

Nitrate Leaching and Nitrous Oxide Flux in Urban Forests and Grasslands

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Urban landscapes contain a mix of land-use types with different patterns of nitrogen (N) cycling and export. We measured nitrate (NO_3^-) leaching and soil:atmosphere nitrous oxide (N_2O) flux in four urban grassland and eight forested long-term study plots in the Baltimore, Maryland metropolitan area. We evaluated ancillary controls on these fluxes by measuring soil temperature, moisture, and soil:atmosphere fluxes of carbon dioxide on these plots and by sampling a larger group of forest, grass, and agricultural sites once to evaluate soil organic matter, microbial biomass, and potential net N mineralization and nitrification. Annual NO_3^- leaching ranged from 0.05 to 4.1 g N m^{-2} yr^{-1} and was higher in grass than forest plots, except in a very dry year and when a disturbed forest plot was included in the analysis. Nitrous oxide fluxes ranged from 0.05 to >0.3 g N m^{-2} yr^{-1} , with few differences between grass and forest plots and markedly higher fluxes in wet years. Differences in NO_3^- leaching and N_2O flux between forests and grasslands were not as high as expected given the higher frequency of disturbance and fertilization in the grasslands. Carbon dioxide flux, organic matter, and microbial biomass were as high or higher in urban grasslands than in forests, suggesting that active carbon cycling creates sinks for N in vegetation and soil in these ecosystems. Although urban grasslands export more N to the environment than native forests, they have considerable capacity for N retention that should be considered in evaluations of land-use change.

URBAN landscapes contain a mix of land-use types that vary in time and space (Cadenasso et al., 2007). In Eastern North America, landscapes that were originally forested were converted to agricultural use in the 18th and 19th Centuries and then reforested to a large extent in the first half of the 20th century (Brush, 2001; Benitez and Fisher, 2004). More recently, there has been a marked expansion in urban and suburban land use such that much of this region is now a mix of relict forest, agricultural, and urban/suburban lands (Goetz et al., 2004; Jantz et al., 2005). The dominant recent (1950–2000) trend has been an increase in “exurban” land use at the expense of agricultural use (Brown et al., 2005).

The changing mix of land-use types has significant effects on multiple ecosystem functions and services (Dale et al., 2005; Burcher et al., 2007; Turner et al., 2007). In coastal regions, there is particular interest in the effects of land-use change on N cycling and export due to widespread concerns about N-induced eutrophication of estuarine ecosystems, such as the Chesapeake Bay and the Gulf of Mexico (Carpenter et al., 1998; Kemp et al., 2005; Paerl et al., 2006). There is particular concern about NO_3^- , the most mobile form of N, which is increased by a wide range of human activities associated with land-use change (Galloway et al., 2008). Alteration of the N cycle can also lead to increases in N_2O flux from soils to the atmosphere. This gas is radiatively active and is a precursor to compounds involved in the destruction of ozone in the stratosphere (Prather et al., 1995).

Evaluating the effects of land-use change on N export from urbanizing landscapes requires an understanding of N cycling in the different components of the landscape (i.e., forests, agriculture, and urban/suburban/exurban ecosystems) (Pouyat et al., 2007). Urban, suburban, and exurban ecosystems are a heterogeneous and variable mix of paved surfaces, trees and shrubs, and grasslands (lawns) (Byrne, 2007; Cadenasso et al., 2007). Although there has been a great deal of research on N cycling in temper-

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Abbreviations: BES, Baltimore Ecosystem Study; CAP, Central Arizona Phoenix, USA; PVC, polyvinyl chloride; SOM, soil organic matter; UMBC, University of Maryland Baltimore County.

ate forest and agricultural ecosystems and in arid and semiarid grasslands, urban grasslands are much less well studied. We define urban grasslands as ecosystems dominated by turf-forming species created and maintained by humans for aesthetic and recreational (not grazing) purposes. We use this term to signal to readers that urban grassland ecosystems cover significant areas and have coherent patterns of ecosystem processes that can be evaluated with the same approaches used to study other ecosystem types (e.g., forests, rangelands, or prairies). There are over 150,000 km² of urban grasslands in the USA (Milesi et al., 2005), but there are few data on N dynamics in these ecosystems (Kaye et al., 2006).

Although urban grasslands can be heavily fertilized and can have high N losses, especially if over-fertilized and over-watered (Morton et al., 1988; Petrovic, 1990; Qian et al., 2003), they also have been shown to have considerable potential for N retention (Gold et al., 1990; Raciti et al., 2008). This retention likely arises from the fact that urban grasslands have young, actively growing vegetation and an extended growing season relative to native and agricultural ecosystems. Although urban grasslands are structurally similar across broad geographic areas, differences between these ecosystems and the native and agricultural ecosystems that they replace vary by region. In arid regions, conversion of native ecosystems to urban grasslands results in increases in soil C and N cycling due to additions of nutrients and especially water (Kaye et al., 2005; Golubiewski, 2006). There is considerable uncertainty about C and N cycling in temperate urban grasslands compared with temperate forests and agricultural ecosystems.

In the Baltimore Ecosystem Study (BES; <http://beslter.org>), one of two urban components of the U.S. National Science Foundation's Long Term Ecological Research network, we have established a series of long-term study plots to evaluate multiple ecological variables in different components of the urban landscape. Eight forest plots were established in 1998 in urban and rural parks and encompass significant natural variation in N cycling (Groffman et al., 2006a). Four grass plots were established from 1999 to 2001 that vary in management intensity, ranging from unfertilized and infrequent mowing to high levels of fertilizer and herbicide input and frequent mowing. Plots were instrumented with lysimeters to measure leaching losses, soil chamber bases to measure soil:atmosphere fluxes of N₂O and CO₂, and sensors to measure soil temperature and moisture. To provide a mechanistic, process-level, and geographic context for these plots, we sampled 14 forest, 10 row crop agriculture (corn), and 10 grass plots in summer 2000 and made measurements of soil organic matter (SOM) content, microbial biomass, and potential net N mineralization and nitrification. Here we present data on NO₃⁻ leaching and N₂O fluxes in four urban grassland and eight forest long-term study plots over a period of significant climatic variability (2001–2005) and use ancillary data collected in 2000 to evaluate factors that control these fluxes. Our objectives were (i) to quantify variation in NO₃⁻ leaching and N₂O flux from different components of the urban landscape under a range of climatic conditions and (ii) to understand the ecosystem properties that control this variation.

Materials and Methods

Baltimore Ecosystem Study Long-term Study Plots

Research of the BES is centered on the Gwynns Falls watershed (76°30', 39°15', and approximately 170 km²) in Baltimore City and Baltimore County, Maryland. Land use varies within the watershed, changing from lower-density residential areas (as low as 220 persons km⁻²) along with agricultural and forest land use in the headwaters to high-density residential (up to 1940 persons km⁻²), commercial, and industrial land uses downstream. Most of the watershed, and all BES research, is in the Piedmont physiographic province. Natural forests occupy approximately 20% of the watershed (Shields et al., 2008) and are dominated by tulip poplar (*Liriodendron tulipifera*) and oaks, primarily chestnut (*Quercus prinus*), scarlet (*Quercus coccinea*), and white (*Quercus alba*) in the uplands and red maple (*Acer rubrum*), green ash (*Fraxinus pennsylvanica*), American elm (*Ulmus americana*), river birch (*Betula nigra*), and sycamore (*Platanus occidentalis*) in the lowlands (Brush et al., 1980). Average annual precipitation is approximately 1060 mm yr⁻¹, and stream discharge is approximately 380 mm yr⁻¹ (Doheny, 1999). Urban grasslands in the region are dominated by Kentucky bluegrass (*Poa pratensis*), tall fescue (*Festuca arundinacea* spp.), fine fescue (*Festuca* spp), and white clover (*Trifolium repens*). Atmospheric N deposition in the Baltimore metropolitan area is estimated at 1.1 g N m⁻² yr⁻¹ (Groffman et al., 2004).

The BES network of long-term study plots consists of eight forest and four grass plots (Table 1). The forest plots have been extensively described elsewhere (Groffman et al., 2006a) and were established in 1998 in remnant forests in Baltimore City and County parks. One of the forest plots had evidence of soil disturbance and extensive invasion by exotic species. Due to continuing vandalism, sampling of this plot was discontinued in 2005.

The grass plots were established in 2001 and represent a range of management intensities from unfertilized, infrequently mowed plots to plots with high inputs of fertilizer and herbicides and frequent mowing. These are "institutional lawns" on the campuses of a secondary school and a university and have been managed in the same way for more than 10 yr. The plots at the McDonogh School represent "low-intensity management" lawns and receive no regular fertilizer inputs, only occasional applications of manure from an on campus stable. The plots on the University of Maryland Baltimore County (UMBC) campus received medium (9.7 g N m⁻² yr⁻¹) or high (19.5 g N m⁻² yr⁻¹) fertilizer applications. Fertilizer was applied to these plots each spring in two applications approximately 2 wk apart. The medium-intensity plots were mowed at 2- to 3-wk intervals (depending on rainfall and subsequent growth) at a height of approximately 10 cm, and the high-intensity plots were mowed at 1- to 2-wk intervals to approximately 5 cm height. Clippings were left in place on all grass plots.

Soil temperature was measured with HOBO H8 Pro Series Temp/External Temp data loggers (Onset Computer Corporation, Pocasset, MA). The external temperature sensor on these units was inserted vertically to a depth of 10 cm in the soil. Measurements were taken once every hour.

Table 1. Soil classification, management regime and dominant vegetation in Baltimore Ecosystem Study long-term study plots in Baltimore, Maryland. Forest plots are described in more detail in Groffman et al. (2006a).

Site	Vegetation	Management/characteristics	Soil classification
McDonogh 1	grass	mowing three or four times a year, horse manure applied occasionally	Chester (fine-loamy, mixed, mesic Typic Hapludult)
McDonogh 2	grass	mowing once or twice a year, no fertilizer	Glenelg (fine-loamy, paramicaceous, mesic Typic Hapludult)
UMBC 1	grass	fertilizer (9.7 g N m ⁻² yr ⁻¹), herbicide (2,4-D, Prodiamine, MCPP, dicamba), bi-weekly mowing	Joppa (loamy-skeletal, siliceous, semiactive, mesic Typic Hapludult)
UMBC 2	grass	fertilizer (19.5 g N m ⁻² yr ⁻¹), herbicide (2,4-D, Dicamba, MCPP), weekly mowing	Brandywine (sandy-skeletal, mixed mesic Typic Dystrudept)
Leakin 1	forest	high inherent fertility, undisturbed vegetation	Legore (fine-loamy, mixed, mesic, Ultic Hapludalf)
Leakin 2	forest	low inherent fertility, undisturbed vegetation	Occaquon (loamy-skeletal, mixed, subactive Typic Dystrudept)
Hillsdale 1	forest	high inherent fertility, undisturbed vegetation	Jackland (fine, smectitic, mesic Typic Haplualf)
Hillsdale 2	forest	high inherent fertility, evidence of soil disturbance, extensive exotic species	Jackland (fine, smectitic, mesic Typic Haplualf)
Oregon topslope 1	forest	low inherent fertility, undisturbed vegetation, top slope position	Glenelg (fine-loamy, paramicaceous, mesic Typic Hapludult)
Oregon topslope 2	forest	low inherent fertility, undisturbed vegetation, top slope position	Glenelg (fine-loamy, paramicaceous, mesic Typic Hapludult)
Oregon midslope 1	forest	low inherent fertility, undisturbed vegetation, mid slope position	Glenelg (fine-loamy, paramicaceous, mesic Typic Hapludult)
Oregon midslope 2	forest	low inherent fertility, undisturbed vegetation, mid slope position	Manor (coarse-loamy, paramicaceous, semiactive, mesic Typic Dystrachrept)

Soil moisture was measured once every 4 to 6 wk at each plot. Time domain reflectometry waveguide probes (Soilmoisture Equipment Corp., Santa Barbara, CA) were installed horizontally into the soil at 10, 20, 30, and 50 cm below ground. A Soilmoisture Trase System I (Model 6050X1; Version 2000 Software) was used to measure soil moisture.

Soil solution chemistry was sampled using zero-tension lysimeters (two or three replicates) of the design described by Johnson et al. (2000) installed at 50 cm depth in two or three subplots at each site. Lysimeter samples were collected monthly, filtered (0.45 µm), and stored at 4°C before analysis for NO₃⁻, ammonium, and phosphate using a Lachat flow injection analyzer (Lachat, Loveland, CO). Only NO₃⁻ data are reported here. Zero-tension lysimeters at the Oregon topslope and Oregon midslope plots (Table 1) did not reliably produce leachate. Therefore, soil solution chemistry comparisons are between the Hillsdale and Leakin forest plots and the McDonogh and UMBC grass plots (Table 1).

Estimates of annual leaching losses were produced in two ways. First, estimates were produced by multiplying annual runoff measured at the BES forested reference watershed by the annual volume-weighted mean NO₃⁻ concentration in lysimeters at 50 cm. Runoff from this watershed, which contains the four rural forest sites, represents water that has passed through the plant canopy and soil profile and is therefore a good estimate of soil solution volume, assuming that surface runoff is negligible (Chang, 2006). A second estimate of annual leaching losses for the grass plots was produced to account for the fact that the grass plots consistently produced less leachate volume than forest plots due to increased evapotranspiration and/or to surface runoff in the grass plots. For these estimates, annual ground water recharge for the grass plots was calculated by multiplying the non-adjusted leaching flux by the annual ratio of grass:forest leachate volume.

Soil:atmosphere fluxes of N₂O and CO₂ were measured using an in situ chamber design. The grass plots had chambers identi-

cal to those used by Bowden et al. (1990, 1991). These (three per plot) consisted of 287-mm inner diameter by 40-mm high polyvinyl chloride (PVC) cylinders that were placed on permanently installed PVC base rings immediately before measurement. The forest plots had the chambers described by Goldman et al. (1995), constructed from 16.5-cm-wide by 20-cm-long pieces of PVC pipe fitted with a septum and an air-tight well cap. These chambers were placed 4 cm into the soil and had a total volume of 2 L. At 0, 10, 20, and 30 min after placement of the chamber on the base or installation of the well cap, 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 (N₂O) or thermal conductivity (CO₂) detection. Fluxes were calculated from the linear rate of change in gas concentration, the chamber internal volume, and soil surface area.

One-time Sampling of Forest, Agricultural, and Grass Plots across the Baltimore Metropolitan Area

In June and July 2000, 14 forest, 10 row crop agriculture (corn), and 10 grass sites throughout the Baltimore metropolitan area, which had been in the same land use for at least 20 yr, were sampled for assessment of soil C and N cycle variables. The long-term forest and grass plots were included in this sampling. Other forest and grass plots were chosen from a set of 202 randomly located sites sampled for an urban forest assessment (Nowak et al., 2004). These plots were chosen to be similar/replicates of the long-term study plots in terms of age, species composition, and management intensity. The agricultural sites included experimental plots cropped to corn on the University of Maryland Experimental Farm and the long-term BES agricultural watershed (Groffman et al., 2004). These sites had received varied agricultural management (crop, fertilizer) typical for the region over the past 20 to 30 yr. Soil samples

(three replicates) were taken with a “bulb corer” sampling tool to a depth of 10 cm and were placed in plastic bags.

Samples were stored at 4°C between sampling and analysis (<1 wk). Soil samples were hand sorted and mixed and held at field moisture for all analyses. Soil moisture content was determined by drying at 60°C for 48 h (McInnes et al., 1994). Soil organic matter content was determined by loss on ignition at 450°C for 4 h (Nelson and Sommers, 1996). Amounts of inorganic N (NO_3^- and NH_4^+) in soil were determined by extraction with 2 mol L^{-1} KCl followed by colorimetric analysis with a Lachat Flow Injection Analyzer.

Microbial biomass C and N content was measured using the chloroform fumigation-incubation method (Jenkinson and Powlson, 1976). Soils were fumigated to kill and lyse microbial cells in the sample. The fumigated sample was inoculated with fresh soil, and microorganisms from the fresh soil grew vigorously using the killed cells as substrate. The flushes of CO_2 and 2 mol L^{-1} KCl-extractable inorganic N (NH_4^+ and NO_3^-) released by the actively growing cells during a 10-d incubation at field moisture content were assumed to be directly proportional to the amount of C and N in the microbial biomass of the original sample. A proportionality constant (0.45) was used to calculate biomass C from the CO_2 flush. Carbon dioxide was measured by thermal conductivity gas chromatography. Inorganic N flush data were not corrected with a proportionality constant.

Inorganic N and CO_2 production was measured in unfumigated “control” samples. These incubations provided estimates of microbial respiration and potential net N mineralization and nitrification. Microbial respiration was quantified from the amount of CO_2 evolved over the 10-d incubation. Potential net N mineralization and nitrification were quantified from the accumulation of NH_4^+ plus NO_3^- and NO_3^- alone during the 10-d incubation. Ammonium and NO_3^- were measured as described above.

Statistical Analysis

Given concerns about unequal sample sizes and non-normally distributed data from the long-term study plots, differences among land-use types and years were evaluated using non-parametric ANOVA (Wilcoxon scores, Kruskal-Wallis test) using the NPARIWAY procedure in the Statistical Analysis System (SAS, 1988). For comparison of site means and evaluation of data from the one-time comparison of forest, agriculture, and urban grassland soils, differences among land-use types were evaluated using one-way ANOVA with a Fisher's protected least significant difference test to determine specific differences among the three land-use classes.

Results

There is variation in the land-use comparisons presented here for different parameters because (i) plots were established at different times, (ii) one of our forest plots was vandalized, and (iii) lysimeters did not collect leaching water in some plots. Nitrate (NO_3^-) leaching comparisons are based on data from four forest versus four grass plots from 2002 to 2004 and from three forest (eliminating the disturbed and vandalized plot) versus four grass

plots from 2002 to 2005. Comparisons of N_2O and CO_2 flux are based on data from seven forest (eliminating the disturbed and vandalized plot) and four grass plots from 2001 to 2005. The full set of soil temperature sensors did not begin to function until 2003; therefore, soil temperature comparisons run from 2003 to 2007. Soil moisture comparisons run from June 2001 through August 2005. To provide mechanistic, process-level, and geographic contexts for the results from the long-term plots, we sampled 14 forest, 10 row crop agriculture (corn), and 10 grass plots in summer 2000 and made measurements of SOM content, microbial biomass, and potential net N mineralization and nitrification.

Soil Temperature and Moisture

Soil temperatures were consistently higher in grass plots than in forest plots, especially in the summer (Fig. 1). There were no consistent differences in soil moisture (Fig. 2) between grass and forest plots, although over the entire record, moisture was significantly ($p < 0.05$) higher in grass than forest plots at 50 cm depth (Fig. 2d). There was an opposite pattern at 30 cm depth, with significantly higher moisture in forest plots in 2001, 2002, and 2003 (Fig. 2c).

Nitrate Leaching

Forest plots produced consistently higher volumes of leachate with lower concentrations of NO_3^- than grass plots (Table 2). The total load of NO_3^- collected in lysimeters was not consistently higher in grass plots when all the forest plots (including the disturbed plot) were included in the analysis (Fig. 3a). Removing the disturbed plot (Hillsdale 2) from the analysis increased mean leaching volume but decreased leaching load due to the very high NO_3^- concentrations in leachate at this site (Fig. 4). When this plot was removed from the analysis, NO_3^- leaching loads in lysimeters were consistently higher ($p < 0.05$) in grass than forest plots except in 2002, which was very dry (68% of normal precipitation) (Fig. 3b). Estimates of annual NO_3^- leaching flux ranged from 0.05 to 4.1 g N m^{-2} yr^{-1} and were consistently higher in grass than in forest plots, even when adjusted for lower leachate volumes in grass plots, except in 2002 (Table 2). Levels of ammonium, which were measured on all samples, and dissolved organic N (measured on selected samples) were low relative to NO_3^- (data not shown).

Nitrous Oxide Flux

Nitrous oxide fluxes did not show a marked seasonal pattern but were higher ($p < 0.05$) in the wet years of 2003 (148% of normal precipitation) and 2004 (123% of normal precipitation) than in the other years (Fig. 5a). Nitrous oxide flux was significantly ($p < 0.05$) higher in the grass plots only in 2003 (Fig. 6a). The disturbed forest plot (Hillsdale 2) had the highest ($p < 0.05$) N_2O fluxes (Fig. 7a). The low-intensity management grass plots (McDonogh) had higher ($p < 0.05$) N_2O fluxes than the more intensively managed grass plots at UMBC (Fig. 7a).

Ancillary Variables

Soil:atmosphere fluxes of CO_2 , or total soil respiration, an index of total soil C cycling activity, showed a marked seasonal pattern, with highest rates in summer (Fig. 5b). Grass plots

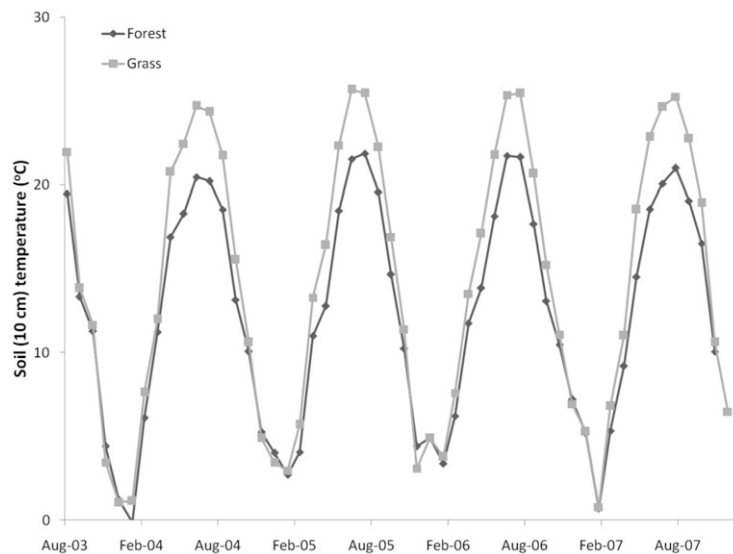


Fig. 1. Mean monthly soil temperature (10 cm) in seven forest and four grass plots in the Baltimore metropolitan area from August 2003 through November 2007.

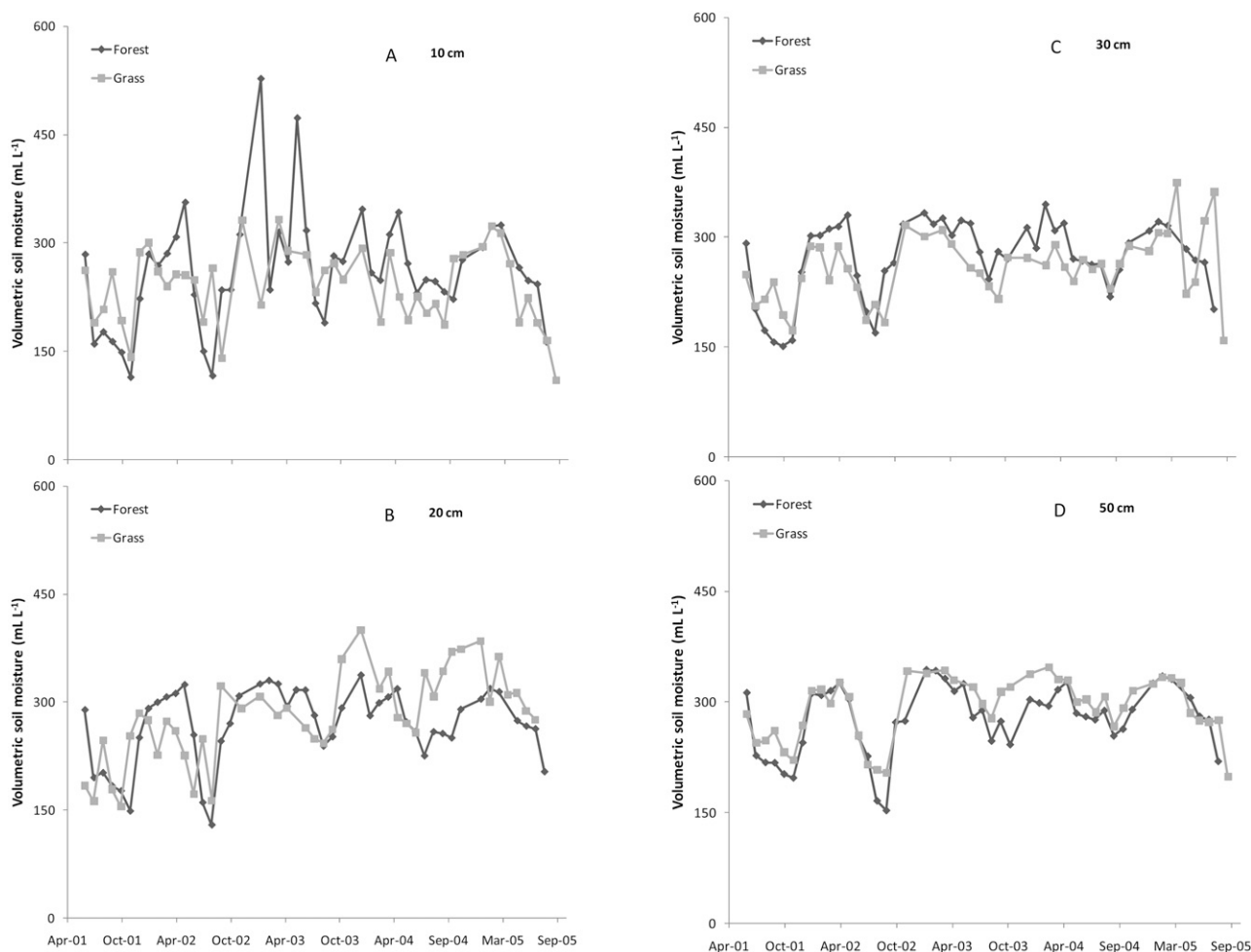


Fig. 2. Volumetric soil moisture at 10 (A), 20 (B), 30 (C), and 50 (D) cm in seven forest and four grass plots in the Baltimore metropolitan area from June 2001 through September 2005.

had higher ($p < 0.05$) CO_2 fluxes than forest plots in 2003 and 2005 (Fig. 6b). The urban forest plots (Leakin, Hillsdale) had

higher ($p < 0.05$) CO_2 fluxes than the rural forest plots (Oregon topslope, Oregon midslope) (Fig. 7b).

Table 2. Annual leachate volume, volume-weighted nitrate (NO_3^-) concentration, and annual NO_3^- leaching flux in grass and forest plots in the Baltimore area, 2002–2005. Values are means with SE in parentheses.

Landuse/ year	Leachate volume collected	Volume- weighted NO ₃ ⁻ concentration	Annual NO ₃ ⁻ leaching flux	
	L yr ⁻¹	mg N L ⁻¹	g N m ⁻² yr ⁻¹	
Forest				
2002	3.8 (0.8)*	1.9 (0.7)*	0.23 (0.08)	
2003	7.9 (0.7)	0.6 (0.2)*	0.30 (0.11)*	
2004	18.21 (4.4)*	1.2 (0.4)*	0.79 (0.25)*	
Forest (disturbed site removed)†				
2002	5.1 (0.8)*	0.9 (0.5)*	0.11 (0.06)	
2003	9.2 (0.7)	0.1 (0.03)*	0.05 (0.01)*	
2004	15.8 (2.9)*	0.34 (0.06)*	0.22 (0.04)*	
2005	9.7 (0.5)*	0.30 (0.10)*	0.17 (0.06)*	
Grass			Non-adjusted	Adjusted‡
2002	0.9 (0.4)	6.4 (1.8)	0.78 (0.2)	0.14 (0.05)
2003	7.5 (1.0)	3.1 (0.5)	1.5 (0.3)	1.2 (0.2)
2004	8.4 (1.2)	5.1 (0.6)	3.3 (0.4)	1.8 (0.2)
2005	6.0 (1.0)	7.3 (1.8)	4.1 (1.0)	2.5 (0.6)

* Significant difference between forest and grass at $p < 0.05$.

† One of the forest plots (Hillsdale 2) was highly disturbed and had much higher leaching than the other forest plots. Sampling of this plot was discontinued in 2005.

‡ Grass plots consistently produced less leachate volume than forest plots. Therefore, estimates of annual leaching flux were calculated by using the same estimate of annual ground water recharge that was used for the forest sites or by multiplying the non-adjusted leaching flux by the annual ratio of grass:forest leachate volume. For example, for 2002, the adjusted flux was calculated by dividing the leaching volume collected in the grass plots (0.9 L) by the volume collected in the forest plots (5.1 L) and then multiplying the non-adjusted flux (0.78) by this number (0.18) to yield an adjusted flux of 0.14.

In the one-time sampling of 14 forest, 10 row crop agriculture (corn), and 10 grass sites, forest sites consistently had the highest values for C-related variables (organic matter, microbial biomass, and respiration) and the lowest values for variables associated with N loss (soil NO_3^- and nitrification potential) (Table 3). For some variables (organic matter, microbial biomass, and soil NO_3^-), urban grasslands were similar to forest sites, but for others (pH and nitrification potential), urban grasslands were similar to agricultural sites.

Discussion

We expected to observe higher NO_3^- leaching and N_2O fluxes from urban grasslands than forest sites due to the higher frequency of disturbance and fertilization in these human-created and maintained ecosystems. Although NO_3^- leaching was higher in urban grasslands than in forest plots, the difference was not as large or consistent as we expected, and the most intensively fertilized plots did not have the highest leaching losses. Our N_2O results were even more surprising because there were few differences between forest and grass plots, and, again, the more intensively fertilized grasslands did not have greater fluxes. These results suggest that N cycling in urban grasslands is complex and that there is significant potential for N retention in these ecosystems. Our ancillary data suggest that this retention was driven by high rates of C cycling, as shown by

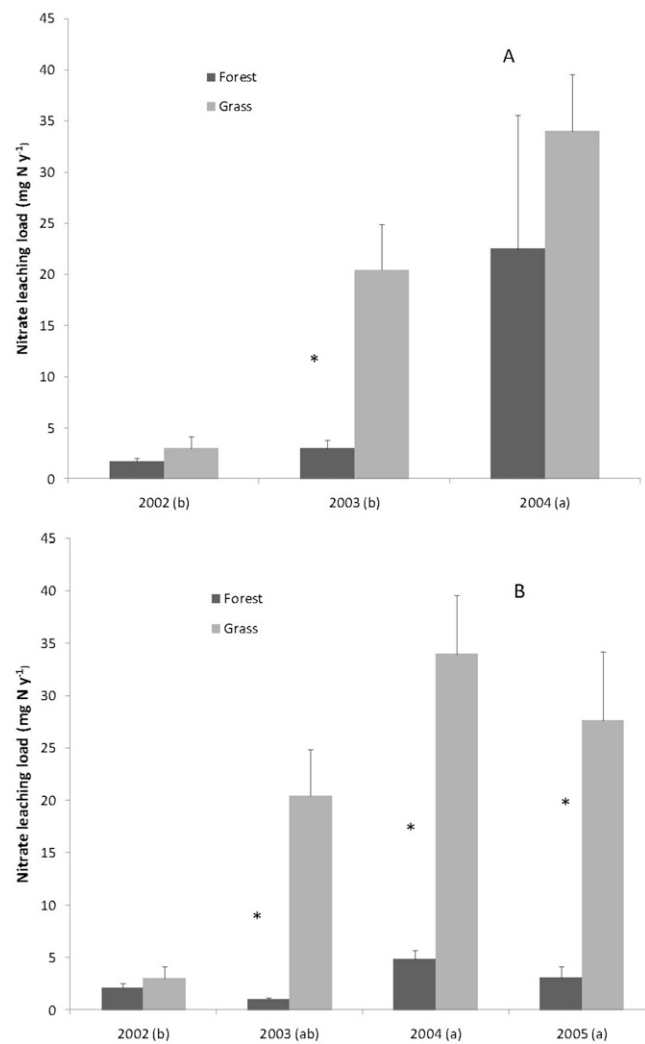


Fig. 3. Nitrate collected in zero tension lysimeters in four (A) or three (B) forest and four grass plots in the Baltimore metropolitan area from 2002 through 2004 (A) or 2005 (B). Panel A includes data from a highly disturbed forest plot that had high leaching. Sampling of this plot was discontinued in 2005. Panel B compares the three undisturbed forest with the four grass plots. *Significant difference between forest and grass at $p < 0.05$. Years followed by different letters are significantly different at $p < 0.05$.

high rates of total soil respiration and pools of SOM and microbial biomass.

NO_3^- Leaching

Differences in NO_3^- leaching between ecosystems were the product of differences in the volume of leaching water and the NO_3^- concentration of that water. Quantifying differences in leaching volume between urban grasslands and forest plots was complicated by differences in evapotranspiration and runoff between these ecosystem types. We collected significantly less leachate in lysimeters in grass plots, but we have no conclusive way to tell if this was due to differences in runoff, evapotranspiration, the way that water moves through the soil profile (percolation), or lysimeter collection efficiency. To account for this uncertainty, we calculated leaching loads in two ways: One way assumed that actual leaching volume did not differ be-

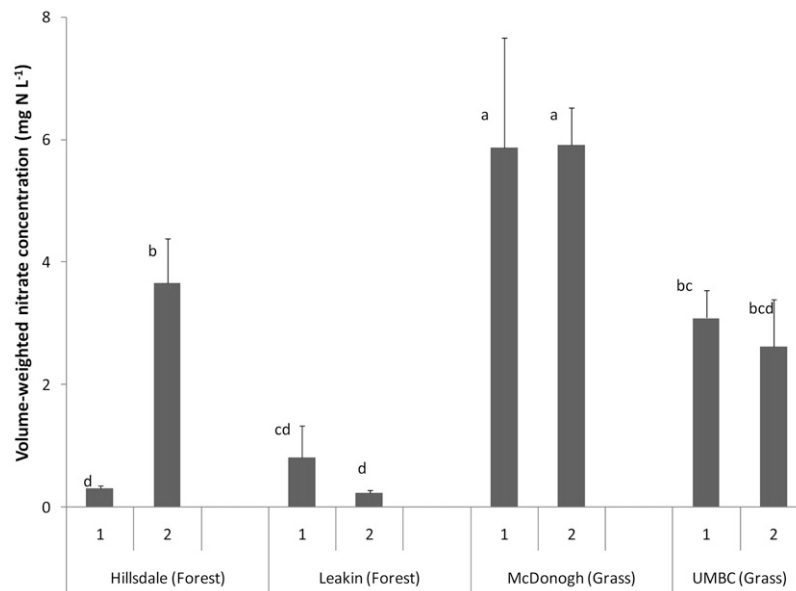


Fig. 4. Volume-weighted nitrate concentrations in leachate in zero-tension lysimeters in four forest and four grass plots in the Baltimore metropolitan area. Values are mean (SE) of three water years (2002–2004). Bars with different superscripts are significantly different at $p < 0.05$.

tween grasslands and forests, and the other assumed that the difference in leachate volume that we collected reflected an actual difference in the volume of water moving through the soil profile in these ecosystem types. We suspect that the difference was due to higher evapotranspiration on the grass plots due to higher soil temperatures and the longer growing season in urban grassland versus forest ecosystems. Differences in percolation and lysimeter collection efficiency may have played a role because we consistently observed similar, or higher, levels of soil moisture at 50 cm in the grass plots. These differences could be driven by disturbance of the soil profile during urban grassland establishment or to the generally high bulk density of urban grasslands relative to forests (Raciti et al., 2008). We observed no visual evidence of runoff on our grass plots.

A second complication in our leaching comparisons was the fact that one of our forest plots was extensively disturbed and had very high N losses. Although leaching from most of the forest plots was very low, consistent with many previous studies of forest ecosystems (Montagnini et al., 1991; Peterjohn et al., 1999; Groffman et al., 2006a; Dittman et al., 2007), data from our highly disturbed forest plot (Hillsdale 2) showed that forests can have hydrologic N losses well in excess of atmospheric inputs. Likely causes of the high N losses from the highly disturbed forest plot include soil disturbance and invasion by exotic plant and earthworm species (Steinberg et al., 1997; Ehrenfeld et al., 2001; Zhu and Carreiro, 2004; Szlavecz et al., 2006). These results suggest that not all forest components of urban landscapes are functioning as strong N sinks. We made comparisons between forests and urban grasslands that included or excluded the disturbed plot so that we could evaluate how urban grasslands compare with undisturbed forests typical of the natural ecosystems that the urban grasslands replaced as well as with the full range of forests likely to be found in urban areas.

In the most conservative comparison of NO_3^- leaching from forests and urban grasslands, which included the highly disturbed forest plot and adjusted leachate volumes in the grass plots, mean annual leaching loss from 2002 to 2004 was more than twice as high in grass ($1.0 \text{ g N m}^{-2} \text{ yr}^{-1}$) as forest ($0.44 \text{ g N m}^{-2} \text{ yr}^{-1}$). In the least conservative comparison, with the highly disturbed forest plot removed and no adjustment of leachate volume in the grass plots, the difference was much more striking (mean annual leaching loss from 2002 to 2005 of 2.4 versus $0.14 \text{ g N m}^{-2} \text{ yr}^{-1}$). There was marked annual variation in flux, with very low losses and no difference between forests and grasslands during a very dry year (2002) and higher losses and bigger differences during wetter years. Here we report only NO_3^- leaching losses. Ammonium was measured on all samples and was low. Dissolved organic N was measured occasionally and did not appear to be important relative to NO_3^- .

The variation in NO_3^- losses among the grass plots was puzzling in that the most intensively fertilized plot (UMBC 2) had the lowest NO_3^- losses among the grass plots and the least intensively fertilized plots (McDonogh 1 and 2) had the highest losses. The McDonogh 1 plot received occasional (and unquantified) applications of manure, and the McDonogh 2 plot was downslope from a fertilized agricultural field and may therefore also have received external inputs of N. Among the UMBC plots, the higher losses from the less intensively fertilized plot (UMBC 1) may have been due to higher slope and/or less dense vegetation cover at this plot. The different grass plots also differed in their exposure to herbicides. Although research has generally shown that these compounds have little effect on N cycling when applied at normal application rates (Martens and Bremner, 1993), effects on specific processes in specific ecosystems can be significant. Further research is necessary to isolate the factors controlling urban grassland response to variation in management.

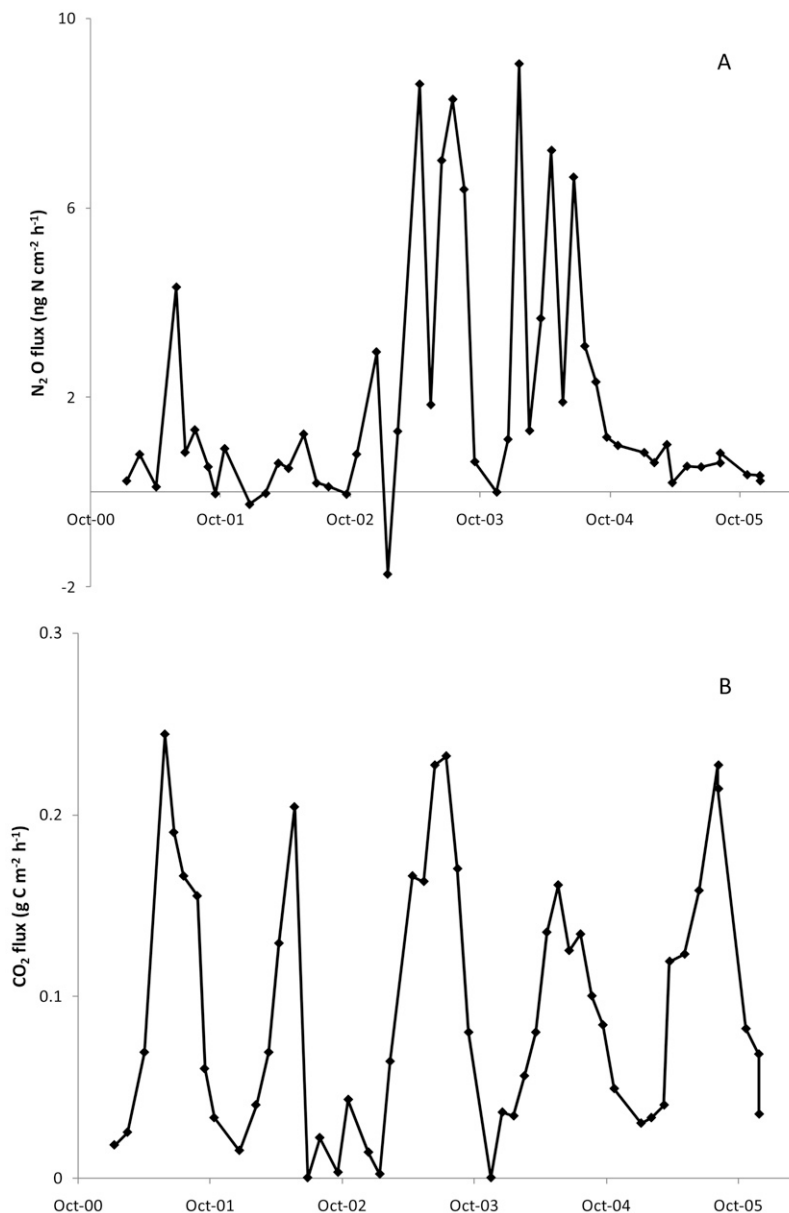


Fig. 5. Soil-atmosphere fluxes of N_2O (A) and CO_2 (B) from February 2001 through December 2005. Values are means of fluxes from three chambers in seven or eight intact forest and four grass plots in the Baltimore metropolitan area.

Data from the UMBC plots support the idea that grass areas have a high capacity for N retention (Gold et al., 1990; Raciti et al., 2008). Given that fertilizer inputs to these plots were $>10 \text{ g N m}^{-2} \text{ yr}^{-1}$ and that losses ranged from <1 to $4 \text{ g N m}^{-2} \text{ yr}^{-1}$, retention on these plots ranged from nearly 100% during the dry year (2002) to $>60\%$ during the wettest year (2004). Our data suggest that much of the high N retention that has been reported for urban mass balance studies (Baker et al., 2001; Groffman et al., 2004; Wollheim et al., 2005) likely takes place in urban grasslands. On the other hand, these data suggest that urban grasslands can be significant sources of NO_3^- to the environment (i.e., 60% retention of a high rate of input [$10 \text{ g N m}^{-2} \text{ yr}^{-1}$], which leaves a significant amount of N to be lost to the environment). The factors controlling N retention in lawns are complex and can include variation in multiple

sinks including thatch, denitrification, and roots (Engelsjord et al., 2004; Horgan et al., 2002; Miltner et al., 1996; Raciti et al., 2008), which likely vary with site conditions, lawn age, and clipping management (Petrovic, 1990; Qian et al., 2003; Frank et al., 2006). Further research is needed into these factors so that this retention can be maintained or increased.

There have been relatively few long-term studies of hydrologic N losses from urban grasslands. Petrovic (1990) reviewed multiple studies and found that most reported $>90\%$ retention of fertilizer input (i.e., $<10\%$ was leached). Newly established lawns (Easton and Petrovic, 2004) and overwatering and/or overfertilization (Morton et al., 1988) can lead to significantly higher (20–50% leached) losses. King et al. (2007a, 2007b) reported nearly 90% retention (11% exported in streamflow) of N fertilizer applied to a golf course in Austin, Texas over

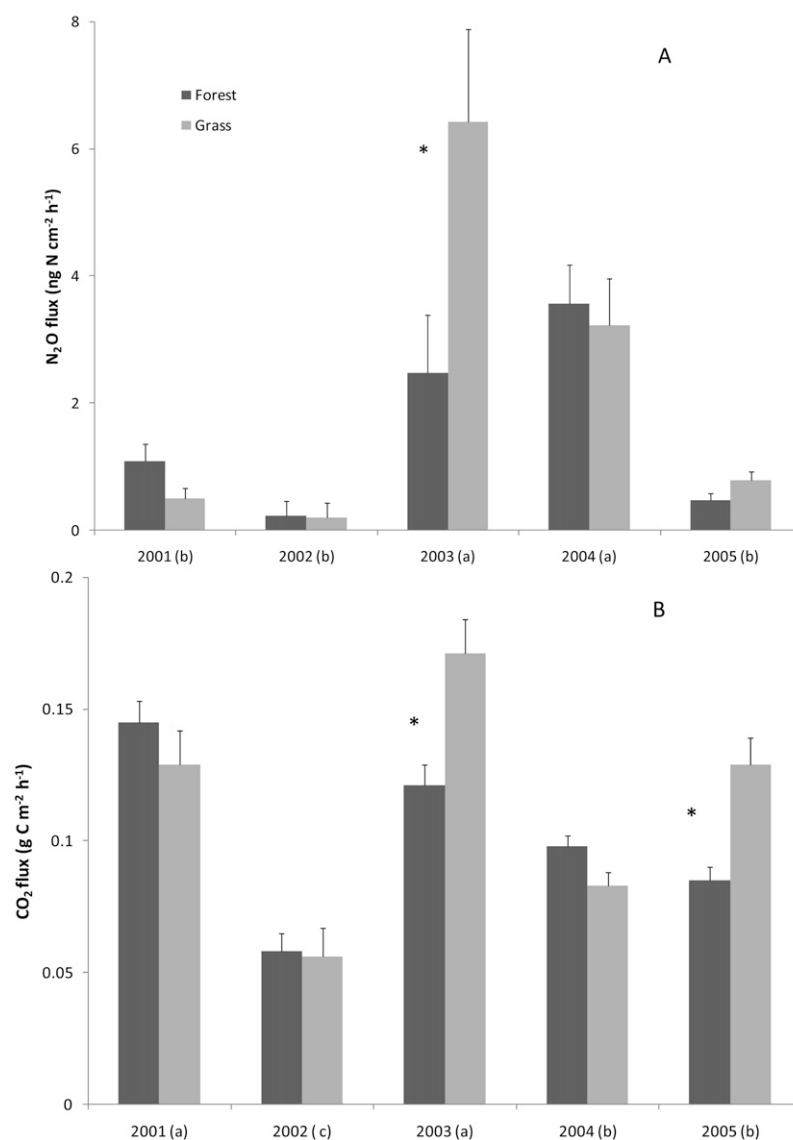


Fig. 6. Soil:atmosphere fluxes of N₂O (A) and CO₂ (B) from forest and grass plots in the Baltimore metropolitan area from June 2001 to December 2005. Values are means from three chambers in seven undisturbed forest and four grass plots. *Indicates significant difference between forest and grass at $p < 0.05$. Years followed by different letters are significantly different at $p < 0.05$.

a 5-yr period, with most of the loss associated with periods of disturbance (turf reconstruction) and high rainfall. Gold et al. (1990) reported N retention of >95% for high applications (24.4 g N m⁻² yr⁻¹) of urea applied to lawns in Rhode Island over 2 yr with near normal precipitation. Guillard and Kopp (2004) reported similar results, with N retention values ranging from 83 to >95% for applications (14.7 g N m⁻² yr⁻¹) of several different fertilizer types applied to lawns in Connecticut over 3 yr with near normal precipitation. Gold et al. (1990) and Guillard and Kopp (2004) found, like we did, that precipitation was a significant driver of variation in losses, with dry seasons and years having lower losses than wetter periods.

Nitrous Oxide Flux

Given that N input and hydrologic losses of N were elevated in grass plots, it was somewhat surprising that N₂O

fluxes were not higher in grass plots than in forest plots and that fluxes from the more heavily fertilized grass sites (UMBC) were lower than those from the less heavily fertilized grass sites (McDonogh). These results are in marked contrast to results from arid regions. Kaye et al. (2004) found that urban grassland soils emitted 10 times more N₂O to the atmosphere than native grassland soils in Colorado, and Hall et al. (2008) found elevated N₂O fluxes in urban lawns relative to native ecosystems in Arizona. The differences between urban grasslands and native ecosystems in Colorado and Arizona were driven by a combination of fertilizer and, most importantly, water inputs to the urban grasslands. Water inputs can increase N₂O fluxes by increasing denitrification and/or nitrification rates and/or the fraction of N₂O released from nitrification (Robertson and Groffman, 2007). Our grass and forest plots did not differ in water inputs or surface soil moisture, and the comparison with

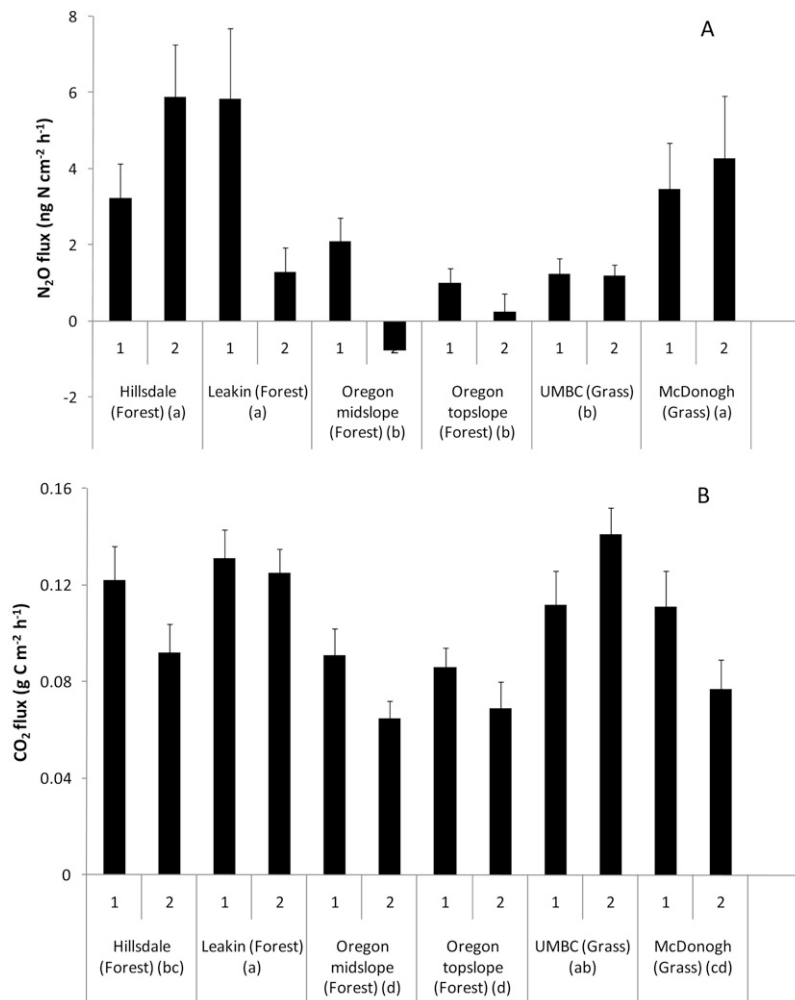


Fig. 7. Soil:atmosphere fluxes of N_2O (A) and CO_2 (B) from forest and grass plots in the Baltimore metropolitan area. Values are means of all fluxes measured in three chambers per plot from June 2001 through May 2004. Sites followed by different superscripts are significantly different at $p < 0.05$.

the Colorado and Arizona results suggests that water is a more important driver of N_2O emissions than N input in urban landscapes (Bijoor et al., 2008). We observed some differences in soil moisture between grass and forest sites at depth (higher in forests at 30 cm; higher in grass at 50 cm), but these did not appear to influence surface emissions of N_2O . Similar to our results, Byrne (2007) found no difference in N_2O flux between fertilized lawns and unmanaged old fields in Pennsylvania. Our sampling was not keyed to fertilizer input events and therefore may have missed periods of high flux associated with these events (Maggiotto et al., 2000). Nitrous oxide is just one of the gaseous forms of N that can be lost from the soil, and it is possible that emissions of other gases (NO , N_2) were elevated in our fertilized grass plots.

The marked annual variation in N_2O emissions that we observed supports the idea that water is a key driver of these emissions in urban landscapes. Extrapolating mean annual rates over the entire year suggests that annual emissions ranged from $<0.05 \text{ g N m}^{-2} \text{ yr}^{-1}$ in dry 2002 to $>0.3 \text{ g N m}^{-2} \text{ yr}^{-1}$ in wet 2003 and 2004. These latter rates are at the high end of rates reported for deciduous forests in the eastern USA (Peterjohn

Table 3. Soil variables in 10 forest, 14 agriculture and 10 grassland plots sampled in summer 2000 in the Baltimore metropolitan area. Values are mean with SE in parentheses.

Variable	Units	Forest	Agriculture	Grassland
Soil organic matter	g kg^{-1}	57 (3)a†	34 (3)b	52 (8)a
Soil moisture	g kg^{-1}	200 (10)a	170 (10)b	140 (20)b
Soil pH		3.9 (0.1)c	5.1 (0.2)b	5.9 (0.4)a
Soil NO_3^-	mg N kg^{-1}	0.4 (0.1)b	8.7 (2.4)a	1.2 (0.3)b
Soil NH_4^+	mg N kg^{-1}	2.1 (0.4)a	0.9 (0.5)b	0.5 (0.1)b
Microbial biomass C	mg C kg^{-1}	346 (29)a	224 (29)b	306 (25)ab
Microbial respiration	$\text{mg C kg}^{-1} \text{ d}^{-1}$	10.3 (0.7)a	6.7 (0.5)b	8.2 (0.9)b
Nitrification potential	$\text{mg N kg}^{-1} \text{ d}^{-1}$	0.5 (0.1)b	63 (23)a	37 (9.2)a

† Values followed different letters in a row are statistically different at $p < 0.05$.

et al., 1998; Groffman et al., 2000, 2006a, 2006b; Bowden et al., 2000).

What Constrains NO_3^- Leaching and Nitrous Oxide Flux in Urban Grasslands?

We suggest that the surprisingly high N retention that we observed in urban grasslands is driven by high rates of C cy-

cling by soil and vegetation in these ecosystems. Carbon cycling drives N retention by plant uptake and microbial immobilization, which is tightly linked to SOM dynamics and the C/N ratio of that organic matter (Hart et al., 1994; Lovett et al., 2002). We observed high rates of total soil respiration (an index of plant and microbial C cycling activity and N demand in the soil) and high levels of SOM in urban grasslands, suggesting that C cycling is similar in urban grasslands and forests and that this underlies the ability of the grasslands to retain N.

The high CO₂ fluxes (total soil respiration) that we observed in the grass long-term study plots were likely driven by high productivity of the grasses and the high temperatures in the grass plots. The high temperatures, which are a result of the lack of tree canopy, were most dramatic during summer but may have had a larger effect on CO₂ fluxes in spring and fall when temperatures were lower and flux was more sensitive to temperature (Davidson et al., 2006).

Further evidence for the importance of high rates of C cycling in urban grasslands comes from our one-time sampling of forest, agricultural, and grass plots across the Baltimore metropolitan area. Results from this sampling showed that grass plots had levels of SOM, microbial biomass C, and microbial respiration that were more similar to forest soils than agricultural soils in the region. Agricultural soils generally have low levels of soil C relative to native ecosystems due to removal of biomass by harvest and stimulation of decomposition by tillage and changes in litter quality (Guo and Gifford, 2002). This depletion of soil C is associated with high rates of N loss in agricultural soils (Drinkwater and Snapp, 2007). More generally, high levels of SOM and rates of C cycling are known to contribute to N retention (Hart et al., 1994). Our urban grasslands had low levels of soil NO₃⁻ relative to agricultural soils despite similarly high rates of nitrification potential, likely due to the high levels of organic matter and microbial biomass in the grassland soils. These results support the idea that C-based N sinks in soil contribute to the generally low NO₃⁻ leaching and N₂O fluxes that we observed in our long-term study plots.

Our results are consistent with other studies that have found relatively active C cycling in urban grasslands (Pouyat et al., 2002, 2006; Qian and Follett, 2002; Kaye et al., 2005; Golubiewski, 2006) but highlight the observation that responses to urban environmental change vary markedly with regional climate. A comparison of urban grasslands and native pine forests in North Carolina produced similar results to ours, with similar levels of total and microbial C and inorganic N in both ecosystem types despite relatively high nitrification potential in the urban grasslands (Shi et al., 2006). Kaye et al. (2005) found that fertilization and irrigation inputs resulted in much higher aboveground net primary productivity, soil respiration, total belowground C allocation, and microbial biomass in urban lawns compared with unmanaged shortgrass steppe ecosystems and unfertilized and non-irrigated wheat agricultural ecosystems in Colorado. Urban lawns had higher soil respiration, total belowground C allocation, and microbial biomass than fertilized and irrigated corn, but aboveground net primary productivity was higher in corn (Kaye et al., 2005). Golubiewski

(2006) also found that urban lawns had higher productivity and soil C than native grasslands or agricultural systems in Colorado. Pouyat et al. (2009) compared soil organic C densities of turf grass and native cover types of the Baltimore and Denver metropolitan areas and found that differences between residential turf grasses were less than differences between native ecosystems (hardwood deciduous forest and shortgrass steppe soils, respectively) despite large differences in precipitation between the regions. In both cases, residential turf grass had up to twofold higher soil organic C densities than the native ecosystems. In the Central Arizona Phoenix (CAP) urban Long Term Ecological Research, SOM was higher in irrigated urban residential and agricultural sites than in native desert sites (Jenerette et al., 2006; Zhu et al., 2006). Urban residential sites in CAP had higher soil NO₃⁻ concentrations than native desert sites but lower NO₃⁻ and nitrification than agricultural sites (Zhu et al., 2006). The main difference between the Colorado and CAP studies and our results is likely due to the addition of water to urban grasslands in Colorado and Arizona, which greatly increases primary production, leading to higher soil C compared with the native ecosystems. In Baltimore and Colorado, agricultural (irrigated in Colorado) systems had lower microbial biomass than urban lawns, which likely reflects the higher levels of soil disturbance and removal of biomass in agricultural systems.

Land-use Change and Nitrogen Losses

Given that urban grasslands cover about 10% of the state of Maryland that was once forest (Milesi et al., 2005), our data suggest that conversion of forest to urban grassland has increased NO₃⁻ leaching statewide in Maryland from 20 to 170% above pre-settlement conditions. However, given the strong recent (1950–2000) trend for urban grassland establishment on agricultural land (Brown et al., 2005) and the high NO₃⁻ losses associated with agricultural lands, increases in the area of urban grasslands have likely decreased NO₃⁻ leaching in the region over the past few decades.

Although our results are consistent with previous studies that suggest that conversion of agricultural land to residential land-use results in lower N delivery to receiving waters (Gold et al., 1990; Miller et al., 1997; Jordan et al., 2003; Weller et al., 2003; Groffman et al., 2004), these analyses do not consider fluxes associated with food imports and sewage outputs, which must be accounted for at a larger scale than the individual urban grassland, crop field, or small watershed. Evaluations of land-use change effects on N delivery must also consider the hydrologic effects of residential land-use development and how these can reduce retention of N in riparian and stream ecosystems in urban watersheds (Groffman et al., 2003; Walsh et al., 2005).

Evaluations of land-use change effects on N delivery must also consider how amenable N exports from different land uses are to reduction and control. In the Chesapeake Bay region, efforts to reduce N export from agricultural areas have had mixed results, whereas N removal techniques used in sewage treatment plants that collect N from residential areas have been

quite effective (Boesch et al., 2001). Control of N exports from urban grasslands has received less attention. There is a great need for information on just how urban grasslands are managed (Law et al., 2004; Osmond and Hardy, 2004) and how this management can be improved to reduce N exports.

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