# Denitrification in Suburban Lawn Soils

Steve M. Raciti,\* Amy J. Burgin, Peter M. Groffman, David N. Lewis, and Timothy J. Fahey

There is great uncertainty about the fate of nitrogen (N) added to urban and suburban lawns. We used direct flux and in situ chamber methods to measure N2 and N2O fluxes from lawns instrumented with soil O2 sensors. We hypothesized that soil O2, moisture, and available NO3- were the most important controls on denitrification and that N<sub>2</sub> and N<sub>2</sub>O fluxes would be high following fertilizer addition and precipitation events. While our results support these hypotheses, the thresholds of soil O2, moisture, and NO3 availability required to see significant N2 fluxes were greater than expected. Denitrification rates were high in saturated, fertilized soils, but low under all other conditions. Annual denitrification was calculated to be 14.0  $\pm$  3.6 kg N ha<sup>-1</sup> yr<sup>-1</sup>, with 5% of the growing season accounting for >80% of the annual activity. Denitrification is thus an important means of removing reactive N in residential landscapes, but varies markedly in space, time, and with factors that affect soil saturation (texture, structure, compaction) and NO<sub>3</sub><sup>-</sup> availability (fertilization). Rates of in situ N<sub>2</sub>O flux were low; however, when recently fertilized soils saturated with water were incubated in the laboratory, we saw extraordinarily high rates of N<sub>2</sub>O production for the first few hours of incubation, followed by rapid N<sub>2</sub>O consumption later in the experiment. These findings indicate a lag time between accelerated N2O production and counterbalancing increases in N2O consumption; thus, we cannot yet conclude that lawns are an insignificant source of N<sub>2</sub>O in our study area.

Copyright © 2011 by the American Society of Agronomy, Crop Science Society of America, and Soil Science Society of America. All rights reserved. No part of this periodical may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying, recording, or any information storage and retrieval system, without permission in writing from the publisher.

J. Environ. Qual. 40:1932–1940 (2011) doi:10.2134/jeq2011.0107 Posted online 26 Aug. 2011. Received 24 Mar. 2011. \*Corresponding author (raciti@bu.edu). © ASA, CSSA, SSSA 5885 Guilford Rd., Madison, WI 53711 USA The developed land area of the United States has grown more than 400% in the past half century (Brown et al., 2005) and continues to grow rapidly (Goetz et al., 2004; Jantz et al., 2005; Brown et al., 2005). The most visible changes that accompany development are increased impervious surface area (e.g., buildings, roads, and sidewalks) and replacement of natural vegetation and agriculture fields with lawns (i.e., turfgrass). Impervious surfaces in the United States are estimated to cover an area nearly the size of Ohio (112,610 km<sup>2</sup>; Elvidge et al., 2004), and the area in lawns is estimated to be even larger (163,812 km<sup>2</sup>; Milesi et al., 2005).

The rapid increase in residential land area has raised concerns about pollution associated with fertilizers and pesticides, which are used for lawn establishment and maintenance (Morton et al., 1988; Gold et al., 1988, 1990; Petrovic, 1990; Milesi et al., 2005). Concern for coastal and freshwater ecosystems is particularly high, where nitrogen pollution has contributed to numerous water quality problems, including harmful algal blooms, decreased biodiversity, fisheries declines, and "dead zones" in areas such as the Gulf of Mexico and Chesapeake Bay (Carpenter et al., 1998; Kemp et al., 2005; Paerl et al., 2006; Dodds et al., 2008).

Residential systems receive higher N inputs than natural systems and may have a high capacity for N retention (Baker et al., 2001; Wollheim et al., 2005; Groffman et al., 2009). Lawns, which are the dominant vegetation cover in residential areas, may play an important role in this outcome. While lawns can have significant N losses, especially when overwatered and overfertilized (Morton et al., 1988; Petrovic, 1990; Qian et al., 2003), they also have considerable potential for organic matter accumulation and N retention (Gold et al., 1990; Qian and Follett, 2002; Kaye et al., 2005; Golubiewski, 2006; Raciti et al., 2008).

Through our studies of the Baltimore Long-Term Ecological Research (LTER) site, we have measured N inputs, outputs, and transformations in residential ecosystems with a particular focus on lawns. In a <sup>15</sup>N-tracer study we found that when a pulse of nitrate ( $NO_3^-$ ) (simulating atmospheric deposition) was added to Baltimore area lawns, the  $NO_3^-$  was rapidly incorporated or retained in microbial biomass, fine roots, aboveground vegetation biomass, thatch, and soil organic matter (Raciti et al., 2008). Overall <sup>15</sup>N retention was similar, and possibly higher, than in

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Abbreviations: BES, Baltimore Ecosystem Study; N-FARM, Nitrogen-Free Atmospheric Recirculation Method; PVC, polyvinyl chloride.

forested reference sites. In a second study, we evaluated soil carbon (C) and nitrogen (N) pools in 32 residential home lawns down to 1-m depth (Raciti et al., 2011a). We found evidence for rapid accumulation of C and N in residential soils, particularly in those with a history of agricultural land use. When we studied NO<sub>3</sub><sup>-</sup> production and consumption in the same lawns (Raciti et al., 2011b), we found that net nitrification and exchangeable NO3<sup>-</sup> were significantly higher in residential soils than in forest soils, but these measures of NO<sub>2</sub><sup>-</sup> production and availability were still notably low and comparable to deciduous forest stands in other studies (Lovett et al., 2004). Finally, while N inputs to our developed watersheds were high (Law et al., 2004), measured leaching losses were a relatively small fraction of total inputs (Groffman et al., 2009). Using information gathered from these experiments, we created a mass balance for our lawn-dominated residential systems (Raciti et al., 2011b); however, a major N flux was missing from our balance-gaseous losses of N<sub>2</sub> from denitrification-a process that has been notoriously difficult to measure in terrestrial ecosystems (Kulkarni et al., 2008).

Direct measurements of denitrification in terrestrial ecosystems have been limited by the difficulty of measuring N<sub>2</sub> fluxes (see review by Groffman et al., 2006a); however, past research suggests that denitrification may be an important pathway for N loss from turfgrass systems (e.g., Horgan et al. 2002a,b). Due to the difficulty in measuring N<sub>2</sub> fluxes, mass balance studies have generally estimated denitrification as the difference between recovered and unrecovered fertilizer N at the end of an experiment (Horgan et al., 2002a). For instance, Miltner and colleagues (1996) recovered 64 to 81% of <sup>15</sup>N-labeled urea in the spring and fall of their experiment, suggesting that gaseous losses might be responsible for incomplete recovery. Engelsjord and colleagues (2004) and Starr and DeRoo (1981) reported a similar range of recovery rates. Horgan and colleagues (2002a,b) attempted to account for gaseous losses by periodically measuring <sup>15</sup>N-N<sub>2</sub>O and <sup>15</sup>N-N<sub>2</sub> fluxes from lawn and greenhouse plots, but overall recoveries (57-84%) were not much improved over previous mass balance studies. Despite less than complete recovery, Horgan and colleagues calculated sizeable N2 and N2O fluxes, particularly following a major rainfall event, confirming that denitrification was an important process in turfgrass systems.

In this study, we sought to complete the N budget for our residential system (Raciti et al., 2011b) using a combination of laboratory and field measurements to quantify denitrification. There is general consensus on the proximate controls of denitrification in terrestrial ecosystems (e.g., soil temperature, moisture, oxygen, organic matter, and available NO<sub>2</sub>). As an anaerobic, primarily heterotrophic process, denitrification in terrestrial environments tends to occur in small areas (hotspots) and during brief periods (hot moments) of activity when these controls converge (Parkin, 1987; McClain et al., 2003). In addition to influencing the total rate of denitrification, these factors influence the relative importance of the end products of denitrification, including N2O, which is an important greenhouse gas (Kulkarni et al., 2008). Two problems have hindered attempts to estimate meaningful rates outside the laboratory: (i) an inability to measure direct N<sub>2</sub> fluxes due to high atmospheric concentrations of this gas, and (ii) an inability to measure and monitor soil oxygen  $(O_2)$  concentrations in the field (Groffman et al., 2006a). Using recent advances in instrumentation (Butterbach-Bahl et al., 2002; Burgin et al., 2010), we were able to overcome these problems to measure field-relevant rates of denitrification from lawns. Our objectives were to (i) measure soil O<sub>2</sub> conditions in home lawns; (ii) determine relationships between soil O<sub>2</sub> conditions, and N<sub>2</sub> and N<sub>2</sub>O fluxes, in the laboratory and field (N<sub>2</sub>O only); (iii) evaluate the role of soil moisture and nitrate levels on these relationships; and (iv) produce estimates of annual N gas fluxes to close the N budget of our residential ecosystem. At the outset of the study, we hypothesized that denitrification (as N2 and N2O) would occur on an episodic basis, with the highest rates coinciding with rainfall and after fertilizer application, when soil moisture and available NO<sub>3</sub><sup>-</sup> would be high and soil oxygen concentrations would be low.

## Materials and Methods Site Description

The lawns used in this study were located in the Baltimore metropolitan area in association with the Baltimore Ecosystem Study (BES; http://beslter.org), a component of the U.S. National Science Foundation LTER network, and have been described in detail elsewhere (Groffman et al., 2009). This area has a temperate climate with warm, humid summers (1220 cooling degree days), cold winters (4720 heating degree days), and mean annual precipitation of approximately 1060 mm distributed relatively evenly throughout the year (NCDC, 2009).

The two lawns (referred to as UMBC1 and South Campus) were located on the grounds of University of Maryland Baltimore County, but were not turfgrass research plots. Campus lawns were chosen because of their known, long-term management regimes, similarities in land-use history (formerly agricultural), and their representativeness of typical residential lawns. Each lawn (or plot) contained a mixture of tall fescue (Festuca arundinacea Schreb.) and fine fescue (Festuca spp.). The UMBC1 lawn, which was less actively managed, also had significant white clover (Trifolium repens L.) cover. UMBC1 was fertilized each spring at a rate of 98 kg N ha-1 using LESCO 14-14-14 (LESCO, Cleveland, OH), applied in two applications, approximately 2 wk apart. Mowing was done at 2- to 3-wk intervals (dependent on rainfall and subsequent growth) during the spring, summer, and fall seasons to a height of approximately 10 cm. South Campus was fertilized each spring and fall at 98 kg N ha<sup>-1</sup> (196 kg N ha<sup>-1</sup> yr<sup>-1</sup> total). Fertilizer was applied over two applications each season, approximately 2 wk apart, using LESCO 18–24–12 in the spring and LESCO 25–5–10 in the fall. The lawn was mowed weekly during the growing season to a height of approximately 10 cm. Neither lawn received irrigation, and clippings were left in place. Management of the lawns was similar to moderate (UMBC1) and moderately high maintenance (South Campus) home lawns in the study area. A lawn management survey by Law et al. (2004) found that lawn fertilizer inputs in the area ranged from zero to >300 kg N ha<sup>-1</sup> yr<sup>-1</sup> with a mean of 83.5 kg N ha<sup>-1</sup> yr<sup>-1</sup> in their suburban watershed (0.13-ha mean lot size). The soils at UMBC1 and South Campus have been classified as Joppa (loamy-skeletal, siliceous, semiactive, mesic Typic Hapludult) and Brandywine (sandy-skeletal, mixed mesic Typic Dystrudept), respectively. Soil pH was between 5.7 and 6.0 for both lawns when measured at the beginning of the study. Atmospheric N deposition in the Baltimore metropolitan area is estimated at 11.2 kg N ha<sup>-1</sup> yr<sup>-1</sup> (Groffman et al., 2004).

### Instrumentation

In early August of 2008, each lawn was instrumented with three Apogee diffusion-head soil  $O_2$  sensors (SO-100 series, Apogee Instruments, Logan, UT) with the diffusion heads at 7-cm depth. The sensors in each lawn were connected to a Campbell Scientific CR-800 data logger (Campbell Scientific, Logan, UT), which was programmed to measure soil  $O_2$  hourly over the course of approximately 1 yr (with monthly interruptions to recharge and replace batteries at each installation). Both lawns have been continually monitored for soil temperature and moisture as part of the BES network of long-term study sites (Groffman et al., 2009).

### Sample Collection and Processing

Soil cores were collected to a depth of 10 cm using a 5-cm-diameter slide-hammer corer (AMS Equipment Corp., American Falls, ID) from 13 May and 4 June 2009. For each experiment (described below) an equal number of soil cores were collected from each of the two lawn areas (UMBC1 and South Campus), with the exception of the field fertilization experiment (Experiment 3), where all of the soil cores came from the UMBC1 site. Soil cores were collected randomly from each lawn area. All cores were transported to the laboratory in coolers and then stored at 4°C until they could be processed (2–4 d). A subset of soil cores from each time point were used to determine soil dry weight, percent moisture, and bulk density. Soil dry weight and percent moisture were determined by the change in mass of 10 g of field-moist soil after 48 h at 105°C. Bulk density (BD) was calculated as BD = (Total Dry Mass - Rock Mass)/ (Total Volume - Rock Volume) (see Boone et al., 1999).

### Direct Measurement of N<sub>2</sub>, Nitrous Oxide, and Carbon Dioxide Fluxes from Intact Lawn Soil Cores

Denitrification measurements were made using the Nitrogen-Free Atmospheric Recirculation Method (N-FARM) system (Burgin et al., 2010), which is based on those built by Swerts et al. (1995) and Butterbach-Bahl et al. (2002). Intact soil cores were encased in 10 glass chambers (each acting as an independent incubator) with gastight lids and Swagelok fittings and valves connected to a gastight flow injection system built from Swagelok connections (Swagelok, Crawford Fitting Co., Solon, OH). These were mounted in-line with Shimadzu (Kyoto, Japan) GC8A gas chromatographs with thermal conductivity (to measure N2, CO2, and O2) and electron capture (to measure N2O) detectors. The glass chambers were submerged under water in a Plexiglas box. This served as a secondary test for leaks (which would be evident from water accumulation in the chambers) and further minimized potential gas diffusion around the chamber seals. Using this system, the ambient soil atmosphere could be replaced with an N2-free helium (He) and O<sub>2</sub> atmosphere using a series of gentle vacuum-flush cycles (Butterbach-Bahl et al., 2002; Burgin et al., 2010). By lowering  $N_2$  concentration in the soil atmosphere (to below the 7.5 µmol mol<sup>-1</sup> detection limit of our thermal conductivity detector), we were able to measure small fluxes of  $N_2$ gas exchange from intact soil cores. The system allowed us to vary soil  $O_2$  concentrations by adjusting the He: $O_2$  ratio used during the vacuum-flush cycle. Regular system pressure checks, empty chambers (two blanks per incubation), and incubation of killed soil cores (autoclaved twice at 125°C for 3 h over the course of 3 d) were used to control for system leaks and residual degassing of  $N_2$  from soil pores. All soil cores were incubated at 25°C and left completely intact (including plant roots and shoots) to minimize disturbance to the soil ecosystem.

### **Field Fluxes**

In the field, soil:atmosphere fluxes of  $CO_2$  and  $N_2O$  were measured using 29-cm (inner diameter) polyvinyl chloride (PVC) cylinder chambers with gas sampling ports (Bowden et al., 1991; Groffman et al., 2006b). Just before sampling, these chambers were mounted on PVC base rings installed to 5-cm depth and flush with the soil surface. These low-profile base rings allowed mowing to take place as usual between sampling intervals. At 0, 10, 20, and 30 min following placement of the chamber on the base, 9-mL gas samples were collected from gas sampling ports in the center of the chamber top by syringe. Samples were transferred to evacuated glass vials which were stored at room temperature before analysis by gas chromatography with electron capture ( $N_2O$ ) or thermal conductivity ( $CO_2$ ) detection.

### Experiments

The first experiment tested the effects of  $O_2$  concentration on  $N_2$  and  $CO_2$  fluxes at field moisture (17–20% volumetric soil moisture). Using intact soil cores,  $N_2$  and  $CO_2$  fluxes were measured at 20, 5, and 0%  $O_2$  concentrations in the N-FARM. Each soil  $O_2$  concentration was tested using fresh soils (n = 4) to avoid unknown effects that might arise from subjecting soil cores to prolonged incubation. Headspace  $N_2$  and  $CO_2$  concentrations were measured after 2, 6, and 24 h of incubation.

Our second experiment tested the effect of soil moisture and NO<sub>3</sub><sup>-</sup> availability on N<sub>2</sub> and CO<sub>2</sub> fluxes at 0% O<sub>2</sub>. Wet soil cores (>30% volumetric soil moisture, n = 4) were collected during a rain event and compared with dry soil cores (18% soil moisture, n = 4) collected before the rain event. Since similarly low N<sub>2</sub> fluxes were obtained for both conditions, a third incubation was conducted at 0% O<sub>2</sub> after injecting 10 mL of NO<sub>3</sub><sup>-</sup> solution (approximately 100 mg N kg<sup>-1</sup> dry soil) into four wet soil cores. Headspace N<sub>2</sub>, N<sub>2</sub>O, and CO<sub>2</sub> concentrations were measured after 2, 6, and 24 h of incubation.

Our third experiment examined changes in soil N<sub>2</sub>, N<sub>2</sub>O, and CO<sub>2</sub> fluxes following a field fertilization experiment. On 13 May 2009, a 3- by 30-m section of the UMBC1 site was amended with LESCO 24–0–11 fertilizer at a rate of 49 kg N ha<sup>-1</sup> using a calibrated spreader. Soil cores were collected from the recently fertilized and "ambient" (i.e., control) areas of the plot. The first N-FARM incubation was performed at 20% O<sub>2</sub> using ambient (n = 4) and recently fertilized (n = 4) soil cores taken 24 h after fertilizer addition. The incubation was performed again at 2% soil O<sub>2</sub> using fresh cores. The experiment was repeated for cores taken 9 d after fertilizer addition. The fertilized area of UMBC1 included three gas rings that were used to measure N<sub>2</sub>O and

 $CO_2$  fluxes in the field. Field fluxes were measured before fertilizer application, and 24 h and 9 d after application (i.e., at the same time that soil cores were collected). All soil cores were incubated at field moisture (18–21% volumetric soil moisture).

We performed two more N-FARM incubations to test the effects of soil saturation (e.g., from a major rainstorm) on denitrification rates in fertilized soils. Field fertilized soil cores (collected 9 d postfertilization) were saturated by slowly dripping water onto them until no further water could be absorbed. These cores were incubated at 20 and 2% O<sub>2</sub> (n = 8 for each O<sub>2</sub> concentration).

### **Calculations and Statistics**

Linear regression (accumulation of N<sub>2</sub>, N<sub>2</sub>O, or CO<sub>2</sub> vs. time) was used to calculate flux rates from N-FARM incubations. We used killed soil cores to correct for low levels of N<sub>2</sub> accumulation that might have originated from degassing from soil pores. Fluxes were expressed on a per-area basis by dividing by the ground surface area of each soil core. Field fluxes (using PVC cylinder chambers described earlier) were calculated from the linear rate of change in gas concentration, the chamber internal volume and soil surface area (Groffman et al., 2006b, 2009). Statistical differences between experimental treatments were tested using analysis of variance followed by Tukey's Honestly Significant Difference post hoc test. All statistical analyses were performed using SAS JMP version 8 statistical software (SAS Institute, 2009). For laboratory Experiments 1 and 2, an equal number of soil cores from each lawn were used on the grounds that the different management regimes would result in differences in N<sub>2</sub>, N<sub>2</sub>O, and CO<sub>2</sub> fluxes. We found no statistically significant differences between the two lawns across laboratory experiments, so the results for both lawns are grouped in the figures and statistics. Using a combination of laboratory and field measurements, we estimated annual N2 fluxes in residential lawns (Table 1). Annual N<sub>2</sub> fluxes were estimated by apportioning flux rates from appropriate N-FARM incubations to the proportion of the growing season (231 d for Baltimore, MD [NCDC, 2009]) when fieldmeasured soil moisture and O<sub>2</sub> conditions fell within that range.

### Results

We measured in situ soil  $O_2$  concentrations hourly for 1 yr and found that concentrations stayed within a relatively small range (Fig. 1A and 1B) near atmospheric concentrations (20%), occasionally dropping as low as 17%. A 3-wk period with two major storm systems (4.3 and 10.4 cm of precipitation) failed to cause a significant drop in bulk soil  $O_2$  concentrations at our sites.

In laboratory incubations we tested for the effect of soil  $O_2$  concentration on  $N_2$  and  $CO_2$  fluxes (at 20% field moisture), and found that  $CO_2$  fluxes (i.e., respiration) decreased as  $O_2$  concentrations were lowered (p < 0.02 for all differences). The

 $N_2$  fluxes increased as  $O_2$  decreased, but the differences were not statistically significant due to high variability within treatments (Fig. 2A and 2B). The  $N_2$  fluxes were low across the  $O_2$ concentration gradient, with means ranging from 4.26 ± 3.91  $\mu$ g N m<sup>-2</sup> h<sup>-1</sup> at 20% O<sub>2</sub> to 28.9 ± 17.0  $\mu$ g N m<sup>-2</sup> h<sup>-1</sup> at 0% O<sub>2</sub>.

We used changes in the field moisture of lawn soils (collected before and during a rain event) to measure the influence of soil moisture on N<sub>2</sub> and CO<sub>2</sub> fluxes at 0% soil O<sub>2</sub>. While wet soils (>30% field moisture) had higher arithmetic means than dry soils (18% field moisture), these differences were not statistically significant (59.8 ± 13.9 µg N m<sup>-2</sup> h<sup>-1</sup> vs. 28.9 ± 17.0 µg N m<sup>-2</sup> h<sup>-1</sup> and 9.1 ± 1.5 mg C m<sup>-2</sup> h<sup>-1</sup> vs. 6.0 ± 1.8 mg C m<sup>-2</sup> h<sup>-1</sup>; Fig. 3A and 3B). However, when a pulse of NO<sub>3</sub><sup>-</sup> was added to the wet soils incubated at 0% O<sub>2</sub>, N<sub>2</sub> fluxes increased dramatically from 59.8 ± 13.9 µg N m<sup>-2</sup> h<sup>-1</sup> to 2216 ± 509 µg N m<sup>-2</sup> h<sup>-1</sup> (p < 0.001). Carbon dioxide fluxes from wet soils amended with NO<sub>3</sub><sup>-</sup> were significantly higher than CO<sub>2</sub> fluxes from dry soils, but not significantly higher than fluxes in unamended wet soil cores (Fig. 3B).

Fertilized and unfertilized ("ambient") soil cores collected 24 h after fertilization in the field (applied at 49 kg N ha<sup>-1</sup>) did not show significantly different N<sub>2</sub> and CO<sub>2</sub> fluxes when incubated at 20 and 2% O<sub>2</sub> (Fig. 4A and 4B). When this experiment was repeated with soil cores collected 9 d after fertilization (Fig. 4A), we found that soils incubated at 2% O<sub>2</sub> had higher denitrification rates than those incubated at 20% soil O<sub>2</sub>; however, differences between fertilized and ambient soil cores were not statistically different at a given O<sub>2</sub> concentration. We found a predictable pattern of lower CO<sub>2</sub> fluxes at lower O<sub>2</sub> concentrations (Fig. 4B), but no differences in CO<sub>2</sub> fluxes between ambient and fertilized soils at a given O<sub>2</sub> concentration. Soil moisture was approximately 20% at both sampling intervals.

When we saturated field-fertilized soil cores (to simulate soil conditions after a major storm event), we found tremendously high N<sub>2</sub> fluxes at both 20 and 2% soil O<sub>2</sub> (Fig. 5A). The N<sub>2</sub> fluxes in saturated soils were 4039 ± 723  $\mu$ g N m<sup>-2</sup> h<sup>-1</sup> and 2959 ± 254  $\mu$ g N m<sup>-2</sup> h<sup>-1</sup> at 20% and 2% O<sub>2</sub>, respectively, compared to 53.3 ± 30  $\mu$ g N m<sup>-2</sup> h<sup>-1</sup> and 243 ± 98  $\mu$ g N m<sup>-2</sup> h<sup>-1</sup> in field-moist soils. Carbon dioxide fluxes were lower at 2% O<sub>2</sub> than at 20% O<sub>2</sub> at each moisture level (Fig. 5B).

Field-measured fluxes of N<sub>2</sub>O and CO<sub>2</sub> showed no significant differences 24 h after fertilization (Fig. 6A and 6B), but after 9 d fluxes had increased significantly compared to prefertilization rates (2.00 ± 0.62  $\mu$ g N<sub>2</sub>O-N m<sup>-2</sup> h<sup>-1</sup> and 43.4 ± 5.5 mg C m<sup>-2</sup> h<sup>-1</sup> vs. -0.07 ± 0.33  $\mu$ g N m<sup>-2</sup> h<sup>-1</sup> and 23.0 ± 3.2 mg C m<sup>-2</sup> h<sup>-1</sup>).

While we were able to measure  $N_2O$  concentrations in the incubation chambers, calculating  $N_2O$  fluxes would have been misleading due to the rapid and dynamic swings in concentration observed between sampling intervals. For instance, when fertilized soils were saturated with water (or when an  $NO_3^-$  solution

Table 1. Annual denitrification rates calculated for study lawns based on laboratory measured N<sub>2</sub> flux rates and field measured soil moisture conditions, University of Maryland Baltimore County.

Volumetric soil moisture	Proportion of growing season	N² flux	Notes
		kg N ha <sup>-1</sup> yr <sup>-1</sup>	
8–35%	0.95	2.95 ± 1.65	Fertilized lawns 18–20% $O_{2'}$ pH = 5.7–6.0
35%+	0.05	223.9 ± 40.1	Rate for saturated soils
Annual N <sub>2</sub> flux		$14.0 \pm 3.6$	

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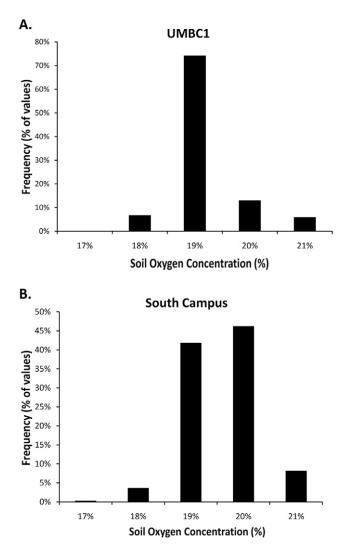


Fig. 1. Macroscale soil oxygen concentrations in two study lawns over a 1-yr time period: (A) UMBC1, and (B) South Campus, University of Maryland Baltimore County. Values for each lawn represent the mean of three sensors at 7-cm depth.

was added to wet soils), we saw extraordinarily high concentrations of  $N_2O$  for the first few hours of the incubation, followed by rapid  $N_2O$  consumption. In some cases, virtually all of the accumulated  $N_2O$  had been consumed before the next sampling interval (see Fig. 7 for examples from individual soil cores).

We estimated annual N<sub>2</sub> fluxes in residential lawns by apportioning flux rates from appropriate N-FARM incubations to the proportion of the growing season when fieldmeasured soil moisture and O2 conditions fell within that range (Table 1). We measured mean N<sub>2</sub> fluxes equivalent to 2.95 ± 1.65 kg N ha<sup>-1</sup> yr<sup>-1</sup> in UMBC1 and South Campus soils at 20% soil O2 and 18 to 30% soil moisture. Based on soil O<sub>2</sub> and moisture measurements at the sites, similar conditions were found during 95% of the year, so a rate of 2.95  $\pm$ 1.65 kg N ha<sup>-1</sup> yr<sup>-1</sup> was assumed for this time period annually. Conversely, we measured very high N<sub>2</sub> flux rates (equivalent to 224 ± 40.1 kg N ha<sup>-1</sup> yr<sup>-1</sup>) at 20%  $O_2$  in saturated, fertilized lawn soils. Based on maximum soil moisture readings at the sites (38%), we estimated that soils at 35% and greater soil water content would be approaching saturated conditions. Saturated conditions were experienced for 5% of the

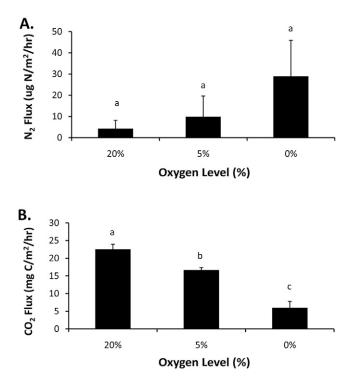


Fig. 2. (A) N<sub>2</sub> and (B) CO<sub>2</sub> fluxes from intact lawn soil cores at approximately 20% volumetric soil moisture across three soil oxygen concentrations (20, 5, and 0%), University of Maryland Baltimore County. Different letters indicate significant differences across treatments (p < 0.05, n = 4).

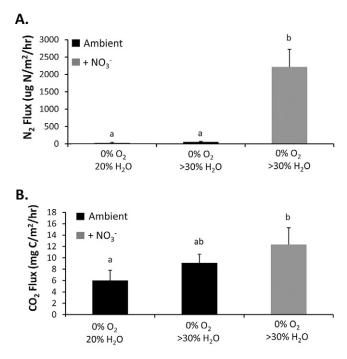


Fig. 3. (A) N<sub>2</sub> and (B) CO<sub>2</sub> fluxes from intact lawn soil cores at 0% oxygen, University of Maryland Baltimore County. Bars represent soil cores under ambient conditions before rainfall (approximately 20% volumetric soil moisture), ambient conditions after rainfall (>30% volumetric soil moisture), and injected with an NO<sub>3</sub><sup>-</sup> solution after rainfall. Different letters indicate significant differences across treatments (p < 0.05, n = 4).

average growing season (based on 5 yr of soil moisture data). By this method, total annual denitrification was estimated at  $14.0 \pm 3.6$  kg N ha<sup>-1</sup> yr<sup>-1</sup>.

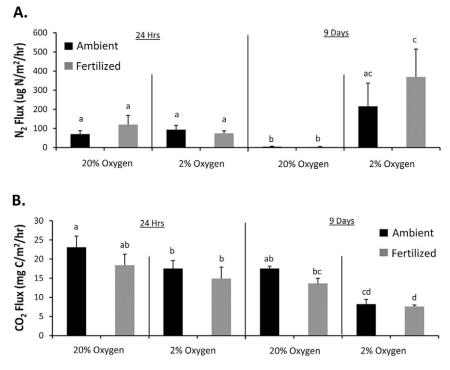


Fig. 4. (A) N<sub>2</sub> and (B) CO<sub>2</sub> fluxes at 20 and 2% oxygen for lawn soil cores collected 24 h and 9 d after a portion of each plot was fertilized in the field (Fertilized) or left untreated (Ambient), University of Maryland Baltimore County. Volumetric soil moisture was approximately 18 to 20%. Different letters indicate significant differences across all treatments and time periods (p < 0.05, n = 4).

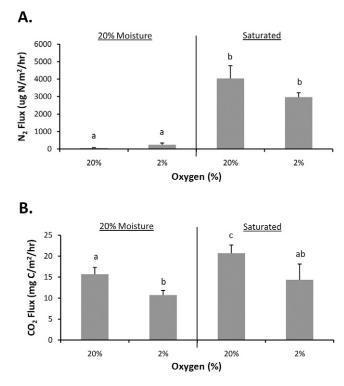


Fig. 5. (A) N<sub>2</sub> and (B) CO<sub>2</sub> fluxes at 20 and 2% oxygen for lawn soil cores collected 9 d after fertilization in the field, then saturated with water in the laboratory, University of Maryland Baltimore County. Different letters indicate significant differences across treatments (p < 0.05, n = 8).

## Discussion

We hypothesized that (i) soil  $O_{2^2}$ , moisture, and available  $NO_{3^2}$  were the most important controls on denitrification in resi-

dential lawns; (ii) denitrification would vary temporally based on these controls; and (iii) N<sub>2</sub> fluxes would be low most of the time, with large pulses following fertilizer addition and precipitation events. While our results generally confirm these hypotheses, the threshold levels of soil O<sub>2</sub>, moisture, and NO<sub>3</sub><sup>-</sup> availability required to see significant rates of denitrification in lawns (relative to N inputs) were greater than expected. For instance, high rates of denitrification were possible when bulk soil O<sub>2</sub> concentrations were high, and for all oxygen concentrations, lawn soils had to be nearly saturated and recently fertilized to see significant N<sub>2</sub> fluxes. Soil oxygen concentrations were less dynamic (Fig. 1A and 1B), and N<sub>2</sub>O fluxes even more dynamic than expected (Fig. 7).

Soil moisture has been linked to soil  $O_2$ in a number of studies (Sexstone et al., 1985; Burgin et al., 2010), so we expected to measure significant drops in soil  $O_2$  concentrations following large storm events; however, this was not the case. Soil  $O_2$  concentrations (measured hourly by three diffusion-head  $O_2$  sensors at each site) never dropped much below ambient atmospheric concentrations over our study period (Fig. 1A and 1B), which included several major storm events.

One storm system brought >10 cm of rainfall over a 3-d period (NCDC, 2009), yet soil  $O_2$  concentrations did not change significantly at the sites. These findings suggest that the soils were well aerated and well drained. A lack of redoximorphic features in these soils further supports this conclusion.

We expected denitrification rates to be low when soil O<sub>2</sub> concentrations were high, but this was not always the case. Under wet or saturated conditions, soils amended with fertilizer or NO3- had high N2 fluxes, even when soil O2 concentrations were at 20% (4039 ± 723  $\mu$ g N m<sup>-2</sup> h<sup>-1</sup>; Fig. 5A). The Apogee sensors likely reflect O<sub>2</sub> levels in macropores, while denitrification likely occurs in anaerobic microsites associated with soil aggregates or particulate organic matter (Parkin, 1987). The fact that soil moisture appeared to be a stronger controller of denitrification rate than soil O<sub>2</sub> thus suggests that factors that influence the flux of O<sub>2</sub> from macropores to denitrifying microsites are critical controllers of denitrification rate. Given that these factors vary from site to site with soil texture, structure, compaction, and other variables, it is likely that relationships between soil O2 and denitrification rates will vary in both time and space across the landscape. Another key factor affecting the levels of O2 in soil microsites is bacterial and plant respiration. Lawn soils, which tend to have high soil organic matter, microbial biomass, and labile C and N, have correspondingly high rates of respiration (Qian and Follett, 2002; Raciti et al., 2008; Qian et al., 2010; Fig. 1B and 6B). Since respiration is the primary oxygen-consuming process in soils, we might expect anoxic microsites to form readily in lawns, especially under warm, moist conditions that favor high soil respiration.

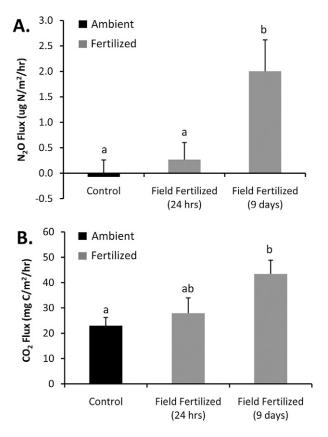


Fig. 6. (A) N<sub>2</sub>O and (B) CO<sub>2</sub> fluxes from in situ gas sampling chambers in each of the lawn plots, University of Maryland Baltimore County. Different letters indicate significant differences across treatments (p < 0.05, n = 6).

The N<sub>2</sub>O fluxes we measured in the field suggest that lawns are not a major source of N<sub>2</sub>O emissions in our study system. When we fertilized part of the UMBC1 site, we expected to see an immediate and rapid increase in N<sub>2</sub>O emissions (one of the intermediary gases in the denitrification process), but N<sub>2</sub>O fluxes remained low after 24 h (Fig. 6A). We saw significantly higher N<sub>2</sub>O fluxes 9 d after fertilizer application. These enhanced fluxes of N<sub>2</sub>O may be the result of greater N availability 9 d after fertilizer application due to the use of a slowrelease, sulfur-coated urea product (per standard management practices at the site). The extra time (9 d), combined with a light rainfall 3 d after fertilizer application, may have increased N availability in the soil. However, it should be stressed that even the enhanced  $N_2O$  fluxes (<0.2 ng N cm<sup>-2</sup> h<sup>-1</sup>) were lower than the mean rates measured in lawn and forest plots at BES (Groffman et al., 2009), which calls into question whether the low but significantly higher N<sub>2</sub>O fluxes are a result of the experimental treatment or merely natural variation in the system.

Results from the N-FARM incubations suggest that soil moisture,  $NO_3^-$  availability, and the balance of  $N_2O$  production and consumption are key factors controlling  $N_2O$  emissions from lawns. Fluxes from wet, fertilizer-amended soils support the hypothesis that high soil moisture and  $NO_3^-$  availability can lead to high rates of  $N_2O$  production (Groffman et al., 2009), but these results also reveal a more complicated relationship between  $N_2O$  production and consumption. In fertilized cores, we sometimes saw extraordinarily high concentrations of  $N_2O$  followed by very low concentrations (near

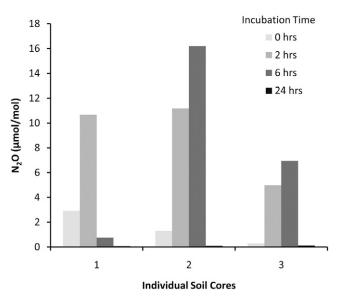


Fig. 7. Laboratory-measured N<sub>2</sub>O concentrations in the headspace of individual soil sampling chambers at 0, 2, 6, and 24 h after the start of incubations for fertilized, saturated soil cores, University of Maryland Baltimore County.

the detection limit of our instrument) at the next sampling interval (Fig. 7). These findings indicate a lag time between accelerated N<sub>2</sub>O production and counterbalancing increases in N<sub>2</sub>O consumption, which may have important implications for N<sub>2</sub>O fluxes from fertilized soils. Nitrous oxide is a by-product of both nitrification and denitrification, and its solubility and diffusivity control fluxes between the soil and the atmosphere (Heincke and Kaupenjohann, 1999). In the closed incubation system, N<sub>2</sub>O could not escape and was generally consumed during the soil incubations. While soil saturation would inhibit N<sub>2</sub>O diffusion to a significant degree (Heincke and Kaupenjohann, 1999), it is difficult to say how much N<sub>2</sub>O would have been lost to the atmosphere. While long-term, in situ N<sub>2</sub>O fluxes from BES lawns suggest that they are not major sources of N<sub>2</sub>O emissions, these measurements are not keyed to fertilizer or rainfall events and may miss periods of high N<sub>2</sub>O emissions (Groffman et al., 2009). Thus, like studies in the western United States (Kaye et al., 2004; Bijoor et al., 2008; Hall et al., 2008; Townsend-Small and Czimczik, 2010; Townsend-Small et al., 2011), we cannot yet conclude that lawns are an insignificant source of N<sub>2</sub>O in the study area.

#### Closing the Nitrogen Budget

Using a combination of laboratory and field measurements, we calculated an annual denitrification rate of  $14.0 \pm 3.6 \text{ kg N}$  ha<sup>-1</sup> yr<sup>-1</sup> for the lawns in this study (see the Calculations and Statistics section and Table 1). This calculation is based on long-term field and laboratory measurements of soil moisture and oxygen conditions, but does not account for other factors that might influence N<sub>2</sub> fluxes, such as temperature, seasonality (soil cores were collected during the spring), plant species, soil type, and climate variation. Further, while the sum of N inputs (109.2 kg N ha<sup>-1</sup> yr<sup>-1</sup>) and losses or sequestration (111.1 kg N ha<sup>-1</sup> yr<sup>-1</sup>) in our mass balance (Table 2) yields a nearly balanced N budget, there is significant uncertainty surrounding some of the numbers in the budget. The term with

Table 2. Nitrogen mass balance calculated for stud	/ lawns, University of Maryland Baltimore County.

Nitrogen flux	Residential	Forest	Source	
Ninputs				
Atmospheric deposition (kg N ha <sup>-1</sup> yr <sup>-1</sup> )	11.2	11.2	Groffman et al., 2004	
Fertilizer (kg N ha <sup>-1</sup> yr <sup>-1</sup> )	98.0	0	This study (UMBC1 lawn plot)	
Hydrologic N losses				
Leaching (kg N ha <sup>-1</sup> yr <sup>-1</sup> )	14.1	4.4	Groffman et al., 2009	
Gaseous N losses				
N <sub>2</sub> O (kg N ha <sup>-1</sup> yr <sup>-1</sup> )	<1	<1	Groffman et al., 2009	
Denitrification as $N_2$ (kg N ha <sup>-1</sup> yr <sup>-1</sup> )	14.0	N/A	This study combined with long-term soil moisture records at Baltimore Ecosystem Study (http://beslter.org).	
N sequestration				
N accumulation in soils (kg N ha <sup>-1</sup> yr <sup>-1</sup> )	83.0	N/A	Residential sites with agricultural land-use history (Raciti et al., 2011a).	

the largest uncertainly is soil N sequestration in residential lawn soils, which was estimated using a chronosequence of lawns in the study area (Raciti et al., 2011a) and may not be an accurate estimate for an individual lawn. Atmospheric N inputs may also be somewhat higher or lower than reported in our budget, since they reflect estimates from a USEPA Clean Air Status and Trends Network (CASTNET) site that is approximately 30 km to the south. Finally, hydrologic N losses are based on the long-term average for the site, but there is interannual variation in this rate (Groffman et al., 2009).

Despite these significant uncertainties, our calculations suggest that denitrification is an important part of the N budget for residential lawns (Table 2). The N<sub>2</sub> flux we calculated (14.0  $\pm$  3.6 kg N ha<sup>-1</sup> yr<sup>-1</sup>) was comparable in magnitude to atmospheric N deposition (11.2 kg N ha<sup>-1</sup> yr<sup>-1</sup>), NO<sub>3</sub><sup>-</sup> leaching losses (14.1 kg N ha<sup>-1</sup> yr<sup>-1</sup>), and was equal to approximately 15% of mean fertilizer N inputs to home lawns in the study area (83.5 kg N ha<sup>-1</sup> yr<sup>-1</sup>; Law et al., 2004). This rate is within the range of denitrification estimates obtained by Horgan et al. (2002a,b) using a <sup>15</sup>N mass balance approach, though a significant fraction of the <sup>15</sup>N tracer used in those studies could not be accounted for at the end of the experiments. Our annual flux calculation indicates that relatively short periods of saturation may be responsible for the majority of denitrification in our well-drained lawn soils. Lawns with limited drainage (or at low points in the landscape) could be hotspots for denitrification in residential areas. Our results suggest that denitrification is an important means of removing reactive N from the residential landscape, but varies markedly in space, time, and with factors that affect soil saturation (texture, structure, compaction) and NO<sub>3</sub><sup>-</sup> availability (fertilization). While the annual denitrification rate we calculated was substantial, there is evidence that soil organic matter may be an even larger N sink in residential landscapes, particularly for sites with a history of agricultural land use before development (see Raciti et al., 2011a). Further work is required before the findings of this, or the aforementioned study, can be generalized to a wider range of residential lawns and soils.

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