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CONTRIBUTION OF BIOGENIC NITRIC OXIDE IN URBAN OZONE: RALEIGH, NC, AS A CASE STUDY

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Abstract—Anthropogenic emissions from industrial and automotive sources within the confines of the city of Raleigh, NC have been documented by the North Carolina Department of Environment, Health and Natural Resources, Division of Environmental Management, but no direct biogenic emissions of nitric oxide (NO) from soils has yet been measured. In this study, emissions of NO were measured in Raleigh, NC, and its surrounding suburbs, in an attempt to determine the portion of the total NO_x (= NO + NO_2) budget which can be attributed to biogenic sources. Residential and commercial lawns, and golf courses receiving normal fertilizer applications were chosen as the primary biogenic source of NO. Soil NO fluxes were measured using a dynamic chamber technique from 11 sites and ranged in value (hourly averages calculated from 15 min readings) from 1.24 to 23.7 ng N m^{-2} s^{-1}. These hour averages were then combined with estimates of lawn acreage within the city proper, and in the surrounding suburbs, in order to develop a budget for biogenic NO emissions in Raleigh. This budget was then compared to the budget used in the Environmental Protection Agency's (EPA) Regional Oxidant Model (ROM) for photochemical modeling. Results from this comparison suggest that less than 1% of the total NO_x budget for Raleigh, NC is emitted by natural processes, and that approximately 1.2% of the nitrogen applied as fertilizer is lost via soil NO emissions. Thus, the effects of biogenic NO may be neglected in the development of a reliable plan for reducing ozone in the urban atmosphere.

Key word index: Biogenic nitric oxide, urban source strength.

INTRODUCTION

NO_x (= NO + NO_2) is a critical component in the photochemistry of the troposphere (World Meteorological Organization (WMO), 1985; Slemr and Seiler, 1991; Trainer *et al.*, 1991; Aneja *et al.*, 1996). Increasing emissions of NO_x are of great concern because NO reacts with hydrocarbons in the atmosphere, in presence of sunlight, to produce ozone (O_3). NO_x in the lower troposphere is emitted from six predominant sources (Yienger and Levy, 1995). The descending order of importance of these sources are: fossil fuel combustion (> 20 T_g N yr^{-1}; Logan, 1983; Hameed and Dignon, 1988; Levy and Moxim, 1989; where $T_g = 10^{12}$ g), soil-biogenic emissions, and biomass burning (4-20 T_g N yr^{-1}; Hao *et al.*, 1990; Davidson *et al.*, 1991; Levy *et al.*, 1991); lightning discharge (< 10 T_g N yr^{-1}; Penner *et al.*, 1991); and upper troposphere aircraft emission, and stratospheric intrusion (< 1 T_g N yr^{-1}; Levy *et al.*, 1980; Kasibhatla *et al.*, 1991; Kasibhatla, 1993).

Efforts to reduce O_3 in the urban atmosphere must account for both NO_x and hydrocarbon emissions, including emissions from natural sources (Chameides *et al.*, 1988). For example, results published by Lindsay *et al.* (1989) for the city of Atlanta, Georgia, document continued exceedances of the National Ambient Air Quality Standard for O_3 (>0.12 ppmv) despite sizeable reductions in anthropogenic emissions of hydrocarbons. These data strongly suggest that in urban environments like Atlanta, Georgia, emissions of natural hydrocarbons are not negligible, and that anthropogenic hydrocarbon emissions are not the dominant source of O_3-producing hydrocarbons. Failure to account for natural hydrocarbon emissions may be a serious flaw in the current national O_3 abatement control strategy, and may in part be related to the apparent lack of success in the U.S. to reduce O_3 in many urban areas.

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A number of studies have now shown that in rural areas, natural emissions of NO can be just as significant as anthropogenic emissions in influencing the chemistry of the atmosphere (Anderson and Levine, 1987; Slemr and Seiler, 1991). However, we are not aware of any studies that have attempted to document biogenic NO emissions from within the confines of moderate to large cities. It is unknown, therefore, whether such emissions have the same potential to influence O_3 formation as do emissions of natural hydrocarbons. In this study, we focus on a relatively large urban center in the southeast U.S. and the contribution of biogenic emissions to the total (biogenic + anthropogenic sources) NO budget in order to evaluate the extent to which such sources should be considered in photochemical modeling for ozone control.

MATERIALS AND METHODS

Physiographic location

Soil NO flux measurements were made in Raleigh, NC and the surrounding suburbs during the summer and fall of 1995. Raleigh, the capital and the second largest city in North Carolina (35.52°N, 78.47°W, ~127 MSL), has a population of 250,000 people and is situated in the north central portion of the state, 150 km west of the Atlantic Ocean and 90 km south of the Virginia border. Raleigh is located in Wake County which has a population of approximately 500,000 people and is located along the geologic border between the Piedmont and Upper Coastal Plain regions of North Carolina. Raleigh is accessible by I-40 from the northwest and southeast, U.S. 64 from the east, and U.S. 1 from the northeast and the south. I-440 is the major thoroughfare in Raleigh, which is a beltline encircling the city. The city is currently experiencing rapid growth in both population and number of businesses moving into the city and surrounding areas.

Sampling scheme

Soil NO flux was measured on a daily basis using a dynamic flow-through chamber technique. Urban areas, which have a multitude of fluctuating emission sources, skew the background NO concentration and introduce a bias into soil NO flux calculations. In order to compensate for this potential bias, zero grade air was used as the carrier gas in the chamber. Figure 1 is a schematic diagram of the dynamic flow-through chamber system utilizing zero grade air as the carrier gas. The use of zero grade air eliminates reactions within the chamber, except wall loss (Parrish *et al.*, 1987; Sullivan *et al.*, 1996), from all subsequent calculations.

NO concentrations within the chamber were measured every 15 min, usually from 9:00 AM until 4:00 PM. The chamber was flushed with zero grade air for approximately 45 min prior to the first measurement to allow the system to reach a steady state. The stainless-steel collar was relocated in the evening after each experiment, which attempted to remove a potential bias from soil NO flux due to soil disturbance generated by insertion of the stainless-steel collar into the soil. Eleven sites were chosen for the collection of this data, nine which represented average fertilized lawn areas, and two which represented golf courses. Figure 2 shows the approximate locations of these 11 sites with Sites 2 and 5 being the two golf course sites.

Flux calculation

The NO flux was calculated from a mass balance equation (Kaplan *et al.*, 1988; Kim *et al.*, 1994). The mass balance equation is:

$$\frac{dC}{dt} = \left(\frac{q[C_{air}]}{V} + \frac{J}{h}\right) - \left(\frac{L}{h} + \frac{q}{V}\right)[C] \quad (1)$$

where h is the internal height of the chamber, J the emission flux per unit area, L the loss by chamber wall per unit area assumed first order in [NO], q the flow rate through the chamber, V the volume of the chamber, C the NO concentration in the chamber, and C_{air} the NO concentration in the stream entering the chamber

Assuming the chamber is well mixed, the concentration $[C]$ which is measured can be assumed to be the same everywhere within the chamber. Additionally, at steady-state conditions, the change of concentration with respect to time will be zero. Because zero grade air was used as the carrier gas, equation (1) can be further simplified. In the presence of zero grade air, the loss term (L) only represents losses due to the reaction of NO with the chamber wall (no other reactions resulting in production or destruction of NO should be occurring in the chamber):

$$\frac{J}{h} = \left(\frac{L}{h} + \frac{q}{V}\right) C_{eq} \quad (2)$$

where C_{eq} is the NO concentration measured at the outlet of the chamber after steady state is reached. For this study, the wall loss term L was assumed to have a value of 0.02 cm s^{-1} as proposed by Kaplan *et al.* (1988).

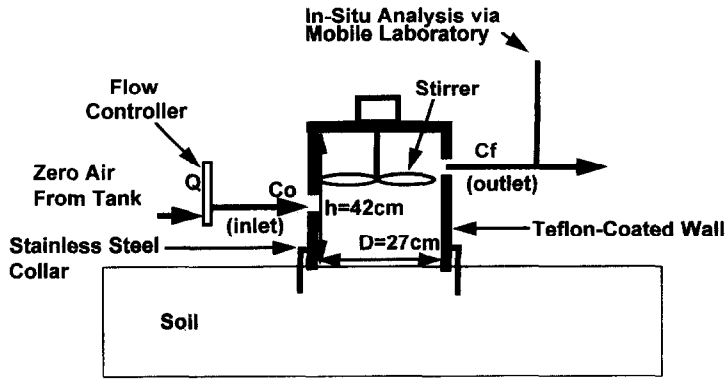

Fig. 1. Schematic of dynamic flow-through chamber.

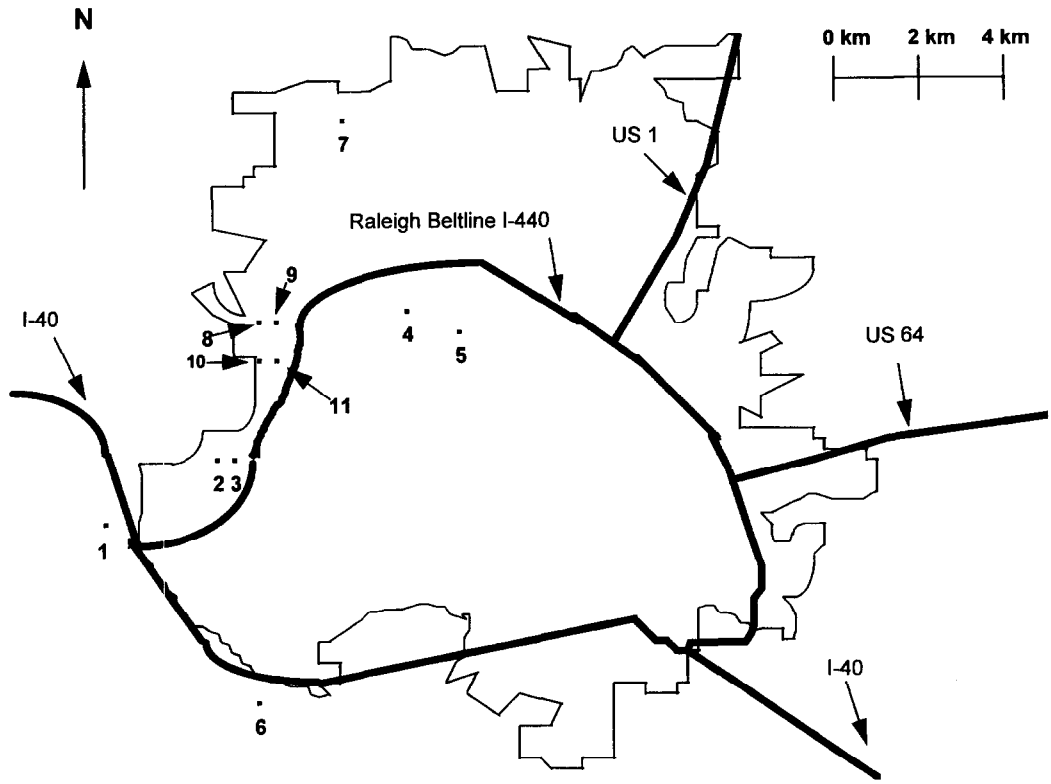

Fig. 2. Map of Raleigh, NC with measurement sites indicated by numbers.

RESULTS AND DISCUSSION

Calculation of Raleigh fertilized lawn area

In order to determine a NO budget for Raleigh, it was critical to determine the amount of land within the city limits that is capable of emitting NO. For example, we wanted to know how much land was paved and built on, versus how much land was grass and forested areas.

Although areas which are not fertilized for many years will emit some NO (Williams *et al.*, 1992; Kim *et al.*, 1994), it has been found that the application of fertilizer can dramatically increase the emissions of NO (Slemr and Seiler, 1991; Jambert *et al.*, 1994; Sullivan *et al.*, 1996; Aneja *et al.*, 1996). Therefore, the contribution from the fertilized acreage will be used to determine the biogenic NO_x budget and the non-fertilized acreage will only be considered when trying to calculate a budget using the most extreme scenario.

The City of Raleigh Planning Department provided the acreage for the following nine land use areas: Vacant, Open Space, Recreational, Industrial, Institutional, Office, Retail, Single, and Multi-Family dwellings. The Raleigh Department of Taxation provided figures on total homes, total apartment complexes, businesses, and approximate acreage for these respective properties. The City Planning Department and Geographical Information Systems Office was unable to provide data on the percentage of lawn area, as opposed to driveway, sidewalk, forest or building area. For the purpose of this study we assumed that 50% of all the land use areas were covered by lawns (personal communication with the North Carolina State University Forestry Department). Table 1 lists these nine different land use categories and their respective acreage, estimated lawn acreage and estimated fertilizer acreage.

Assuming that the only fertilized land use areas are those lawns in the industrial, institutional, office, retail, golf courses, multi-family, and single-family home areas, an estimate can be obtained for the land area which will emit the majority of biogenic NO. We assumed that approximately 90% of the industrial, institutional, office, retail, and multi-family land use areas use commercial lawn care. Using statistics provided by the National Gardening Survey, approximately 45% of the single-family home areas use fertilizer (see section on Calculation of Nitrogen Fertilizer Applied). Additionally, the lawn areas of the three golf courses in Raleigh were added, bringing the total to 6961 hectares (ha) of fertilized lawn area in Raleigh, NC.

Calculation of anthropogenic emissions

The total anthropogenic NO_x budget for the Raleigh, NC area was calculated from a report provided by the North Carolina Department of Environment, Health and Natural Resources (DEHNR), Division of Environmental Management – Air Quality Section. This report (North Carolina Inventory

Table 1. Land-use categories in Raleigh, NC and associated acreage. The manner in which grass acreage and fertilized acreage was determined can be found in the section: Calculation of Raleigh Fertilized Grass Area

Use	Total acreage (ha)	Lawn acreage (ha)	Estimated fertilized acreage (ha)
Vacant	15,204	N/A	
Open space	4886	N/A	
Recreational	3866 (255)[a]	127	127
Industrial	1645	822	740
Institutional	1766	883	794
Office	1252	626	563
Retail	2901	1451	1305
Multi-family	2200	1100	495
Single-family	13,042	6521	2934
Totals	46,766	11,531	6961

[a]The only acreage which is considered in this land use category is from the golf courses, listed in parenthesis.
Source: City of Raleigh, Planning Department.

– tons/day) contains all of the counties in North Carolina and an emissions inventory, by county, for the following categories: NO_x Point, defined as those facilities/plants/activities for which individual records are maintained in the inventory; NO_x Mobile, defined as a source which can travel on roads; NO_x Non Road (NR) Mobile, defined as vehicles which do not travel on roads, for example, tractors, railroad locomotives, and aircraft; NO_x Area, defined as sources that are too small and/or too numerous to be handled individually in the point source inventory; and NO_x Biogenic, defined as tree, crop and vegetation species (EPA-450/4-91-016; Mobile Source Inventory, Charlotte Maintenance Plan). It is the sum of the first four of these sources which make up the anthropogenic sources.

Although these figures represent the entire Wake County, they were refined to be representative of only Raleigh. NO_x Area and Point sources, according to the report, emitted 2449 kg and 1633 kg d^{-1}, respectively. These values needed to be reduced to represent only the City of Raleigh. A separate report, also provided by DEHNR, lists all facilities in Raleigh and their NO_x emissions. The total of all the facilities in Raleigh summed to 272,486 kg of NO_x emitted per year. The total for the entire County of Wake was 1,490,076 kg of NO_x emitted per year (2449.4 and 1633.0 kg NO_x per day * 365 d y^{-1}). This suggests that Raleigh emits approximately 18% of all the area and point sources of NO_x for Wake County. The Area and Point source emissions, in Raleigh, for the 43 d period from 22 August to 3 October 1995 totaled 32096.7 kg of NO_x.

The total NO_x emissions from both mobile and non-road mobile sources, in Raleigh, for the 43 d period were 1,123,131 kg. This value was obtained from the following calculation provided by DEHNR, Division of Environmental Management:

$$\frac{\text{Total Wake County mobile and non-road mobile sources}}{\text{Wake County population}} * \text{Raleigh population.}$$

Summing both estimates (Area and point source emissions + mobile and non-road mobile source emissions) brings the total to 1,155,228 kg of NO_x emitted by anthropogenic sources during the time period under investigation (22 August–3 October 1995).

Calculation of nitrogen fertilizer applied

The total nitrogen (N) fertilizer that was applied in Raleigh, NC was calculated by using the 1994 North Carolina Fertilizer Tonnage Report and through personal communication with both the Fertilizer Institute and the Professional Lawn Care Association of America. The total amount of N fertilizer that was shipped to Wake County between 1 July 1993 and 30 June 1994 was 3,339,403 kg.

In order to estimate the amount of N fertilizer applied to the average lawn, we spoke with various lawn care companies which operate in Raleigh, NC. The spokespersons for these companies agreed that, on average, 1.36 kg of N per 92.94 m^2 per year are applied to the average maintained lawn (TruGreen Chemlawn, Raleigh, NC; Barefoot Grass Lawn Service, Raleigh, NC, personal communication). This total is distributed through 3–4 applications throughout the year with the heaviest dose of nitrogen being applied in the fall. Additionally, the Professional Lawn Care Association of America in Marietta, Georgia, provided the most recent National Gardening Survey. The city of Raleigh, NC falls into a demographic region where approximately 45% of the households are estimated to apply fertilizer to their yards. Applying this average (1.36 kg N^{-1} per 92.94 m^2) to the total fertilized lawn acreage translates to 1,019,692 kg of N applied in Raleigh, which represents approximately 30% of the 3,339,403 kg which was shipped to Wake County.

Biogenic NO budget using data from urban measurements

The budget that we calculated represents only the period during which the measurements were made (22 August–3 October 1995). The total acreage for the lawn area (Industrial, Institutional, Office, retail, multi-family, and single-family) assumed to be fertilized in typical quantities (1.36kg N per 92.94 m^2 yr^{-1}) is 6834 ha. The average flux from the nine measurement locations representative of these land-use areas was 5.66 ± 5.61 ng $N\,m^{-2}\,s^{-1}$. Applying this average to the total acreage for the 43 d period produces 1433 kg of N. It should be noted that this estimate may slightly overestimate NO emissions, because we obtained our daily average flux from measurements between 9:00 AM and 4:00 PM and previous studies have shown that soil NO emissions tend to follow soil temperature with afternoon maximum and a daytime minimum values (Williams *et al.*, 1988; Shepherd *et al.*, 1991; Valente and Thorton, 1993; Sullivan *et al.*, 1996). Experimental constraints precluded diurnal experiments. Table 2 lists the average flux from the 11 different measurement sites.

The total fertilized acreage for the lawn areas at the three golf courses located in Raleigh, NC is 127 ha. The average flux for the two measurement locations representative of this land-use area was 10.9 ± 6.61 ng $N\,m^{-2}\,s^{-1}$. Applying this average to the total golf course acreage produces 51.7 kg of N for the 43 d period. Therefore, the total NO budget from fertilized lawns in Raleigh, NC is 1485 kg of N for the period during which the measurements were made.

Biogenic NO budget used in the EPA regional oxidant model (ROM)

The regional oxidant model (ROM) (Pierce and Novak, 1991) is used by the Environmental Protection Agency (EPA) in order to estimate natural sources of nitrogen oxides (NO_x) and nonmethane hydrocarbon (NMHC). The model uses an algorithm developed by Williams (1991) to assess the emissions of NO due to microbial processes in the soil. The equation used to calculate the flux is

$$\text{Flux (ng N m}^{-2}\text{ s}^{-1}) = C\,\text{Exp}(0.071\,T_s)$$

where C is the experimentally derived coefficient for each land-use category, and T_s the soil temperature (°C), which is derived from functional relationships with air temperature.

Table 3 lists all the land use categories in the algorithm, their respective C values and the functions for calculating soil temperature.

Table 2. The average flux at the 11 different sites which were measured during the Raleigh, NC urban study. See Fig. 2 for the location of these sites

Site	Date	Number of 15 min average NO flux measurements	Average NO flux (ng $N\,m^{-2}\,s^{-1}$)	
1	22 August 1995	28	8.69[a]	($\pm$ 8.89)[b]
2 (Golf course)	24 August 1995	20	5.64	($\pm$ 2.66)
3	25 August 1995	30	3.74	($\pm$ 0.24)
4	29 August 1995	29	4.39	($\pm$ 0.76)
5 (Golf course)	30 August 1995	29	16.2	($\pm$ 4.04)
6	31 August 1995	35	3.50	($\pm$ 0.30)
7	26 September1995	38	18.1	($\pm$ 1.19)
8	28 September 1995	20	1.43	($\pm$ 0.12)
9	29 September 1995	15	3.59	($\pm$ 0.77)
10	2 October 1995	30	2.73	($\pm$ 0.39)
11	3 October 1995	21	3.77	($\pm$ 0.50)

[a]Simulated rain event to study pulsing.
[b]Number in parentheses are one standard deviation.

Table 3. Land use categories and their respective C values and soil temperature functions (Source: Williams *et al.*, 1990; Pierce and Novak, 1991)

Land use	c	Function for computing soil temperature (T_s°C) from air temperature (T_A°C)
Grasslands and pasture	0.9	$T_s = 0.67 * T_A + 8.8$
Forest	0.07	$T_s = 0.84 * T_A + 3.6$
Wetlands	0.004	$T_s = 0.92 * T_A + 4.4$
Agriculture		
Upper bound	9.0	$T_s = 0.72 * T_A + 5.8$
Lower bound	0.2	$T_s = T_A + 2.9$

Table 4. The air temperature, as recorded at the Raleigh-Durham International Airport, and the soil temperature as calculated by the temperature algorithm used in the EPA Regional Oxidant Model are listed for the 11 urban sites which were studied. The average flux calculated using a mass balance equation and the flux calculated using the Regional Oxidant Model are also listed

Date	Average air temp (°C)	Average soil temp (°C)	Average flux[a] (ng N $m^{-2} s^{-1}$)	EPA ROM average flux (ng N $m^{-2} s^{-1}$)
Aug 22	30.2	29.0	8.69	7.10
Aug 24	28.6	27.9	5.64	6.56
Aug 25	29.1	28.3	3.74	6.73
Aug 29	25.6	26.0	4.39	5.70
Aug 30	28.0	27.6	16.2	6.39
Aug 31	27.9	27.5	3.50	6.35
Sept 26	21.6	23.3	18.1	4.71
Sept 28	21.1	22.9	1.43	4.59
Sept 29	20.4	22.4	3.59	4.44
Oct 2	24.0	24.9	2.73	5.27
Oct 3	24.0	24.9	3.77	5.27

[a]This study.

For urban areas, the EPA assumes that 20% of the acreage is grass ($C = 0.9$) and a corresponding temperature function ($T_s = 0.67\,T_A + 8.8$) to model NO emissions. Table 4 lists air temperature, and soil temperature, as calculated by the soil temperature function. Additionally, the table displays side-by-side comparisons of daily average NO fluxes using our mass balance approach and the NO flux algorithm used in the ROM. Except for the two high fluxes which occurred on 30 August and on 26 September 1995, the algorithm tended to slightly overestimate biogenic emissions. Using the estimates generated by the ROM and applying them to the fertilized land areas in Raleigh (see section on Calculation of Raleigh Fertilized Land Area) for the 43 d period produces a total NO budget of 1487 kg of N.

CONCLUSIONS AND RECOMMENDATIONS

The urban measurements of NO conducted in Raleigh, NC suggest that biogenic emissions make up a minor portion of the overall NO_x budget. The 11 sites measured, in addition to land estimates, show that for the 43 d period from 22 August to 3 October 1995 approximately 1485 kg of N are emitted from the fertilized soils. This estimate represents less than 1% of the anthropogenic emissions emitted in Raleigh for the same time period. The most liberal estimate would be to assume that all of the vacant and open space land use areas were lawn (total acreage = 31,623 ha) and that all these acres emitted at the highest flux calculated (18.1 ng N $m^{-2} s^{-1}$). Using these values would produce 21,273 kg of N emitted which is still less than 2% of the anthropogenic emissions emitted in Raleigh from 22 August to 3 October 1995.

Comparing the estimates obtained using the urban measurements (1485 kg of N emitted during the 43 d period) and the algorithm used in the Regional Oxidant Model (1487 kg of N emitted during the 43 d period) shows no significant differences. However, there is a difference in the methods used for estimating the amount of lawn area in the urban centers. The comparisons made between the two techniques were conducted using identical lawn acreages. Through communication with the EPA, it became evident that we were not making the same assumptions of lawn acreage. The EPA model assumes that 20% of all the acreage in urban areas is grassland whereas we assumed 50% of certain land use categories are grassland. There is no way to substantiate either claim without a detailed land analysis. However, the results suggest that biogenic emissions, which account for such a small fraction of the total NO_x budget, makes any differences in the lawn acreage's inconsequential.

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