Nitrogen Availability and Denitrification in Urban Agriculture and Regreened Vacant Lots

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Abstract

Many cities demolish abandoned homes and create regreened vacant lots (RVLs), and an increasingly popular, high-intensity use of RVLs is as urban agriculture (UA) sites. UA may potentially result in higher nitrogen (N) runoff to aquatic ecosystems, but this potential has not been quantified. We examined the role that varying land reuse intensity plays in determining potential for N export via runoff or leaching, focusing on soil N availability and N removal capacity via denitrification. We contrasted three levels of land use intensity for vacant parcels: intact vacant properties, turfgrass RVLs, and regreened UA lots in Buffalo, NY. We examined soil N and C availability, denitrification potential, and isotopic evidence of denitrification.

Land use intensity only affected soil properties in surficial soil horizons. Total N was 2.5x higher in UA soils (mean = 0.51%) than non-UA (mean = 0.21%). Soil nitrate was 2.6x higher in winter (mean = 12.4 μg NO_3^--N g^{-1}) than summer (mean = 4.7 μg NO_3^--N g^{-1}) and was generally higher in UA soils. Despite higher soil N availability at UA sites, there were no differences in denitrification potential between UA and non-UA sites (mean = 620 ng N_2O-N g^{-1} h^{-1}). Isotopic evidence further confirms that denitrification was not a major sink of N. Although UA had high N availability compared to non-UA sites and low rates of denitrification, UA only has moderate potential for runoff-driven N export, as nitrate concentrations were substantially lower than values typical for conventional agricultural soils.

Keywords: urban agriculture, vacant lots, green infrastructure, nitrogen, nitrate, denitrification

Introduction

Urban environments are hotspots of nitrogen (N) and phosphorus export to aquatic ecosystems, where pollution by these important macronutrients can drive eutrophication and harmful algal blooms (Grogan et al., 2023). Nutrient export to aquatic systems from the urban environment is primarily driven by runoff during precipitation events that results from a large percentage of impervious surfaces (Brezonik & Stadelmann, 2002). In cities with combined sewer systems, stormwater combines with sewage during high flows and overwhelms the capacity of wastewater treatment plants, with excess untreated water containing high nutrient loads routed to waterways (Field & Struzeski, 1972). While sewage from these combined sewer overflow (CSO) events can be an important component of overall nutrient loads to receiving aquatic ecosystems, nutrients mobilized by runoff from green spaces can also contribute substantial amounts to these nutrient loads. For example, Hobbie et al. (2017) found that, in St. Paul, MN, residential fertilizer comprised 37-59% of N supplied to a watershed, and that stormwater runoff, exclusive of sewage inputs, comprised 37-79% of total N export from the watershed. Similarly, in a study of a high-to-medium housing density area in Florida, fertilizer runoff contributed 6-25% of N export from the watershed (Yang & Toor, 2017). Runoff N from lawns is likely to be highest when the flow path to the nearest impervious surface is short, such as in dense urban areas (Suchy et al., 2021).

To reduce stormwater pollution from urban ecosystems, cities have implemented management plans that increasingly focus on engineered green infrastructure (such as rain gardens) as a pathway to mitigation of runoff volumes and resulting nutrient pollution (Hopkins et al., 2018). Many Rust Belt cities such as Detroit, Michigan and Buffalo, New York have experienced population decline and widespread abandonment and subsequent decay of properties

(Hackworth, 2016; Silverman et al., 2013). To combat this, many of these cities have engaged in programs of active demolition and regreening of abandoned properties. The resulting regreened vacant lots (RVLs), have been recognized over the past decade for their usefulness as a low intensity but extensive form of green infrastructure (Kelleher et al., 2020; Newman et al., 2019; Shuster et al., 2014, 2015). Demolition of abandoned structures decreases impervious surface cover of RVLs, and planting of vegetation potentially increases evapotranspiration and improves soil hydraulic properties (Qiu et al., 2013, 2017), in turn reducing storm flows in sewer systems and mitigating CSOs (Kelleher et al., 2020). For example, in Buffalo, NY, infiltration capacity of RVLs was increased by greater than 50% compared to pre-demolition state (Kelleher et al., 2020). Buffalo includes RVLs, produced as a result of its urban blight management program, in its EPA-mandated CSO control plan (Buffalo Sewer Authority, 2014). Despite their recognized hydrologic benefits, little attention has been paid to whether RVLs act as sinks of nutrients, as in the case of other, engineered green infrastructure, or whether they can produce nutrient pollution in surface runoff, partially counteracting their hydrologic benefits.

RVLs have documented costs and benefits, the balance of which largely depends on how they are managed. RVLs targeted for high-intensity reuse, such as debris removal and replanting, are associated with many community health outcomes including decreased levels of violence, decreased mortality, and increased feelings of safety (Garvin et al., 2013; Kondo et al., 2018) while unmanaged RVLs, in addition to being hotspots for crime, can increase the incidence of zoonotic diseases (Gulachenski et al., 2016). A common, high-intensity use of RVLs is urban agriculture (UA). UA has been the focus of increasing interest in recent decades (Heckler, 2012; Kleszcz, 2018) and can provide nutrition benefits to low income individuals in inner-city communities (Gudzune et al., 2015) as well as fostering community engagement (Ohmer et al., 2009). As UA is often associated with intensive organic agriculture, UA also has the benefit of not contributing new inorganic N to the global N cycle, sourcing N instead from manure, compost or from N already present in the urban environment (Erisman et al., 2008). RVLs used for UA are characterized by a high degree of soil amendments, with nutrient rich materials such as compost or manure imported to increase levels of N and P (Taylor & Lovell, 2015; Wielemaker et al., 2019). These high levels of nutrient inputs to UA suggest high potential for export of these nutrients in runoff, and this potential needs to be quantified to properly weigh the costs and benefits of UA as a potential use for RVLs (Meharg, 2016; Sieczko et al., 2023).

Denitrification can remove N from ecosystems by converting nitrate (NO_3^-) to inert N_2 gas, a highly desirable outcome from a nutrient runoff perspective. Denitrification is an anaerobic microbial process that requires anoxic environments and that uses labile organic carbon as a substrate to reduce NO_3^- and obtain energy. Denitrification rates are negatively correlated with nitrate runoff in urban lawns (Suchy et al., 2023). Although denitrification requires anoxic environments, substantial denitrification occurs in oxic soils in microsites where oxygen has been depleted (e.g. soil aggregate interiors), especially in fine-textured soils (Tiedje et al., 1984). Researchers frequently measure potential denitrification in upland agricultural environments where typical rates range from 27 ng N_2O-N g^{-1} h^{-1} to 932 ng N_2O-N g^{-1} h^{-1} (D’Haene et al., 2003; Wang et al., 2022). Potential denitrification rates have been measured in urban lawn environments as well, and in a meta-analysis rates ranged widely, from <1 ng N_2O-N g^{-1} h^{-1} to >62000 ng N_2O-N g^{-1} h^{-1} (Reisinger et al., 2016), though other studies show a much narrower range of rates, comparable to agricultural soils (Suchy et al., 2021).

The contribution of RVLs to N export from urban watersheds is a function of the balance of N inputs to these systems and the capacity for these systems to retain and ultimately remove these nutrients. The quantities of inputs are in turn likely to be driven by reuse intensity of RVLs (e.g. unmaintained lawn vs. urban agriculture) and the associated management practices that are employed. RVL reuse intensity is also likely to change the rates and occurrence of denitrification by modifying substrate supply and the favorability of environmental conditions. For example, the soils of RVLs have been altered as a byproduct of demolition and regrading, resulting in compaction that can result in more anaerobic conditions favorable to denitrifiers (Li et al., 2014). Variable demolition procedures also contribute greatly to the high variability of soil hydraulic properties that have been observed in RVLs in Buffalo (Kelleher et al., 2020). Finally RVLs that have UA are frequently tilled and amended with compost and manure, altering soil structure and greatly increasing organic carbon and nitrogen available to microbes for denitrification (Wielemaker et al., 2019).

This study aims to address how vacant lot regreening may impact the N cycle in these urban ecosystems, with the objective of understanding the potential for these ecosystems to be a source or sink of N that can result in pollution of urban aquatic ecosystems. Specifically, we ask: How do various land reuses of vacant lots determine a) N content available for export and b) N removal via denitrification? We hypothesized that, compared to undemolished vacant properties, soil N content and denitrification activity would be higher in urban agriculture sites and lower in regreened turfgrass. We reasoned that urban agriculture receives soil amendments from farmers and so can be expected to have higher N content including NO_3^- as well as labile organic carbon. By contrast, turfgrass sites have experienced soil disturbances such as burial and mixing which could be expected to decrease nutrient content, and also generally receive no applied fertilizer. We examined sites in Buffalo, NY, a city with a high amount of property vacancy and RVLs, to test the hypothesis.

Methods

Site Description

Buffalo, New York (42°53.187′ N, 78°52.7022′ W) is located in the far west of the state, on the eastern shore of Lake Erie. The climate is humid continental (Köppen classification: Dfb/Dfa) with mean annual precipitation of 640 mm and mean annual temperature of 9 °C. The natural vegetation of the area consists of temperate hardwood forest, although most land within the region is in agriculture or developed land uses (Multi-Resolution Land Characteristics Consortium (U.S.), 2019). Soils consist predominantly of urban anthrosols developed from glacial till and glaciolacustrine sediments (Cline & Marshall, 1977). As a result of city-led demolitions from 2001-2013, there have been 404 acres (163.5 ha) of impervious surfaces converted to RVLs across the city (Buffalo Sewer Authority, 2014). Demolished lots have typically been converted to lawns, although more intensive redevelopment has occurred in some areas.

Work for this study was conducted on lots within the urban core of Buffalo (Figure 1), focusing on the west and southeast regions of the city, regions that have experienced substantial depopulation and urban decay. Sites were selected for proximity to one another and availability for research purposes. All sites were privately owned. Work was conducted at four sites with intact vacant homes (hereafter intact sites), four demolished home sites that were replanted in turfgrass (turfgrass RVL sites), and four demolished home sites that have been converted to UA (agriculture sites). The intact and turfgrass sites are mowed periodically. The UA sites are used for intensive vegetable production, receiving regular tillage and soil amendments of manure and/or compost.

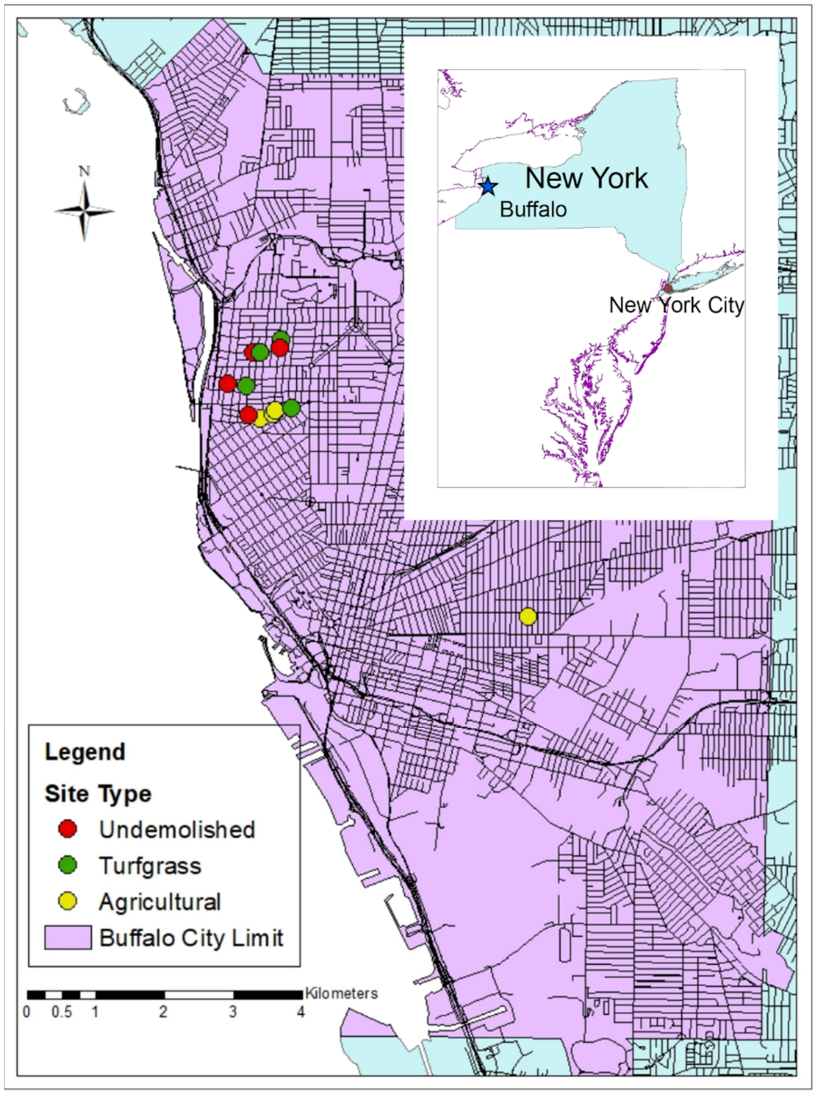

Figure 1 Location of study sites within the city of Buffalo, NY.

Soil Sampling

Two soil sampling campaigns were conducted between October and December 2021 (non-growing season) and between May and July 2022 (growing season), as plant demand for N varies substantially between these seasons. At the agriculture and turfgrass sites, two soil profiles were taken at each site, one within the former foundation (fill soil) and one within the yard

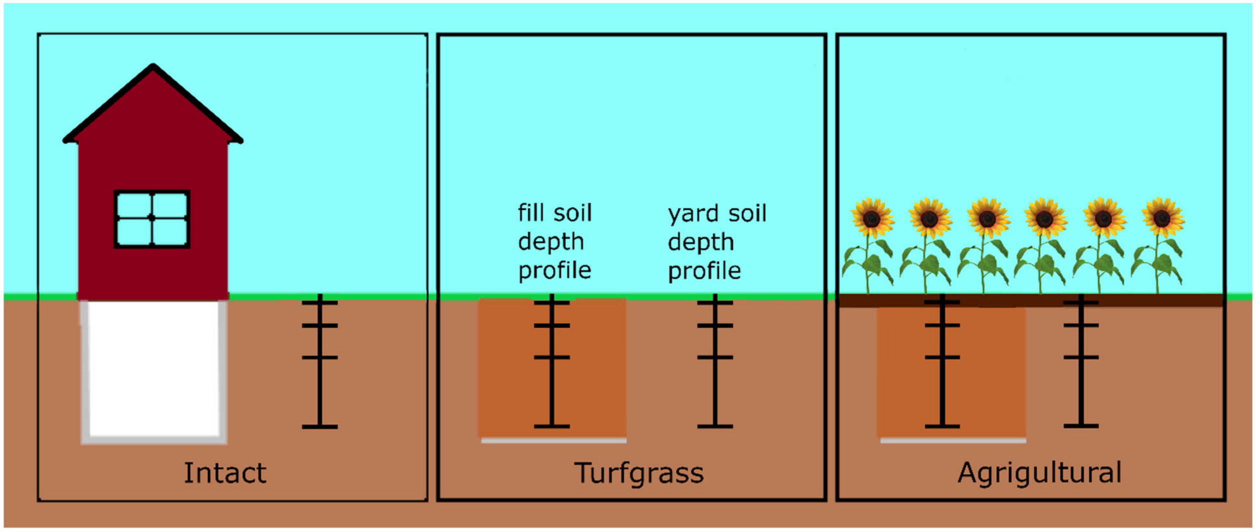

Figure 2 Sampling regime: sampling in fill and yard soils at agricultural and turfgrass sites and in yard soils at intact sites. Four sites of each type were sampled. Abbreviations for each of these location types are; AF: agricultural fill, AY: agricultural yard, IY: intact yard, TF: turfgrass fill, TY: turfgrass yard

(Figure 2), as pervious work has shown that soil properties can differ substantially between former foundation and yard locations on regreened vacant lots (Kelleher et al., 2020; Shuster et al., 2014, 2015). For the intact sites, only one soil profile was taken from the yard. Sampling locations within each lot were randomly determined using ArcGIS. Soil samples were collected using an 8.26 cm bucket auger at the following intervals: 0-10 cm, 15-25 cm, 50-60 cm, and 95-105 cm. Intact soil cores (77 mm x 51 mm) were taken at the same intervals for bulk density analysis and were collected using a slide hammer corer. To maintain somewhat uniform soil moisture conditions among samples, no soil samples were taken within 24 h of a precipitation event greater than 7 mm. Soils were stored at field moist conditions at 4 °C between sampling and analysis (approximately 1 week for all chemical analyses except for pH and elemental analysis). All soils were sieved through a < 2 mm sieve prior to analysis.

Soil Physical and Chemical Analyses

Soil texture was determined via the hydrometer method, following the protocol of Gee and Bauder (1986). Gravimetric water content was measured on the sieved < 2 mm soil fraction by heating the soil in an oven at 115 °C to a constant weight. Soil cores were oven dried and weighed to determine bulk density. Soil pH was measured in a 2:1 water:soil slurry (Robertson et al., 1999) using a Fisherbrand pH meter with Orion probe (Fisher Scientific, Hampton, NH).

Soil nitrate (NO_3^-) and nitrite (NO_2^-) were extracted using 2M KCl at a 5:1 solution:soil ratio. Soil subsamples (9 g) were shaken for two hours on an end-over shaker and filtered through a 0.2 μm nylon membrane filter. Concentrations were determined by colorimetric analysis on a San ++ segmented flow analyzer (Skalar Analytical B.V., Breda, Netherlands), using the EPA cadmium reduction method (Eaton & Franson, 2005; U.S. EPA, 1993). Total soil carbon and nitrogen were measured by combustion analysis. Samples were dried at 40 °C to a constant weight and then ground on a roller mill so that 88% or more of the sample passed through a 100 mesh sieve. Ground samples were sent to the Cornell Nutrient Analysis Laboratory for elemental analysis on a Primacs SNC-100 analyzer (Skalar Analytical B.V., Breda, Netherlands).

Water-extractable organic carbon (WEOC) was measured on all samples as an index of microbially-available carbon substrates, following the protocol of Elliot et al. (1999). Briefly, 13g of soil (field moist weight) was mixed with Type 1 water at a ratio of 3:1 water:soil. Soils were shaken overnight on an end-over shaker, filtered through a 0.2 μm nylon membrane filter, and analyzed for dissolved organic carbon using a TOC-V_{CSH} combustion analyzer (Shimadzu Corporation, Kyoto, Japan). WEOC was then calculated on a per gram of dry soil basis using the gravimetric water content of each soil.

Soil Denitrification Activity

Soil denitrification potential was measured using denitrification enzyme assays following the methods outlined in Groffman et al. (1999). To summarize, 25 g of sample was weighed into 125 ml Erlenmeyer flasks. One quarter of all samples were run in triplicate for quality control. 25 ml of DEA medium containing 100 mg l^{-1} NO_3^--N, 40 mg l^{-1} dextrose, and 10 mg l^{-1} chloramphenicol was added to each flask, and the flasks were stoppered with a butyl rubber stopper. The flasks were then purged of oxygen by four cycles of flushing with N_2 gas followed by evacuation for one minute. Acetylene was then added to each flask, which inhibits the last step of denitrification, the reduction of nitrous oxide (N_2O) to N_2, allowing the quantification of denitrification via measurement of N_2O production. Acetylene was purified by running industrial grade acetylene gas through two traps of concentrated sulfuric acid followed by a water trap, and purified acetylene gas was added to the headspace of each flask at the equivalent of 10% of headspace volume. Flasks were incubated at 22 °C on a rotary shaker table and headspace gas samples were taken at 30 and 90 minutes, with an additional quality control sample taken at 60 minutes in the case of replicates. Headspace gas samples were placed in evacuated 11 ml Exetainer vials. The headspace gas samples were analyzed for N_2O concentration using a GC-2014 GHG-3 gas chromatograph equipped with an electron capture detector (Shimadzu Corporation, Kyoto, Japan).

To complement these laboratory assays, we measured the isotopic composition of soil NO_3^- . This provides an integrated, semi-quantitative measure of the total amount of denitrification a pool of NO_3^- has undergone, as denitrification strongly fractionates against heavy isotopes. Remaining NO_3^- in the soil thus becomes progressively enriched in the heavy isotope as the extent of denitrification progresses in soils (Burns et al., 2009). The isotopic composition of extracted NO_3^- was analyzed using the denitrifier method (Casciotti et al., 2002). Briefly, KCl solutions of NO_3^- were added to colonies of denitrifying bacteria that have been genetically modified to only produce nitrous oxide (N_2O) rather than N_2. The isotopic composition of the precursor NO_3^- is then calculated from the isotopic values of nitrogen and oxygen measured on the N_2O gas using an isotope ratio mass spectrometer (IRMS). Samples were pre-treated for removal of (NO_2^-) following the procedure outlined in Granger & Sigman (2009) if they contained NO_2^- concentrations greater than 5% of NO_3^-. KCl extracts from the non-growing season were analyzed at UC Davis Stable Isotope Facility using a ThermoFinnigan GasBench + PreCon trace gas concentration system interfaced to a Delta V Plus IRMS (Thermo Scientific, Bremen, Germany). Growing season KCl extracts were analyzed at the UC Riverside Facility for Isotope Ratio Mass Spectrometry on a Delta-V Advantage IRMS interfaced to a GasbenchL (Thermo Scientific, Bremen, Germany).

Statistical Analysis

Statistical analysis was performed in R (R Core Team, 2022). For analysis, we grouped data by location type, comprised of the unique combinations of land use and soil type, for a total of five location types: UA on foundation fill (AF), UA on former yards (AY), turfgrass on foundation fill (TF), turfgrass on former yards (TY), and intact yards (IY). We analyzed data from both seasons (growing and non-growing season) jointly, and we constructed separate models for each sampling depth interval.

For each soil property of interest at each depth, we tested for differences between location types by performing a Location Type x Season two-way ANOVA. In no model was the Location Type x Season interactive term significant, so we removed the interactive term from all models via a stepwise selection procedure. The results presented here are thus from models that only include terms for the main effects of Location Type and Season. For ANOVAs where the Location Type term was determined to be significant, we used Tukey's test (Tukey, 1949) for post-hoc comparisons among location types. In these models, all parameters except pH were log_{10}-transformed for variance stabilization. When reporting group means and standard errors in the results, however, we report the arithmetic mean of untransformed data.

To analyze the isotopic NO_3^- data for semi-quantitative evidence of denitrification, we jointly examined $\delta^{15}N$ and $\delta^{18}O$ values, comparing these to literature values of the isotopic composition of known NO_3^- sources (Kendall, 1998). We then visually looked for evidence of increases in isotopic enrichment with each increase in depth along the "denitrification line," the slope of which (a 0.5 ‰ increase in $\delta^{18}O$ with a 1 ‰ increase in $\delta^{15}N$) describes how denitrification typically enriches ^{15}N and ^{18}O in residual NO_3^- pools. This approach assumes that most NO_3^- is sourced from surficial soil layers and that progressive enrichment at depth is a signal of denitrification as nitrate migrates vertically in the soil profile.

Results

Although our analysis examined soil properties throughout a 1 m soil profile, significant differences among land uses for these soil properties were almost exclusively confined to the uppermost soil sampling interval (0-10 cm). We therefore focus the following results and discussion on the results from this uppermost sampling interval, unless explicitly noted otherwise in the text. Full results for all sampled depths are presented in the Supporting Information (**Error! Reference source not found.**, **Error! Reference source not found.**), and additional figures that display data for all soil depths are also provided in the Supporting Information (**Error! Reference source not found.**, **Error! Reference source not found.**). Full tables of

ANOVA results and post hoc comparisons are presented in the Supporting Information (**Error! Reference source not found.**).

Soil Biogeochemical Properties

Soil NO_3^- concentrations differed greatly between seasons, but there were few differences in NO_3^- concentrations among location types. Across all location types, NO_3^- concentrations were 2.6x higher in the winter (mean = 12.4 µg NO_3^--N g^{-1}) than in the summer (mean = 4.6 ug NO_3^--N g^{-1})($p < 0.001$) (**Error! Reference source not found.**). Across both the growing and non-growing season, NO_3^- concentrations tended to be higher at agricultural locations compared to other location types, but the only significant differences were between the agricultural location types (AY: mean = 12.6 µg NO_3^--N g^{-1}; AF: mean = 12.7 µg NO_3^--N g^{-1}) and the TY location type (TY: mean = 4.5 µg NO_3^--N g^{-1}) (p = .011 and .0097 for comparisons of TY with AY and AF, respectively) (Figure 3A).

Total N tended to be higher at both UA locations (AF and AY, pooled mean = 0.52%) than non-UA locations (pooled mean = 0.21%) ($p<0.001$), though AF sites were not significantly higher than IY sites (Figure 3C). There was no effect of season on total N. Differences between location types ranged from a 2.9x difference at AY (mean = 0.58%) compared to TY (mean = 0.20%) to 2.5x greater at AY compared to IY (mean = 0.23%) (**Error! Reference source not found.**).

Water-extractable organic carbon was significantly higher at UA sites compared to non-UA sites, but there were no seasonal effects (Figure 3B). AF and AY sites were 2.8x higher in WEOC (pooled mean = 0.11 mg C g^{-1}) than non-UA location types (pooled mean = 0.04 mg C d^{-1}) ($p<0.001$) (**Error! Reference source not found.Error! Reference source not found.**).

Differences ranged from a 4.4x greater concentration at AY (mean = 0.11) than TY (mean = 0.03) to a 2.1x greater concentration at AF (mean = 0.10) than TF (mean = 0.05).

Total carbon tended to be higher at UA locations than non-UA locations and showed no obvious seasonal trends across location types. UA location types (pooled mean = 8.74%) were 1.9x higher than non-UA location types (pooled mean = 4.61%) (**Error! Reference source not found.**, Figure 3A). Differences ranged from a 2.1x greater proportion at AY (mean = 9.51%) than TY (mean = 4.48%) ($p<0.001$) to a 1.7x greater proportion at AF (mean = 7.97%) than IY (mean = 4.78%) ($p<0.05$) (**Error! Reference source not found.**).

Turfgrass sites generally had a higher pH than intact and agricultural sites and showed no obvious seasonal trends across location types. Although turfgrass location types showed higher pH (pooled mean = 7.94) than agricultural and intact (pooled mean = 7.57) (**Error! Reference source not found.**AFigure 3) the only significant difference between location types was that pH was 0.43 units greater at TF (mean = 7.96) sites than AY (mean = 7.53) ($p<0.05$) (**Error! Reference source not found.**).

Soil Physical Properties

All soils had high clay content, with the majority of soils classified as clay soils (USDA-NRCS, 2018). The mean clay content of surface soils was 44% and there were no significant differences in clay content between location types. The proportion of the coarse fraction (> 2 mm) in samples likewise varied widely (229% to <1% of the weight of the > 2mm fraction), typically composed of patches of building rubble that likely contributed to preferential flow. Bulk density differed between location types, with UA soils having generally lower bulk densities than non-UA soils (Figure 3E). AY sites had lower bulk density (mean = 0.69 g cm^{-3})

than all other location types, containing high amounts of organic debris in the sites we sampled. AF (mean = 1.11 g cm^{-3}) was not significantly lower only than any non UA soil types.

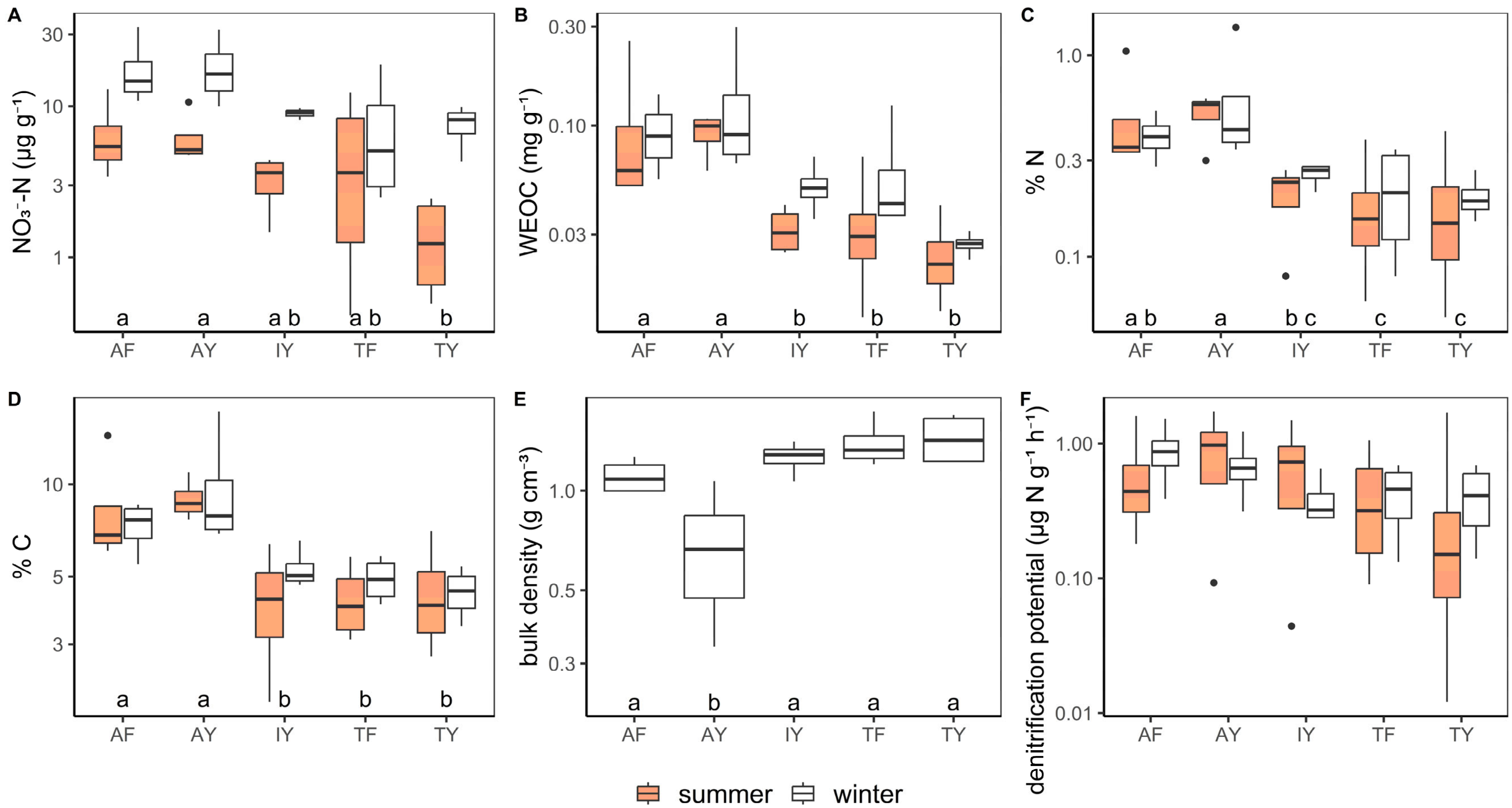

Figure 3 Physical and chemical soil properties by location type and season at the 0.05 m depth. (Location type abbreviations; AF: agricultural fill, AY: agricultural yard, IY: intact yard, TF: turfgrass fill, TY: turfgrass yard). Note that the y axis for each plot is log scale. Shared letters between two or more location types indicate no significant difference between respective location types. Bulk density was only measured in the non-growing season.

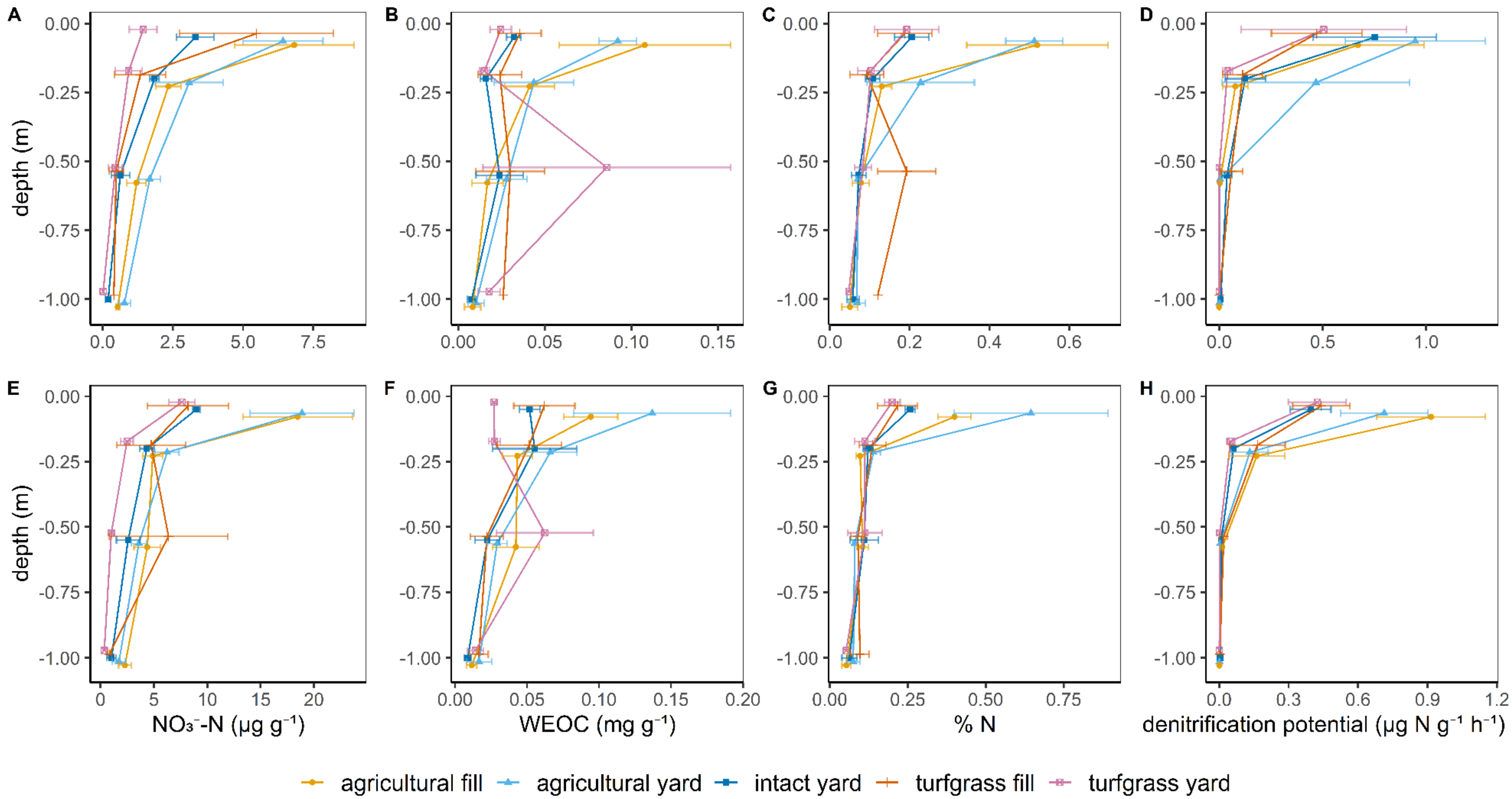

Figure 4 Chemical soil properties by location type and depth. Dots are mean values and error bars represent the standard error of the mean. Points are vertically staggered at each depth interval for ease of comparison. Plots A-D are summer data and E-H are winter. Note that the scales are different between seasons.

Denitrification Activity

Denitrification potential was not significantly different among any of the site types at any depth. The mean denitrification rate in the surficial sampling interval was 200 ng N_2O-N g^{-1} h^{-1} (Figure 3F). Across all sites, denitrification potential decreased substantially with depth (Figure 4D,H), consistent with lesser substrate availability in lower horizons (Figures 4A,E,C,G). Although there were no differences between denitrification potential at location types, the availability of substrates for denitrification were significantly, positively correlated with denitrification potential across all land uses and depths. Denitrification potential was significantly positively correlated with WEOC (R^2=.3837, p<.001, Figure 5A), NO_3^- (R^2=.3257, p < 0.001, Figure 5B), total N (R^2=.4342, p< 0.001, Figure 5C), and total C (R^2=.2483, p < 0.001, **Error! Reference source not found.**B), and negatively correlated with soil pH (R^2=.2326, p <.001, **Error! Reference source not found.**A). There was no significant effect of season on the slopes of these linear regression relationships, although for the relationship between denitrification potential and NO_3^-, the intercept of the relationship was higher in summer than winter.

Very few sites exhibited progressive enrichment of NO_3^- $\delta^{15}N$ and $\delta^{18}O$ along the expected slope of denitrification with increasing soil depth, indicating that little denitrification occurred in these soils as soil water infiltrates deeper soil horizons, or that the signal of any denitrification activity was overwhelmed by endogenous NO_3^- production in these horizons. $\delta^{15}N$ and $\delta^{18}O$ values of extracted NO_3^- fell almost entirely within the envelope of expected values for fertilizer and manure inputs (Figure 6). Four of the 34 0.95-1.05m samples (all from non-UA location types) with low NO_3^- concentrations did show an increase in both $\delta^{15}N$ and $\delta^{18}O$ between 0.50-0.60m and 0.95-1.05m depths, though these did not follow the consistent slope expected in the case denitrification.

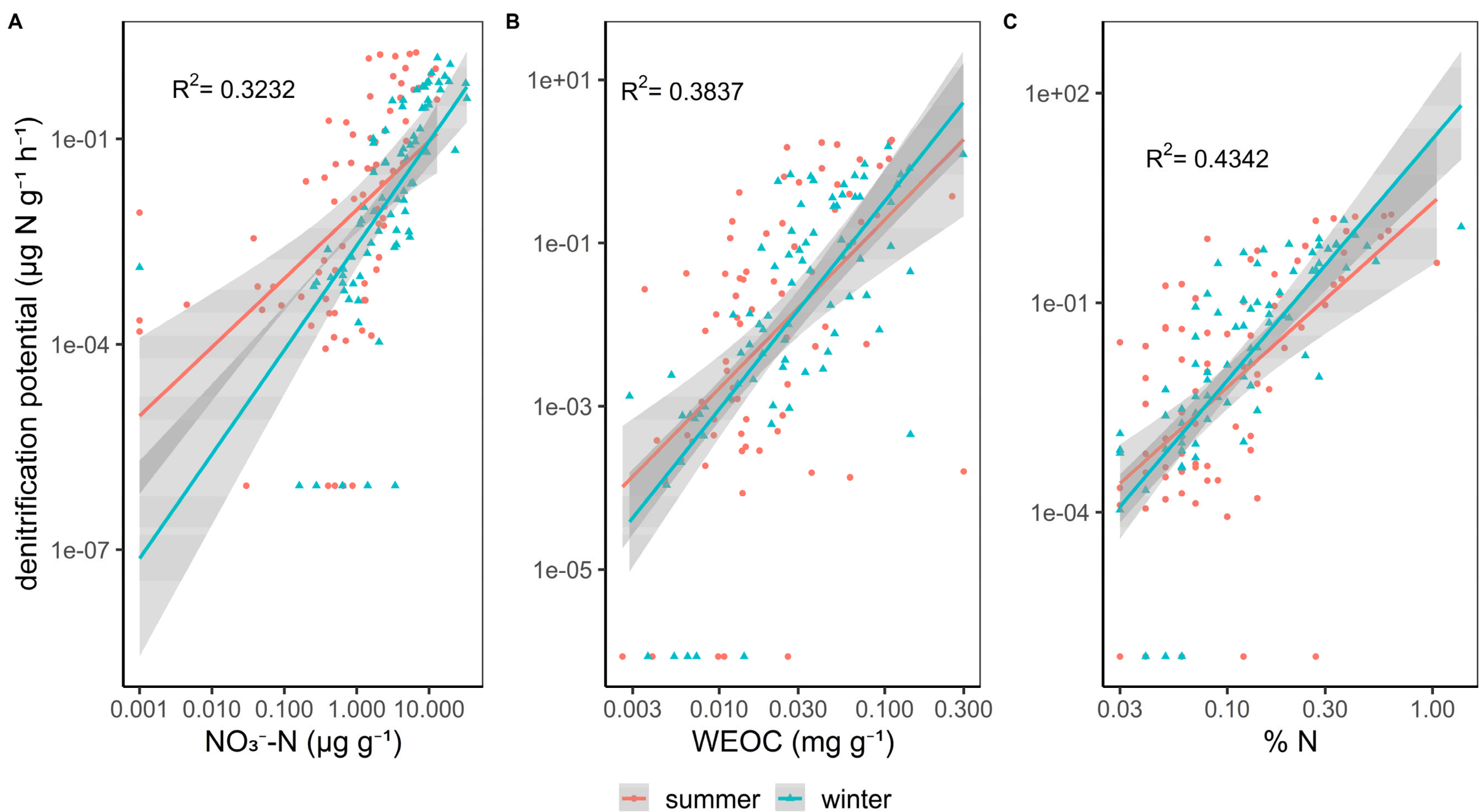

Figure 5 Multiple linear regressions of denitrification potential by NO_3^-, WEOC, and total N for all depths. Shaded areas represent the 95% confidence interval of the regression lines. Note that both axes are log scale.

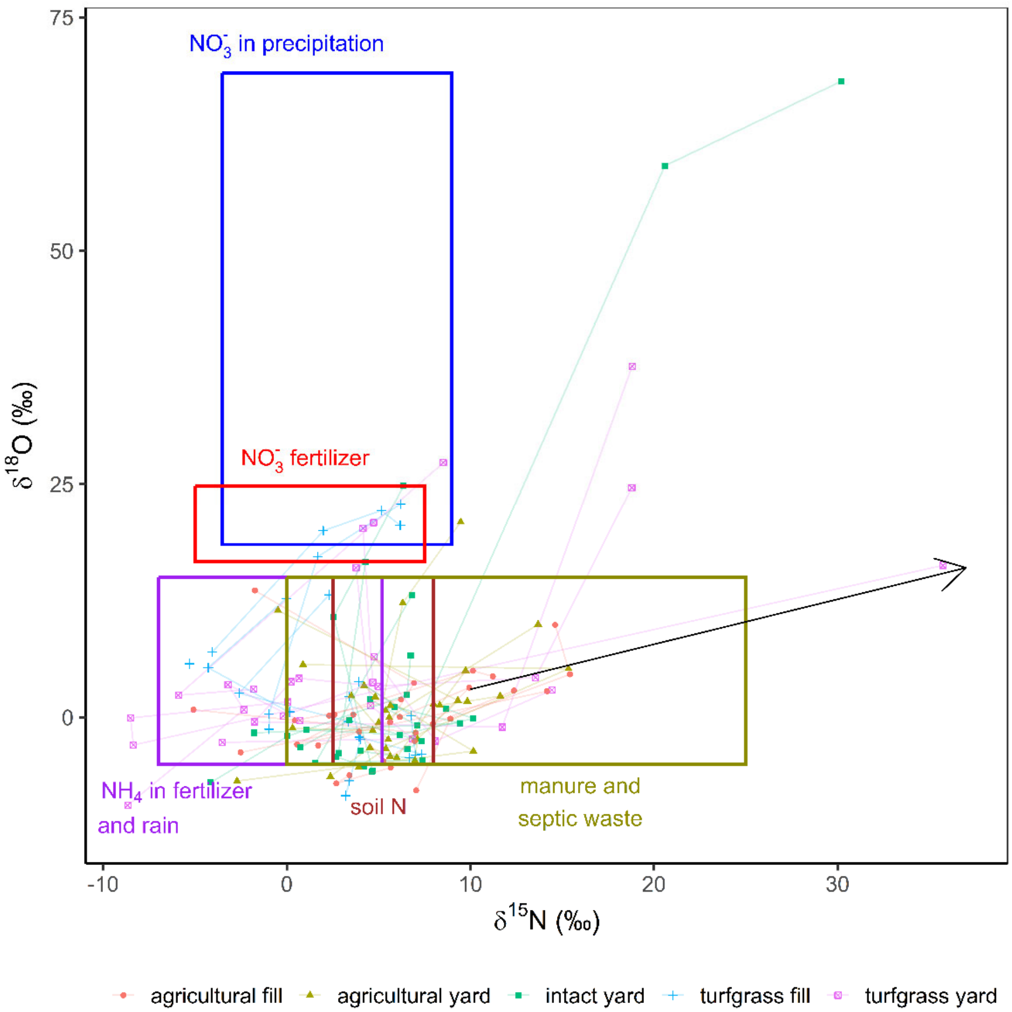

Figure 6 NO_3^- isotopic ratios of samples at all depths, with lines connecting samples sharing the same depth profile. Boxes indicate ranges of expected isotopic ratios of $\delta^{15}N$ and $\delta^{18}O$ based on sources of NO_3^- and the black arrow is the slope that isotopic enrichment with denitrification is expected to follow (Kendall, 1998).

4. Discussion

4.1. Potential for N Runoff from RVLs

Urban agriculture has a moderate potential to be an increased source of N to local water bodies via surface runoff compared to other uses of RVLs, particularly in winter, when NO_3^- concentrations are elevated. Soil N concentrations, including NO_3^-, were moderately higher at agricultural locations than non-agricultural locations, with NO_3^- in particular being higher in surface soil horizons during winter. Despite higher N concentrations and higher availability of carbon substrate, soils at agricultural locations did not exhibit significantly higher denitrification than non-agriculture, as measured either through denitrification potential or increasing isotopic enrichment of NO_3^- with depth. Increased N supply is thus not coupled to increased removal capacity, and this decoupling results in conditions that are favorable to surface N runoff (Suchy et al. 2023).

Although the decoupling of N supply from denitrification, documented here, will likely favor increased N runoff, this is tempered by the fact that our observed soil NO_3^- concentrations are not anomalously high, compared to other measurements found in the literature. Nitrate has long been understood to be the most leachable form of N, and NO_3^- tends to dominate N export in anthropogenic landscapes (Basu et al., 2011). The farms that participated in this study used only organic fertilizers, and the lack of inorganic NO_3^- fertilizers applied in this setting is likely to be a major factor responsible for the low soil NO_3^- concentrations compared to conventional agriculture. Growing-season NO_3^- concentrations for UA soils in this study are comparable to other UA soils found in temperate climate zones (mean = 6.4 $\mu g\ N\ g^{-1}$), as reported by Alvarez-Campos & Evanylo (2019). Our observed concentrations were at the low end compared to values reported for organic farms, where summer concentrations ranged from 9.6-94 $\mu g\ N\ g^{-1}$ (Ouyang et al., 2018; Xie et al., 2021; Zhang et al., 2019). These concentrations are also considerably lower than the 20 $\mu g\ N\ g^{-1}$ end-of-season values recommended for maximum crop yields in conventional agriculture in the US (Sullivan et al., 2003). The NO_3^- concentrations of this study's non-UA sites were also low compared to those in soils of similar plant communities. These concentrations were between the values observed by others for suburban lawns (mean = 9.4 $\mu g\ NO_3^-\text{-}N\ g^{-1}$) (Martinez et al., 2014) and those observed in unfertilized pastures (mean =

3.1 μg NO_3^--N g^{-1}) (Jarvis & Hatch, 1994). Leaching of N to groundwater is also unlikely to be substantial because of the soils' high clay content that limits hydraulic conductivity and low NO_3^- concentrations at depth at all locations. Although we thus assess the risk of N leaching to groundwater to be low due to the heavy clay soils at our sites, localities with particularly course textured soils should conduct similar studies to confirm that this still holds in such conditions.

Although we conclude that the potential for nitrate runoff from RVLs is only moderate, the potential for export of particulate organic N and dissolved organic N may exist at our UA sites. Although nitrate is often the dominant N source of concern in runoff, organic N forms can contribute substantially to total N loads (Hobbie et al., 2017; Jani et al., 2020). Total N at UA locations were similar to 0.7 %N measured in raised garden beds (Salomon et al., 2020) and 0.38 %N in urban agriculture allotments (Edmondson et al., 2014) and were much higher than typical values measured in farms across the Midwest that use chemical fertilizers (mean = 0.21 %N) (Laboski et al., 2008). Total N percentages at TY, TF, and IY sites, in counter to this, were toward the lower end of the range of values between 0.05 %N and 0.6 %N in a nationwide study of lawns (Selhorst & Lal, 2012). The higher values for total N in UA soils suggest that particulate N and dissolved organic N thus may drive increased N export at UA compared to lower intensity uses (Mulvaney et al., 2009). Erosion control, careful timing of fertilizer application, and appropriate tillage practices are key controls on organic N export that should be implemented in the context of UA and other uses of RVLs (Sieczko et al., 2023; Whittinghill & Sarr, 2021).

Despite the increased N supply, the potential for lower runoff may exist in UA compared to other landscape use types, driven by the physical properties of the soil. We observed generally lower bulk density in UA than other land uses. Organically amended soils are often lower in bulk density and greater porosity associated with the formation of soil aggregates (Aggelides & Londra, 2000). This has been shown in several cases to increase infiltration, resulting in lower runoff amounts with rainfall (Spargo et al., 2006). Evanylo et al, (2008) for example found lower bulk density and greater porosity, time to runoff generation, and infiltration rates in a compost fertilized soil with total N similar to this study's sites than an adjacent unfertilized soil, resulting in lower NO_3^- and total N loads in addition to lower runoff volumes.

The observation of higher NO_3^- in winter is typical of non-growing season conditions, where assimilatory N demand by plants is negligible (Laine et al., 1994, Sieczko et al. 2023). Elevated winter NO_3^- concentrations in UA is of particular concern for runoff events given the common occurrence of springtime eutrophication events, even in locations relatively unimpacted by anthropogenic nutrient loading (Venugopalan et al., 1998). The occurrence of winter runoff events is potentially increased in climates that experience substantial snowfall. While early snowmelt infiltrates completely, late snowmelt can contribute to overland flow and runoff at rates similar to impervious surfaces when soils infiltration capacity is reduced and exceeded by snowmelt (Bengtsson & Westerström, 1992). Rain on snow events further contribute to runoff in a similar manner. Adding to this concern is that rapid snowmelt, rain on snow, and other extreme variability in winter weather are expected to increase with climate change (Casson et al., 2019). We thus assess that, if UA does contribute substantially to nutrient export to aquatic ecosystems, it is most likely to occur during the non-growing season. Though the setup of runoff collectors on private property accessible by the public was not feasible for this study, runoff generation and concentrations should be investigated in future studies, as should the concentration and loads of possible runoff events.

4.2. Drivers of Denitrification

We found that total N was a better predictor of denitrification potential than NO_3^- , even though NO_3^- is the immediate substrate requirement for denitrification. NO_3^- is highly mobile in the soil and is readily taken up by plants, and NO_3^- concentrations are known to respond rapidly to precipitation events (Nangia et al., 2010; Yahdjian & Sala, 2010). We also found that soil NO_3^- concentrations were more highly variable within location types (average CV=0.75) than total N, (average CV=0.52). These results suggest that NO_3^- levels fluctuate more so than total N and that individual point measurements of NO_3^- may not be highly representative of total nitrate availability over the weekly time scales that denitrification enzymes persist in soils.

In addition to measures of N and C, bulk density was a moderately strong predictor of denitrification, but with a counterintuitively inverse relationship. It may be expected that higher bulk density and lower pore volumes would favor anaerobic conditions for denitrification, but denitrification was higher in low-bulk density soils. This is likely driven by high levels of soil amendments at UA sites that increase fertility and decrease bulk density. We thus conclude that bulk density is likely not directly driving denitrification rates but is instead acting as a proxy for soil amendment levels (Aggelides & Londra, 2000). Similarly, while denitrification is known to be suppressed at low soil pH (<5) (ŠImek & Cooper, 2002), we found an inverse relationship between soil pH and denitrification potential, across the relatively limited pH gradient (7.03-8.90) examined here. We speculate that the inverse relationship between soil pH and denitrification is again due to organic amendments in the surface horizon of UA locations that contribute organic acidity to the soil and lower pH, and pH is thus a proxy for substrate availability and does not directly influence denitrification at the circumneutral pH levels of the soils examined.

Denitrification potential in UA sites was fairly typical for that of organic agriculture (Ouyang et al., 2018; Yin et al., 2015). Although not significant, denitrification potential at UA sites had higher mean values (UA pooled mean = 811 ng N_2O-N g^{-1} h^{-1}) than at almost all non-UA location types (non-UA pooled mean = 498 ng N_2O-N $g^{-1}h^{-1}$). Compared to agriculture using inorganic fertilizers in temperate regions (D'Haene et al., 2003; Malique et al., 2019; Yin et al., 2015), denitrification potential rates at the UA sites were fairly high. Denitrification potential rates were fairly low among non-UA soils compared to the values found by other researchers, though denitrification rates in lawns tend to be quite variable (Reisinger et al., 2016). Despite this, other researchers have found lawns with similar denitrification potential (Hall et al., 2016; Suchy et al., 2021). A possible explanation for lower rates in this study is that lawns measured in most studies are occupied properties, and are generally fertilized and watered regularly, in contrast to the non-UA sites in this study. While denitrification potential was lower at these sites, N inputs are also much lower on these unfertilized turfgrass sites, compared to residential lawns and UA sites.

Conclusion:

Urban agriculture has the potential to modestly increase N export through runoff. Nitrogen availability is higher in UA than other land uses, but this is not counteracted by higher denitrification rates that result in N removal. In particular NO_3^-, the most leachable form of N, is only slightly higher at UA sites, compared to other land use types. Runoff may be a larger concern in the winter largely due to elevated NO_3^- concentrations in the non-growing season combined with the increased risk of runoff during snowmelt. Overall, we assess that the small increase in N availability from UA use of RVLs does not pose a sizeable risk of increased N export, particularly when its land cover percentage is relatively low, such as in Buffalo. Given the risk of small increased N export and the positive impacts that UA can provide such as social cohesion, nutritional benefits, and reuse of N from imported nutrients, we conclude that UA is most likely a net socio-ecological and economic benefit for the communities it serves.

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