

1 TITLE

2 Spatial and temporal patterns of nitrogen mobilization in residential lawns

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4 Shortened title: Nitrogen mobilization in residential lawns

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ABSTRACT

Identifying locations prone to exporting nitrogen (N), also called export control points, within residential landscapes is key to determining N mitigation strategies. Within residential landscapes, lawns have the potential to act as either a sink of N via uptake and denitrification, or a source of N via additions such as fertilizer. Lawns draining to impervious surfaces are more likely to be sources of N loading to receiving water bodies through directly connected curb and sewer flow paths. We utilized small-scale rainfall experiments to examine whether hydrobiogeochemical measurements of potential denitrification and saturated infiltration rates were predictive of N mobilization, and how potential export control points (locations within the upper quartile of N mobilization values) varied spatially and temporally on residential lawns in Baltimore, Maryland. We found potential denitrification, but not infiltration, was predictive of N mobilization in runoff and leachate, only on fertilized lawns. Potential export control points occurred more often in the late summer and fall and 85% were on fertilized lawns. Applying fertilizer shortly before a rainfall event increased the N mobilization in runoff and leachate by an order of magnitude. Suburban front yards also had more potential export control points compared to backyards, which is notable as front yards are surrounded by impervious surfaces increasing their vulnerability to transporting N to downstream ecosystems. These findings highlight the spatial and temporal variability of N mobilization on lawns. Targeting locations such as vulnerable front yards, or behaviors, such as timing of fertilizer application, may be useful N mitigation strategies.

65 KEY WORDS

66 Denitrification, flow paths, nitrate, urban, topography, storm water, hydrology, biogeochemistry

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68 MANUSCRIPT HIGHLIGHTS

- 69 • N mobilization is more frequent on fertilized lawns and in the fall.
- 70 • Elevated N mobilization occurs more frequently on front lawns.
- 71 • Proximity of front lawns to impervious areas raise the chance of offsite transport.

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INTRODUCTION

Nutrient transport and transformation in watersheds occur as water moves solutes through a series of biogeochemical patches with diverse characteristics. A major challenge in understanding - and managing - these dynamics is the presence of small areas (hotspots) and periods of time (hot moments) that have a disproportionate influence on both transport and transformation (McClain and others 2003). The transport of nutrients can be facilitated by the presence of locations that disproportionally accumulate or process nutrients, and by locations that are prone to conveying water relative to other locations within the landscape. “Ecosystem control points” are one way to incorporate the spatial and temporal components of hotspots and hot moments into one framework that accounts for both biogeochemical and hydrological processes (for more details see Bernhardt and others 2017). Understanding and managing nutrient transport thus depends on identification and quantification of ecosystem control points. For this study, we will utilize the ecosystem control points framework to examine where and when “potential *export* control points” of nitrogen (N) occur within residential lawns. Export control points are locations that must have both an accumulation of N and be located where water may mobilize and transport N downhill or downstream. We examined *potential* export control points by creating extreme rain events using small-scale rainfall experiments in the field and measuring N mobilization during these events.

Lawns have the potential to act as “export control points” of N within residential watersheds. Lawns can accumulate N due to either varied biogeochemical process rates, such as low plant uptake or low denitrification rates (a microbial process that reduces NO_3^- to N_2), or from inputs such as N-fixing legumes, run-on from the surrounding landscape, applications of fertilizer, or atmospheric deposition (Groffman and others 2004; Bigelow and others 2022). Natural variation and human factors can also affect the vulnerability of lawns to transporting N

via water. For example, low infiltration rates due to soil characteristics could make a location vulnerable to producing runoff and thus transporting N from lawns onto impervious surfaces (Gregory and others 2006; Yang and Zhang 2011). The positioning of a downspout can also increase the likelihood of overland runoff by saturating the lawn and by shortening the flow path of water off a lawn and onto impervious surfaces (Miles and Band 2015).

In non-urban catchments, nitrogen export occurs when N is transported via overland runoff or subsurface flow to surface waters. Catchment properties such as topography, soils, area of wetlands, and contributing area can affect how much N is exported from non-urban catchments (Creed and Beall 2009). Flows from uplands to streams can move through locations such as riparian wetlands where plant uptake and denitrification can remove or transform the N exported (Gold and others 2001). In urban areas, natural flow paths are often replaced by engineered flow paths, such as rooftop gutters and stormwater pipes, that may bypass natural N sinks such as riparian wetlands (Kaushal and Belt 2012; Miles and Band 2015; Fork and others 2018). Additionally, urban overland flows may travel through a patchwork of impervious and pervious surfaces that can vary greatly in their potential for biogeochemical activity and transformations of N. Thus, flow paths on biogeochemically active soils may be shorter than in nonurban environments due to interruptions by impervious surfaces and drainage infrastructure thus limiting opportunities for N transformation and uptake. In residential parcels, overland flow paths often begin on impervious rooftops with little biogeochemical activity, with the potential exception of drainage eaves (Fork and others 2018). Water then runs from these rooftops onto pervious lawns with biogeochemical activity. From lawns, water can move onto impervious sidewalks or streets with little biogeochemical activity, and finally into storm drains which discharge runoff to streams. Urban subsurface flow is less well understood than surface flow, but

151 still may be susceptible to similar interruptions by impervious surfaces or leakage into storm or
152 sanitary sewer pipes. Because lawns are often the most biogeochemically active patch along
153 these residential flow paths, what happens on the lawn will impact full flow path retention or
154 transport of N. Therefore, understanding drivers of N mobilization on lawns is important for
155 understanding N transport in residential watersheds more broadly.

156 Currently, there are few direct measurements of N mobilization on lawns with coincident
157 measurements of hydrobiogeochemical properties that may be predictive of mobilization.
158 Several prior studies have made direct measurements of vertical N leaching under various
159 fertilizer and irrigation applications (Morton and others 1988; Gold and others 1990; Guillard
160 and Kopp 2004) with the finding that lawns overall are retentive of fertilizer, and thus N,
161 applications. However, lawns are more vulnerable to lateral leaching of N by runoff when
162 overwatering occurs or when fertilization occurs close in time to irrigation or a storm. Relatively
163 fewer studies have examined N mobilization in overland flow directly (Kelling and Peterson
164 1975; Morton and others 1988; Spence and others 2012) and none to our knowledge have
165 examined what hydrobiogeochemical properties of lawns are associated with N mobilization and
166 transport in a residential setting.

167 While direct measurements, watershed budgets (Baker and others 2001; Groffman and
168 others 2004; Hobbie and others 2017) and process based studies (Raciti and others 2008) all
169 suggest that lawns are generally retentive, fertilizer application is a large input, and N
170 concentrations in streams in residential landscapes can be high (Boesch and others 2001;
171 Kaushal and others 2011; Bettez and others 2015; Reisinger and others 2018; Jani and others
172 2020). Fertilizer is a potential source of N to residential streams during large storms (Jani and
173 others 2020) and is a target of management strategies. The aim of this study was to determine the

roles and interactions of biogeochemical and hydrologic processes and human management in the production of potential N export control points from residential lawns. We call these experiment locations *potential export control points* because we made point measurements within a lawn but did not directly quantify whether runoff from that location would reach impervious surface or not. To that end, we generated extreme experimental rainfall events that produced runoff to investigate dynamics of N mobilization via runoff and leachate in lawns. Lawns were located in two neighborhoods and one institution in Baltimore, MD that varied in their urban form (lawn management and parcel size) and both short and long-term fertilizer input practices. We compared flow path lengths from lawns to streams or directly connected impervious surfaces between the two study neighborhoods to assess differences or similarities in vulnerability among neighborhoods to transporting N from lawns to streets and storm drains. We hypothesized that hydrobiogeochemical properties, specifically low denitrification potential and/or fertilizer applications paired with low infiltration rates, would be associated with larger N fluxes (H1), locations of potential export control points would be spatially and temporally variable (H2), fertilizer application would affect what are important predictors of N fluxes (H3) and timing of fertilizer relative to a rain event would affect the magnitude of the flux (H4).

METHODS

Site description

The lawns in this study are in Baltimore County, Maryland, USA and were categorized into four lawn types: exurban, suburban front yard, suburban backyard, and institutional. Exurban lawns (n=4) were in the Baisman Run watershed, a 3.82 km² watershed about 10 km north of Baltimore City. Suburban front yards (n=4) and backyards (n=4) were in the Dead Run watershed, a 14.11 km² watershed in Baltimore County near the Baltimore City limits.

Institutional lawns were located on the University of Maryland Baltimore County campus (n=2). Average annual precipitation is approximately 1030 mm distributed evenly throughout the year (World Climate, <http://www.worldclimate.com/climate/us/maryland/baltimore>). Lawns were comprised of mostly cool season grasses- *Poa pratensis* (Kentucky bluegrass), *Festuca arundinacea* (tall fescue) and *Lolium perenne* (perennial rye)- and often had a mixture of two species. More detailed descriptions of watershed land cover, vegetation and soils of the study lawns can be found in Suchy and others (2021).

Flow path analysis

To assess the vulnerability of the suburban and exurban neighborhoods to transporting N from lawns to a stream, we calculated the horizontal flow distance (i.e., the flow path length) from lawns to nearest draining stream or nearest road draining through a directly connected impervious flow path to a stream. In the suburban neighborhood, there is a dense road network that routes runoff directly to streams through storm drains and thus we treated roads as drainage paths that function as streams when calculating horizontal flow distance. Conversely, in the exurban neighborhood, which has a much lower density of urban development, we did not include roads as streams. This is because most of the water that runs off the roads is not released directly to streams, but to downstream soils.

To calculate horizontal flow distance, we first extracted the stream network using the r.watershed tool in GRASS GIS (<https://grass.osgeo.org/grass82/manuals/r.watershed.html>), which yielded a network slightly more extensive than the NHDPlus high resolution flowlines by USGS (<https://www.usgs.gov/national-hydrography/nhdplus-high-resolution>). The stream network was delineated using a 1-meter digital elevation model from Maryland's GIS Data Catalog (<https://data.imap.maryland.gov>) and the land use/cover map from the Chesapeake Bay

Program (<https://www.chesapeakeconservancy.org/conservation-innovation-center/high-resolution-data/lulc-data-project-2022>), which had a 1-meter resolution and enabled us to identify lawn patches. The horizontal flow distance from lawns to nearest draining stream or nearest road draining to a stream was then calculated using the `r.stream.distance` tool in GRASS GIS (Jasiewicz and Metz 2011).

Long- and short-term fertilizer classifications

Lawns were categorized either as fertilized in the long-term or fertilized in the short-term. Lawns were categorized as fertilized long-term if the homeowner reported that they fertilized within the last year. Two exurban lawns were fertilized by lawn care companies and two were not. Two suburban front yards and two suburban backyards were fertilized by the homeowner within the year prior to the study. One suburban front and one suburban backyard were not fertilized. Institutional lawns were managed and fertilized by campus maintenance staff at a rate of approximately 100 kg N ha⁻¹ yr⁻¹. One suburban lawn that we initially classified as unfertilized based on information provided by the homeowner unexpectedly received two treatments during this study. Rather than removing this lawn from the study entirely we removed it from the comparisons of long-term fertilized and unfertilized lawns and instead refer to this lawn as a short-term fertilized lawn. The two fertilizer additions to this lawn occurred 24 hours prior to two of our experiments (April 2018 and March 2019) thus allowing us to examine the effects of short-term fertilization on N mobilization and lawn biogeochemistry in two seasons. Although our initial design included two front and backyard lawns in the suburban unfertilized category (based on homeowner responses), because of the unexpected fertilizer treatments, we lost one front and backyard lawn from the suburban unfertilized category. We do not have the

exact fertilizer application rates of homeowner fertilized lawns because we wanted them to continue their practices as usual and to not be influenced by the experiment as much as possible.

Sampling design

Sampling locations within lawns for this study were derived from the analysis reported by Suchy and others (2021) that generated predictions of areas likely to act as hotspots N mobilization or removal based on measurements of denitrification potential (DNP; which removes reactive N) and saturated infiltration rate (which controls mobilization of N during rain events). Thus, we expected that sampling locations with values in the lower quartile of denitrification potential and saturated infiltration rates were more likely to function as hotspots of N mobilization during storm events (i.e., potential export control points) with locations in the upper quartiles being more retentive of N. Sampling locations for this study were selected to both (a) encompass the locations hypothesized to be hotspots of N mobilization or removal, but also to (b) distribute locations among different lawns, topographic gradients (described below) and fertilizer usage (Table 1). All final sampling locations (n=48 located across the 14 study lawns) were categorized into four groups based on where they fell on the denitrification potential and saturated infiltration rate axes (potential N-mobilization groups):

Group 1: sampling locations with low DNP and low saturated infiltration rates (n=10)

Group 2: sampling locations with low DNP and high saturated infiltration rates (n=11)

Group 3: sampling locations with high DNP and low saturated infiltration rates (n=12)

Group 4: sampling locations with high DNP and high saturated infiltration rates (n=15)

At each study lawn, sampling locations were positioned along a topographic gradient and were classified as the top or bottom of a hillslope. Top positions were located on the upper portion of the hillslope, where water was not likely to accumulate during rain events. Bottom

positions were located on lower positions of hillslopes where water was more likely to accumulate during rain events. This sampling design allowed us to compare N mobilization among potential N-mobilization groupings, topographic position, fertilizer usage, and lawn type.

Sampling was conducted in four seasons April 2018, September 2018, November 2018 and March 2019. At each sampling location, we conducted simulated rainfall experiments using Cornell Sprinkling Infiltrimeters, followed by collection and analysis of runoff and leachate (details described below). Soil cores were collected at each event for measurement of gaseous N losses (details described below). Rainfall experiments were conducted in the same location in each season. Soil cores were collected a maximum distance of 30 cm from the rainfall experiment. April and November sampling periods were meant to capture spring and fall fertilization periods recommended by the University of Maryland Cooperative Extension Service (<https://extension.umd.edu/resource/fertilizing-home-lawns>).

Rainfall experiments and N mobilization measurements

Rainfall experiments were run in the same sampling locations in every season. Artificial rainfall was generated with Cornell Sprinkle Infiltrimeters (hereafter infiltrimeter; Ogden and others 1997). Infiltrimeters are designed to simulate rainfall to gain more realistic measurements of saturated infiltration rates. Water sprinkles from the infiltrimeter body into an infiltration ring (457.3 cm²) with a hole and tubing that allows for the collection of runoff into a beaker (Figure 1). Rainfall experiments were conducted for 45 minutes at a rainfall rate of approximately 20 cm hr⁻¹. It is important to note that rainfall of this magnitude is not representative of typical storms in Baltimore, MD. A rainfall of 20 cm hr⁻¹ has a greater than 1000-year return interval. However, a rainfall of this intensity over a shorter duration has approximately a 10-year return interval for a duration of 5 minutes and approximately a 100-year return interval for a duration of 10 minutes

(https://hdsc.nws.noaa.gov/hdsc/pfds/pfds_map_cont.html?bkmrk=md). Roughly 90% of our infiltration runs generated runoff in under 5 minutes, with all but one generating runoff in under 10 minutes. The rainfall simulations were conducted at a high rainfall rate to ensure runoff was generated at all locations during the experiment. During the rainfall experiments, we collected data on saturated infiltration rates (details in Suchy and others 2021) and collected runoff (n=191) and leachate (n=141, 134 for NO_3^- and NH_4^+ respectively) water samples to estimate N fluxes during rainfall. To minimize the introduction of N to the lawns, we used deionized water for the experimental rainfall. Additionally, a control sample was collected from the infiltrometer before the start of the experiment to check for N contamination. Runoff volume was measured in three-minute “blocks” (Supplemental Figure 1). Runoff samples for N analysis were collected at four of these “blocks” during the simulated rainfall. Runoff was collected for three minutes in a plastic beaker, the volume was recorded, and a 20 ml subsample was collected and filtered in the field using Titan3 0.7 μm glass microfiber syringe filters. The first sample for N analysis was taken from the 3-minute block containing the first observation of runoff as we anticipated most N loss would likely occur at this time (Supplemental Figures 1-3; Lee and others 2002). If the onset time of runoff was close to the end of the three-minute block, the collection was carried over to the next three-minute block. Subsequent samples were taken at the 3-minute blocks ending at 15 minutes, 30 minutes, and 45 minutes after the start of the simulation.

Leachate was collected using Macrorhizons®, which are small (~10 cm in length, 4.5 mm diameter) samplers that extract small volumes of pore water from soils by applying suction to a microfiltration membrane made of a blend of polyvinylpyrrolidone and polyethersulfone with a mean pore size of 0.15 μm (www.rhizosphere.com). Macrorhizons® were installed at 15 cm depth, horizontal to the soil profile and one month prior to the first sampling (Figure 1). Care

was taken to not disturb the soil below the rainfall experiment. PVC tubing was used to connect Macrorhizons® to the soil surface and was capped between sampling periods to avoid contamination with water and debris (Figure 1). During the experimental rainfall, suction was continuously applied to the Macrorhizon® using a 60 mL syringe held open with a wooden block. Samples were collected at 15 minutes, 30 minutes and 45 minutes after the start of the rainfall experiment. If no sample was drawn during a given time period, suction was checked. If a Macrorhizon® appeared to break or lose suction thus resulting in no leachate sample, it was replaced after the conclusion of the experiment for the next sampling effort. Leachate samples were filtered in the field using Titan3 0.7 µm glass microfiber syringe filters. Leachate was not always collected at each sampling period due to broken Macrorhizons®, poor suction or clay soils; thus, our leachate sample size is smaller than that of our runoff sample size. Runoff and leachate water samples were stored on ice in the field until they were brought back to the lab and stored at 4°C until analysis. Water samples were analyzed for NO₃⁻-N and NH₄⁺-N colorimetrically using a Molecular Devices SpectraMax M2.

Fluxes of NO₃⁻ and NH₄⁺ in runoff and runoff volume were not correlated as NO₃⁻ and NH₄⁺ concentrations generally declined to undetectable values over the course of each rainfall experiment ($r = 0.07, 0.09$ respectively, Supplemental Figures 2 and 3). Therefore, we calculated the flux of NO₃⁻ and NH₄⁺ for each experimental rainfall by first determining the mass of N in runoff for each sampling interval (Eq 1) and then summing N across all sampling intervals and standardizing to mass per m² per hour (Eq 2):

$$N_{\text{mass}(i)} \text{ mg} = N_{\text{conc}(i)} \text{ mg L}^{-1} \times \text{volume}(i) \text{ L} \quad (1)$$

$$N_{\text{runoff}} \text{ mg m}^{-2} \text{ h}^{-1} = N_{\text{mass}(\text{total})} \text{ mg} / 0.04573 \text{ m}^2 / 0.75 \text{ h} \quad (2)$$

$N_{\text{mass}(i)}$ is the mass of NO_3^- -N or NH_4^+ -N at a given interval (i). $N_{\text{conc}(i)}$ is the concentration of NO_3^- -N or NH_4^+ -N in a runoff sample. $N_{\text{mass}(\text{total})}$ is the sum of NO_3^- -N or NH_4^+ -N mass for all sampling intervals (i.e., the total mass of N collected during the rainfall experiment). Volume is the runoff volume between two sampling times (i.e. 3-minute block containing first runoff, first runoff – 15 minutes, 15 – 30 minutes, and 30 – 45 minutes). We assumed the concentration of N collected at a given sampling time applied to the volume of runoff prior to that sampling time (Supplemental Figure 1). For example, the concentration of NO_3^- -N collected in runoff at the 30-minute interval applied to the volume of runoff between 15 and 30 minutes. We opted for this estimation method rather than fitting an exponential curve for two reasons. First, we wanted to avoid overestimating N flux between the samples containing the first runoff and the 15-minute samples. Often, samples had undetectable concentrations of N at 15 minutes (Supplemental Figures 2 and 3); thus, we could not confidently fit a recession curve without potential overestimation of N loss. Second, not all samples fit an exponential decay pattern and we selected a method we could apply to all samples (Supplemental Figures 2 and 3).

Concentrations of NO_3^- and NH_4^+ in leachate were generally stable over the course of a rainfall experiment (Supplemental Figures 4 and 5), in contrast to the pattern of N concentrations in runoff. This resulted in correlations between fluxes of NO_3^- and NH_4^+ in leachate and volume of leachate during the rainfall experiment ($r=0.38, 0.19$ respectively). Because the total volume of water infiltrating could be affected by variability in initial soil moisture conditions and variability in infiltrometer rainfall rates, we calculated a standardized infiltration volume for each sampling location under a rainfall rate of 20 cm hr^{-1} and initial soil moisture conditions of 25% (Ogden and others 1997). We then used the standardized infiltration volume for each sampling location to calculate N fluxes in leachate for each sampling event.

Standardized infiltration volume for each of the 48 infiltrometer sampling locations (i.e., experimental rainfall locations) was determined by first solving equations 3 and 4 (Ogden et al., 1997) for each location in each season for sorptivity (S ; Eq 5) and then for matric flux potential (ϕ_m ; Eq 6). These equations rely on measured time to ponding (tr_{actual} in hours), initial soil moisture ($SM_{initial}$), saturated soil moisture (SM_{sat}) and rainfall rate (r_{actual} in $cm\ hr^{-1}$). SM_{sat} was standardized to one value for each sampling location by averaging the seasonal SM_{sat} measurements at that location. Percent initial and saturated volumetric soil moisture were measured for each rainfall experiment with a Field Scout TDR 300 with 7.5 cm rods. We computed a standardized time to runoff ($tr_{standard}$, Eq 7) for each location by using the average of the seasonally calculated matric flux potentials (ϕ_{m_avg}) from each location along with a fixed rainfall value of 20 $cm\ hr^{-1}$ rainfall (r_{20}) and a 25% initial volumetric soil moisture (SM_{25}). This was then used to calculate the standardized infiltration volume ($V_{leachate}$ in L) of water that would infiltrate at that sampling location under 20 $cm\ hr^{-1}$ rainfall and 25% initial volumetric soil moisture (Eq 8). For simplification purposes, we assumed saturated infiltration rates after runoff began- which reflects the relatively stable runoff rates observed following ponding and runoff under the high rates of rainfall used with the infiltrometer.

$$tr_{actual} = S^2 / (2 * r_{actual})^2 \quad (3)$$

$$tr_{actual} = \phi_m * (SM_{sat} - SM_{initial}) / (2 * r_{actual}^2) \quad (4)$$

$$S = (2 * tr_{actual})^{0.5} * r_{actual} \quad (5)$$

$$\phi_m = S^2 / (SM_{sat} - SM_{initial}) \quad (6)$$

$$tr_{standard} = \phi_{m_avg} * (SM_{sat} - SM_{25}) / (2 * r_{20}^2) \quad (7)$$

$$V_{leachate} = [(r_{20} * tr_{standard}) + (inf_{avg} * (1 - tr_{standard})) * 457.3\ cm^2] / 1000 \quad (8)$$

Additional variables are the seasonally averaged saturated infiltration rate in cm hr^{-1} for each sampling location (inf_{avg}) and 457.3 cm^2 is the area of the experimental rainfall. To account for measurement error that can affect ϕ_m estimates we removed ϕ_m outliers for each location and standardized the minimum difference between SM_{sat} and $\text{SM}_{\text{initial}}$ to 1 %. It is important to note that ϕ_m estimates approach infinity when initial and saturated soil moisture are very similar and thus small differences can result in large estimates. Outliers of ϕ_m for each sampling location were defined as falling 1.5 x the interquartile range below or above quartile 1 and quartile 3 respectively.

We then calculated the flux of NO_3^- and NH_4^+ in leachate over 1 hour for each experimental rainfall by averaging the concentrations of NO_3^- or NH_4^+ ($\text{N}_{\text{conc}(\text{avg})}$) in leachate across sampling intervals and then using the standardized volume of leachate and experimental area to convert to mass $\text{m}^{-2} \text{ hr}^{-1}$ (Eq 9):

$$\text{N}_{\text{leachate}} \text{ mg m}^2 \text{ h}^{-1} = \text{N}_{\text{conc}(\text{avg})} \text{ mg L}^{-1} \times \text{V}_{\text{leachate}} \text{ L} / 0.04573 \text{ m}^2 \quad (9)$$

Soils

Our aim was to measure N dynamics of soils during the rainfall experiment. Because we could not take soil cores in the infiltrometer ring without disrupting future sampling efforts, we collected two soil cores up to 30 cm away from the sampling ring. At the beginning of each rainfall experiment, we installed two split PVC corers of 5 cm diameter x 10 cm depth. We then wet the soil with deionized water to mimic the conditions of the soils in the infiltrometer ring. We removed the soil cores at the conclusion of the rainfall experiment. All cores were stored on ice in the field until they were brought back to the lab and stored at 4°C until analysis.

One core of each pair was kept intact for the measurement of in situ N_2 and N_2O fluxes utilizing the nitrogen-free air recirculation method (Kulkarni and others 2008; Burgin and

Groffman 2012; Morse and others 2015). The other core of each pair was homogenized and subsampled for measurements of soil moisture, organic matter content, extractable NO_3^- and NH_4^+ , and potential net N mineralization and nitrification rates. We determined soil moisture gravimetrically by drying soils at 60°C for 48 hours. Soil organic matter content was determined by mass loss on ignition at 450°C for 4 hours. We measured soil NO_3^- and NH_4^+ by shaking 7.5 g (wet weight) soil with 30 mL 2M KCl for 1 hour. KCl extract was then decanted onto a pre-leached Whatman 42 ashless filters. Samples were stored at 4°C until analyzed colorimetrically on a Lachat QC8000 flow-injection analyzer. We measured potential net nitrogen mineralization and nitrification by incubating 10 g (wet weight) of soil for 10 days in 946 mL “mason” jars. We then extracted soil NO_3^- and NH_4^+ after the incubation period as described above. We calculated net nitrogen mineralization as the change in soil NH_4^+ plus NO_3^- , and nitrification as the accumulation of NO_3^- alone over the 10-day incubation period.

Statistical Analyses

To assess whether potential N mobilization groupings were predictive of NO_3^- in runoff and leachate we used two-way repeated measures ANOVA (H1). Tukey’s HSD post hoc tests were used to determine pairwise significance levels of potential N mobilization groupings. To determine if fertilizer application affected predictability of potential N mobilization groupings, we ran models including all data and including just long-term fertilized lawns. We did not run a separate model for unfertilized lawns due to low sample size in some potential N mobilization groupings as a result of the loss of the short-term fertilized lawn from this group. Runoff and leachate values were log-transformed so model residuals would conform to assumptions of normality and equal variance. It is important to note that we only applied this test to fluxes of

NO₃⁻, and not NH₄⁺, because the potential N mobilization groupings were determined using denitrification potentials, thus potentially directly affecting NO₃⁻ fluxes but not NH₄⁺ fluxes.

Logistic regression was used to examine spatial and temporal distribution of export control points in lawns as well as the effects of long-term fertilizer use on the locations of export control points (H2). Export control points were defined as samples of runoff or leachate that fell into the upper quartile of the data distribution of lawns (excluding the short-term fertilized lawn) for fluxes of NO₃⁻ and NH₄⁺. The binary variable (upper quartile versus quartiles 1-3) for each flux was then regressed against lawn type, season, fertilizer use (yes or no) and hillslope location (top or bottom). Firth's logistic regression was utilized for the analysis of hotspots of leachate N fluxes due to smaller sample size resulting from broken or faulty Macrorhizons® (Firth 1993).

The relationships among potential drivers of NO₃⁻ flux in runoff were examined using linear regression (H3). Comparisons of interest were based on investigation of pairwise correlations among data and inclusion of relationships among variables that made theoretical sense. We modeled unfertilized and long-term fertilized lawns separately to determine if relationships among drivers were different between these treatments. To account for temporal clustering (i.e. repeated sampling of location across seasons) we included season as a fixed effect in each regression (McNeish and Stapleton 2016). We used clustered standard errors to account for spatial clustering of data within each study lawn. Flux of NO₃⁻ in runoff, soil NO₃⁻, and N₂O flux were log-transformed so model residuals would conform to assumptions of normality.

Comparisons of fluxes of NO₃⁻ and NH₄⁺ in runoff and leachate, soil NO₃⁻, soil NH₄⁺, N₂ flux and N₂O flux in each season between unfertilized, long-term fertilized lawns and the short-term fertilized lawn were made using Kruskal-Wallis H test. Fertilizer treatments within each

season were compared using a Dunn's post-hoc test (H4). All tests were run using Stata 16 (StataCorp 2019).

RESULTS

A repeated measures ANOVA testing for NO_3^- flux differences among potential N mobilization groupings (H1) found no significant difference between the groupings for NO_3^- fluxes in runoff ($F_{(3,122)} = 1.50$, $p > 0.05$) or leachate ($F_{(3,80)} = 0.49$, $p > 0.05$). However, within the locations classified as long-term fertilized lawns, potential N mobilization groupings did show significant differences in NO_3^- fluxes in runoff ($F_{(3,86)} = 3.97$, $p = 0.02$) and marginally significant differences in leachate ($F_{(3,60)} = 2.68$, $p = 0.07$). Specifically, groupings classified as having high potential denitrification rates (groups 3 and 4) were associated with lower NO_3^- fluxes in both runoff and leachate (Figure 2).

Potential export control points of NO_3^- and NH_4^+ were defined as locations with fluxes in the fourth quartile of the data distribution. Therefore, locations with fluxes greater than 3.02 NO_3^- -N $\text{mg m}^{-2} \text{hr}^{-1}$ in runoff, 1.67 NH_4^+ -N $\text{mg m}^{-2} \text{hr}^{-1}$ in runoff, 48.72 NO_3^- -N $\text{mg m}^{-2} \text{hr}^{-1}$ in leachate, and 2.58 NH_4^+ -N $\text{mg m}^{-2} \text{hr}^{-1}$ in leachate were coded as potential export control points for logistic regression analysis. Logistic regression revealed lawn type and season affected the probability of a location being defined as a potential export control point (H2). Potential export control points of NO_3^- in runoff and leachate were less likely to occur in suburban backyards compared to suburban front yards and exurban yards (Table 2, Figure 3). Additionally, potential export control points of NO_3^- in runoff and leachate were more likely to occur in the sampling months of September and November compared to March and April (Table 2, Figure 3). The patterns of potential export control points of NH_4^+ in runoff and leachate differed from that of NO_3^- . Potential export control points of NH_4^+ in runoff were more likely to occur in exurban

yards and during the September sampling period (Table 2, Figure 3). While potential export control points of NH_4^+ in leachate were not different among yard types they were least likely to occur during the September sampling period (Table 2, Figure 3). Fertilized lawns were more likely to act as export control points than unfertilized lawns for all fluxes (Table 2, Figure 3). Hillslope location was not a good predictor of export control points as tops of hillslopes were more likely to be export control points of only NO_3^- in leachate (Table 2).

Potential drivers of NO_3^- flux could be related directly or indirectly to NO_3^- flux, thus we display the pairwise comparisons as such (Figure 4). Hypothesized relationships (Figure 4a) reflect expected direction of relationship among variables based on previous studies of N dynamics in soils (Booth and others 2005; Seitzinger and others 2006). We found relationships among drivers of N dynamics and NO_3^- fluxes in runoff differed between unfertilized and long-term fertilized lawns (H3). In unfertilized lawns, soil organic matter and soil moisture, two important drivers of N cycling in soils, were significantly related to soil NH_4^+ and denitrification (N_2 flux), and nitrification respectively (Figure 4, Table 3). Nitrification and denitrification were significant predictors of soil NO_3^- as expected, and soil NO_3^- was a significant predictor of NO_3^- flux in runoff (Figure 4, Table 3). In fertilized lawns soil organic matter, soil moisture and denitrification were not predictive of N dynamics (Figure 4, Table 3). Rather, soil NH_4^+ and nitrification were significant predictors of soil NO_3^- and NO_3^- flux in runoff (Figure 4, Table 3), suggesting a simplification of N dynamics in soils where NH_4^+ inputs from fertilizer applications, rather than mineralization of organic matter or denitrification rates, was a more important driver of soil NO_3^- .

Short-term fertilizer applications (fertilization of one lawn 24 hours prior to sampling) occurred in the April 2018 and March 2019 sampling periods (hereafter April and March), with

no applications in September 2019 and November 2019 sampling periods (hereafter September and November). Results of Kruskal-Wallis H test revealed differences in N dynamics among all fertilizer treatments in each season (Table 4, Figure 5); however, we will focus on comparisons between short-term fertilizer applications to other treatments on N mobilization and dynamics (H4) as comparisons between unfertilized and long-term fertilized lawns are discussed in previous analyses. Notably, in April and March soil NH_4^+ and NH_4^+ fluxes in runoff and leachate were 1-2 orders of magnitude higher in the short-term fertilized lawn than the other fertilizer treatments but were not statistically different than long-term fertilized lawns in September and November (Figure 5). Soil NO_3^- and NO_3^- fluxes in runoff and leachate were 2-3 times higher in April and March for the short-term fertilized lawn but were not statistically different than long-term fertilized lawns in September and November (Figure 5). Additionally, N_2O fluxes were significantly higher in the short-term fertilized lawn following fertilizer applications in April and March, while they were of similar magnitude to lawns of other fertilizer treatments in September and November. Short-term fertilizer applications did not affect N_2 fluxes in any season.

We found flow path lengths differed between the suburban and exurban neighborhood (Figure 6a). The suburban neighborhood had a lower mean (101.7m) and median (66.8m) flow path length than the exurban neighborhood (mean = 297.4m, median = 291.5m).

DISCUSSION

Residential lawns have the potential to be important for the retention, transformation and mobilization of N in urban watersheds (Groffman and others 2004; Raciti and others 2008; Reisinger and others 2016; Thompson and Kao-Kniffin 2019). Previous studies have found that lawns have high potential to remove biologically reactive N via plant uptake (Herrmann and Cadenasso 2017) and biogeochemical transformations such as denitrification (Shi and others

2006; Raciti and others 2008, 2011), but only a few have measured N in runoff directly (Kelling and Peterson 1975; Morton and others 1988; Spence and others 2012; Toor and others 2017). Further, none, to our knowledge, have paired measurements of N in runoff with measurements of hydrobiogeochemical properties of lawns to examine what might drive N mobilization. In this study, we generated high intensity artificial rainfall events to produce runoff and examined the spatial and temporal variation of N mobilization (i.e., potential export control points) on residential lawns. Additionally, we paired these measurements with measurements of soil properties and processes to examine if aspects of the hydrology and biogeochemistry of lawns was predictive of where N mobilization may occur. We found that unfertilized lawns minimally contributed to N mobilization, and most export control points occurred on fertilized lawns. Additionally, more export control points occurred in exurban lawns and suburban front yards, with fewer in suburban backyards. Finally, denitrification potential, but not infiltration rates or in situ denitrification rates, were predictive of N mobilization on fertilized lawns.

N mobilization on fertilized lawns is temporally and spatially variable

The magnitude of N fluxes and location of potential export control points differed among seasons and lawn types (H2). We selected our sampling periods to capture temporal variability in fertilizer applications such that the April and November sampling events occurred after the anticipated spring and fall fertilizer application period recommended by the Maryland Cooperative Extension Service; thus, we anticipated more N mobilization in April and November. Rather, we found low N fluxes in April and highest N fluxes in September and November on fertilized lawns and in November on unfertilized lawns, suggesting that changes to uptake/removal processes or changes to other N inputs likely also play an important role in seasonal patterns. The differences between N fluxes in the “post-fertilizer application” sampling

periods of April and November could be due to inadequately capturing fertilizer applications, but also may be the result in shifting plant N demand. In April, temperatures are warming and plant N demand could be higher than in November, as grass enters a more dormant phase with lower N demand (Bauer and others 2012).

Changes to N sources or inputs could also contribute to the high N fluxes during the September and November sampling period. Several studies have found an important source of N in residential streams is atmospheric deposition, in addition to chemical fertilizers (Kaushal and others 2011; Hobbie and others 2017; Jani and others 2020). Given the proximity of residential lawns to high density areas with many motorized vehicles, lawns are likely to also receive inputs from elevated atmospheric deposition and thus also have the capacity to either retain or transport N from this source (Bettez and others 2013). The combination of declines in soil N between April and September (as would be expected with increased uptake or microbial processing associated with warmer weather and more plant growth) paired with increases in runoff and leachate N during this period point to atmospheric deposition as one possible source. Nitrogen deposition generally increases in summer months (Li and others 2016) potentially resulting in greater accumulation of N on vegetation surfaces, which is then mobilized during a rain event.

We observed more potential export control points located in exurban and suburban front yards than suburban backyards (H2). Differences between suburban front and backyards are notable as these locations are managed by the same resident. Prior studies have found, however, that residents may manage these spaces differently (Locke and others 2018b). For example, residents are more likely to fertilize public facing front yards for aesthetic reasons, while using backyards for more functional purposes, and as a result apply less fertilizer. How this management disparity translates to soil N dynamics is less clear as some studies have found

some differences between front and backyards (Suchy and others 2021), while others have not (Martinez and others 2014; Locke and others 2018a).

In addition to differences in management, we also speculate that N deposition could contribute to differences between N mobilization in front and backyards, Suburban front yards are closer to roads and driveways where N deposition is greatest (Cape and others 2004; Bettez and others 2013). Backyards are further from the source and thus may receive less N deposition overall. This could explain why even unfertilized front yards had occasional export control points, while unfertilized backyards did not. However, more explicit investigations into N deposition patterns within neighborhoods are needed to confirm this hypothesis.

Fertilizer matters in the long- and short-term

We found both long and short- term fertilizer applications were predictive of whether a location was a potential export control point of N (H3). Unfertilized lawns minimally contributed to N mobilization with about 90% having zero or near zero flux values. The majority (83%) of potential N export control points (or locations with N fluxes in the upper quartile) occurred on long-term fertilized lawns. While fertilizer has long been recognized as having the potential to runoff of lawns and contribute to downstream N pollution, several studies have found that lawns are quite retentive of fertilizer applications (Morton and others 1988; Petrovic 1990; Raciti and others 2008; Bachman and others 2016). In addition, several studies have noted that fertilizer application prior to irrigation or rain events can significantly increase the mobilization of fertilizer derived N from lawns (Gold and others 1990; Linde and Watschke 1997; Bachman and others 2016), similar to what we observed in our short-term fertilized lawn.

While we find effects of fertilizer application on the probability of a lawn acting as an export control point, the magnitude of the flux is important to consider. In long-term fertilized

lawns, runoff export control point fluxes ranged from 3 – 81 NO_3^- -N $\text{mg m}^{-2} \text{hr}^{-1}$ and 2 – 37 NH_4^+ -N $\text{mg m}^{-2} \text{hr}^{-1}$. Maximum runoff N fluxes on the short-term fertilized lawn were 23 NO_3^- -N $\text{mg m}^{-2} \text{hr}^{-1}$ and 1349 NH_4^+ -N $\text{mg m}^{-2} \text{hr}^{-1}$. While we cannot make direct calculations of what percent of fertilizer N was transported in runoff, we can make some generalizations. If we assume a fertilization rate of 10 $\text{g m}^{-2} \text{yr}^{-1}$, applied over 4 applications (2.5 g m^{-2} per application) (Law and others 2004), we can determine that for long-term fertilized lawns as little as 0.2% and as much as 4.7% of fertilizer N (NO_3^- -N + NH_4^+ -N) from an application could be mobilized in a runoff event. For short term fertilized lawns, as much as 54.9% of applied fertilizer could be mobilized in a runoff event – but these hot moments are likely to occur very infrequently as they require fertilization within 1-3 days of a runoff generating rain event. It is important to note that our experimental method generated a rain event exceeding a 1000-year return interval. Additionally, our estimates do not account for transformations that may occur along a flow path. Thus, we consider these estimates to be of potential N mobilization, or an upper boundary estimate of what loss may occur on these lawns.

While we found that NO_3^- fluxes were elevated at the short-term fertilized lawn, NH_4^+ fluxes were orders of magnitude higher than the other lawns. Ammonium can contribute to eutrophication of streams similar to NO_3^- , but NH_4^+ is less mobile in soils than NO_3^- , and thus the fate of an NH_4^+ flush before it reaches streams is less clear. For example, NH_4^+ may be nitrified or adsorbed to soils along flows paths before reaching a stream.

Dissolved organic nitrogen (DON) is another form of nitrogen that can be taken up by organisms or mineralized into inorganic N, potentially promoting denitrification (Liu and others 2022). We did not measure DON in this study, but it is important to note that DON losses in leachate from lawns can be of a greater magnitude than losses of inorganic N (Lusk and others

2018), and fertilizer additions have been shown to increase leaching of DON (Dijkstra and others 2007), possibly due to increases on the amount of plant material available for decomposition (van Kessel and others 2009). Additionally, DON can comprise a large portion of N in stormwater (Lusk and others 2020) and urban runoff (Kaushal and others 2014). Taken together, this suggests that it is important to quantify DON when investigating N losses from leaching and runoff in lawns.

We also found that fertilizer decouples common drivers of the soil nitrogen cycle (H4), primarily soil moisture and soil organic matter, from accumulation of soil N and ultimately N mobilization in runoff (Boyer and others 2006). This highlights how external sources, such as fertilizer and possibly atmospheric deposition, can overwhelm internal cycling drivers. Generally, more research is needed to understand N transformation along flow paths in lawns and engineered flow paths such as stormwater pipes (Pennino and others 2014).

Identification of export control points and landscape context

Identification and prediction of export control points are necessary to adequately target N pollution mitigation strategies. We investigated whether previous measurements of potential denitrification rates and saturated infiltration rates would be predictive of the magnitude of the NO_3^- flux. We hypothesized that low potential denitrification rates and low saturated infiltration rates would be predictive of locations that would have larger N fluxes during and experimental rainfall (H1). We found that pre-defining sites along these two axes (potential denitrification and saturated infiltration rate) was somewhat effective for predicting N fluxes on fertilized lawns, but ineffective on unfertilized lawns likely due to the overall low N fluxes on unfertilized lawns. More specifically, we found low saturated infiltration rates were not significantly related to locations with larger NO_3^- fluxes in runoff or lower fluxes in leachate. Rather, locations with low

potential denitrification generated significantly larger NO_3^- fluxes in runoff or leachate than locations with high potential denitrification- suggesting this axis is more predictive of whether a location may be a potential export control point. However, saturated infiltration rates would become an important consideration when predicting which locations would generate runoff during a storm. Interestingly, contemporaneous measurements of denitrification rates (as opposed to potential denitrification measured in prior season) of soil cores collected at the time of rainfall experiments were not predictive of NO_3^- in runoff. Potential denitrification rates measure denitrification when the soil is anaerobic and plenty of NO_3^- and carbon are available. These study lawns are carbon limited (Suchy and others 2021); thus, it is possible that denitrification may be stimulated when pulses of water and carbon enter the lawn. Alternatively, small differences in low denitrification rates over long periods of time may produce large differences in the pool of N available for transport over a long-time scale. These small differences may not be discernable in our denitrification rate measurements but may be more adequately reflected in potential denitrification measurements.

It is important to note that the measurements in this study are of points on a lawn, thus high N in runoff suggests a location with *potential* to act as an export control point. When determining whether a location would act as an *actual* export control point one must also consider the flow path of water from the lawn and onto impervious surfaces. Thus, the landscape context relative to the location of the potential export control points are important to consider. In this study we found, exurban lawns and suburban front yards generated the largest N fluxes in runoff; however, the flow paths for runoff from lawns to streams differ between these locations. When considering the flow path water may take from a lawn to a stream, or to a storm drain that drains to a stream, the exurban neighborhood has fewer roads and storm drains directly

connected to streams compared to the suburban front yards, which are surrounded by impervious surfaces and roads that drain to streams (Figure 6b). This difference in neighborhood configuration results in longer flow paths through biogeochemically active patches in the exurban neighborhood compared to the suburban neighborhood (median of 291.5m versus 66.8m respectively; Figure 6a). It is important to note that the flow path length estimates for the suburban neighborhood includes all lawn patches, and, thus, suburban front yards specifically likely have flow path lengths below the median. The consequence of shorter flow paths in suburban front yards is decreased opportunity for uptake or transformation of N along the flow path (Onderka and others 2012) and increased vulnerability to transporting the N off the lawn and into storm drains and streams. It is also important to note that the leachate flux was often higher than the runoff flux of N; however, there is uncertainty about subsurface flow paths in residential environments making it difficult to predict the importance of these flow paths to N transport to downstream ecosystems.

CONCLUSIONS

Our study utilized a novel method of generating runoff to examine variability in N mobilization within and among lawns. Predicting locations of export control points is a critical but challenging task. We found that denitrification potential measurements may be useful in identifying potential N export control points. However, the ability of a location to generate runoff and the juxtaposition of the location relative to impervious surfaces must also be considered. Additionally, understanding fertilizer application relative to rain events and flow paths off lawns will be key to assessing vulnerability of residential areas to N transport.

Unsurprisingly, application of fertilizer soon before a large rain event creates a huge potential for N export and preventing these hot moments of export will be essential for reducing

N transport. This will require better understanding of flow paths through and off lawns and transformations of N along those flow paths, as well as an understanding of how frequently fertilization occurs close to a runoff generating rain event. Unfertilized yards rarely contributed significant amounts of N fluxes in runoff.

While this study is of a limited number of lawns, it reveals some important patterns to consider in future research. We found that N fluxes in runoff showed distinct seasonal and spatial patterns with larger N fluxes in runoff occurring in fall and winter seasons, and more potential export control points located in the exurban and suburban front yards than suburban backyards. Our study highlights that lawns are not homogenous - even when considering the front and back lawn of the same home. Understanding the causes of these seasonal and spatial patterns will be necessary to determine the generalizability of these results and to develop effective and efficient mitigation strategies. For example, export associated with fertilizer can be addressed with homeowner education or restrictions on fertilizer use. However, if N deposition is also a source of N from front lawns, then managing hydrology and flow paths to prevent runoff from lawns to impervious surfaces would be a necessary, but more challenging mitigation strategy.

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DATA AVAILABILITY

Suchy, A.K. and P.M. Groffman. 2023. Seasonal N dynamics and fluxes of nitrogen in leachate and runoff from experimental rainfalls on fertilized and unfertilized lawns in Baltimore County, Maryland ver 2. Environmental Data Initiative. <https://doi.org/10.6073/pasta/6b6208c3075b9ffe206a7af26f00b93a>

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918 TABLES
 919 Table 1: Table of sampling distribution by quadrants.

	Quadrant				
	1	2	3	4	Total
<i>Fertilizer</i>					
Fertilized- long term	5	8	6	11	30
Fertilized- short term	0	0	4	2	6
No fertilizer	5	3	2	2	12
<i>Yard type</i>					
Exurban	8	1	3	2	14
Suburban: front yard	1	5	4	4	14
Suburban: backyard	1	3	5	3	12
Institutional	0	2	0	6	8
<i>Location</i>					
Top	5	5	2	8	20
Bottom	5	6	10	7	28

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Table 2: Results of logistic regressions.

Variable	Runoff NO ₃ ⁻		Runoff NH ₄ ⁺		Leachate NO ₃ ⁻		Leachate NH ₄ ⁺	
	OR P-value	95% CI	OR P-value	95% CI	OR P-value	95% CI	OR P-value	95% CI
<i>Lawn type</i>	<i>*χ^2 (3) = 12.97</i>		<i>*χ^2 (3) = 10.99</i>		<i>*χ^2 (3) = 8.05</i>			
Exurban	base	-	base	-	base	-	base	-
Suburban: Backyard	<i>0.02</i> <i><0.001</i>	0.002, 0.23	<i>0.16</i> <i>0.006</i>	0.05, 0.59	<i>0.06</i> <i>0.01</i>	0.007, 0.57	2.86 0.14	0.72, 11.35
Suburban: Front yard	0.70 0.50	0.24, 1.98	<i>0.34</i> <i>0.03</i>	0.13, 0.88	1.55 0.59	0.32, 7.58	2.11 0.27	0.56, 7.95
Institutional	<i>0.22</i> <i>0.03</i>	0.06, 0.83	<i>0.26</i> <i>0.02</i>	0.08, 0.80	0.86 0.84	0.20, 3.67	0.85 0.79	0.24, 2.98
<i>Season</i>	<i>*χ^2 (3) = 30.24</i>		<i>*χ^2 (3) = 10.35</i>		<i>*χ^2 (3) = 19.66</i>		<i>*χ^2 (3) = 15.88</i>	
April 2018	base	-	base	-	base	-	base	-
Sept 2018	<i>8.39</i> <i>0.003</i>	2.01, 35.00	<i>3.24</i> <i>0.03</i>	1.12, 9.31	<i>192.08</i> <i><0.001</i>	9.20, 4010.95	<i>0.13</i> <i>0.01</i>	0.03, 0.61
Nov 2018	<i>27.09</i> <i><0.001</i>	6.22, 118.00	1.77 0.30	0.6, 5.22	<i>65.18</i> <i>0.006</i>	3.31, 12183.33	2.87 0.07	0.92, 8.97
March 2019	0.63 0.63	0.10, 4.15	0.53 0.33	0.15, 1.89	7.68 0.20	0.34, 175.07	0.57 0.40	0.15, 2.09
<i>Fertilizer use</i>	<i>*χ^2 (1) = 6.68</i>		<i>*χ^2 (1) = 6.82</i>		<i>*χ^2 (1) = 7.17</i>		<i>*χ^2 (1) = 6.63</i>	
Unfertilized	base	-	base	-	base	-	base	-
Fertilized	<i>4.46</i> <i>0.01</i>	1.43, 13.84	<i>3.86</i> <i>0.01</i>	1.40, 10.62	<i>70.83</i> <i>0.007</i>	3.13, 1600.21	<i>7.44</i> <i>0.01</i>	1.61, 34.25
<i>Hillslope location</i>					<i>*χ^2 (1) = 3.97</i>			
Top	base	-	base	-	base	-	base	-
Bottom	0.65 0.36	0.27, 1.61	0.78 0.53	0.36, 1.70	<i>0.28</i> <i>0.05</i>	0.08, 0.98	0.89 0.82	0.34, 2.33
Sample size	167		167		124		117	

Italicized font denotes significant comparison to base factor. OR = odds ratio; CI = confidence interval. * Denotes significant (P<0.05) predictors in model and χ^2 value if significant. Note Firth logistic regression was used for leachate analysis due to low sample sizes and zero count cells.

Table 3: Results of linear regressions.

Outcome	Predictor	Fertilizer treatment	Coef.	SE	R ²
Runoff NO ₃ ⁻ Flux	Soil NO ₃ ⁻	Unfertilized	0.22*	0.06	0.47
		Fertilized	0.40**	0.10	0.35
Soil NO ₃ ⁻	N ₂ flux	Unfertilized	-0.06*	0.02	0.43
		Fertilized	0.01	0.005	0.38
Soil NO ₃ ⁻	Nitrification	Unfertilized	0.54*	0.14	0.59
		Fertilized	0.33**	0.07	0.49
N ₂ O flux	Soil NO ₃ ⁻	Unfertilized	1.03	0.44	0.23
		Fertilized	1.01**	0.22	0.22
N ₂ O flux	Nitrification	Unfertilized	1.27*	0.39	0.44
		Fertilized	0.13	0.13	0.04
N ₂ flux	Soil organic matter	Unfertilized	-0.70*	0.20	0.30
		Fertilized	-0.72	0.40	0.05
N ₂ flux	Soil moisture	Unfertilized	-0.03	0.19	0.20
		Fertilized	0.10	0.10	0.04
Soil NH ₄ ⁺	Soil organic matter	Unfertilized	0.09*	0.02	0.44
		Fertilized	0.02	0.06	0.35
Nitrification	Soil moisture	Unfertilized	-0.07*	0.02	0.14
		Fertilized	-0.02	0.02	0.08
Nitrification	Soil NH ₄ ⁺	Unfertilized	0.97*	0.26	0.28
		Fertilized	0.96*	0.32	0.34

Coef is unstandardized regression coefficient; SE is standard error of coefficient clustered by site. Note that season was included in all models as a control for repeated seasonal sampling; therefore, results of season are not included in table. *= $P < 0.05$, **= $P < 0.01$, ***= $P < 0.001$

Table 4: Kruskal-Wallis H test for seasonal effect of fertilizer treatments.

Outcome	April*		September		November		March*	
	χ^2	<i>df</i>	χ^2	<i>df</i>	χ^2	<i>df</i>	χ^2	<i>df</i>
RO NO ₃ ⁻	8.76	2	9.86	2	1.14	2	17.36	2
RO NH ₄ ⁺	17.11	2	16.59	2	1.65	2	15.23	2
L NO ₃ ⁻	5.82	2	9.51	2	4.16	2	5.27	2
L NH ₄ ⁺	9.28	2	2.48	2	4.51	2	13.43	2
Soil NO ₃ ⁻	3.02	2	2.22	2	4.48	2	7.67	2
Soil NH ₄ ⁺	4.20	2	3.41	2	1.42	2	7.19	2
N ₂ flux	0.53	2	3.51	2	0.50	2	1.76	2
N ₂ O flux	8.58	2	2.54	2	7.30	2	6.38	2

* Sampling season when short-term fertilizer application occurred. Bolded χ^2 represent significant test at P<0.05. RO is runoff; L is leachate

FIGURES

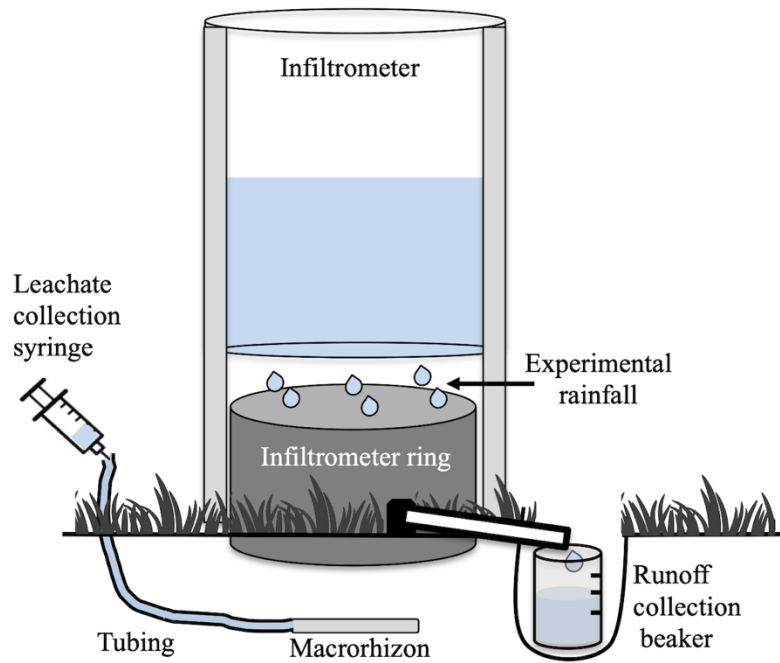


Figure 1: Schematic of rainfall experiment.

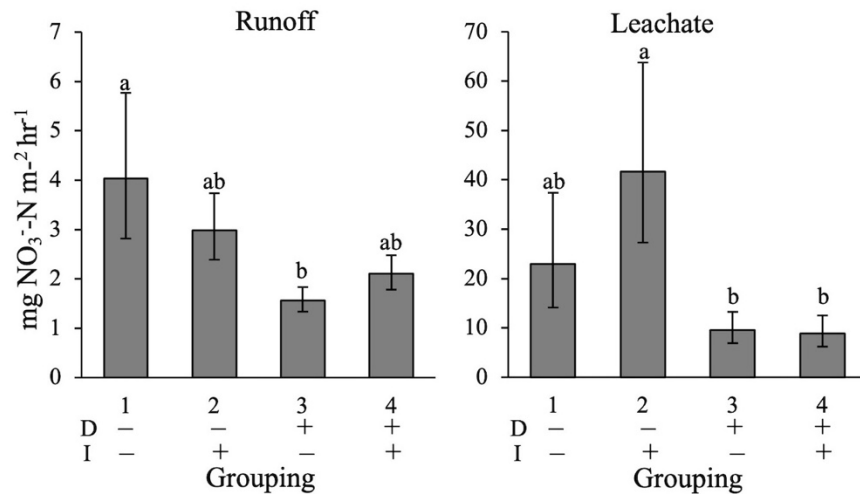


Figure 2: NO₃⁻ flux in runoff and leachate for each potential N-mobilization grouping for long-term fertilized lawns. Different letters denote significant differences at P < 0.05. “D” denotes denitrification potential grouping with “-” representing low and “+” representing high rates. “I” denotes saturated infiltration rate grouping with “-” representing low and “+” representing high rates. Error bars indicate ±1 standard error.

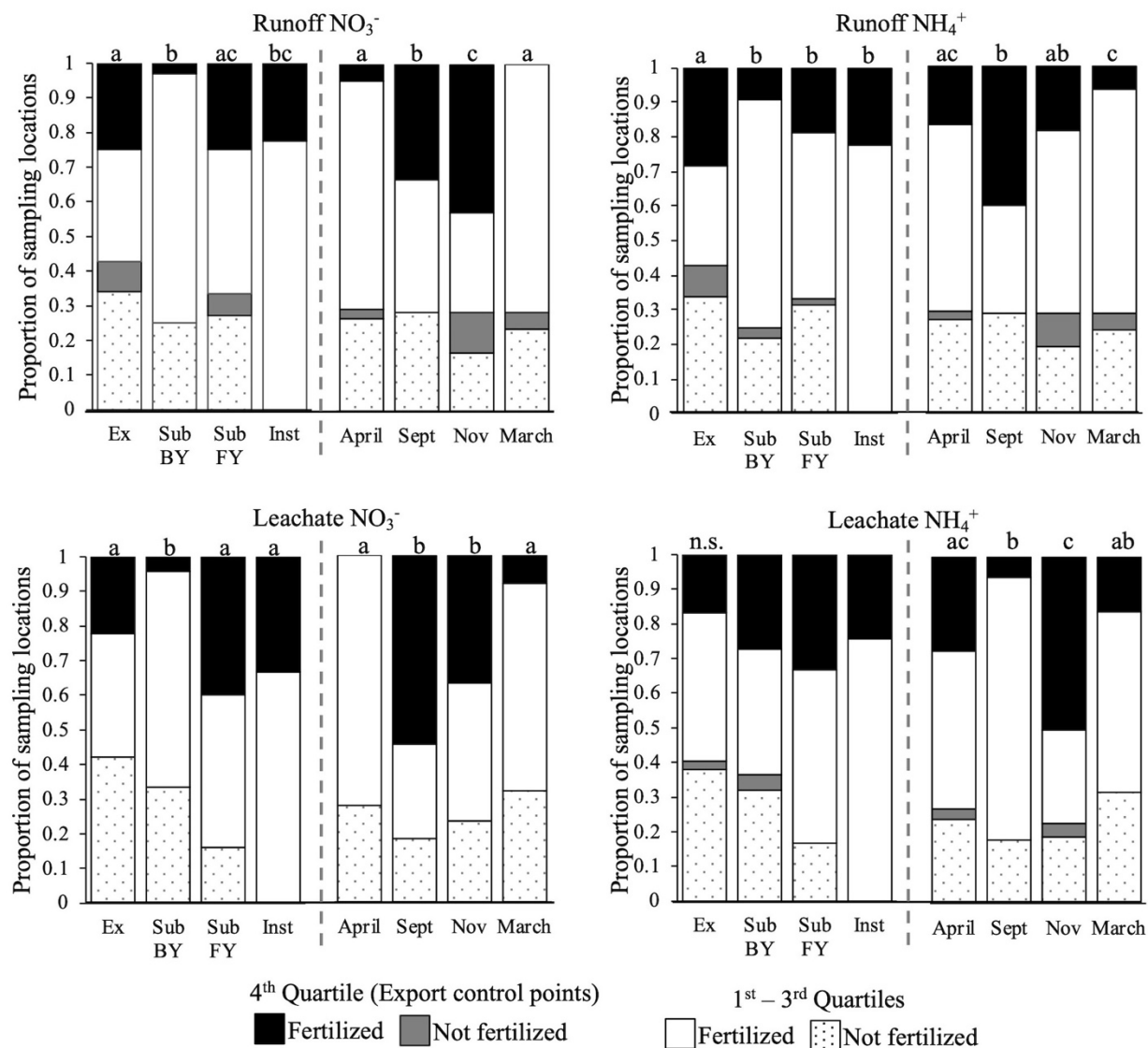


Figure 3: Proportion of sampling locations that were designated as potential export control points (i.e. were in upper quartile of data distribution) and were not designated as potential export control points (in quartiles 1-3) for long-term fertilized and unfertilized yards. Comparisons are shown for each yard type and each season. Different letters denote significant differences ($P < 0.05$) among yard types or seasons for each flux. Ex= exurban, sub=suburban, BY= backyard, FY= front yard, inst= institutional.

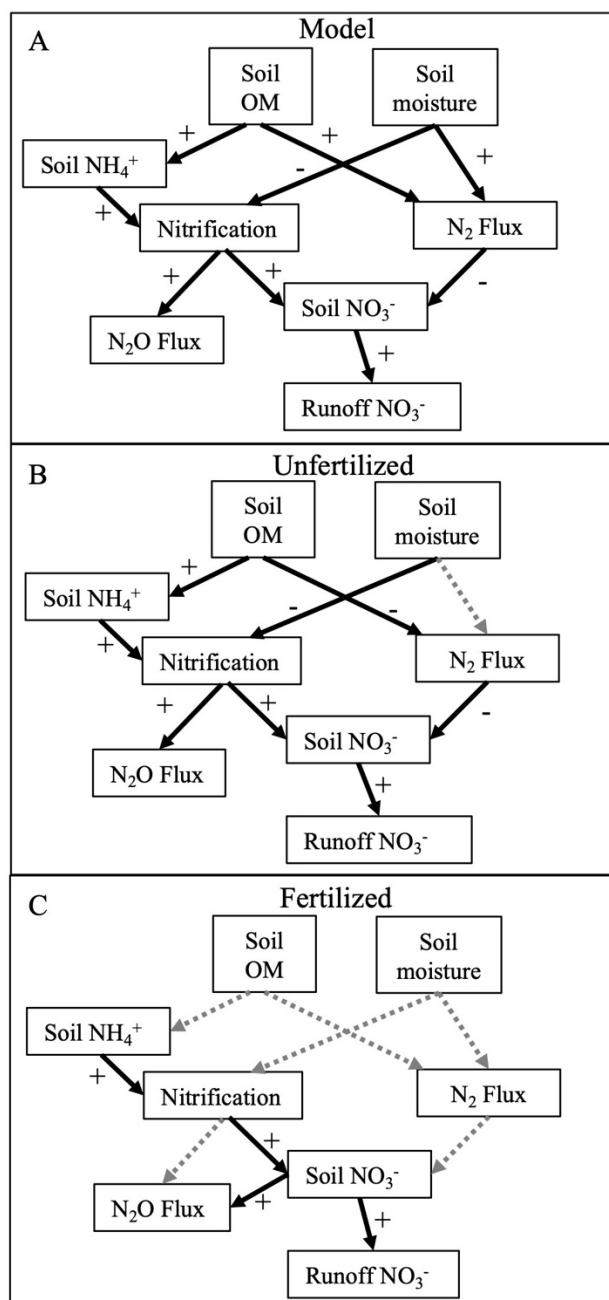


Figure 4: Hypothesized (A) and actual relationships among drivers of NO₃⁻ fluxes in runoff in unfertilized (B) and long-term fertilized (C) lawns. Arrow points from predictor to outcome of regression. Direction of coefficients of linear regression represented by (+) for positive and (-) for negative relationships. Solid black lines represent significant pathways. Dashed gray lines represent insignificant pathways.

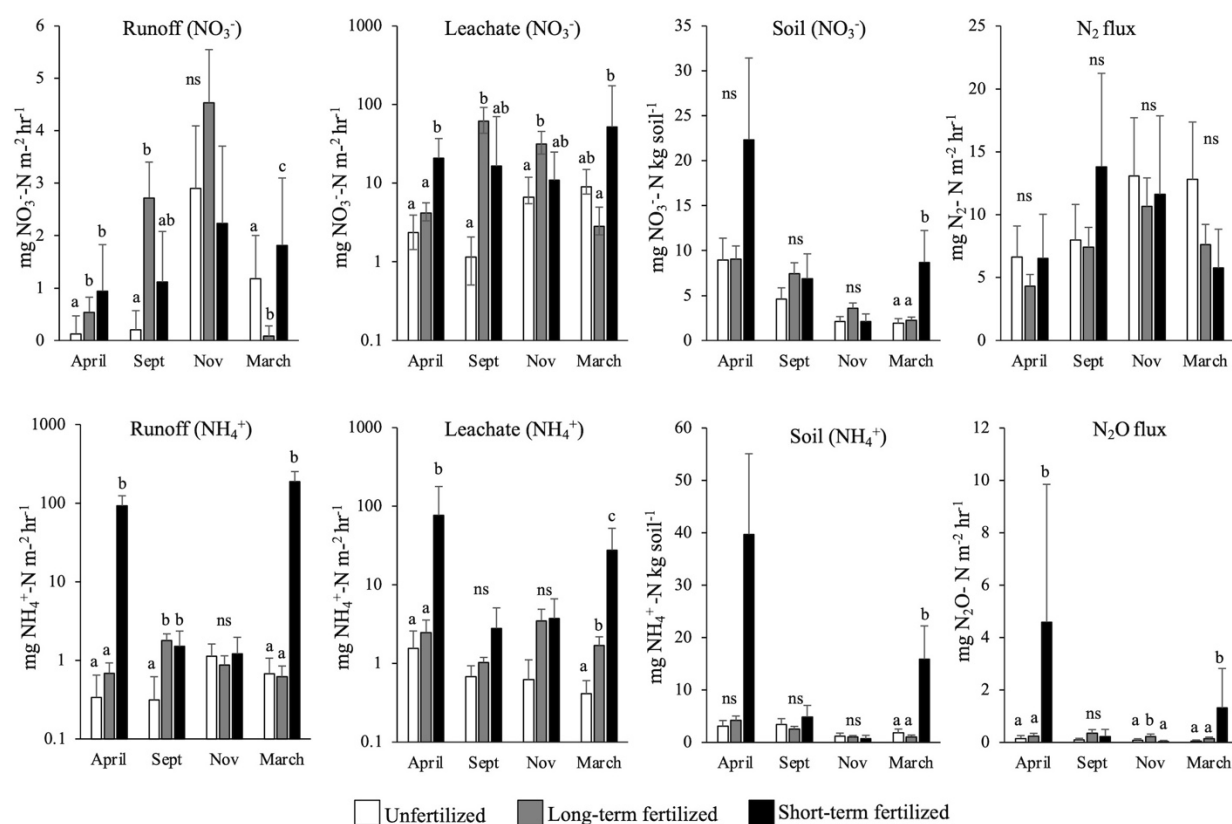


Figure 5: Log-normal mean values for N flux in runoff and leachate, soil NO_3^- , soil NH_4^+ , N_2 flux and N_2O flux in unfertilized, long-term fertilized and short-term fertilized lawns. Error bars indicate ± 1 standard error. Different letters denote significant differences within season from nonparametric Dunn's pairwise comparison tests at $p < 0.05$. Note log y-axis for NO_3^- leachate and NH_4^+ runoff and leachate fluxes.

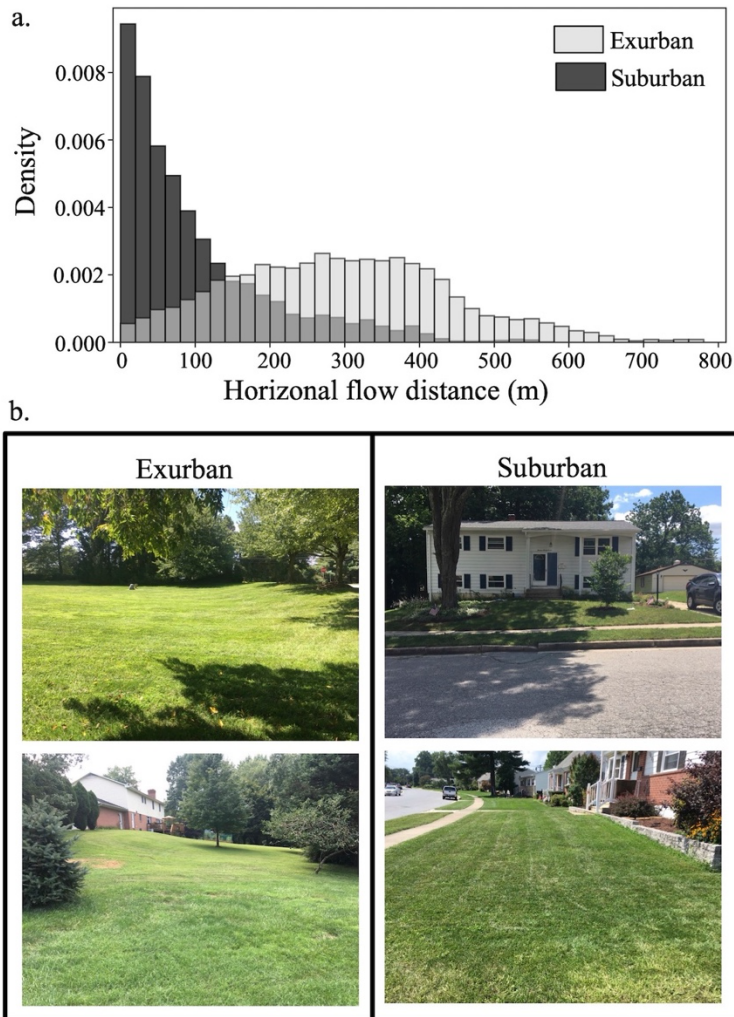


Figure 6. (a) Density distributions of horizontal flow distances from lawn patches to nearest draining stream or road draining to a stream (20-m interval) for exurban and suburban watersheds. (b) Examples of lawns in exurban and suburban neighborhoods that illustrate the differences in length of potential flow paths and proximity to impervious surfaces.