal waters in the United States: Implications for achieving coastal water quality goals. *Estuaries* **25**:656-676.
- John, E. G. 1998. Simplified Curve Fitting using Spreadsheet Add-ins. *International Journal of Engineering Education* **14**:375-380.
- Jones, D. L., L. T. Hughes, D. V. Murphy, and J. R. Healey. 2008. Dissolved organic carbon and nitrogen dynamics in temperate coniferous forest plantations. *European Journal of Soil Science* **59**:1038-1048.
- Kirchner, M., G. Jakobi, E. Felcht, M. Bernhardt, and A. Fischer. 2005. Elevated NH₃ and NO₂ air concentrations and nitrogen deposition rates in the vicinity of a highway in Southern Bavaria. *Atmospheric Environment* **39**:4531-4542.
- Lajtha, K., B. Seely, and I. Valiela. 1995. Retention and Leaching Losses of Atmospherically-Derived Nitrogen in the Aggrading Coastal Watershed of Waquoit Bay, Ma. *Biogeochemistry* **28**:33-54.
- Lilleskov, E. A., T. J. Fahey, and G. M. Lovett. 2001. Ectomycorrhizal fungal aboveground community change over an atmospheric nitrogen deposition gradient. *Ecological Applications* **11**:397-410.
- Lindberg, S. E., and G. M. Lovett. 1985. Field-Measurements of Particle Dry Deposition Rates to Foliage and Inert Surfaces in a Forest Canopy. *Environmental Science & Technology* **19**:238-244.
- Lindberg, S. E., G. M. Lovett, D. D. Richter, and D. W. Johnson. 1986. Atmospheric Deposition and Canopy Interactions of Major Ions in a Forest. *Science* **231**:141-145.
- Lovett, G. M., and S. E. Lindberg. 1984. Dry Deposition and Canopy Exchange in a Mixed Oak Forest as Determined by Analysis of Throughfall. *Journal of Applied Ecology* **21**:1013-1027.
- Lovett, G. M., and S. E. Lindberg. 1993. Atmospheric Deposition and Canopy Interactions of Nitrogen in Forests. *Canadian Journal of Forest Research-Revue Canadienne De Recherche Forestiere* **23**:1603-1616.
- Lovett, G. M., S. E. Lindberg, D. D. Richter, and D. W. Johnson. 1985. The Effects of Acidic Deposition on Cation Leaching from 3 Deciduous Forest Canopies. *Canadian Journal of Forest Research-Revue Canadienne De Recherche Forestiere* **15**:1055-1060.

- Lovett, G. M., K. C. Weathers, M. A. Arthur, and J. C. Schultz. 2004. Nitrogen cycling in a northern hardwood forest: Do species matter? *Biogeochemistry* **67**:289-308.
- Marino, R., R. W. Howarth, N. D. Bettez, and E. A. Davidson. In Prep.
- Massachusetts Highway Department. 2008. Executive Office of Transportation, Traffic Volume Counts. *in* On-line database <http://www.mhd.state.ma.us/>.
- McNulty, S. G., J. D. Aber, and R. D. Boone. 1991. Spatial Changes in Forest Floor and Foliar Chemistry of Spruce-Fir Forests across New-England. *Biogeochemistry* **14**:13-29.
- Nadelhoffer, K. J., M. R. Downs, B. Fry, J. D. Aber, A. H. Magill, and J. M. Melillo. 1995. The Fate of N-15-Labeled Nitrate Additions to a Northern Hardwood Forest in Eastern Maine, USA. *Oecologia* **103**:292-301.
- National Atmospheric Deposition Program (NRSP-3). 2009. NADP Program Office, Illinois State Water Survey, 2204 Griffith Dr., Champaign, IL 61820.
- National Oceanic and Atmospheric Administration. 2008. Office of Ocean and Coastal Resource Management, National Estuarine Research Reserve System-wide Monitoring Program, Centralized Data Management Office, Baruch Marine Field Lab, University of South Carolina. *in* on-line database, <http://cdmo.baruch.sc.edu/>.
- National Research Council. 2000. Which Nutrients Matter. Pages 65-83 *in* R. W. Howarth, editor. *Clean Coastal Waters: Understanding and Reducing the effects of Nutrient Pollution*. National Academy Press, Washington.
- Neirynck, J., I. A. Janssens, P. Roskams, P. Quataert, P. Verschelde, and R. Ceulemans. 2008. Nitrogen biogeochemistry of a mature Scots pine forest subjected to high nitrogen loads. *Biogeochemistry* **91**:201-222.
- Padgett, P. E., H. Cook, A. Bytnerowicz, and R. L. Heath. 2009. Foliar loading and metabolic assimilation of dry deposited nitric acid air pollutants by trees. *Journal of Environmental Monitoring* **11**.
- Pardo, L. H., P. H. Templer, C. L. Goodale, S. Duke, P. M. Groffman, M. B. Adams, P. Boeckx, J. Boggs, J. Campbell, B. Colman, J. Compton, B. Emmett, P. Gundersen, J. Kjonaas, G. Lovett, M. Mack, A. Magill, M. Mbila, M. J. Mitchell, G. McGee, S. McNulty, K. Nadelhoffer, S. Ollinger, D. Ross, H. Rueth, L. Rustad, P. Schaberg, S. Schiff, P. Schleppi, J. Spoelstra, and W. Wessel. 2006. Regional assessment of N saturation using foliar and root delta N-15. *Biogeochemistry* **80**:143-171.

- Parker, G. G. 1983. Throughfall and stemflow in the forest nutrient cycle. Pages 58-136 in A. Macfadyen and E. D. Ford, editors. *Advances in Ecological Research*. Academic Press Inc, New York.
- Peterson, B. J., and B. Fry. 1987. Stable Isotopes in Ecosystems Studies. *Annual Review of Ecology and Systematics* **18**:293-320.
- Pocewicz, A., P. Morgan, and K. Kavanagh. 2007. The effects of adjacent land use on nitrogen dynamics at forest edges in northern Idaho. *Ecosystems* **10**:226-238.
- Raivonen, M., B. Bonn, M. José Sanz, T. Vesala, M. Kulmala, and P. Hari. 2006. UV-induced NO_y emissions from Scots pine: Could they originate from photolysis of deposited HNO₃? *Atmospheric Environment* **40**:6201-6213.
- Riitters, K. H., and J. D. Wickham. 2003. How far to the nearest road? *Frontiers in Ecology and the Environment* **1**:125-129.
- Schwendenmann, L., and E. Veldkamp. 2005. The role of dissolved organic carbon, dissolved organic nitrogen, and dissolved inorganic nitrogen in a tropical wet forest ecosystem. *Ecosystems* **8**:339-351.
- Seely, B., K. Lajtha, and G. D. Salvucci. 1998. Transformation and retention of nitrogen in a coastal forest ecosystem. *Biogeochemistry* **42**:325-343.
- Spangenberg, A., and C. Kolling. 2004. Nitrogen deposition and nitrate leaching at forest edges exposed to high ammonia emissions in Southern Bavaria. *Water Air and Soil Pollution* **152**:233-255.
- Sparks, J. P. 2009. Ecological ramifications of the direct foliar uptake of nitrogen. *Oecologia* **159**:1-13.
- Stachurski, A., and J. R. Zimka. 2000. Atmospheric input of elements to forest ecosystems: a method of estimation using artificial foliage placed above rain collectors. *Environmental Pollution* **110**:345-356.
- Stadler, B., S. Solinger, and B. Michalzik. 2001. Insect herbivores and the nutrient flow from the canopy to the soil in coniferous and deciduous forests. *Oecologia* **126**:104-113.
- Valiela, I. 2009. NLoad. NLOAD is a web-based modeling tool that allows users to: estimate land-derived nitrogen loads, identify sources of land-derived nitrogen loads, ascertain effects of nitrogen loading on estuarine producers, investigate possible options to manage nitrogen loads. (<http://nload.mbl.edu/>).
- Valiela, I., and J. L. Bowen. 2002. Nitrogen sources to watersheds and estuaries: role of land cover mosaics and losses within watersheds. *Environmental Pollution* **118**:239-248.

- Valiela, I., G. Collins, J. Kremer, K. Lajtha, M. Geist, B. Seely, J. Brawley, and C. H. Sham. 1997. Nitrogen loading from coastal watersheds to receiving estuaries: New method and application. *Ecological Applications* **7**:358-380.
- Watts, R. D., R. W. Compton, J. H. McCammon, C. L. Rich, S. M. Wright, T. Owens, and D. S. Ouren. 2007. Roadless space of the conterminous United States. *Science* **316**:736-738.
- Weathers, K. C., M. L. Cadenasso, and S. T. A. Pickett. 2001. Forest edges as nutrient and pollutant concentrators: Potential synergisms between fragmentation, forest canopies, and the atmosphere. *Conservation Biology* **15**:1506-1514.
- Wuyts, K., A. De Schrijver, J. Staelens, M. Gielis, G. Geudens, and K. Verheyen. 2008. Patterns of throughfall deposition along a transect in forest edges of silver birch and Corsican pine. *Canadian Journal of Forest Research-Revue Canadienne De Recherche Forestiere* **38**:449-461.

CHAPTER 3:

FOREST RESPONSE TO CHRONIC LOW LEVEL N DEPOSITION ALONG A ROADSIDE DEPOSITION GRADIENT.

Introduction

Nitrogen (N) has been shown to limit primary production in both forested and coastal ecosystems (Vitousek and Howarth 1991). Under low N deposition, forest growth tends to be limited by N availability, and N is retained in biomass, forest floor organic layer, and the mineral soil. As N deposition increases, the availability of NH_4^+ and NO_3^- can occur in excess of plant and microbial demand and forests can show decreased N retention efficiency or N saturation (Aber et al. 1989, Aber et al. 2003). Negative consequences of this excess N have been documented across a broad range of ecosystems, including declining health of forests and lakes because of long-term (chronic) N deposition associated with acid rain (Aber et al. 1982, Schindler et al. 1985, Driscoll et al. 2003), and degradation of coastal rivers and estuaries are also by chronic N loading from multiple sources (Bricker et al. 1999, Howarth et al. 2000, National Research Council 2000, Howarth 2008a).

While the sources of this N vary by site and region, they are primarily wastewater, fertilizer, agricultural sources, and wet and dry atmospheric deposition (Howarth 2000, Howarth et al. 2002b). Unlike the rest of the world where N emissions from fossil fuel combustion are only one quarter the amount applied as fertilizer (Howarth et al. 2002a), N emissions in the U.S. are equal to three quarters of the amount of N applied as fertilizer (US EPA 2008a, IFA 2008). In the US between 1940 and 1998, N emissions have more than tripled. These increases are largely due to increases in emissions from mobile sources (i.e., motor vehicles and construction equipment) which have increased 5 fold and since 1940 and have replaced stationary

sources such as power plants as the largest source of N emissions in the US (US EPA 2008a).

Recently, mobile sources (i.e., vehicle traffic) have been recognized as a potentially important source of N to local N budgets, especially in areas near roads (Kirchner et al. 2005, Howarth 2008a, Bettez Chapter 2, Marino et al. In Prep). This N comes from mobile source emissions of NO_x (NO and NO₂) created during combustion and NH₃, a secondary pollutant made from the over reduction of NO_x by catalytic converters (Heeb et al. 2006). While most of these emissions are carried into the larger atmosphere and deposited broadly across the landscape, a portion of them are deposited close to roads (near-source deposition). In a study along a transect away from a major highway in Germany, Kirchner et al. (2005) found up to 3x higher NH₃ and NO₂ concentrations and 2x higher N deposition at sites near the highway than at sites just 500 meters away. Similar patterns in gas concentration and deposition have also been found along transects adjacent to moderately sized roadways (~15,000 vehicles day⁻¹) on Cape Cod (MHD 2008). Marino et al. (In Prep) estimate that 10-25% of the NH₃ and 1% of the NO_x is deposited within 50 m of a roadway, and Bettez et al. (Chapter 2) finds deposition along roadside edges to be elevated over both forest interiors and non-roadside edges. This gradient in ambient chronic N deposition adjacent to roads creates an ideal natural experiment in which to evaluate the impacts of long-term deposition on adjacent forest environments while removing variability in forest-type, climate, and land-use history that have confounded earlier studies.

Over the last two decades, understanding how forest ecosystems respond to chronic N deposition has been the focus of a great deal of work in both the US and Europe. This research has included regional transects across the northeastern US, Michigan, and northern Europe that capture long-term landscape scale deposition gradients (Dise and Wright 1995, Aber et al. 2003, McNulty et al. 1991) and whole

forest ecosystem experiments in which N deposition is manipulated (Tietema et al. 1998, Jefts et al. 2004, Magill et al. 2004, McNulty et al. 2005, Pregitzer et al. 2004). The whole ecosystem manipulations have included: the chronic N experiments at the Harvard Forest Long-Term Ecological Research site in which N has been added for 15 years to pine and hardwood forests in Massachusetts (Magill et al. 2004), the northern hardwood gradient experiment in which N has been added $\sim 3\times$ the ambient N deposition ($30 \text{ kg ha}^{-1} \text{ yr}^{-1}$) since 1994 to four different northern hardwood forests located along a 500 km geographic gradient, and the NITrogen saturation EXperiments (NITREX) in Europe in which N was either added to throughfall at sites with low or moderate N deposition or removed from throughfall at sites with high N deposition for four to six years (Wright and van Breemen 1995, Tietema et al. 1998).

Changes in N cycling have been observed in both the gradient studies and the whole ecosystem N manipulations. For example along the deposition gradients positive relationships between N deposition and N cycling variables such as net nitrification, mineralization, and forest floor N have been measured in multiple studies (Lovett and Rueth 1999, McNulty et al. 1991, Dise et al. 1998a). While in the whole-ecosystem manipulations changes in N leaching (Pregitzer et al. 2004, McDowell et al. 2004), leaves (Zak et al. 2004), and forest floor N (McNulty et al. 2005) were found.

However, both types of studies have their drawbacks. The whole ecosystem N additions are often at very high levels (3-10 x ambient loading), and the gradients span long distances 10-100's of kilometers). There are several drawbacks to comparing distant sites along deposition gradient. One is that they often have different land use histories or other varying conditions (Emmett et al. 1998a). Another is that some variables such as foliar N and deposition can co-vary with climate and elevation (Aber et al. 2003).

In this study I use the short (<150 meters) deposition gradient adjacent to a roadway that results from near-source deposition of mobile source emissions in order to address how chronic, low-level N deposition affects forest N cycling and retention. As part of this study, I measured N pools (foliage, forest floor), inputs (N deposition), and N outputs (leaching) from July 2006 until July 2007 in plots at 10, 50, 100, and 150 meters away from a moderately traveled roadway. I evaluated 6 metrics commonly used to calculate N budgets and evaluate N cycling in forests: N deposition (bulk and throughfall), leaf C:N, leaf decomposition rates, forest floor C:N and pH, and N leaching. I expected that areas closer to the roadway would have higher N deposition, and would be more likely to show signs of chronic N loading such as changes in forest floor C:N, decreased decomposition, and increased leaching of N.

Methods

This study was conducted in the Waquoit Bay Estuarine Research Reserve (N41 35.834 W70 30.090) on Cape Cod in Massachusetts (Figure 3.1). In 2006, the average wind direction was predominantly from the south-south west to the north-west and average annual wind speed, precipitation, and temperature were 0.76 m sec⁻¹, 121 cm, and 10.5 °C respectively (NOAA 2008). Soils are a Carver loamy coarse sand (CcA) from parent material deposited in the Sandwich Moraine outwash during the Wisconsinian glaciation (Fletcher 1993). The research was conducted in a mid successional stage aggrading red oak (*Quercus rubra*) and red pine (*Pinus resinosa*) forest (Seely and Lajtha 1997). Research plots were located at 10, 50, 100, and 150 meters along a transect perpendicular to Route 28, a class 3 road (rural minor arterial and urban extensions) which contained an integral curb that diverted road runoff to drywells and had an average daily traffic volume of 13,300 vehicles day⁻¹ (MHD 2008). Above-ground forest biomass was determined using diameter at breast height

measurements and allometric equations from (Jenkins et al. 2003). Leaf-area-index (LAI) estimates were made by applying a leaf area: leaf weight ratio to the amount of leaves collected in each plot during litter fall. The ratio was made by collecting leaves from 3 trees in each plot, measuring their area using a LI-COR LI-3100 area meter (LI-COR Lincoln, NE, USA) followed by drying and weighing each set of samples. This ratio was then applied to the litter fall estimates in each plot to obtain leaf area index (Table 3.1).

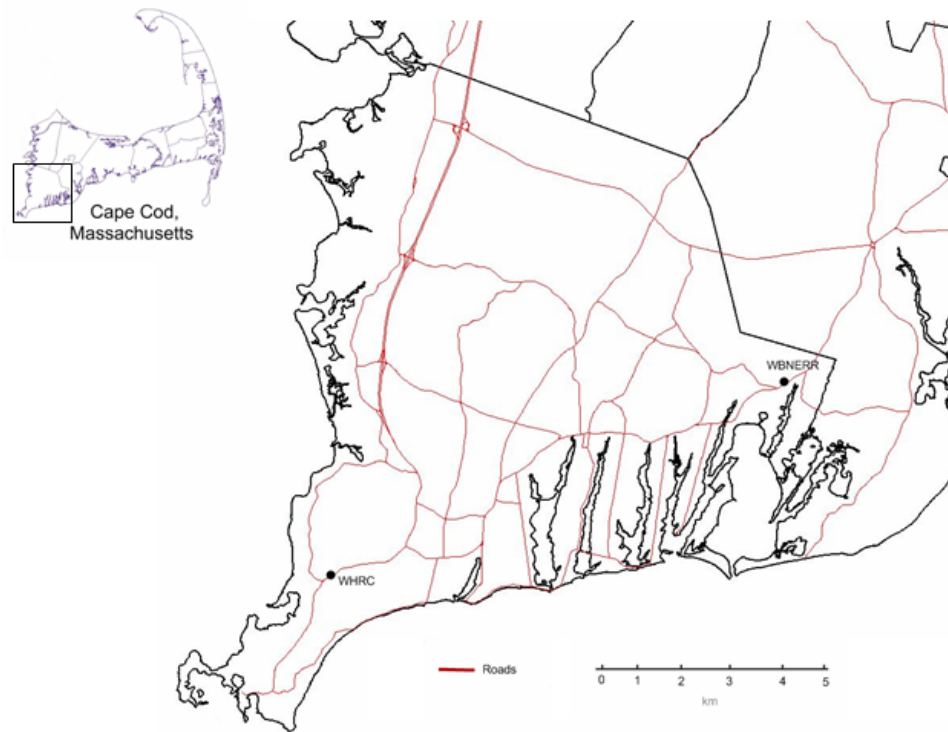


Figure 3.1. Study site at the Waquoit Bay Road and non-road study sites were located within the Waquoit Bay Watershed on Cape Cod in Falmouth, Massachusetts.

Deposition was estimated using measurements made with both bulk deposition and throughfall collectors placed along transects perpendicular to the roadway. Bulk collectors were located in an open field at 10, 50, and 100 m from the road and throughfall collectors were located in forest plots at 10, 50, 100, and 150 m from the roadway. Collectors, which were suspended ~ 1m off the ground, consisted of a 20-cm

diameter polyethylene funnel with a polyester fiber filter plug (to keep out coarse debris) attached to a 2-l amber HDPE bottle. Following each precipitation event from Jul 2006 – Jul 2007, collectors were brought back to the laboratory where the volume in each was measured and sub-samples were taken for nutrient analysis (total dissolved nitrogen, NO_3^- , and NH_4^+). Sub-samples were filtered using an ashed Whatman® GF/F (nominal pore size of $0.7\mu\text{m}$) glass fiber filter and stored at -20°C until analysis on a Lachat quick chem. auto analyzer (Hach Company Loveland, CO, USA). Mean annual N deposition for each distance was calculated by averaging the mean annual N flux for each distance. The N flux for each collector was calculated by converting the concentration to mass [(bottle volume (L) * concentration (mg L^{-1}) / funnel area (m^2) = mg m^{-2}], summing these for all the events over the period of interest, and dividing by the length of time in order to get either $\text{mg m}^{-2} \text{ day}^{-1}$ or $\text{kg ha}^{-1} \text{ yr}^{-1}$ for each collector.

Table 3.1. Site characteristics for plots along roadside gradients at WBNERR (\pm S.E.). One-Way ANOVA and Tukey's HSD pair wise comparison: ***P < 0.001, **P < 0.01, *P < 0.05.

Distance (meters)	Above ground biomass (Mg ha^{-1})	Mean DBH (cm)	Basal Area ($\text{m}^2 \text{ ha}^{-1}$)	LAI ($\text{m}^2 \text{ m}^{-2}$)
10	215 (.85)	17 (1.0)	34 (.11)	3.6 (.18)
50	82 (.67)	16 (1.0)	14 (.10)	3.8 (.12)
100	151 (1.4)	18 (1.6)	27 (.24)	3.4 (.31)
150	162 (1.7)	19 (1.7)	30 (.91)	2.6 (.23)

Foliage samples were collected during the growing season in 2006 from the mid canopy of red oak trees in each plot using a 6-m long pole pruner. Three samples were collected from each plot, with each sample consisting of leaves from 3 areas of the mid canopy of an individual tree, which were combined, dried @ 70°C , ground using a Cyclone mill (UDY Corporation, Fort Collins, CO, USA), and analyzed for C

and N using a LECO C, N, H, S analyzer (LECO Corporation, St. Joseph, Michigan USA).

Litter bags were used to determine litter mass loss across the deposition gradient. In 2004 litter was collected throughout each plot using six 0.212-m² baskets per plot, allowed to air dry, separated by species, and sub-sampled for lignin, C, and N analysis. Sub-samples were ground and analyzed for the following carbon fractions: cell solubles; hemicellulose and bound protein; cellulose; and lignin and other recalcitrants, which were determined on an ash-free dry mass basis using an ANKOM Fiber Analyzer (Ankom Technology, Macedon, NY, USA) (Van Soest 1994). I also analyzed samples for C and N on a PerkinElmer 2400 analyzer (PerkinElmer Corporation, Waltham, Massachusetts, USA). Four litter bags for each distance along the transect were made by filling a 20-cm² bag constructed from 1 mm nylon mesh with ~10g of red oak litter from that site. Litter bags were deployed for two years from 21 Nov-04 - 21 Nov-06, retrieved, dried for 1 week @ 70°C, and reweighed to calculate mass loss.

Litter fall was collected each week throughout the fall of 2006 using 8 baskets spread throughout each plot. Each week litter was collected from the baskets and dried for 48 h @ 70°C; once leaf fall was complete; all litter from each distance was combined, separated by species, weighed to obtain a seasonal litter mass, and sub-sampled. Sub-samples were ground using a Cyclone mill and analyzed for C and N using a LECO elemental (C, N, H, S) analyzer.

To measure changes in the forest floor across the deposition gradient, samples were collected from three different areas within the plot each month from July-December and in May and June. Each sample consisted of a composite of 3 cores taken within 20-30 cm of one another. Cores were taken by clearing away the O_i or L horizon (the litter that is still largely intact and recognizable as litter) and inserting a

sharpened 5 x 30 cm PVC tube to a depth of 20 cm. The depth of the organic horizon was calculated by difference using the distance from the top of the core to the surrounding forest floor and the distance from the bottom of the core to top of the mineral soil. Upon removing the core, it was separated into organic and mineral horizons which were then combined with the other two cores that comprised the sample. Samples were then stored on ice and transported back to the laboratory where they were passed through a 4.75mm sieve, thoroughly mixed, weighed, and subsampled for moisture content, pH, and N and C content. Samples for N and C were dried @65 °C, ground using an 8000D Dual Mixer/Mill (SPEX), and analyzed using a LECO C, N, H, S analyzer. Samples for pH were analyzed according to Robertson et al. (1999). Briefly, 30 mls of deionized water were added to 15g of un-dried sieved soil. The mixture was stirred and allowed to stand for 30 minutes to equilibrate with atmospheric CO₂, stirred again, and the pH was then read to nearest 0.1 pH unit on an Orion Research digital pH/millivolt meter model 611.

Nitrogen leaching was measured along the N deposition gradient using ion exchange resin (IER) bags and zero-tension lysimeters. Although resin bags only provide relative indicators of NO₃⁻ leaching, their ease of use and low cost enables larger numbers to be deployed compared to lysimeters, which are difficult to install. By combining use of resin bags with lysimeters, I was able to capture larger spatial patterns and provide rigorous quantification of N leaching. The resin bags were similar to those used by Lovett et al. (2004), although deployment times were shortened as suggested by Giblin et al. (1994). Resin bags were prepared by placing ~10g of Sybron IONAC ASB-1P in nylon stocking. The resin bags were then cleaned and charged by soaking in 10% HCl for 1 hour, rinsing with Deionized (DI) water, and soaking in 0.5 NaOH overnight. Three groups of resins bags were placed in each plot, with each group consisting of 5 individual bags joined with 2 m of mason's twine.

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 each month from July - December, December - May, and May - June. 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^- using a Lachat auto-analyzer and cadmium reduction.

To calculate N flux and retention along the deposition gradient, 10 lysimeters were installed in each plot with 6 below the forest floor at ~10-12 cm and 4 below the rooting zone at ~ 50 cm. 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-l HDPE bottle. Following each precipitation event, lysimeter samples were collected and brought back to the laboratory where they were processed similarly to the precipitation samples. Mean annual flux was calculated for each collector similarly to the precipitation collectors. 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). Annual N retention efficiency was calculated as $1 - (\text{N inputs} - \text{N outputs}) / \text{N inputs}$ (Lajtha et al. 1995). Similarly to Lajtha et al. (1995), retention was calculated using Total (DIN + DON) dissolved N in throughfall corrected for canopy uptake and zero-tension lysimeters from below maximum rooting depth (50 cm).

Data analysis was performed using StatPlus Professional (Analystsoft, Vancouver, BC Canada). Differences in fluxes N in precipitation and through-fall away from roads were tested by one-way analysis of variance (ANOVA) and Tukey's HSD multiple comparison test for pair-wise comparisons between distances. Single pair comparisons were performed between measurement means from sites 10 meters from the road and those from farther away using paired two tailed Students t-Test. Differences were considered statistically significant at $p < 0.05$ unless otherwise noted.

Results

In this study I used an N deposition gradient that resulted from near source deposition of motor vehicle emissions away from a roadway to investigate the effects of increased N loading on forest N cycling. The deposition gradient was measured using bulk and throughfall collectors positioned along transects perpendicular to the roadway. There were no significant differences in N inputs via bulk deposition among collectors along the transect away from the road in the open field. Therefore, measurements of N inputs from the collectors at 10, 50, and 100 meters were averaged to give a bulk precipitation estimate of $4.76 \text{ (SE } \pm 0.17) \text{ kg TDN N ha}^{-1} \text{ yr}^{-1}$. The throughfall collectors were placed in forest plots along a transect in which there were no significant differences in characteristics such as DBH, biomass, or LAI (One-Way ANOVA and Tukey's HSD multiple comparison test (Table 3.1). There were significant differences in throughfall measurements between sites along the gradient, with throughfall N deposition near the road 37% to 48% higher than at sites farther away for TDN and DIN respectively (Table 3.2).

There were significant differences between the sites near the road and those farther away in several forest floor properties such as, thickness and mass (Table 3.3) and C:N ratio (Figure. 3.2). The forest floor at the 10 meter site was 2.9 cm thicker

and 4.9 kg m² greater in mass than the average of the sites farther away (Table 3.3). The forest floor at 10 meters had a C:N ratio of 34 (\pm 0.7) (Figure 3.2) and pH values of 4.02 (\pm 0.1) (Figure 3.3) compared to the forest floor at 150 meters which had a C:N of 39.5 (\pm 0.5) and a pH of 4.43 (\pm 0.15). These differences do not appear to be driven by differences in the amount of litter because there was no difference in the litter fall flux of either N or C across the gradient (Table 3.4). However, in litter collected in 2004 and used for a decomposition experiment there were significant differences in the percent N and C:N ratios, but not in carbon quality indicators such as lignin:N ratios or lignocellulose index (LCI) (Table 3.5) between sites near the road and those farther away.

Table 3.2. N flux for bulk and throughfall along roadside gradients at WBNERR (\pm S.E., n=4). One-Way ANOVA and Tukey's HSD pair wise comparison: ***P < 0.001, **P < 0.01, *P < 0.05.

Distance (meters)	NH ₄ ⁺ - N kg ha ⁻¹ yr ⁻¹	NO ₃ ⁻ - N kg ha ⁻¹ yr ⁻¹	TDN - N kg ha ⁻¹ yr ⁻¹	DON - N kg ha ⁻¹ yr ⁻¹	DIN - N kg ha ⁻¹ yr ⁻¹
Bulk	1.70 (.08)	2.07 (.07)	4.76 (.17)	.99 (.07)	3.77 (.14)
10	2.07 (.15)	3.05 (.22)	7.51 (.35)	2.39 (.20)	5.12 (.31)
50	1.25 (.06) **	2.25 (.08)*	5.33(.19) **	1.83 (.16) [†]	3.50 (.05) **
100	1.13 (.03) ***	2.12 (.05) **	5.35 (.09) ***	2.10 (.09)	3.25 (.04) **
150	1.13 (.03) ***	2.50 (.25)	5.85 (.40) *	2.22 (.14)	3.63 (.28) *

Table 3.3. Forest floor characteristics along roadside gradients at WBNERR (\pm S.E., n=8). Students T-Test comparing 10 meters to 50, 100, and 150 meters: ***P < 0.001, **P < 0.01, *P < 0.05, [†]P < 0.10.

Distance (meters)	Forest Floor mass (kg m ⁻²)	Forest floor thickness (cm)	Forest floor turnover (yrs)	Forest floor (pH)
10	21 (1.9)**	12.8 (.34)*	12.7 (1.16)	4.02 (.10)*
50	17 (1.6)	9.9 (.22)	10.1 (.96)	4.26 (.11)
100	16 (1.3)	9.5 (.19)	9.5 (.79)	4.37 (.15)
150	16 (1.6)	10.2 (.26)	10.9 (1.1)	4.43 (.15)

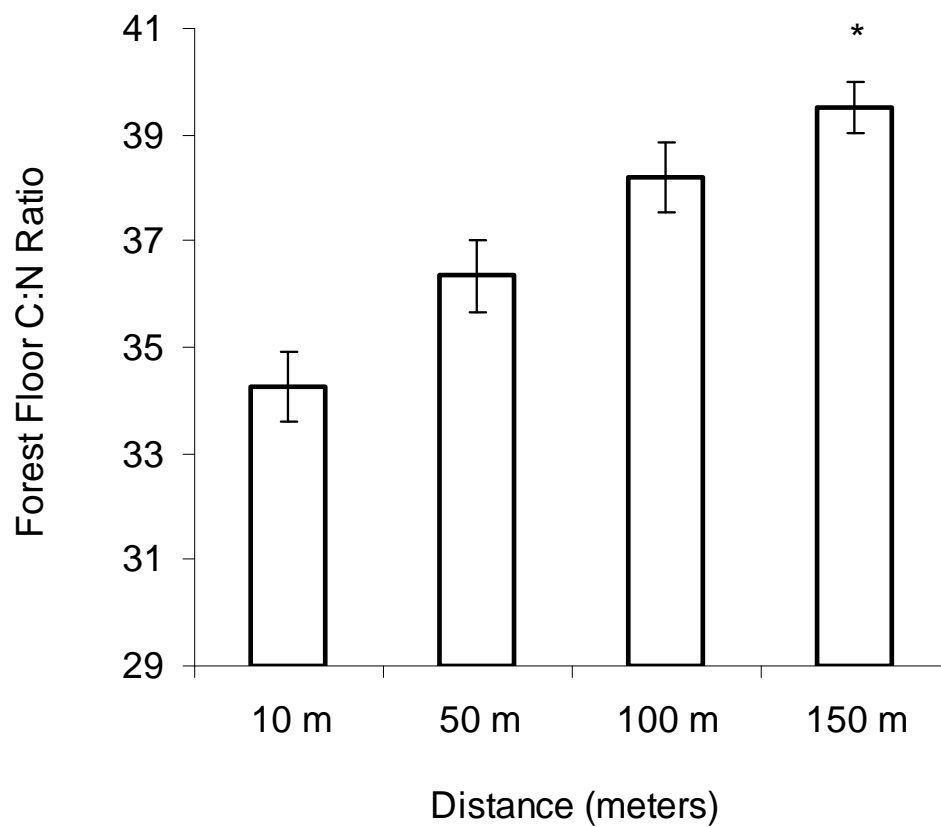


Figure 3.2. Forest floor C:N ratio at 10, 50, 100, and 150 meters from roadway (\pm SE, $n = 8$). One-Way ANOVA and Tukey's HSD pair wise comparison: *** $P < 0.001$, ** $P < 0.01$, * $P < 0.05$.

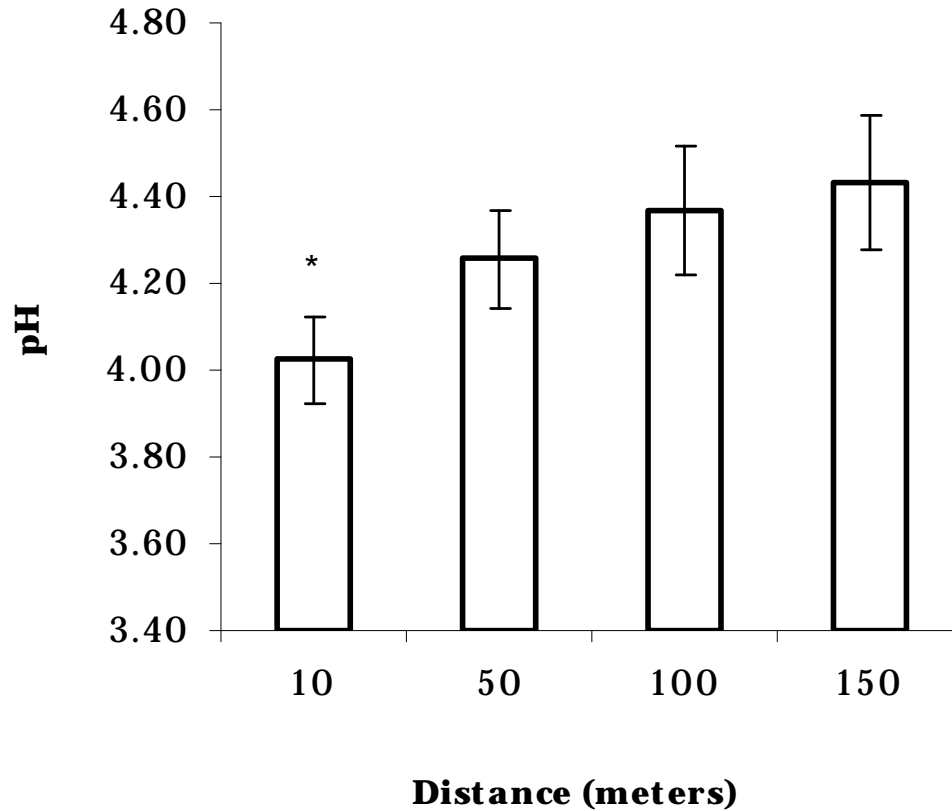


Figure 3.3. Average pH of forest floor organic matter collected at 10, 50, 100, and 150 meters (\pm SE, $n = 8$) at all sites. For students T-Test comparing pH at 10 meters to each distance: *** $P < 0.001$, ** $P < 0.01$, * $P < 0.05$, † $P < 0.10$.

Table 3.4. Leaf flux (concentration*mass) in plots along roadside gradients at WBNERR (\pm S.E., $n=6$). One-Way ANOVA and Tukey's HSD pair wise comparison: *** $P < 0.001$, ** $P < 0.01$, * $P < 0.05$.

Distance (meters)	Leaf flux C ($\text{g m}^{-2} \text{yr}^{-1}$)	Leaf flux N ($\text{g m}^{-2} \text{yr}^{-1}$)
10	164.8 (10.5)	2.3 (0.1)
50	168.1 (3.2)	2.0 (0.5)
100	165.0 (11.1)	2.4 (0.1)
150	143.4 (11.3)	2.8 (0.3)

Table 3.5. Litter characteristics along roadside gradients at WBNERR (\pm S.E., n=3). One-Way ANOVA and Tukey's HSD pair wise comparison: ****P < 0.0001, ***P < 0.001, **P < 0.01, *P < 0.05.

Distance (meters)	Percentage N	C:N	Lignin:N	LCI
10	0.90 (.01)	55.2 (.77)	18.4 (.12)	0.53 (.01)
50	0.84 (.01)****	60.1 (.94)****	18.9 (.71)	0.51 (.03)
100	0.77 (.01)***	66 (.60)****	21.4 (.50)	0.49 (.01)
150	0.70 (.01)**	71.3 (.68)**	21.8 (4.23)	0.45 (.05)

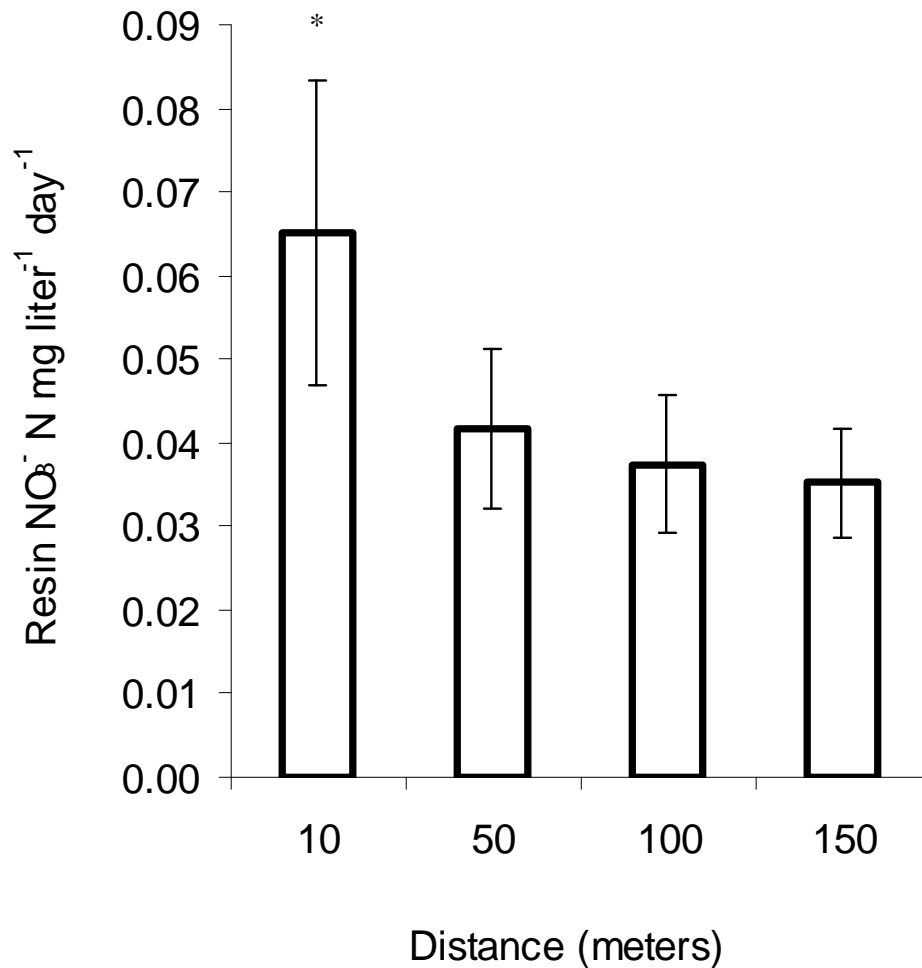


Figure 3.4. Nitrate collected on ion exchange resins at 10, 50, 100, and 150 meters (\pm SE, n = 8). For students T-Test comparing nitrate collected at 10 meters to each distance: ***P < 0.001, **P < 0.01, *P < 0.05, †P < 0.10.

Table 3.6. Leaching along roadside gradients at WBNERR measured with ion exchange resins and zero tension lysimeters placed beneath the forest floor at 15 cm and below the maximum rooting depth at 50 cm (\pm S.E., n=8). One-Way ANOVA and Tukey's HSD pair wise comparison: ***P < 0.001, **P < 0.01, *P < 0.05.

Distance (meters)	Beneath forest floor		Beneath rooting zone	
	DON - N kg ha ⁻¹ yr ⁻¹	DIN - N kg ha ⁻¹ yr ⁻¹	DON - N kg ha ⁻¹ yr ⁻¹	DIN - N kg ha ⁻¹ yr ⁻¹
10	5.7 (0.6)**	1.5 (.02)	3.0 (1.1)	0.7 (0.2)
50	3.9 (0.2)	1.3 (0.2)	0.9 (0.2)*	0.7 (0.1)
100	4.2 (0.2)	1.0 (0.3)	1.4 (0.3) *	0.5 (0.1)
150	4.5 (0.6)	1.3 (0.1)	1.4 (0.5)*	0.4 (0.1)

There were significant differences along the deposition gradient in N leaching beneath both the forest floor and the rooting zone. Leaching beneath the forest floor near the road was elevated regardless of how it was measured, either with ion exchange resins (Figure 3.4) or with zero-tension lysimeters (Table 3.6). However, although there were generally decreasing amounts of NO₃⁻ collected on ion exchange resins and smaller fluxes of all species of N in lysimeters along the transect, only differences between 10 m and the other sites were significant, while differences among the 50, 100, and 150 meter sites were not significant. There were no significant differences between 10 meters and the sites further away in DIN flux either beneath the forest floor or the rooting zone.

Discussion

Collectively, my results indicate that there is a significant gradient in N deposition that results in differences in N cycling between sites near the road (i.e., 10 meters away) and those farther away (50, 100, and 150 meters). The differences along the deposition gradient are primarily in the throughfall, forest floor organic layer and result in decreased C:N ratio and increased N leaching in areas near the road that experience higher deposition.

In order to estimate N deposition, total inputs of both wet and dry N need to be accounted for. While measuring wet inputs of N via precipitation are straightforward, measuring inputs of gaseous and particulate N is more difficult. There are several different methods of estimating dry N input. It can be inferred based on nitrogen content of atmospheric gases and particulates, along with their computed deposition rates. In the U.S., two networks are using this approach: NOAA's Atmospheric Integrated Research monitoring Network (AIRMoN-dry) and the EPA sponsored Clean Air Status and Trends Network (CASTNet). Some researchers have used either proxy collectors such as artificial trees (Dambrine et al. 1998, Stachurski and Zimka 2000), and Petri plates (Lindberg and Lovett 1985), or a ratio of wet:dry deposition (Lovett and Lindberg 1993, Valiela et al. 1997). Others 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 (Lovett and Lindberg 1984, Lajtha et al. 1995). Throughfall is likely an underestimate of total deposition for several reasons. The first is that the different forms of N enter the leaf through different pathways with nitric acid vapor, ammonium, and nitrate ions that accumulate on leaf surfaces from gaseous and particulate deposition (i.e., dry deposition) being transported into the leaf through cuticular diffusion (i.e., leaf surface uptake) while gaseous NH_3 , NO and NO_2 are taken up via the stomata (Draaijers et al. 1996). Thus, any of the NH_3 , and NO_x that is taken by the canopy and not washed off the leaf surface results in throughfall underestimating dry deposition. Therefore in order to estimate total deposition using this method it is necessary to account for net canopy exchange which is the amount of N either taken up or leached by the canopy (Lovett and Lindberg 1984).

Our estimate of wet N input by way of bulk precipitation (which measures mostly wet as well as some dry) is comparable to other measurements made at our

site, as well as those made 60 km away by the NADP. For the period of Jul 2006 – Jul 2007, our estimate of bulk DIN (NO_3^- and NH_4^+) deposition was $3.77 (\text{SE} \pm 0.14) \text{ kg N ha}^{-1} \text{ yr}^{-1}$ (Table 3.2) which is similar to deposition estimates made at the nearest NADP site for 2006 ($3.02 \text{ kg N ha}^{-1} \text{ yr}^{-1}$) (NADP 2009) as well as those of Lajtha et al. (1995) ($4.2 \text{ kg N ha}^{-1} \text{ yr}^{-1}$) and Seeley et al. (1998) ($2.8 \text{ kg N ha}^{-1} \text{ yr}^{-1}$).

In this study in order to get a range of estimates for deposition I calculated deposition using both DIN, which is an underestimate because of canopy uptake and conversion of DIN to DON and TDN, which may overestimate N deposition if some of the organic N is leached from canopy surfaces as opposed to resulting from conversion of deposited DIN. In order to account for canopy uptake I corrected the DIN inputs (Table 3.2) which were similar to those of Lajtha et al. (1995) ($3.7 \text{ kg ha}^{-1} \text{ yr}^{-1}$) using the net-throughfall (throughfall-bulk) measurements of DIN made at our non-road site (Bettez chapter 2). The average canopy uptake across the transect was $0.16 \text{ mg DIN m}^{-2} \text{ day}^{-1}$ ($\pm \text{S.E } 0.05$). Assuming this canopy uptake occurs from May-Nov when foliage is present, the throughfall inputs along the transect need to be adjusted upward by 8%. When applied to our throughfall measurements, total DIN inputs along our roadside transect range from $5.42 (\text{SE} \pm 0.35) \text{ kg N ha}^{-1} \text{ yr}^{-1}$ at 10 m, to $3.93 (\text{SE} \pm 0.32) \text{ kg N ha}^{-1} \text{ yr}^{-1}$ at 150 m.

I have chosen, similarly to Lajtha et al. (1995), Valiela et al. (1997), and Bowen et al. (2001), to use TDN (DIN + DON) as an estimate of N inputs in our study because TDN captures any conversions to DON by microorganisms on canopy surfaces. While there are fewer reported results for TDN in the literature, our estimate of TDN inputs in bulk deposition ($4.76 (\text{SE} \pm 0.17) \text{ kg N ha}^{-1} \text{ yr}^{-1}$) (Table 2) are similar to those of Seeley et al. (1998) ($5.1 \text{ kg ha}^{-1} \text{ yr}^{-1}$).

Our estimates of TDN inputs in throughfall (Table 3.2) are lower than those of Lajtha et al. (1995) ($11.3 \text{ kg ha}^{-1} \text{ yr}^{-1}$) and Seeley et al. (1998) ($9.5 \text{ kg ha}^{-1} \text{ yr}^{-1}$) which

is reasonable considering that throughfall measurements can be variable from year to year (Parker 1983). In a study investigating retention and leaching losses of atmospherically derived N in the Waquoit Bay watershed, Lajtha et al. (1995) estimated total N inputs to be $13.1 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ by adjusting the measured total N inputs in throughfall ($3.7 \text{ kg ha}^{-1} \text{ yr}^{-1}$ DIN and $7.6 \text{ kg ha}^{-1} \text{ yr}^{-1}$ DON) by 16% ($\sim 1.8 \text{ kg N ha}^{-1} \text{ yr}^{-1}$) to account for canopy uptake. Canopy uptake was calculated using an Integrated Forest Study (IFS) regression of net canopy uptake vs. throughfall total N (Lovett and Lindberg 1993). If similar estimates of canopy uptake are applied to our throughfall measurements, total N inputs along our roadside transect range from $8.71 \text{ (SE } \pm 0.40) \text{ kg N ha}^{-1} \text{ yr}^{-1}$ at 10 m, to $6.78 \text{ (SE } \pm 0.47) \text{ kg N ha}^{-1} \text{ yr}^{-1}$ at 150 m. While our deposition estimates are lower than those of Lajtha et al. (1995) it is the gradient in N deposition away from the road that examined here.

The N saturation hypothesis provides a framework to describe the response of forests to chronic N deposition. In general, in response to increases in N availability, forest soils and plants are expected to progress through several stages, from N limitation where there is high N retention, to N saturation where N limitation is alleviated and nitrate mobility (leaching) in soil is elevated (Aber et al. 1998). I have included DON in our N retention efficiency calculations because the majority of N losses ($78\% (\pm 1.5)$) in our system are in the form of DON (which is similar to the 76% found by Lajtha et al. (1995)). Our N retention efficiencies range from 58-73% across the gradient (with the lowest retention rate occurring near the road) (Table 3.7). These retention rates, although higher than the 40-62% retention rates calculated by Lajtha et al. (1995) are comparable to the 65% forest N retention rates of Valiela et al. (1997).

Table 3.7. N retention estimates in forest plots along roadside gradients at WBNERR calculated as $1 - (\text{annual N export below the rooting zone} / \text{estimated annual N inputs in throughfall collectors corrected for canopy uptake using IFS regression of net canopy uptake and throughfall total N})$

Distance (meters)	Percent N Retention
10	58
50	73
100	69
150	73

The decreases in forest floor C:N ratios and increases in N leaching associated with areas of greater N deposition (closer to roads) are similar to results from several studies in the US and Europe that investigated the impact of increased N on forests using either regional deposition gradients (Dise et al. 1998b, Aber et al. 2003) or whole ecosystem N manipulations (Gundersen et al. 1998, Magill et al. 2004). However unlike in these other studies, which required considerable effort either in data collection to compare between sites across large transects (100 km or more) or in continued non-natural N additions, with ongoing deposition along the roadside, the issues of loading rates and of site differences that affect other studies are overcome. Our deposition spatial gradient is short, leading to far greater homogeneity in forest conditions and the road-side sites in this study have likely been experiencing increased deposition for many decades since emissions were many times higher in the past. Even though emission rates from individual vehicles have decreased by 99% since the Clean Air Act was enacted in 1970 (NRC 2006), emissions of NO_x from highway vehicles have increased by ~6% (US EPA 2000) due to the number of miles driven having more than doubled (~2.5 x) over the same time period (FHWA 2008). Based on our current deposition estimates for TDN ($0.75 \text{ mg m}^{-2} \text{ yr}^{-1}$) and our observed forest floor mass, it would it over take ~38 years to shift the forest floor C:N ratio the 5.3 units seen between our 10 and 150 meter sites along the deposition gradient.

Studies investigating the effects of chronic N additions find different responses in the fluxes and pools of N in forests depending on the type of study. These different responses are the result of the lag time between when parameter is manipulated and when a response is observed. This is related to the size of the N pool being impacted with small pools responding quickly and large pools responding more slowly. These response times have been characterized as fast (within the first year) (i.e., dissolved N in soil), intermediate (2-4) years (i.e., foliar N), or slow (>5) years (i.e., forest floor N). For example, after manipulating N inputs by either adding or removing N, corresponding increases (McDowell et al. 2004) or decreases (Gundersen et al. 1998) were measured in fluxes of N in soil solutions within a few years. Studies that use the deposition gradients that have been occurring for decades (i.e., those across the Northeastern US and Northern Europe) find increases in N leaching as well as decreases in forest floor C:N (Dise and Wright 1995, Aber et al. 2003). However, while these transect studies document changes in slow turnover pools because of differences between sites in climate and land use history they have difficulties comparing differences within the fast turnover pools.

In contrast to N manipulation studies which tend to document changes in short-term turn-over but not long-term turn-over pools, and transect studies which have difficulties comparing differences in short term pools between sites, I document significant changes along a 150 meter gradient in both smaller faster turnover pools such as fluxes of N, and larger slower turnover pools such as the forest floor C:N and pH.

With regard to changes in the intermediate turnover pools such as foliar N, our results were variable. While I did find difference in foliage and litter samples from 2004, with samples taken near the road having higher % N, I did not find any significant difference in samples taken in 2006. This is possibly due to recent

outbreaks of an introduced pest, *Operophtera brumata* (L.) (winter moth) which has appeared in increasing numbers in our study sites throughout the experiment. In early spring of 2006, much of the canopy was defoliated resulting in a flush of secondary leaves which as litter have been shown to have lower nitrogen content (May and Killingbeck 1995). These results highlight the multiple variables that affect N cycling and N pools in forests, and illustrates the how year to year variability can, at times, overwhelm, the effect of N deposition. Multiple year and multiple metric assessments are clearly required to assess and quantify impacts of chronic N deposition.

While insect defoliations are known to impact foliar chemistry their impact on soil solution N and N retention appears to not be as significant. In a study that investigated the effects of aphids and leaf-feeding lepidopterous larvae Stadler et al. (2001) found little difference between the chemistry of soil solutions collected from the forest floor beneath infested and uninfested trees. Lovett et al. (2002) used ^{15}N labeled oak litter to investigate the fate of the foliar N that is consumed by insects and deposited to the forest floor as frass, greenfall, and insect biomass. They found that very little N is leached from the system and that most of the N that is deposited on forest floor as frass is immobilized by microbes and retained in the soil organic matter. Similar retention was also reported at Hubbard Brook following an insect defoliation event which appeared to have no effect on watershed N export (Bormann and Likens 1979) although other studies have shown more significant effects (Swank et al. 1981, Webb et al. 1995).

I also found no difference in litter fall flux of C across the gradient, thus the increased mass and thickness of the forest floor near the road is likely due to difference in the decomposition rate. Along our gradient there are differences in forest floor turnover time, a commonly used index of decomposition rate. The forest floor turnover time, which is estimated as the forest floor mass divided by the C deposited

annually in litter fall (Chapin and Chapin 2006), is 25% longer at 10 meters than it is farther away ($P < 0.05$). A longer turnover time means less decomposition and greater potential for litter accumulation on the forest floor. Using this method the turnover time of litter 10 meters from the road was 12.7 ($SE \pm 1.2$) years compared to average of 10.1 ($SE \pm .40$) years for the other sites (Table 3.3). Similar results of longer turnover times near the road were also found with the litter decomposition experiment carried out from 2004-2006.

Litter near the road had a mass loss $\sim 15\%$ lower over the two year experiment than litter from farther away (Figure 3.5). Litter decay patterns have been attributed to differences in substrate quality (C and N) and the amount of externally supplied N. A simple assessment of substrate quality that takes both C and N into account is its C:N ratio. The quality of either C or N can also be assessed individually using the lignocellulose index (LCI), which is the ratio of the lignin mass to the ratio of either the combined lignin plus cellulose mass for carbon, or lignin:N ratio for N. In studies that have compared decomposition with litter quality, litter from different species spanning a large range in either C:N, LCI or lignin:N ratio have been used, often with oak representing the lowest quality litter (Carreiro et al. 2000, Hobbie 2005). In general, higher quality litter with either a lower LCI or lower lignin:N ratio, decomposes faster.

The different indices of litter quality in our study gave contradictory results, with the litter from the site near the road having lower C:N and lignin:N ratios, which would be indicative of more degradable litter, but also having a higher LCI, which would be indicative of a more slowly degrading litter. However, these differences in lignin:N and LCI across the deposition gradient were small and not significant, especially when compared to difference in other studies in which different types of litter were used (Carreiro et al. 2000, Hobbie 2005).

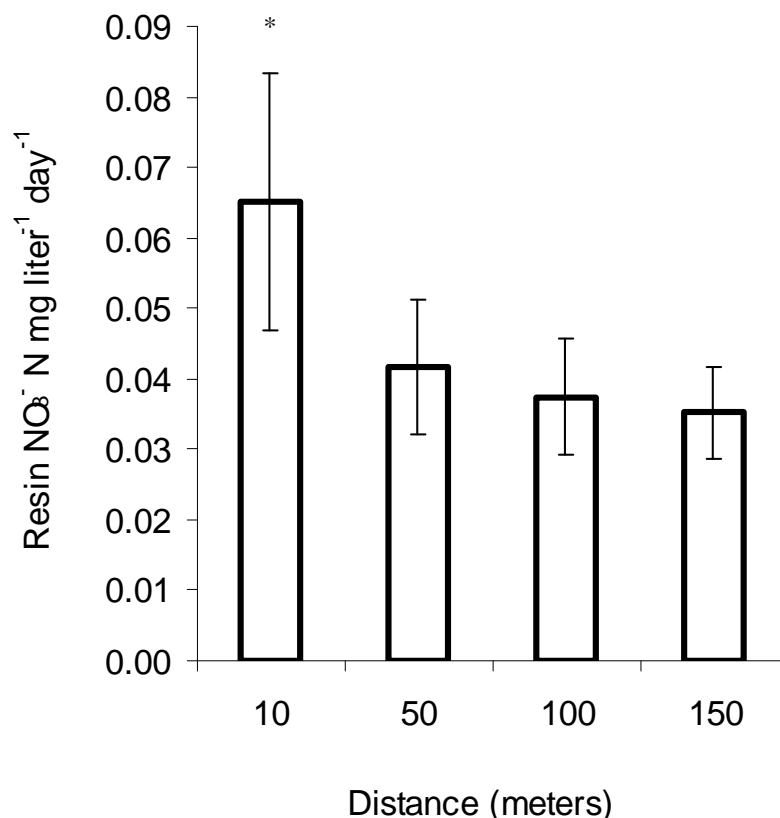


Figure 3.5. Mass loss of oak litter collected and incubated at 10, 50, 100, and 150 meters for twenty four months (\pm SE, $n = 4$) at all sites. One-Way ANOVA and Tukey's HSD pair wise comparison: *** $P < 0.001$, ** $P < 0.01$, * $P < 0.05$.

Another possible explanation for the decreased decomposition rate near the road is that with increased deposition the low quality litter used in this study decomposed more slowly. While additional N has been shown to increase (Hobbie 2000) decrease (Magill and Aber 1998) or have no effect (Fog 1988) on decomposition, both the amount of added N and the type of litter have been shown to have an effect on decomposition. In a meta-analysis of the effects of N addition on litter decomposition Knorr et al. (2005) found that at low fertilization rates (2-20 times the anthropogenic N deposition level) litter decomposition was inhibited (Knorr et al. 2005). While Fog (1988) found inconsistent results when adding fertilizer, the author noted that decomposition rates in the litters with the highest lignin content were often depressed with increased N. This increased N is thought to suppress microbial

production of the ligninolytic enzymes which are much more important for decomposing “low quality” lignin rich litter such as oak (Magill and Aber 1998). In a study that investigated the effects of increased N deposition on decomposition of different quality litters Carreiro et al. (Carreiro et al. 2000) found that in high lignin oak litter similar to ours, the activity of the lignin-degrading phenol oxidase declined substantially with increased N. This decrease in enzyme activity found by others is a possible explanation for the decreased decomposition and increased forest floor mass found in our site closest to the road.

Along the deposition gradient there was a significant change in the percent of TDN due to DIN, which decreased from 68% at 10 m to 62% at 150 m due mainly to changes in NH_4^+ (Figure 3.6). This higher NH_4^+ near the road is likely due to deposition of motor vehicle emissions of NH_3 which is later ionized into NH_4^+ in the canopy. NH_3 has a high deposition velocity and I estimate that approximately 10% to 25% of ammonia emissions from vehicles at our site are deposited within 50 m of the road (Marino et al. In Prep). Unlike NO_x (NO & NO_2) emissions which are formed during combustion, NH_3 is a secondary pollutant in motor vehicle emissions that results from the over-reduction of NO by three-way catalytic converters. While NH_3 is not regulated or widely monitored, the US EPA currently uses an estimate of $\sim 70 \text{ mg NH}_3\text{-N km}^{-1}$ per vehicle for their emission models compared to $\sim 116 \text{ mg NO} - \text{N km}^{-1}$ per vehicle (US EPA 2001), although others have found higher levels ($\sim 118 \text{ mg N-NH}_3 \text{ km}^{-1}$) under urban driving conditions resulting in vehicles, at least in urban areas, being an important source of NH_3 (Heeb et al. 2008). Furthermore, this over reduction to NH_3 has been increasing and NH_3 's percentage of overall emissions is now thought to account for up to 40-80% of total motor vehicle emissions (Heeb et al. 2008).

Based on other research at our site comparing road and non-road edges, the deposition gradient away from the roadway documented here is the result of near

source deposition of car and truck emissions (Marino et al. in prep), not simply an edge effect (Bettez Chapter 2). Marino et al. (In Prep) have found that 10-25% of the NH_3 and 1 % of the NO_x is deposited within 50 m of a roadway. In a study comparing road and non-road edges Bettez et al. (Chapter 2) found that compared to non-road edges deposition along road side edges was elevated. Results from this study indicate that the deposition gradient extends ~ 150 meters from the roadway with the plots near the road receiving ~ 1.25-1.5x the normal deposition, or an additional $1.4 \text{ kg ha}^{-1} \text{ year}^{-1}$ of N. As a result of this increased deposition there were significant differences between samples from 10 meters and those from farther away for decomposition, forest floor mass, forest floor C:N, and resin leaching.

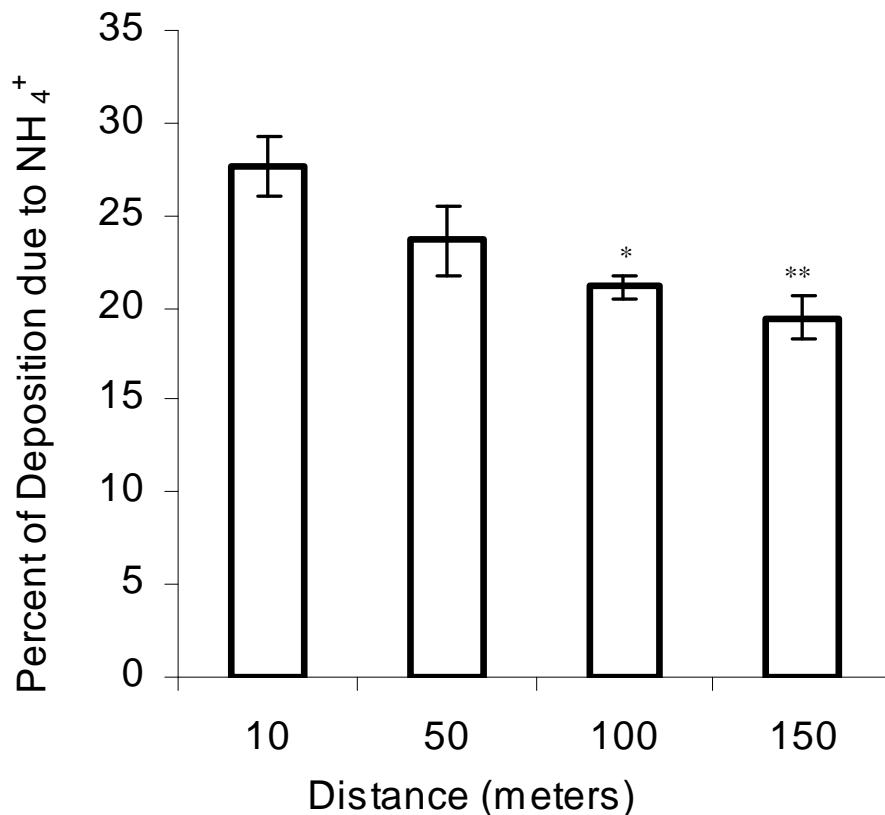


Figure 3.6. Percent of TDN in throughfall that is NH_4^+ at 10, 50, 100, and 150 meters from roadway for 38 events from 12 July 2006 – 12 July 2007 (\pm SE, $n = 4$). One-Way ANOVA and Tukey's HSD pair wise comparison: *** $P < 0.001$, ** $P < 0.01$, * $P < 0.05$.

One criticism of the applicability of this work to the larger question of how chronic N deposition affects forest ecosystems is how other roadside pollutants from vehicle exhaust such as salt, ozone and heavy metals, may also affect the forests along this gradient. While numerous studies investigating these elements have found higher concentrations of many of these near roads (Lytle et al. 1995, Zechmeister et al. 2005, Sabin et al. 2006, Hooda et al. 2007, Zereini et al. 2007), these pollutants have an exponential-like decrease with distance from the road, usually reaching background levels within 5 - 10 m from the edge of the road (Zehetner et al. 2009). Furthermore, the few studies that have examined the impacts of these pollutants on ecosystem processes such as decomposition (Post and Beeby 1996) or mineralization (Kalbitz et al. 2008) have not found any. While there is the possibility that these other elements may also play a role in the patterns seen along our gradient, multiple lines of evidence such as changes in decomposition, forest floor C:N, pH, and leaching indicate that the changes are driven by the N deposition gradient.

The results from this study indicate that areas near the road that have most likely been experiencing increased deposition for decades are showing signs of N saturation with higher fluxes of N and lower forest floor C:N ratios. Understanding the impacts mobile source emissions near roadways is important. Indeed, road impacted areas are fast becoming the rule and not the exception, it is estimated that about 20% of the US is affected by roads in one way or another such as altered drainage, noise, and introduction of invasive species, (Forman 2000). With more than 6.3 million km of roads in the conterminous US (Forman 2003) roads are so ubiquitous that it is difficult to get more than 35 km away from a road (Watts et al. 2007), and 20% of the land area is within 127 meters of one (Riitters and Wickham 2003). The results from this study highlight that N deposition is elevated near roadways and that estimates of N deposition based on collectors in rural areas are probably underestimates. These

deposition gradients away from roadways have been occurring for decades and are useful for investigating the effects of chronic low-level N deposition on forest N cycling.

REFERENCES

- Aber, J., W. McDowell, K. Nadelhoffer, A. Magill, G. Berntson, M. Kamakea, S. McNulty, W. Currie, L. Rustad, and I. Fernandez. 1998. Nitrogen saturation in temperate forest ecosystems - Hypotheses revisited. *Bioscience* **48**:921-934.
- Aber, J. D., C. L. Goodale, S. V. Ollinger, M. L. Smith, A. H. Magill, M. E. Martin, R. A. Hallett, and J. L. Stoddard. 2003. Is nitrogen deposition altering the nitrogen status of northeastern forests? *Bioscience* **53**:375-389.
- Aber, J. D., G. R. Hendrey, D. B. Botkin, A. J. Francis, and J. M. Melillo. 1982. Potential Effects of Acid Precipitation on Soil-Nitrogen and Productivity of Forest Ecosystems. *Water Air and Soil Pollution* **18**:405-412.
- Aber, J. D., K. J. Nadelhoffer, P. Steudler, and J. M. Melillo. 1989. Nitrogen Saturation in Northern Forest Ecosystems. *Bioscience* **39**:378-386.
- Bettez, N. D. Chapter 2. Near-source deposition of mobile source emissions, roads as N deposition hotspots.
- Bormann, F. H., and G. E. Likens. 1979. Pattern and process in a forested ecosystem : disturbance, development, and the steady state based on the Hubbard Brook ecosystem study. Springer-Verlag, New York.
- Bowen, J. L., and I. Valiela. 2001. Historical changes in atmospheric nitrogen deposition to Cape Cod, Massachusetts, USA. *Atmospheric Environment* **35**:1039-1051.
- Bricker, S. B., C. G. Clement, D. E. Pirhalla, S. P. Orlando, and D. R. G. Farlow. 1999. National Estuarine eutrophication assessment: Effect of Nutrient enrichment in the Nation's Estuaries. NOAA, National Ocean Service, Special Projects Office and National Centers for the Coastal Ocean Service, Silver Springs, MD.
- Carreiro, M. M., R. L. Sinsabaugh, D. A. Repert, and D. F. Parkhurst. 2000. Microbial enzyme shifts explain litter decay responses to simulated nitrogen deposition. *Ecology* **81**:2359-2365.
- Chapin, F. S., and M. C. Chapin. 2006. Alaska's changing boreal forest. Oxford University Press, Oxford ; New York.
- Dambrine, E., B. Pollier, M. Bonneau, and N. Ignatova. 1998. Use of artificial trees to assess dry deposition in spruce stands. *Atmospheric Environment* **32**:1817-1824.

- Dise, N. B., E. Matzner, and M. Forsius. 1998a. Evaluation of organic horizon C: N ratio as an indicator of nitrate leaching in conifer forests across Europe. *Environmental Pollution* **102**:453-456.
- Dise, N. B., E. Matzner, and P. Gundersen. 1998b. Synthesis of nitrogen pools and fluxes from European forest ecosystems. *Water Air and Soil Pollution* **105**:143-154.
- Dise, N. B., and R. F. Wright. 1995. Nitrogen leaching from European forests in relation to nitrogen deposition. *Forest Ecology and Management* **71**:153-161.
- Draaijers, G. P. J., J. W. Erisman, T. Spranger, and G. P. Wyers. 1996. The application of throughfall measurements for atmospheric deposition monitoring. *Atmospheric Environment* **30**:3349-3361.
- Driscoll, C. T., D. Whitall, J. Aber, E. Boyer, M. Castro, C. Cronan, C. L. Goodale, P. Groffman, C. Hopkinson, K. Lambert, G. Lawrence, and S. Ollinger. 2003. Nitrogen pollution in the northeastern United States: Sources, effects, and management options. *Bioscience* **53**:357-374.
- Emmett, B. A., D. Boxman, M. Bredemeier, P. Gundersen, O. J. Kjonaas, F. Moldan, P. Schleppi, A. Tietema, and R. F. Wright. 1998. Predicting the effects of atmospheric nitrogen deposition in conifer stands: Evidence from the NITREX ecosystem-scale experiments. *Ecosystems* **1**:352-360.
- Federal Highway Administration. 2008. Traffic Volume Trends. U.S. Dept. of Transportation Federal Highway Administration, Washington, D.C.
- Fletcher, P. C. 1993. Soil Survey of Barnstable County, Massachusetts. The Massachusetts Agricultural Experiment Station. United States Service Soil Conservation Service, Washington, D.C.
- Fog, K. 1988. The Effect of Added Nitrogen on the Rate of Decomposition of Organic-Matter. *Biological Reviews of the Cambridge Philosophical Society* **63**:433-462.
- Forman, R. T. T. 2000. Estimate of the area affected ecologically by the road system in the United States. *Conservation Biology* **14**:31-35.
- Forman, R. T. T. 2003. Road ecology: science and solutions. Island Press, Washington, DC.
- Giblin, A. E., J. A. Laundre, K. J. Nadelhoffer, and G. R. Shaver. 1994. Measuring Nutrient Availability in Arctic Soils Using Ion-Exchange Resins - a Field-Test. *Soil Science Society of America Journal* **58**:1154-1162.

- Gundersen, P., I. Callesen, and W. de Vries. 1998. Nitrate leaching in forest ecosystems is related to forest floor C/N ratios. *Environmental Pollution* **102**:403-407.
- Heeb, N. V., A. M. Forss, S. Bruhlmann, R. Luscher, C. J. Saxer, and P. Hug. 2006. Three-way catalyst-induced formation of ammonia-velocity- and acceleration-dependent emission factors. *Atmospheric Environment* **40**:5986-5997.
- Heeb, N. V., C. J. Saxer, A.-M. Forss, and S. Brühlmann. 2008. Trends of NO-, NO2-, and NH3-emissions from gasoline-fueled Euro-3- to Euro-4-passenger cars. *Atmospheric Environment* **42**:2543-2554.
- Hobbie, S. E. 2000. Interactions between litter lignin and soil nitrogen availability during leaf litter decomposition in a Hawaiian Montane forest. *Ecosystems* **3**:484-494.
- Hobbie, S. E. 2005. Contrasting effects of substrate and fertilizer nitrogen on the early stages of litter decomposition. *Ecosystems* **8**:644-656.
- Hooda, P. S., A. Miller, and A. C. Edwards. 2007. The distribution of automobile catalysts-cast platinum, palladium and rhodium in soils adjacent to roads and their uptake by grass. *Science of the Total Environment* **384**:384-392.
- Howarth, R. W. 2000. Nutrient Over-Enrichment of Coastal Waters in the United States: Steps Toward a Solution. Pew Oceans Commission.
- Howarth, R. W. 2008. Coastal nitrogen pollution: A review of sources and trends globally and regionally. *Harmful Algae* **8**:14-20.
- Howarth, R. W., D. M. Anderson, T. M. Church, H. Greening, C. S. Hopkins, W. C. Huber, N. Marcus, R. J. Naiman, K. Segerson, A. N. Sharpley, and W. J. Wiseman, editors. 2000. *Clean Coastal Waters: Understanding and Reducing the Effects of Nutrient Pollution*. National Academy Press, Washington, D.C.
- Howarth, R. W., E. W. Boyer, W. J. Pabich, and J. N. Galloway. 2002a. Nitrogen use in the United States from 1961-2000 and potential future trends. *Ambio* **31**:88-96.
- Howarth, R. W., A. Sharpley, and D. Walker. 2002b. Sources of nutrient pollution to coastal waters in the United States: Implications for achieving coastal water quality goals. *Estuaries* **25**:656-676.
- International Fertilizer Industry Association. 2008. Nitrogen, phosphate and potash statistics. *in* International Fertilizer Industry Association Data Bank. (<http://www.fertilizer.org/ifa/statistics/IFADATA/dataline.asp>).

- Jefts, S., I. J. Fernandez, L. E. Rustad, and D. B. Dail. 2004. Decadal responses in soil N dynamics at the Bear Brook Watershed in Maine, USA. *Forest Ecology and Management* **189**:189-205.
- Jenkins, J. C., D. C. Chojnacky, L. S. Heath, and R. A. Birdsey. 2003. National-scale biomass estimators for United States tree species. *Forest Science* **49**:12-35.
- Kalbitz, K., D. Schwesig, and W. Wang. 2008. Effects of platinum from vehicle exhaust catalyst on carbon and nitrogen mineralization in soils. *Science of the Total Environment* **405**:239-245.
- Kirchner, M., G. Jakobi, E. Felcht, M. Bernhardt, and A. Fischer. 2005. Elevated NH₃ and NO₂ air concentrations and nitrogen deposition rates in the vicinity of a highway in Southern Bavaria. *Atmospheric Environment* **39**:4531-4542.
- Knorr, M., S. D. Frey, and P. S. Curtis. 2005. Nitrogen additions and litter decomposition: A meta-analysis. *Ecology* **86**:3252-3257.
- Lajtha, K., W. M. Jarrel, D. W. Johnson, and P. Sollins. 1999. Collection of Soil Solution. Pages 166-184 *in* P. G. Robertson, D. C. Colman, C. S. Bledso, and P. Sollins, editors. *Standard Soil Methods for Long-Term Ecological Research*. Oxford University Press, New York.
- Lajtha, K., B. Seely, and I. Valiela. 1995. Retention and Leaching Losses of Atmospherically-Derived Nitrogen in the Aggrading Coastal Watershed of Waquoit Bay, Ma. *Biogeochemistry* **28**:33-54.
- Lindberg, S. E., and G. M. Lovett. 1985. Field-Measurements of Particle Dry Deposition Rates to Foliage and Inert Surfaces in a Forest Canopy. *Environmental Science & Technology* **19**:238-244.
- Lovett, G. M., L. M. Christenson, P. M. Groffman, C. G. Jones, J. E. Hart, and M. J. Mitchell. 2002. Insect defoliation and nitrogen cycling in forests. *Bioscience* **52**:335-341.
- Lovett, G. M., and S. E. Lindberg. 1984. Dry Deposition and Canopy Exchange in a Mixed Oak Forest as Determined by Analysis of Throughfall. *Journal of Applied Ecology* **21**:1013-1027.
- Lovett, G. M., and S. E. Lindberg. 1993. Atmospheric Deposition and Canopy Interactions of Nitrogen in Forests. *Canadian Journal of Forest Research- Revue Canadienne De Recherche Forestiere* **23**:1603-1616.
- Lovett, G. M., and H. Rueth. 1999. Soil nitrogen transformations in beech and maple stands along a nitrogen deposition gradient. *Ecological Applications* **9**:1330-1344.

- Lovett, G. M., K. C. Weathers, M. A. Arthur, and J. C. Schultz. 2004. Nitrogen cycling in a northern hardwood forest: Do species matter? *Biogeochemistry* **67**:289-308.
- Lytle, C. M., B. N. Smith, and C. Z. McKinnon. 1995. Manganese accumulation along Utah roadways: a possible indication of motor vehicle exhaust pollution. *Science of the Total Environment* **162**:105-109.
- Magill, A. H., and J. D. Aber. 1998. Long-term effects of experimental nitrogen additions on foliar litter decay and humus formation in forest ecosystems. *Plant and Soil* **203**:301-311.
- Magill, A. H., J. D. Aber, W. S. Currie, K. J. Nadelhoffer, M. E. Martin, W. H. McDowell, J. M. Melillo, and P. Steudler. 2004. Ecosystem response to 15 years of chronic nitrogen additions at the Harvard Forest LTER, Massachusetts, USA. *Forest Ecology and Management* **196**:7-28.
- Marino, R., R. W. Howarth, N. D. Bettez, and E. A. Davidson. In Prep.
- Massachusetts Highway Department. 2008. Executive Office of Transportation, Traffic Volume Counts. *in* On-line database <http://www.mhd.state.ma.us/>.
- May, J. D., and K. T. Killingbeck. 1995. Effects of Herbivore Induced Nutrient Stress on Correlates of Fitness and on Nutrient Resorption in Scrub Oak (*Quercus-Ilicifolia*). *Canadian Journal of Forest Research-Revue Canadienne De Recherche Forestiere* **25**:1858-1864.
- McDowell, W. H., A. H. Magill, J. A. Aitkenhead-Peterson, J. D. Aber, J. L. Merriam, and S. S. Kaushal. 2004. Effects of chronic nitrogen amendment on dissolved organic matter and inorganic nitrogen in soil solution. *Forest Ecology and Management* **196**:29-41.
- McNulty, S. G., J. D. Aber, and R. D. Boone. 1991. Spatial Changes in Forest Floor and Foliar Chemistry of Spruce-Fir Forests across New-England. *Biogeochemistry* **14**:13-29.
- McNulty, S. G., J. Boggs, J. D. Aber, L. Rustad, and A. Magill. 2005. Red spruce ecosystem level changes following 14 years of chronic N fertilization. *Forest Ecology and Management* **219**:279-291.
- National Atmospheric Deposition Program (NRSP-3). 2009. NADP Program Office, Illinois State Water Survey, 2204 Griffith Dr., Champaign, IL 61820.
- National Oceanic and Atmospheric Administration. 2008. Office of Ocean and Coastal Resource Management, National Estuarine Research Reserve System-wide Monitoring Program, Centralized Data Management Office, Baruch Marine

Field Lab, University of South Carolina. *in* on-line database,
<http://cdmo.baruch.sc.edu/>.

- National Research Council. 2000. Which Nutrients Matter. Pages 65-83 *in* R. W. Howarth, editor. Clean Coastal Waters: Understanding and Reducing the effects of Nutrient Pollution. National Academy Press, Washington.
- National Research Council. 2006. State and Federal Standards for Mobile-Source Emissions. National Academies Press.
- Parker, G. G. 1983. Throughfall and stemflow in the forest nutrient cycle. Pages 58-136 *in* A. Macfadyen and E. D. Ford, editors. Advances in Ecological Research. Academic Press Inc, New York.
- Post, R. D., and A. N. Beeby. 1996. Activity of the Microbial Decomposer Community in Metal-Contaminated Roadside Soils. The Journal of Applied Ecology **33**:703-709.
- Pregitzer, K. S., A. J. Burton, D. R. Zak, and A. F. Talhelm. 2008. Simulated chronic nitrogen deposition increases carbon storage in Northern Temperate forests. Global Change Biology **14**:142-153.
- Pregitzer, K. S., D. R. Zak, A. J. Burton, J. A. Ashby, and N. W. MacDonald. 2004. Chronic nitrate additions dramatically increase the export of carbon and nitrogen from northern hardwood ecosystems. Biogeochemistry **68**:179-197.
- Riitters, K. H., and J. D. Wickham. 2003. How far to the nearest road? Frontiers in Ecology and the Environment **1**:125-129.
- Robertson, P. G., P. Sollins, B. G. Ellis, and K. Lajtha. 1999. Exchangeable Ions, pH, and Cation Exchange Capacity. Pages 106-114 *in* P. G. Robertson, D. C. Colman, C. S. Bledso, and P. Sollins, editors. Standard Soil Methods for Long-Term Ecological Research. Oxford University Press, New York.
- Sabin, L. D., J. H. Lim, M. T. Venezia, A. M. Winer, K. C. Schiff, and K. D. Stolzenbach. 2006. Dry deposition and resuspension of particle-associated metals near a freeway in Los Angeles. Atmospheric Environment **40**:7528-7538.
- Schindler, D. W., K. H. Mills, D. F. Malley, D. L. Findlay, J. A. Shearer, I. J. Davies, M. A. Turner, G. A. Linsey, and D. R. Cruikshank. 1985. Long-Term Ecosystem Stress - the Effects of Years of Experimental Acidification on a Small Lake. Science **228**:1395-1401.
- Seely, B., and K. Lajtha. 1997. Application of a N-15 tracer to simulate and track the fate of atmospherically deposited N in the coastal forests of the Waquoit Bay Watershed, Cape Cod, Massachusetts. Oecologia **112**:393-402.

- Seely, B., K. Lajtha, and G. D. Salvucci. 1998. Transformation and retention of nitrogen in a coastal forest ecosystem. *Biogeochemistry* **42**:325-343.
- Stachurski, A., and J. R. Zimka. 2000. Atmospheric input of elements to forest ecosystems: a method of estimation using artificial foliage placed above rain collectors. *Environmental Pollution* **110**:345-356.
- Stadler, B., S. Solinger, and B. Michalzik. 2001. Insect herbivores and the nutrient flow from the canopy to the soil in coniferous and deciduous forests. *Oecologia* **126**:104-113.
- Swank, W. T., J. B. Waide, D. A. Crossley, and R. L. Todd. 1981. Insect Defoliation Enhances Nitrate Export from Forest Ecosystems. *Oecologia* **51**:297-299.
- Tietema, A., A. W. Boxman, M. Bredemeier, B. A. Emmett, F. Moldan, P. Gundersen, P. Schleppei, and R. F. Wright. 1998. Nitrogen saturation experiments (NITREX) in coniferous forest ecosystems in Europe: a summary of results. *Environmental Pollution* **102**:433-437.
- United States Environmental Protection Agency. 2000. National air pollutant emission trends. electronic resource EPA 454/R-00-002, U.S. Environmental Protection Agency Office of Air Quality Planning and Standards, Research Triangle Park, N.C.
- United States Environmental Protection Agency. 2001. Methods Used to Estimate Emissions, 1985-1999. EPA-454/R-01-006, U.S Environmental Protection Agency.
- United States Environmental Protection Agency. 2008. National Emissions Inventory (NEI) database. *in*. Environmental Protection Agency.
- Valiela, I., G. Collins, J. Kremer, K. Lajtha, M. Geist, B. Seely, J. Brawley, and C. H. Sham. 1997. Nitrogen loading from coastal watersheds to receiving estuaries: New method and application. *Ecological Applications* **7**:358-380.
- Vitousek, P. M., and R. W. Howarth. 1991. Nitrogen Limitation On Land and in the Sea - How Can It Occur. *Biogeochemistry* **13**:87-115.
- Webb, J. R., B. J. Cosby, F. A. Deviney, K. N. Eshleman, and J. N. Galloway. 1995. Change in the acid-base status of an Appalachian mountain catchment following forest defoliation by the gypsy moth. *Water Air and Soil Pollution* **85**:535-540.
- Wright, R. F., and N. van Breemen. 1995. The NITREX project: an introduction. *Forest Ecology and Management* **71**:1-5.

- Zak, D. R., K. S. Pregitzer, W. E. Holmes, A. J. Burton, and G. P. Zogg. 2004. Anthropogenic N deposition and the fate of (NO₃-)-N-15 in a northern hardwood ecosystem. *Biogeochemistry* **69**:143-157.
- Zechmeister, H. G., D. Hohenwallner, A. Riss, and A. Hanus-Illar. 2005. Estimation of element deposition derived from road traffic sources by using mosses. *Environmental Pollution* **138**:238-249.
- Zehetner, F., U. Rosenfellner, A. Mentler, and M. H. Gerzabek. 2009. Distribution of Road Salt Residues, Heavy Metals and Polycyclic Aromatic Hydrocarbons across a Highway-Forest Interface. *Water Air and Soil Pollution* **198**:125-132.
- Zereini, F., C. Wiseman, and W. Puttmann. 2007. Changes in palladium, platinum, and rhodium concentrations, and their spatial distribution in soils along a major highway in Germany from 1994 to 2004. *Environmental Science & Technology* **41**:451-456.