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δ^{15}N and δ^{18}O Reveal the Sources of Nitrate-Nitrogen in Urban Residential Stormwater Runoff

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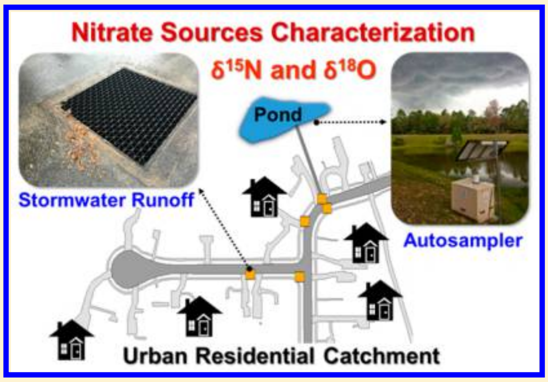
S Supporting Information

ABSTRACT: Nitrogen (N) sources are widely distributed in the complex urban environment. High-resolution data elucidating N sources in the residential catchments are not available. We used stable isotopes of N and oxygen (O) of nitrate (δ^{18}O-NO_3^- and δ^{15}N-NO_3^-) along with δ^{18}O and hydrogen (δD) of water (H_2O) to understand the sources and transformations of N in residential stormwater runoff. Stormwater runoff samples were collected over 25 stormwater events at 5 min intervals using an autosampler installed at the residential catchment outlet pipe that drained 31 low-density homes with a total drainage area of 0.11 km^2. Bayesian mixing model results indicated that atmospheric deposition (range 43−71%) and chemical N fertilizers (range <1−49%) were the dominant NO_3-N sources in the stormwater runoff and that there was a continuum of source changes during the stormwater events. Further, the NO_3-N transport in the stormwater runoff from the residential catchment was driven by mixing of multiple sources and biotic (i.e., nitrification) processes. This work suggests that a better understanding of N transport and sources is needed to reduce N export and improve water quality in urban water systems.



INTRODUCTION

Sources of nitrate−nitrogen (NO_3-N) in urban waters may include a combination of atmospheric deposition, fertilizers, organic materials, and leaking sanitary sewers.[1,2] These nonpoint sources of NO_3-N are a leading contributor to water quality impairment,[3] and result in eutrophication, hypoxia, and loss of biodiversity and habitat.[4,5] To prevent and remediate eutrophication in urban coastal systems, the sources and transport mechanisms of NO_3-N in stormwater runoff need to be determined and quantified.[6,7]

Dual nitrogen (N) and oxygen (O) stable isotope ratios of nitrate (δ^{18}O-NO_3^- and δ^{15}N-NO_3^-) coupled with chemical data are a powerful tool to distinguish the NO_3-N sources and investigate N transport from land to water bodies.[8,9] In general, δ^{15}N-NO_3^- values have been used to distinguish NO_3-N derived from ammonium (NH_4^+) fertilizer, soil organic matter, and animal manure/septic waste, whereas δ^{18}O-NO_3^- values are more useful to distinguish NO_3-N derived from NO_3^- fertilizer and atmospheric deposition.[10,11] However, abiotic (e.g., volatilization) and biotic (e.g., nitrification and denitrification) processes transform N during transport from land to water bodies[2,8,12] making it difficult to distinguish the contributing N sources in urban systems.

Studies have used the dual stable isotope ratios of NO_3^- to discriminate inorganic (e.g., chemical fertilizers) and organic (e.g., human and animal waste) N sources using biweekly to monthly sampling regimes in urban streams during storm and baseflow conditions.[2,13,14] These urban studies have suggested that NO_3^- in surface waters is commonly derived from the atmospheric deposition and sewage.[2,15] Atmospheric deposition is highly variable in space and time and is a major source of NO_3-N due to the high density of automobile traffic in urban areas.[6,16,17] Divers et al.[12] in an urban stream in Pittsburgh, PA observed that atmospheric deposition contributed 34% of NO_3-N during storm events with the remainder (66%) of NO_3-N contributed by sewage-derived sources. Buda and DeWalle[18] reported that wash-off of atmospheric deposition was the main NO_3-N source during storm flow conditions in a central Pennsylvania urban watershed.

Transport of N from land to water is controlled by a complex interaction of hydrological and biogeochemical mechanisms.[2,19−21] Previous research had found that biogeochemical mechanisms are dominant in watersheds,[22,23] whereas some studies found that transport of stormwater driven N is primarily a function of hydrology, with biogeochemical processes playing a minor role.[20,24,25] The dynamics of NO_3-N transport in urban stormwater runoff from residential areas have not yet been fully investigated. Among different N forms, NO_3-N is one of the main form of concern in the stormwater runoff.[26] Stormwater runoff sampling during rain events may reveal N transport mechanisms and contributing NO_3-N sources in residential

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catchments. The objective of this study was to investigate the contributing NO_3-N sources and elucidate the processes controlling NO_3-N transport using dual stable N and O isotopes in a residential catchment. To our knowledge, this is the first study to illustrate the source identification and transport of NO_3-N in residential stormwater runoff using consecutive 5 min intervals sampling from a low-density residential catchment. This data can help develop strategies to reduce NO_3-N transport from residential catchments to downstream urban waters.

STUDY LOCATION AND METHODS

Site Description. The study site is a low-density residential neighborhood of 31 single-family homes, with an average lot area of 2400 m^2 and home area of 409 m^2. The site is located along Florida's Gulf Coast in Hillsborough County, Florida (latitude 27°86′63.17" N, longitude 82°19′37.73" W) and is part of the metropolitan area of Tampa, Florida. The total area of the catchment including stormwater pond is 0.11 km^2; of which 37% is impervious (rooftops: 15%, patios: 4%, driveways and sidewalks: 12%, roads: 6%) and 61% is pervious (lawns in and around homes: 29%, tree canopies: 32%), and 2% is occupied by pond (Supporting Information (SI) Figure S1). The dominant vegetation in the catchment is live oak (*Quercus virginiana*) and St. Augustine turfgrass (*Stenotaphrum secundatum*). Soils in the catchment are predominantly Seffner fine sand series (Sandy, siliceous, hyperthermic Aquic Humic Dystrudepts). The climate in the area is subtropical with 2014 average monthly annual air temperature of 14−27 °C and daily extremes of 4−29 °C.[27] The average annual rainfall in the area over the last 10 years (2004−2014) was 94−153 cm (mean 130 cm), of which 47−77% (mean 65%) occurred during the wet season (June to September) (SI Figure S2A). In 2014, total rainfall was 144 cm, and monthly rainfall ranged from 1.52 to 34.24 cm, of which 58% occurred during the wet season. During the study period, monthly rainfall was highest in September (34 cm), followed by July (24 cm) and August (14 cm) (SI Figure S2B).

Sample Collection and Nitrogen Analysis. An ISCO Avalanche 6712 refrigerated autosampler (Teledyne Isco, Inc., Lincoln, NE, USA) was installed at the end of the stormwater outlet pipe that delivered runoff from the residential catchment to the stormwater pond. The autosampler was equipped with 14 plastic sample bottles of 950 mL each and was programmed to collect runoff entering the pond at the onset of flow and to take samples every 5 min until end of the runoff. An ISCO 674 rain gauge (Teledyne Isco, Inc., Lincoln, NE) was installed at the site for rainfall measurements and collection. Due to the need to have sufficient flow (and water depth) in the outlet pipe for ISCO sampler to operate, it was only possible to collect runoff samples when there was a minimum of 0.25 cm rainfall occurring in 15 min (equivalent to rainfall intensity of 1 cm/h). Thus, samples could not be collected during those rainfall events when the rainfall intensity was lower than 1 cm/h. The samples were collected in airtight plastic bottles and stored in a refrigerator at 4 °C until analysis (<24 h). The range of runoff samples collected during 25 individual events (July to September 2014) varied from 1 to 13 (SI Table S1), resulting in 121 stormwater samples; this corresponds to runoff occurring from 5 to 65 min as each runoff sample was collected at 5 min intervals. Twelve rainfall samples (10 samples were analyzed for isotopes) were also collected from the catchment during the wet season.

A subsample of collected water samples was vacuum-filtered (0.45 μm Pall Corporation, Ann Arbor, MI) within 24 h of collection and placed in 20 mL HDPE scintillation vials (Fisher Scientific, PA) either refrigerated (N and water isotope analysis) or frozen (N isotopic analysis). Aliquots of the filtered water samples were quickly transferred in 2 mL GC vials (Fisher Scientific, PA), sealed without headspace to eliminate water evaporation, and refrigerated until the water isotope analysis. The filtered samples were analyzed for NO_3-N using an AutoAnalyzer 3 (AA3, Seal Analytical, Mequon, WI) with EPA method 353.2.[28] The unfiltered water samples were analyzed for total N (TN) using the alkaline persulfate digestion method[29] followed by NO_3-N analysis as described above. The detection limits for both NO_3-N and TN were 0.001 mg/L.

Isotopic Analysis. Stable isotopes of water (H_2O), that is, oxygen ($\delta^{18}O-H_2O$) and hydrogen (δD-H_2O) were conducted in the Stable Isotope Laboratory at the University of California, Davis. The detailed description of the analysis technique is given by Lis et al.[30] For simultaneous D/H and $^{18}O/^{16}O$ ratios measurements of H_2O, an off-axis integrated cavity output spectroscopy (OA-ICOS) water isotope analyzer (LWIA, Los Gatos Research, Mountain View, CA) was coupled to a CTC LC-PAL liquid autosampler. Analysis of $\delta^{18}O$-NO_3^- and $\delta^{15}N$-NO_3^- was conducted using Coplen et al.[31] at the Isotope Ratio Mass Spectrometry (IRMS) facility at University of California, Riverside. All stable isotope results are expressed as δ values, representing deviations in per mil (‰) from Vienna Standard Mean Ocean Water standards for O, N, and deuterium such that

$$\delta(‰) = 1000 \times [(R_{\text{sample}}/R_{\text{standard}})] - 1$$

where R_{sample} and R_{standard} are the measured isotopic ratios (e.g., D/H, $^{15}N/^{14}N$ or $^{18}O/^{16}O$) for the sample and standard, respectively. The ratio of $^{15}N/^{14}N$ reference is N_2 in air, the D/H and $^{18}O/^{16}O$ reference is Vienna Standard Mean Ocean Water.

Bayesian Mixing Models. The proportion of the NO_3-N source contributions was estimated using Bayesian stable isotope mixing models as described in Parnell et al.[32,33] The Stable Isotope Analysis in R (SIAR) graphical user interface package (MixSIAR version 3.0.2) incorporating sources of uncertainty, isotope fraction, and multiple NO_3-N sources was used in this study. In brief, the isotope mixing analysis was used to determine fraction of NO_3-N in stormwater runoff from four sources (i.e., atmospheric deposition, NH_4^+ fertilizer, NO_3^- fertilizer, and soil and organic N) with two isotope systems. End member isotopic compositions were defined as follows. Atmospheric deposition was estimated from measured $\delta^{15}N$-NO_3^- (2.7 ± 4.90‰, n = 10) and $\delta^{18}O$-NO_3^- (44.8 ± 18.07‰, n = 10) values of rainfall samples collected during the wet season. NH_4^+ fertilizer ($\delta^{15}N$-NO_3^-: −0.2 ± 2.28‰, $\delta^{18}O$-NO_3^-: −2.0 ± 8.0‰),[10,34−41] NO_3^- fertilizer ($\delta^{15}N$-NO_3^-: 1.1 ± 2.78‰, $\delta^{18}O$-NO_3^-: 21.3 ± 3.01‰),[10,35,36,38,39,42] and soil and organic N ($\delta^{15}N$-NO_3^-: 7.5 ± 5.23‰, $\delta^{18}O$-NO_3^-: −2.0 ± 8.0‰)[2,10,12,35,37−39,42−46] end members were based on literature values. Measured $\delta^{15}N$-NO_3^- and $\delta^{18}O$-NO_3^- values of individual stormwater runoff samples (n = 121) were treated as "customers" and mean values of four NO_3-N sources were "sources". It should be acknowledged that the use of stable isotopes for source identification is complicated when the mixing of multiple N sources with overlapping isotopic ranges occurs together with microbial processes such as assimilation,

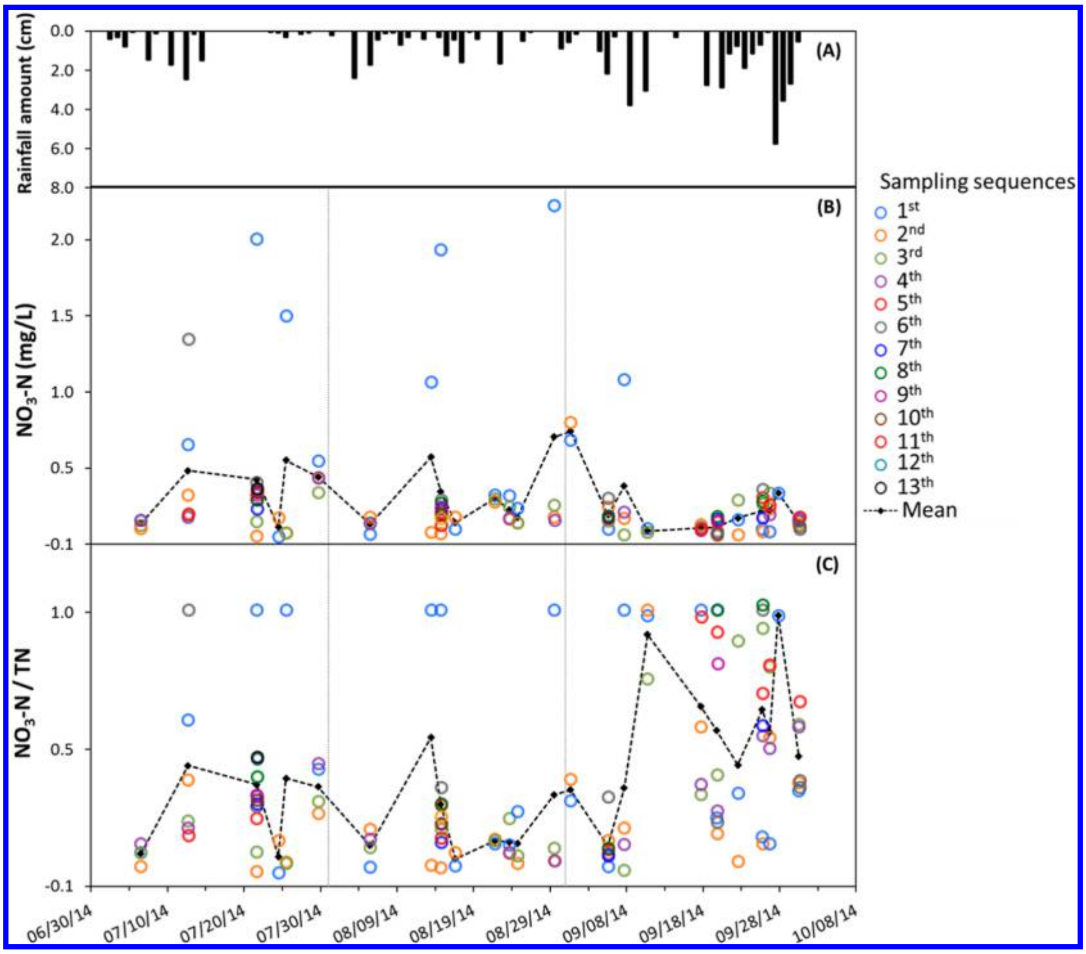

Figure 1. Temporal variability of (A) daily rainfall, (B) NO$_3$-N concentrations, and (C) NO$_3$-N/TN in stormwater runoff (n = 121) from 25 events during July−September 2014. The colors of circles and labels indicate sampling sequences. The dashed line shows change of mean values from individual events.

nitrification, and denitrification. Studies have reported that denitrification process causes increase in δ^{15}N-NO$_3^-$ and δ^{18}O-NO$_3^-$ in roughly 2:1 ratio.[10,12,47] The observed linear relationship between the δ^{15}N-NO$_3^-$ and δ^{18}O-NO$_3^-$ values of the stormwater runoff implied that no obvious denitrification occurred during the sampling events (data not shown). Further, the mean dissolved oxygen (DO) concentration in stormwater runoff during the wet season were high (>2 mg/L), suggesting that denitrification did not cause enrichment of δ^{15}N-NO$_3^-$ and δ^{18}O-NO$_3^-$ in the study catchment as denitrification generally occurs under the low DO concentration (<2 mg/L) condition.[10,48] Thus, the enrichment factors for denitrification were not evaluated in the mixing models. We determined the potential nitrification process using a calculation widely used in previous studies,[10,49] which is discussed in the later section. More detail on the mixing model and calculations can be found in SI.

■ RESULTS AND DISCUSSION

Nitrogen Concentration in Rainfall and Urban Stormwater Runoff. Concentrations of TN and NO$_3$-N in rainfall (n = 12) were 0.09−2.32 mg/L (mean 0.8 mg/L) and <0.001−1.15 mg/L (mean 0.18 mg/L), respectively. Mean concentrations of TN and NO$_3$-N in individual 25 stormwater runoff events (July−September) varied from 0.04 to 2.49 mg/L (mean 0.96 mg/L) and 0.04 to 0.69 mg/L (mean 0.24 mg/L), respectively (SI Table S1). The decrease in monthly NO$_3$-N concentrations from the beginning to the end of wet season could be due to the exhaustion of N sources in the residential catchment. We were not able to evaluate the relationship between N export and hydrological factors due to the lack of flow data and collection of runoff samples when the rain intensity was >1 cm/h. However, the mean concentrations of N in runoff were similar to a Tampa Bay residential stormwater runoff study (mean TN 1.25 mg/L; mean NO$_3$-N 0.21 mg/L)[50] but TN was lower than other urban stormwater runoff studies conducted in the United States (TN 2.0 mg/L).[6] Within individual stormwater events, the ratio of NO$_3$-N:TN varied between 0 and 1, with mean monthly values of 0.29 in July, 0.21 in August, and 0.47 in September, respectively (Figure 1).

Source of Water in Urban Stormwater Runoff. Stable isotopes of δ^{18}O−H$_2$O and δD-H$_2$O are ideal conservative environmental tracers that can provide essential information about the origin of the water, hydrological processes, and insights into the likely N sources.[51−53] In urban residential areas, stormwater runoff can be a combination of various water sources such as rainfall, municipal water, and reclaimed water used for lawn irrigation. Thus, we used water isotopes to determine the water source in stormwater runoff. The δ^{18}O−H$_2$O and δD−H$_2$O values in the rainfall (n = 10) ranged from −8.4‰ to −2.6‰ (mean −4.1‰) and −51.7‰ to −10.8‰

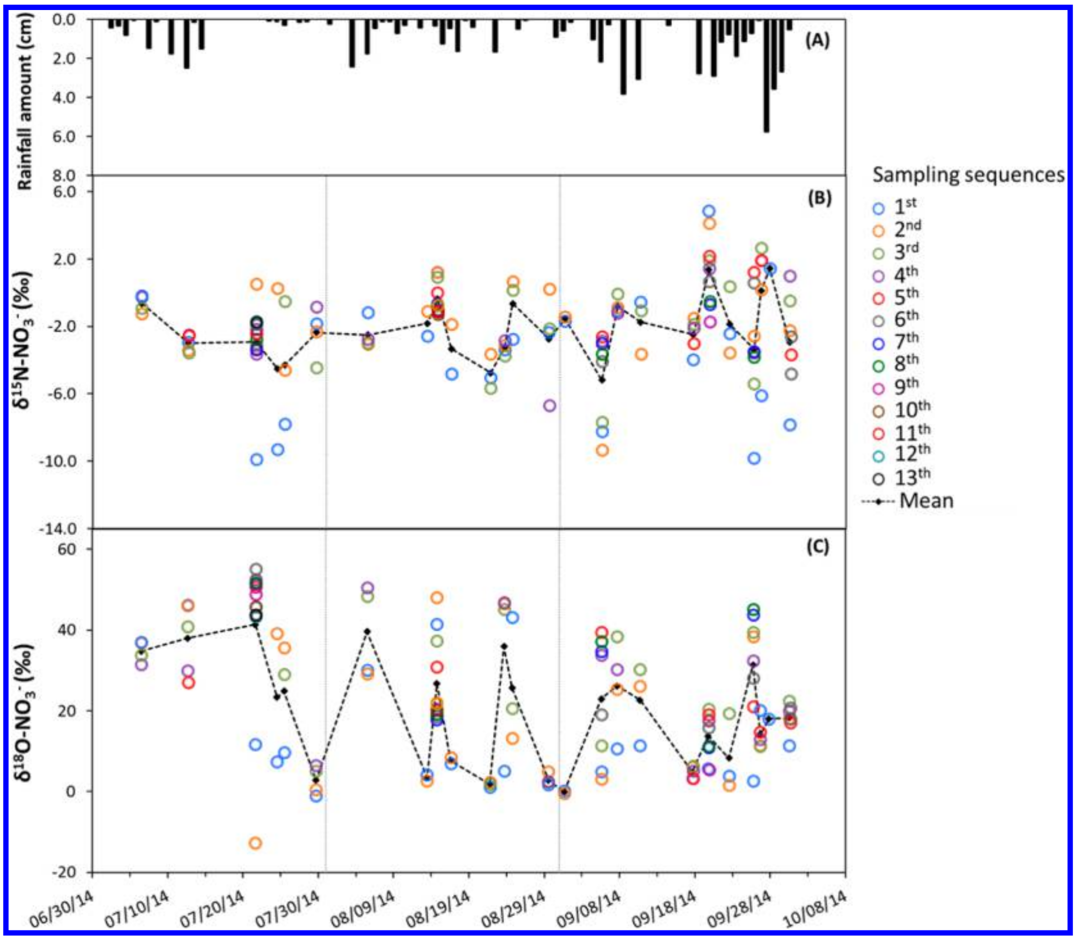

Figure 2. Temporal variability of (A) daily rainfall, (B) δ^{15}N-NO_3^-, and (C) δ^{18}O-NO_3^- in stormwater runoff (n = 121) from 25 events during July−September 2014. The colors of circles and labels indicate sampling sequences. The dashed line shows change of mean values from individual event.

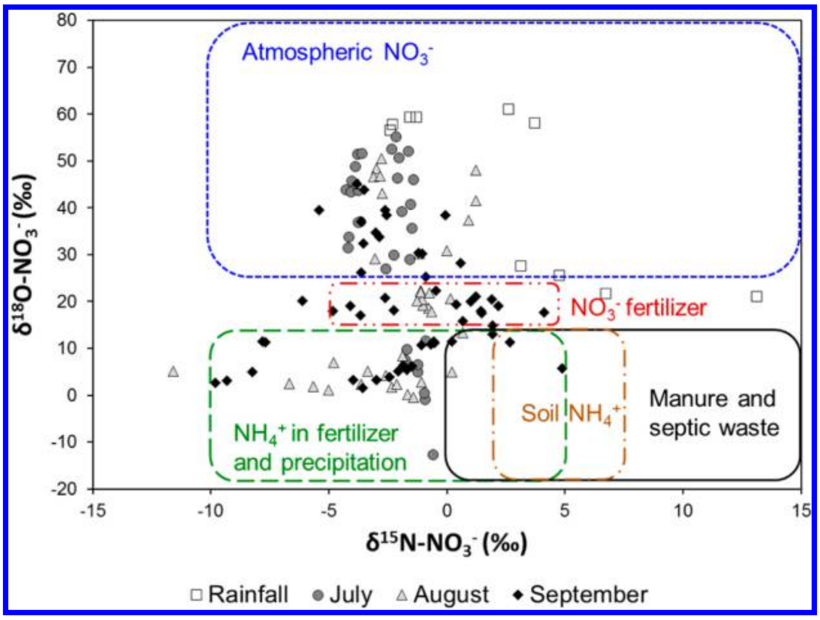

Figure 3. Dual δ^{15}N-NO_3^- and δ^{18}O-NO_3^- in rainfall and stormwater runoff during the wet season in 2014. Area shows the range of the δ^{15}N-NO_3^- and δ^{18}O-NO_3^- values from Kendall et al. (2007)[10]

(mean −24.0‰), respectively (SI Figure S3A). In the stormwater runoff samples (n = 121), δ^{18}O−H_2O and δD−H_2O varied from −8.3‰ to 0.8‰ (mean −2.6‰) and −50.1‰ to −12.1‰ (mean −12.1‰), respectively. Most of the δ^{18}O−H_2O and δD-H_2O of stormwater runoff samples (SI Figure S3A) were close to the global meteoric water line (GMWL), defined as δD−H_2O = 8δ^{18}O−H_2O + 10.[54] Further, the y-intercept (deuterium excess, d-excess = δD-H_2O−8δ^{18}O−

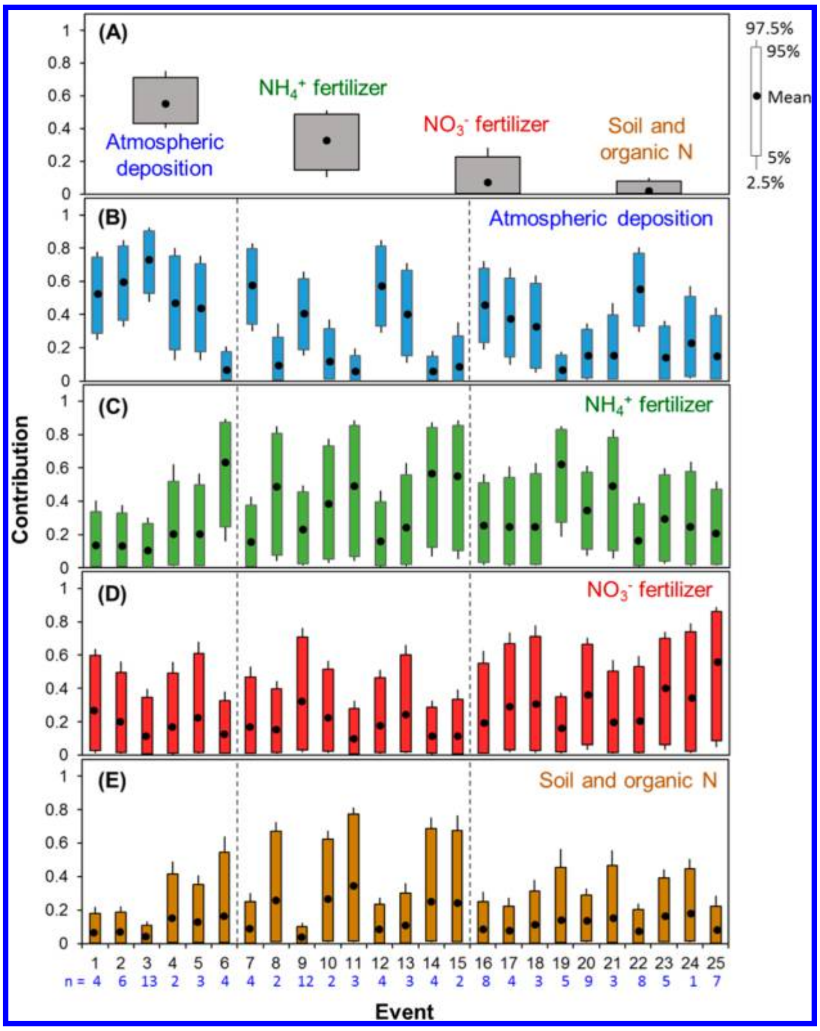

Figure 4. (A) Fractional contribution of different NO_3-N sources to stormwater runoff from 25 events (n = 121) based on Bayesian stable isotope mixing models, and Bayesian credible intervals for the probability distribution calculated for (B) atmospheric deposition, (C) NH_4^+ fertilizer, (D) NO_3^- fertilizer, and (E) soil and organic N sources. Events 1−6, 7−15, and 16−25 occurred in July, August, and September 2014, respectively. Numbers in blue represents total number of sequential 5 min samples collected during each event.

H_2O) was used a diagnostic tool to measure the contribution of evaporated moisture.[55] The mean *d*-excess value in our stormwater runoff samples were lower than GMWL (10‰), indicating enrichment due to the evaporation (SI Figure S3B). Some evaporation is expected in our residential catchment due to the higher temperature (23−29 °C) during study period and presence of 37% impervious area, which may have caused evaporation as water traveled over impervious areas to reach stormwater pond. Overall, our data indicated that all runoff water during 25 stormwater events originated from the local rainfall and evaporation slightly changed the isotopic composition. This suggests that no other sources of water (e.g., groundwater, municipal water, reclaimed water, leaking sanitary sewers) contributed any water and thus N in our stormwater runoff samples.

Source of Nitrate-Nitrogen in Urban Stormwater Runoff. The δ^{15}N-NO_3^- in rainfall (n = 10) and stormwater runoff (n = 121) varied from −2.4‰ to 13.1‰ (mean 2.7‰) and −11.5‰ to 4.9‰ (mean −2.2‰), respectively (Figure 2). There was a narrow range of δ^{15}N-NO_3^- in the runoff samples, with 65% of samples between −4‰ and 0‰. The δ^{18}O-NO_3^- in rainfall and stormwater runoff samples ranged from 21.0‰ to 61.0‰ (mean 44.8‰) and −12.8‰ to 55.2‰ (mean 22.6‰), respectively. Isotopic signatures of potential NO_3-N sources suggest that atmospheric deposition, chemical fertilizers, soil based N, and organic N sources contributed NO_3-N to stormwater runoff in our residential catchment (Figure 3). To estimate the potential contributions from each of these sources, we used a Bayesian mixing model to determine the different sources of NO_3-N during the wet season. The mixing model outputs revealed a high variability in contributions of the four potential NO_3-N sources over 25 stormwater events (Figure 4). In the below sections, we examine the isotopic signatures of different sources of NO_3-N in stormwater runoff based on mixing model results.

Atmospheric Deposition. The δ^{15}N-NO_3^- in the atmospheric deposition is reported to range from −15‰ to 15‰.[10,11] Atmospheric N is known to be enriched in δ^{18}O-NO_3^- due to the exchange of O atoms with ozone.[56] The pattern of δ^{18}O-NO_3^- is considered more useful than δ^{15}N-NO_3^- in identifying NO_3^- sources as there is a large variability in the δ^{18}O-NO_3^- among the different sources.[10] The highest δ^{18}O-NO_3^- values in stormwater runoff were >25‰, which indicated largest contribution from atmospheric N (Figure 3). In addition, high δ^{18}O-NO_3 values in the stormwater runoff samples with low NO_3-N concentrations were observed, suggesting the importance of atmospheric sources in stormwater runoff (SI Figure S4A). Based on the mixing model results, the contribution of NO_3-N from atmospheric deposition to stormwater runoff ranged from 43 to 71% (mean 56%) over 25 stormwater events (Figure 4 and SI Figure S5; Table S2), and observations of fractional contribution for individual samples within events ranged more widely from 1 to 90%. Overall, atmospheric deposition was an important source of NO_3-N in the stormwater runoff during the wet season. Our results are in agreement with previous studies.[2,14,18] For example, Anisfeld et al.[14] observed that atmospheric deposition contributed greater stream NO_3-N (∼50%) during stormflow in urbanized rivers of central New York. Kaushal et al.[2] reported that source contributions of NO_3-N changed with storm magnitude and atmospheric deposition accounting for ∼50% of NO_3-N during storms in Baltimore, Maryland. Earlier studies conducted by Ging et al.[57] and Silva et al.[58] in Austin, Texas also pointed out the importance of atmospheric deposition in urbanized stormflow due to the influence of runoff from impervious surfaces. In summary, these findings suggest that in urban systems, wet atmospheric deposition combined with accumulated dry atmospheric deposition and wash-off from impervious surfaces has the potential to enhance delivery of atmospheric N to waters during storm events.[2,59,60]

Inorganic Fertilizers. Research suggests that δ^{15}N-NO_3^- in the inorganic fertilizers range from −4‰ to 4‰.[10,11] The δ^{18}O-NO_3^- in NO_3^- fertilizers is 17−25‰, which overlaps with atmospheric values (ca. 23.5‰)[10] whereas NO_3^- derived from NH_4^+ fertilizers has lower δ^{18}O-NO_3^- values, usually in the range of −5 to 15‰.[10,11] The δ^{15}N-NO_3^- and δ^{18}O-NO_3^- values in our stormwater runoff samples were in the range of both NH_4^+ fertilizers and NO_3^- fertilizers. The mixing model results suggests that NH_4^+ fertilizers contributed 15−49% (mean 34%) and NO_3^- fertilizers contributed <1 to 23% (mean 8%) of NO_3-N in stormwater runoff over 25 stormwater sampling events (Figure 4 and SI Table S2). Chemical fertilizers as the sources of NO_3-N in urban watersheds have been investigated in previous studies.[2,20,61] For example, fertilizer was the main source of NO_3^- in stormwater runoff, contributing 44% NO_3^- loads in an urban watershed in Phoenix, Arizona.[20] However, a study conducted in an urban watershed in Baltimore, Maryland found fertilizer as a minor component of NO_3^- in stormwater runoff.[2] Lawn fertilizers can be an important source of N in residential catchments depending upon the frequency and quantity of fertilizer use and climatic factors such as high rainfall. Fertilizers are frequently used in Florida's urban neighborhoods due to the sandy texture of soils and subtropical climate (up to ∼60% rainfall occurs during wet season). The fertilizer N input to the residential areas in Hillsborough County (our study region) is estimated to be ∼105 kg/ha, with an average 2.5 applications in a year and 16−22% (18% on average) of fertilizer application during wet season.[50] In our study, we found that N fertilizers contributed ∼42% (on average) of NO_3-N to stormwater runoff during the wet season, which is due to the fertilizers use in the residential catchment and excess rainfall. We hypothesize that NO_3-N in the stormwater runoff might have originated due to the runoff of improper application and/or spillage of N fertilizers on the impervious areas.

Soil and Organic N. The δ^{15}N-NO_3^- values of organic sources of N such as sewage and animal waste generally have much wider range of compositions (2−30‰) than inorganic fertilizers due to their more diverse origins.[10,11] In general, the δ^{18}O-NO_3^- of NO_3-N derived from organic N sources range from −5 to 15‰ based on the literature values.[10] Our mixing model results suggested that <1 to 8% of NO_3-N in stormwater runoff originated from soil and organic N sources (Figure 4 and SI Table S2). It is important to consider the hydrologic connectivity of N sources with surface waters when estimating N sources in water bodies.[62] For example, septic systems have been suggested as major sources of NO_3^- in groundwater and connected surface waters.[6,63] Studies conducted in Baltimore, Maryland found that older leaking sewer systems were the source of NO_3^-.[2] There are no known sources of septic waste in our residential catchment due to the fact that all wastewater is piped and conveyed to a central wastewater treatment plant and there are no septic systems. Further, water isotope results showed that all stormwater runoff originated from the local rainfall, thus it is unlikely that sewer leaks contributed N in stormwater runoff. Another organic N source such as pet waste has been identified in urban catchments.[60,64] Thus, the organic N sources observed in the residential catchment may be derived from the pet waste. In addition, it is important to recognize that there can be multiple organic N sources in urban stormwater runoff as organic N is the dominant N form in urban water systems.[65,66] The estimated area of tree canopy and lawns in our residential catchment is 61% of total drainage area. Therefore, the mineralization of lawn grass clippings and tree leaves likely contribute NO_3-N in stormwater runoff. Research is needed to determine the contribution of organic N sources to NO_3-N in residential stormwater runoff.

Processes Controlling NO_3-N Transport. The isotopic composition of NO_3-N is influenced by nitrification and denitrification in soil. The values of δ^{18}O-NO_3^- can be used to identify the contribution of nitrification, as δ^{18}O-NO_3^- from −10‰ to 10‰ suggests in situ soil nitrification.[10] In theory, the δ^{18}O of NO_3-N produced by nitrification could be calculated using the O value (23.5‰) of the air and experimental O value of stormwater runoff samples using this formula: $\delta^{18}\text{O-NO}_3^- = 1/3\ \delta^{18}\text{O}-\text{O}_2 + 2/3\ \delta^{18}\text{O}-\text{H}_2\text{O}$.[10] Based on this calculation, the expected δ^{18}O-NO_3^- values in our stormwater runoff from nitrification ranged from 2.3‰ to 8.4‰, which suggests that in situ soil nitrification contributed a part of NO_3-N in stormwater runoff (SI Figure S6).

Denitrification is an important process in which bacteria utilize NO_3^- as an electron donor instead O_2 to reduce NO_3^- to N_2 or N_2O in the environment. Combined evaluation of N isotope data and NO_3-N concentrations was pursued to gain a better understanding of denitrification in our stormwater samples. If denitrification occurs, δ^{15}N-NO_3^- increase with decrease in NO_3-N concentrations and there is be 2:1 ratio between δ^{15}N-NO_3^- and δ^{18}O-NO_3^-.[10,67] None of these two conditions were present in our data, suggesting no denitrification in any of the stormwater runoff samples (see Figure 3 and SI Figure S4B).

In contrast, increasing δ^{15}N-NO_3^- values with increase in NO_3-N concentrations were observed in some stormwater runoff samples indicating mixing of NO_3-N from multiple sources (SI Figure S4B). Of 25 stormwater events, 13 events had N isotopic signatures that were dominated by atmospheric deposition (mean credible interval of feasible 33−73%), eight events were dominated by NH_4^+ fertilizer (mean 38 to 63%), and four events were dominated by NO_3-N fertilizer (mean 35 to 56%) (SI Table S2).

Fractional contribution of different NO_3-N sources to stormwater runoff during the wet season indicates that atmospheric deposition had more effect on NO_3-N in the beginning of the wet season (SI Figure S7), which decreased from July (55−88%) to August (32−65%) and September (18−55%). Meanwhile, chemical fertilizer (NH_4^+ fertilizer and NO_3-N fertilizer) showed an increasing contribution from July (1−32%) to August (1−57%) and September (1−59%). Higher contributions of atmospheric deposition in July can be due to the longer antecedent dry weather period prior to the beginning of wet season. It is not possible in this study to estimate the relative importance of wet and dry deposition due to the lack of dry deposition measurements. The increasing trend of sources of N fertilizers as season progressed could be due to the amount and duration of precipitation events as runoff of soil based N fertilizers from residential area to the stormwater runoff is more likely to occur during periods of high rainfall as compared to low rainfall where runoff will primarily occur from impervious areas. These findings are supported by previous research, which found that variation in isotope composition in urban waters is primarily result of mixing sources rather than biogeochemical processes during storm runoff events.[18,20,68]

Environmental Implications. Stormwater runoff from the residential catchments located in subtropics represents a unique scenario of N pollution in urban coastal water bodies. The different NO_3-N sources in residential catchments present a challenge for effectively mitigating N enrichment in urban waters. In this study, combining dual isotope source identification techniques with chemical analysis was used to elucidate the transport and sources of NO_3-N from a low-density residential catchment. Long-term studies in residential catchments of different landscape patterns, community stormwater systems, residential landscape, and resident behaviors are needed to better understand the contribution of urban residential catchments to N pollution in water bodies. Nevertheless, the results from the mixing model suggest that both atmospheric deposition and chemical fertilizers are important NO_3-N sources in urban stormwater runoff. Further, the transport of NO_3-N in the residential catchment was due to the mixing of sources and their changing contributions during the wet season. We are first to report and quantify the contribution of N fertilizers (average of 42%) to NO_3-N in urban stormwater runoff from a residential catchment. This data suggests that proper application of urban N fertilizers in residential areas dominated by turfgrass is important to reduce NO_3-N concentrations in stormwater runoff. This can be achieved by careful application of urban fertilizers on urban lawns and avoiding any accidental spillage on impervious areas that have the high potential for transport during stormwater events. In addition, the use of green infrastructure such as bioswales in residential neighborhoods to slow and direct runoff waters away from impervious areas may provide additional opportunities to remove NO_3-N contributed by atmospheric deposition, chemical fertilizers, and other sources before it reaches stormwater retention ponds and enters the hydrological network in urban watersheds.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b05353.

Detailed descriptions of Bayesian mixing models; Source of Water in Urban Stormwater Runoff; Table S1, S2 and Figures S1−S7 (PDF)

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Notes

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