Downpour dynamics: outsized impacts of storm events on unprocessed atmospheric nitrate export in an urban watershed

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Received: 17 February 2023 – Discussion started: 27 February 2023
Revised: 4 May 2023 – Accepted: 17 May 2023 – Published: 29 June 2023

Abstract. Water quality impacts of stream water nitrate ($\text{NO}_3^-$) on downstream ecosystems are largely determined by the load of $\text{NO}_3^-$ from the watershed to surface waters. The largest $\text{NO}_3^-$ loads often occur during storm events, but it is unclear how loads of different $\text{NO}_3^-$ sources change during storm events relative to baseflow or how watershed attributes might affect source export. To assess the role of storm flow and baseflow in $\text{NO}_3^-$ source export and how these roles are modulated by hydrologic effects of land-use practices, we measured nitrogen ($\delta^{15}\text{N}$) and oxygen ($\Delta^{17}\text{O}$) isotopes of $\text{NO}_3^-$ and oxygen isotopes ($\delta^{18}\text{O}$) of water in rainfall and stream water samples from before, during, and after eight storm events across 14 months in two Chesapeake Bay watersheds of contrasting land use. Storms had a disproportionately large influence on the export of unprocessed atmospheric $\text{NO}_3^-$ and a disproportionately small influence on the export of terrestrial $\text{NO}_3^-$ relative to baseflow in the developed urban watershed. In contrast, baseflow and storm flow had similar influences on $\text{NO}_3^-$ export in the mixed agricultural–forested watershed. An equivalent relationship between $\text{NO}_3^-$ deposition on impervious surfaces and event $\text{NO}_3^-$ stream water export in the urban watershed suggests that impervious surfaces that hydrologically connect runoff to channels likely facilitate the export of $\text{NO}_3^-$ during rainfall events. Additionally, larger rainfall events were more effective at exporting $\text{NO}_3^-$ in the urban watershed, with increased rainfall depth resulting in a greater fraction of event $\text{NO}_3^-$ deposition exported. Considering both projected increases in precipitation amounts and intensity and urban/suburban sprawl in many regions of the world, best management practices that reduce the hydrologic connectivity of impervious surfaces will likely help to mitigate the impact of storm events on $\text{NO}_3^-$ export from developed watersheds.

1 Introduction

Increasing stream water nitrate ($\text{NO}_3^-$) export over the past century has negatively impacted many downstream ecosystems globally (Kemp et al., 2005; Camargo and Alonso, 2006; Steffen et al., 2015; Stevens, 2019). The severity of impacts on receiving waters is partially determined by the magnitude of $\text{NO}_3^-$ loads (i.e., the product of concentration and discharge; National Research Council, 2000). As such, riverine $\text{NO}_3^-$ loads are greatest during periods of high discharge, which often follow large precipitation events, and can therefore have an outsized impact on annual stream water $\text{NO}_3^-$ loads (Vaughan et al., 2017; Kincaid et al., 2020). Sources of $\text{NO}_3^-$ comprising storm event loads can be variable and associated with changing hydrologic flow paths during precipitation events (Buda and DeWalle, 2009). Exported loads of individual $\text{NO}_3^-$ sources (e.g., atmospheric $\text{NO}_3^-$) are less often quantified during storm events than routine baseflow samples, however (Divers et al., 2014; Sabo et al., 2016). Thus, it is not clear whether storm events have a disproportionate impact relative to non-storm (i.e., baseflow) conditions on different $\text{NO}_3^-$ sources. The impact of storm events relative to baseflow on sources of stream water $\text{NO}_3^-$ is particularly relevant given the increases in precipitation amount and intensity projected to be associated with future climate change (Walsh et al., 2014).
Precipitation can affect the amount and source of NO$_3^-$ exported in surface waters via the surface-to-stream flow path. During storms, NO$_3^-$ can be transported to streams by either overland or subsurface pathways. Overland flow is associated with NO$_3^-$ sources deposited or present on the land surface, such as unprocessed atmospheric NO$_3^-$ (NO$_3^-$ Atm; Rose et al., 2015a). Subsurface flow is associated with NO$_3^-$ sources abundant in soils and groundwater, such as fertilizer, microbial, and/or sewage (Cook and Herczeg, 2012). Both hydrologic flow paths (and the respective NO$_3^-$ sources) can be affected by human land-use activities (Paul and Meyer, 2001; Barnes and Raymond, 2010; Jarvis, 2020). For example, previous studies report that developed watersheds export relatively more NO$_3^-$ Atm than less developed watersheds, presumably due to hydrologic changes created by impervious surfaces (Buda and DeWalle, 2009; Burns et al., 2009; Kaushal et al., 2011; Bostic et al., 2021). However, evidence is lacking for (1) the mechanism generating increased NO$_3^-$ Atm export in developed watersheds and (2) quantitative impacts of storm event loads relative to baseflow, both of which could be useful for mitigating the effects of storms on stream water NO$_3^-$ export.

The stable isotope compositions of NO$_3^-$ and water (H$_2$O) are powerful tools for distinguishing NO$_3^-$ sources and hydrologic flow paths, respectively. For example, the oxygen isotope values ($\Delta^{17}$O) of NO$_3^-$ allow for the quantification of atmospheric and terrestrial sources of NO$_3^-$ in stream water (Michalski et al., 2003), and $\delta^{15}$N and $\delta^{18}$O values of NO$_3^-$ permit inferences into the relative contributions of terrestrially sourced NO$_3^-$ (NO$_3^-$ Terr), such as fertilizer or sewage N (Kendall et al., 2007). Additionally, $\delta^{18}$O values of H$_2$O can be used to assess the importance of overland versus subsurface flow through the partitioning of streamflow into pre-event and event contributions (Sklash et al., 1976; McGuire and McDonnell, 2007). Few studies have coupled these isotopic tracers (Buda and DeWalle, 2009), however, despite their suitability for assessing the effect of storm events on both hydrologic flow paths and the export of different NO$_3^-$ sources. Such information could provide mechanistic evidence for the commonly reported relationship between developed watersheds and NO$_3^-$ Atm export.

Here we address the following research questions: how do storm events affect the total amount and sources of NO$_3^-$ exported in streams relative to baseflow? More specifically, what is the relationship between hydrologic and biogeochemical effects of land use and the export of unprocessed atmospheric NO$_3^-$ (NO$_3^-$ Atm) and terrestrial NO$_3^-$ (NO$_3^-$ Terr) during storm events and baseflow? These questions were addressed in two Chesapeake Bay watersheds of contrasting land use. A two-watershed study is inherently comparative, potentially limiting the inferences that can be made regarding land-use effects. However, given the contrasting land uses (i.e., predominantly developed compared to mixed forest/agriculture) in these watersheds, we believe that this study can adequately address our research questions while presenting a "proof of concept" for future studies. To address these research questions, we collected moderate-frequency (45 min–12 h) stream water samples before, during, and after eight rainfall events, bulk rainfall samples corresponding to these events, and monthly baseflow samples in two catchments within the broader Chesapeake Bay watershed. We then used $\delta^{15}$N, $\delta^{18}$O, and $\Delta^{17}$O of NO$_3^-$ and $\delta^{18}$O of H$_2$O to determine NO$_3^-$ sources and hydrologic flow paths, respectively. The Chesapeake Bay region is ideal for our study: it is one of the most ecologically and economically important estuaries in the world (NOAA, 1990) that has experienced recent improvements in ecosystem health associated with declining N loads (Chanat et al., 2016; Lefcheck et al., 2018; Zhang et al., 2018), but uncertainty surrounds continued water quality improvements, in part due to the effects of projected increases in precipitation intensity across its diverse land-use watershed (Najjar et al., 2010).

2 Materials and methods

2.1 Study watersheds and field methods

To assess NO$_3^-$ export dynamics during storm events, stream water and rainfall samples were collected synchronously during eight events from two watersheds with outlets in Maryland, USA – Gwynns Falls at Villa Nova (GWN) and Gunpowder Falls at Glencoe (GUN) (Fig. 1) – from September 2018 to October 2019. These watersheds have similar geology (Piedmont physiographic province; Fenneman, 1946) and climate (humid subtropical; Kottek et al., 2006) but differing land use (one predominantly developed and the other mixed forest and agriculture), impervious surface coverage (Fig. S1 in the Supplement), and area (Table 1). Events were targeted based on forecast precipitation amounts of at least
2.2 Laboratory methods

Stream water and rainfall samples for NO$_3^-$ concentration and isotope analyses were filtered (0.45 µm) and frozen within 48 h of collection. Aliquots for water isotope measurements were stored in completely filled (i.e., no headspace) 20 mL bottles at room temperature prior to analysis. NO$_3^-$ and nitrite (NO$_2^-$) concentrations were measured using flow-injection colorimetric analysis (Lachat Quikchem 8000 FIA+).

The $\Delta$$^{17}$O, $\delta^{18}$O, and $\delta^{15}$N values of stream and rainfall NO$_3^-$ were measured using a Thermo Delta V+ isotope ratio mass spectrometer (Bremen, Germany) via the denitrifier method (Sigman et al., 2001; Casciotti et al., 2002) with thermal decomposition (at 800 °C) of N$_2$O to N$_2$ and O$_2$ (Kaiser et al., 2007) at the Central Appalachians Stable Isotope Facility. NO$_2^-$ was denitrified using this method as well, but NO$_2^-$ concentrations in stream and rainfall samples were low relative to NO$_3^-$ (NO$_2$/ (NO$_2^-$ + NO$_3^-$) mean = 0.006, range = 0.00–0.027). Measured isotope ratios were normalized using international reference standards USGS 34 ($\delta^{17}$O = −14.8 ‰; $\delta^{18}$O = −27.9 ‰) and USGS 35 ($\delta^{17}$O = 51.5 ‰; $\delta^{18}$O = 57.5 ‰) for O isotopes (Böhlke et al., 2003) and USGS 32 ($\delta^{15}$N = 180 ‰) and USGS 34 ($\delta^{15}$N = −1.8 ‰) for N isotopes (IAEA, 1995). Reference standards were measured throughout sample analysis in equal concentrations to samples (ranging from 100 to 200 nmol depending on the sample NO$_3^-$ concentration). The analytical precision of $\Delta$$^{17}$O ($\Delta$$^{17}$O ≈ $\delta^{17}$O-0.52 × $\delta^{18}$O) was estimated as 0.5 ‰, $\delta^{18}$O as 1.4 ‰ and $\delta^{15}$N as 1.8 ‰ (1σ), based on repeated measurements ($n \geq 200$) of reference standards USGS 32 and USGS 35 and a laboratory reference standard “Chile NO$_3^-$” (Duda Energy 1sn 1 lb. Sodium Nitrate Fertilizer 99 + % Pure Chile Saltpeter). Accuracies of $\Delta$$^{17}$O, $\delta^{18}$O, and $\delta^{15}$N were tracked using repeated measurements of IAEA-N3 ($n = 19$; mean $\Delta$$^{17}$O = −0.1 ‰; $\delta^{18}$O = 24.3 ‰; $\delta^{15}$N = 4.5 ‰) and closely agreed with published values (IAEA, 1995; Michalski et al., 2002; Böhlke et al., 2003). Each stream water and rainfall sample was measured three to six times to reduce analytical uncertainty, and the mean of each sample was used in all analyses. The standard error of the mean ranged from 0.1 ‰–0.6 ‰, 0.1 ‰–1.6 ‰, and 0.1 ‰–1.6 ‰ for replicate measurements of $\Delta$$^{17}$O, $\delta^{18}$O, and $\delta^{15}$N, respectively.

Oxygen ($\delta^{18}$O-H$_2$O) isotopes of rainfall and stream water were measured using Picarro L2130-i via cavity ring-down spectroscopy at the University of Wyoming’s Stable Isotope Facility. Measured isotope ratios were normalized to Vienna Standard Mean Ocean Water using internal laboratory standards that were calibrated to international standards. The precision based on repeated measurements of internal standards was 0.2 ‰.

2.3 Quantification of atmospheric NO$_3^-$ deposition

Event NO$_3^-$ deposition was quantified using the measured rainfall NO$_3^-$ concentration and mean rainfall depth (Lovett et al., 2019).
of each individual grab sample collected during a particular event. We compared these estimated loads with the “true” load (calculated using Eq. 5) and calculated bias as the difference between the true load and loads estimated using a single sample and daily average discharge. Because traditional methods commonly use mean daily discharge, we only investigated bias for two events that included samples collected over 1 full day. We also calculated the event fraction of unprocessed atmospheric NO$_3^-$ ($f_{Atm}$) using $\Delta^{17}O$ (Eq. 2) and $\delta^{18}O$ (substituting $\delta^{18}O$ for $\Delta^{17}O$ in Eq. (2) and assuming that baseflow samples for a corresponding storm represent the terrestrial NO$_3^-$ end-member $\delta^{18}O$ value).

Event mean concentrations (EMCs) of NO$_3^{–}$Total and NO$_3^{–}$Atm and event mean values (EMVs) of $\Delta^{17}O$, $\delta^{18}O$, and $\delta^{15}N$ were calculated as

$$EMC, EMV = \frac{\sum_{i=1}^{n} (C_i \times V_i)}{\sum_{i=1}^{n} V_i},$$  

where EMC is the event mean concentration (mg N L$^{-1}$, NO$_3^{–}$Total and NO$_3^{–}$Atm), EMV is the event mean value (‰, $\Delta^{17}O$, $\delta^{18}O$, and $\delta^{15}N$), $C_i$ is either the concentration of NO$_3^{–}$Total or NO$_3^{–}$Atm (mg N L$^{-1}$) or the value of $\Delta^{17}O$, $\delta^{18}O$, or $\delta^{15}N$ (‰) corresponding to sample $i$, and $V_i$ is the volume of water exported corresponding to sample $i$ (L).

Monthly loads of NO$_3^{–}$Total were estimated using Weighted Regressions on Time, Discharge, and Season Kalman Filter (WRTDS-K; Zhang and Hirsch, 2019). Regressions were calibrated using the entire period of record for NO$_3^{–}$ (excluding our storm samples) to generate coefficients representing a greater range of hydroclimatological conditions than was realized in 13 months. NO$_3^{–}$ concentration data for the entire period of record were obtained from the Chesapeake Bay Program water quality database (Chesapeake Bay Program, 2021). Our storm samples were excluded to generate similar estimates of monthly and annual loads used by monitoring agencies (e.g., Maryland Department of Natural Resources, US Environmental Protection Agency) in these watersheds. Monthly yields (g N ha$^{-1}$) were calculated by dividing monthly loads by watershed area, and monthly flow-weighted concentrations (mg N L$^{-1}$) were calculated by dividing monthly loads by monthly discharge. The uncertainty of NO$_3^{–}$Total was estimated using block bootstrapping methods for WRTDS-K (Zhang and Hirsch, 2019) and was propagated through all analyses using NO$_3^{–}$Total loads and/or yields.

Biogeosciences, 20, 2485–2498, 2023  
https://doi.org/10.5194/bg-20-2485-2023
The fraction of rainfall NO$_3^-$ exported on an event basis was calculated as

\[
\text{fraction of rainfall NO}_3^-\text{exported} = \frac{\text{NO}_3^-_{\text{Atm,yield}} (\text{g N ha}^{-1})}{\text{NO}_3^-_{\text{Atm,deposition}} (\text{g N ha}^{-1})},
\]

(7)

where event NO$_3^-$ deposition was calculated using Eq. (1) and event NO$_3^-$ yield was calculated using Eq. (5).

2.6 Terrestrial $\delta^{18}$O and $\delta^{15}$N calculation

Stream water storm samples of $\delta^{18}$O and $\delta^{15}$N were corrected to remove the influence of NO$_3^-$ deposition (Dejwakh et al., 2012), which has higher $\delta^{18}$O values and can have lower $\delta^{15}$N values than terrestrial NO$_3^-$ (Elliott et al., 2007; Kendall et al., 2007). This was done to more carefully infer how terrestrial sources of NO$_3^-$ might change during storm events, and it uses the following equations:

\[
\delta^{15}\text{N}_{\text{Terr}} = \frac{(\delta^{15}\text{N}_{\text{Stream}} - \delta^{15}\text{N}_{\text{Atm}}) \times f_{\text{Atm}}}{f_{\text{terr}}},
\]

(8)

\[
\delta^{18}\text{O}_{\text{Terr}} = \frac{(\delta^{18}\text{O}_{\text{Stream}} - \delta^{18}\text{O}_{\text{Atm}}) \times f_{\text{Atm}}}{f_{\text{terr}}},
\]

(9)

where $\delta^{15}\text{N}/\delta^{18}\text{O}_{\text{Stream}}$ is measured $\delta^{15}\text{N}$ or $\delta^{18}\text{O}$ of stream water storm samples, $\delta^{15}\text{N}/\delta^{18}\text{O}_{\text{Atm}}$ is rainfall $\delta^{15}\text{N}$ or $\delta^{18}\text{O}$ for a given event, $f_{\text{Atm}}$ is the fraction of NO$_3^-$ Atm as calculated using Eq. (2), and $f_{\text{terr}} = 1 - f_{\text{Atm}}$.

2.7 Hydrograph separation

Water isotopes were used to quantify the proportion of event and pre-event water during storm events at or near peak discharge. The direct routing, or translation of rainfall to stream water during the same event, was quantified as the event-water fraction (i.e., rainfall), whereas water present in the catchment prior to the storm event was classified as the pre-event-water fraction (i.e., baseflow) using the following equations (Sklash et al., 1976):

\[
f_{\text{Event Water}} + f_{\text{Pre-Event Water}} = 1,
\]

(10)

\[
f_{\text{Event Water}} = \frac{\delta^{18}\text{O}_{\text{Peak Q}} - \delta^{18}\text{O}_{\text{Baseflow}}}{\delta^{18}\text{O}_{\text{Precipitation}} - \delta^{18}\text{O}_{\text{Baseflow}}},
\]

(11)

where $\delta^{18}\text{O}_{\text{Peak Q}} = \delta^{18}\text{O}_{\text{H}_2\text{O}}$ at or near peak discharge during storm events, $\delta^{18}\text{O}_{\text{Baseflow}} = \delta^{18}\text{O}_{\text{H}_2\text{O}}$ of stream water just prior to storm event and hydrograph rise, and $\delta^{18}\text{O}_{\text{Rainfall}} = \delta^{18}\text{O}_{\text{H}_2\text{O}}$ of bulk rainfall samples during a given storm event. Event and pre-event-water runoff can be quantified using these equations by multiplying runoff during peak storm flow by fractions of event and pre-event water. Uncertainty was estimated using published methods to account for analytical uncertainty and separation, or lack thereof, of end-members (Genereux, 1998). It has been shown that some of the assumptions of isotope-based hydrograph separation may be violated in mesoscale catchments (e.g., spatiotemporally constant end-member values; Klaus and McDonnell, 2013), and thus we estimate event-water fractions and runoff for peak discharge only and apply these data cautiously.

2.8 Framework for interpreting baseflow and storm flow contributions

The importance of storm events relative to baseflow in stream water NO$_3^-$ export can be evaluated using a fractional export plot (Fig. 2). In this plot the $y$ axis shows the fraction of annual nitrate loads exported during a single event ($f_{\text{NO}_3}$), and the $x$ axis shows the fraction of annual discharge exported during a single event ($f_{\text{Runoff}}$). For example, if NO$_3^-$ concentrations remain constant with changing discharge during a storm, the data would fall on the 1 : 1 line because their load is perfectly explained by discharge and both storm events and baseflow have an equal impact on loads (Fig. 2). If NO$_3^-$ concentrations decrease with increasing discharge during a storm, the data would plot below the 1 : 1 line. Watersheds with events consistently plotting below the 1 : 1 line indicate that baseflow, relative to storm events, has an outsized impact on riverine NO$_3^-$ loads. If NO$_3^-$ concentrations increase with increasing discharge, the data would plot above the 1 : 1 line. Watersheds with events consistently plotting above the 1 : 1 line indicate that storm events have an outsized impact on riverine NO$_3^-$ loads. This framework can be expanded fur-
ther by quantifying the (potential) disproportionate effect of storm events on stream water constituent loads relative to water yields. Dividing \( f_{\text{NO}_3} \) by \( f_{\text{Runoff}} \) provides a single value to quantify the level of disproportionality:

\[
\text{disproportionality factor (DF)} = \frac{f_{\text{NO}_3}}{f_{\text{Runoff}}}. \tag{12}
\]

DF can be interpreted using Fig. 2: a value falling on the 1:1 line would have DF = 1, a value below the 1:1 line would have DF < 1, and a value above the 1:1 line would have DF > 1. For example, an event with DF = 4 indicates that a given storm exported 4 times more \( \text{NO}_3^- \) than water, whereas an event with DF = 0.5 indicates that a storm exported 2 times less \( \text{NO}_3^- \) than water after both have been normalized to annual amounts.

2.9 Statistical analyses

All statistical tests were performed in R (R Development Core Team, 2019). A Wilcoxon ranked-sum test was used to compare the EMC and EMV of paired stream water storm and baseflow samples. Due to the presence of outliers, Theil–Sen slopes (calculated using the senth function in R) were used to assess relationships between most continuous variables (Helsel et al., 2020). Least-squares linear regression was used when outliers were absent. Confidence intervals (95%) and p values of Theil–Sen slopes were computed using bootstrapping (10,000 replicates) to incorporate uncertainty into DF and event-water fractions.

3 Results

Rainfall depth and chemistry (\( \text{NO}_3^- \) concentrations and isotopes, \( \text{H}_2\text{O} \) isotopes) were similar between watersheds for sampled events (\( p > 0.1 \), Table S1 in the Supplement). Rainfall depths ranged from 1.90 to 8.10 cm, which corresponds to a range of 24 h precipitation depth return intervals of < 1 year (1-year return interval \( \approx 6.75 \) cm) up to 2 years (2-year return interval \( \approx 8.3 \) cm) in this region (Bonnin et al., 2004). Rainfall \( \text{NO}_3^- \) concentrations ranged from 0.05 to 0.26 mg N L\(^{-1} \), \( \delta^{15}\text{N-NO}_3^- \) from -8.7%e to -1.4%e, \( \delta^{18}\text{O-NO}_3^- \) from 48.0%e to 69.6%e, and \( \Delta^{17}\text{O-NO}_3^- \) from 13.6%e to 24.9%e. Streamflow was slightly more variable in GWN during storm events (Table S2): event mean runoff and event maximum runoff were higher in GWN (\( p < 0.05 \) and \( p < 0.01 \), respectively), but event median runoff was not different between the watersheds (\( p = 0.11 \)). Across all flow conditions, \( \text{NO}_3^- \) concentrations were lower at GWN (median = 0.78 mg N L\(^{-1} \)) than GUN (median = 2.60 mg N L\(^{-1} \)). Baseflow \( \text{NO}_3^- \) concentrations were higher than storm flow \( \text{NO}_3^- \) EMCs in both watersheds, but differences were more pronounced at GWN (baseflow median = 1.79 mg N L\(^{-1} \), storm median = 0.66 mg N L\(^{-1} \), \( p < 0.05 \)) than GUN (baseflow median = 3.06 mg N L\(^{-1} \), storm median = 2.55 mg N L\(^{-1} \), \( p < 0.05 \), Fig. 3 and Table S3).

At GWN, values of \( \delta^{15}\text{N} \) were higher in baseflow (median \( \delta^{15}\text{N} = 7.6 \%) \) than storm flow (EMV median \( \delta^{15}\text{N} = 5.0 \%) \), respectively, \( p < 0.05 \)), whereas values of \( \delta^{18}\text{O-NO}_3^- \) were lower in baseflow (median \( \delta^{18}\text{O} = 3.9 \%) \) than storm flow (EMV median \( \delta^{18}\text{O} = 7.4 \%) \), \( p < 0.05 \). In contrast, values of \( \delta^{15}\text{N} \) and \( \delta^{18}\text{O-NO}_3^- \) did not differ between baseflow and storm flow at GUN (baseflow median \( \delta^{15}\text{N} = 6.2 \%) \), \( \delta^{18}\text{O} = 3.3 \%) \); storm flow EMV median \( \delta^{15}\text{N} = 6.1 \%) \), \( \delta^{18}\text{O} = 3.0 \%) \), Fig. 3 and Table S3). Values of \( \delta^{18}\text{O-NO}_3^\text{Terr} \) were higher during baseflow at both sites (\( p < 0.05 \), Fig. 3), whereas \( \delta^{15}\text{N-NO}_3^\text{Terr} \) was higher during baseflow at GWN only (\( p < 0.05 \), Fig. 3). Similarly, \( \Delta^{17}\text{O} \) was not significantly different between baseflow (median = 0.4%e) and storm flow (EMV median = 0.5%e) at GUN but was lower during baseflow (median = 0.7%e) than storm flow (EMV median = 2.0%e) \( p < 0.05 \), Fig. 3 and Table S3) at GWN.

Concentrations of \( \text{NO}_3^\text{Terr} \) were more temporally variable than \( \text{NO}_3^\text{Atm} \). Concentrations of \( \text{NO}_3^\text{Terr} \) showed similar patterns to \( \text{NO}_3^\text{Total} \) at both watersheds: higher during baseflow than storm events (GWN baseflow median = 1.72 mg N L\(^{-1} \), storm flow median = 0.59 mg N L\(^{-1} \); \( p < 0.001 \), GUN baseflow median = 3.03 mg N L\(^{-1} \); storm flow median = 2.50 mg N L\(^{-1} \); \( p < 0.005 \), Fig. S3). Both GWN and GUN had similar \( \text{NO}_3^\text{Atm} \) concentrations between baseflow and storm events (GWN baseflow median = 0.05 mg N L\(^{-1} \); storm flow median = 0.06 mg N L\(^{-1} \); \( p > 0.05 \); GUN baseflow median = 0.04 mg N L\(^{-1} \); storm flow median = 0.06 mg N L\(^{-1} \); \( p > 0.05 \), Fig. S3).

Similar to \( \text{NO}_3^- \) concentrations and isotopes, \( \delta^{18}\text{O-H}_2\text{O} \) values exhibited greater variability between baseflow and peak streamflow in GWN than in GUN. From baseflow to approximately peak streamflow, \( \delta^{18}\text{O-H}_2\text{O} \) shifted by an absolute average of 2.1%e at GWN but only 0.6%e at GUN (Table S2). These shifts correspond to average event-water fractions at peak storm discharge of 0.75 ± 0.13 at GWN and 0.27 ± 0.23 at GUN (Table S2). Event-water fraction uncertainty was relatively large for several events due to small separation between \( \delta^{18}\text{O-H}_2\text{O} \) end-members. For example, rainfall and pre-event baseflow end-members were separated by only 0.5%e during the 22 July 2019 event at GUN, resulting in uncertainty of event-water fractions exceeding 1 (Tables S1 and S2).

Storm events have an outsized impact, relative to baseflow, on \( \text{NO}_3^\text{Terr} \) export at GWN, as indicated by DF > 1 for seven of eight sampled events (mean = 2.6 ± 0.4; Fig. 2). The opposite relationship was observed for \( \text{NO}_3^\text{Terr} \) export at GWN (DF ≤ 1 for all sampled events, mean = 0.5 ± 0.1), indicating that baseflow has an outsized impact on \( \text{NO}_3^\text{Terr} \) loads relative to storm events. Conversely, DF values at GUN were approximately 1 for both \( \text{NO}_3^\text{Atm} \) (mean = 1.1 ± 0.2) and \( \text{NO}_3^\text{Terr} \) (mean = 1.0 ± 0.1), indicating that neither baseflow nor storm flow disproportionately impacted stream \( \text{NO}_3^- \) loads (Fig. 2). Event-water fractions were positively, though not significantly, related to the DF of \( \text{NO}_3^\text{Atm} \) (\( r = 0.32, p = 0.09 \)) and negatively related to the DF of \( \text{NO}_3^\text{Terr} \) across

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https://doi.org/10.5194/bg-20-2485-2023
Figure 3. Event mean NO$_3^-$ concentrations and $\delta^{15}$N, $\delta^{15}$N$_{Terr}$, $\delta^{18}$O, $\delta^{18}$O$_{Terr}$, and $\Delta^{17}$O values of NO$_3^-$ for samples collected during storm events paired with the corresponding baseflow sample preceding the event. An asterisk (*) indicates a significant difference at $p < 0.05$ as determined using a Wilcoxon ranked-sum test.

4 Discussion

Hydrologic effects of impervious surfaces likely drive the disproportionate impact of storm events on NO$_3^-$ atms and...
of baseflow on NO$_3$$_{\text{Terr}}$ in the more developed watershed (GWN). Impervious surfaces increase peak storm runoff (Arnold and Gibbons, 1996; Walsh et al., 2005), but differences in peak discharge alone are not the sole explanation for the contrasting results of DF for NO$_3$$_{\text{Terr}}$ and NO$_3$$_{\text{Atm}}$ between the watersheds. Sampled events with overlapping $f_{\text{runoff}}$ between sites (i.e., similar x-axis values in Fig. 2) indicate that the difference between $f_{\text{NO}_3}$ for NO$_3$$_{\text{Terr}}$ and NO$_3$$_{\text{Atm}}$ is much greater at the more developed (GWN) than less developed watershed (GUN, i.e., different y-axis values in Fig. 2). Thus, it is the overland routing of rainfall, and NO$_3$$_{\text{Atm}}$, dissolved therein, that likely contributes to the outsized impact of storm events on NO$_3$$_{\text{Atm}}$ in the developed watershed. Although both watersheds show a positive relationship between event-water fractions and DF of NO$_3$$_{\text{Atm}}$ ($p = 0.09$, Fig. 4), event-water fractions are much greater in the more developed watershed, GWN (green triangles in Fig. 4). Higher event-water fractions promote greater export of NO$_3$$_{\text{Atm}}$ by reducing the potential for biological processing or retention. Our results provide evidence (i.e., increased event-water fractions, proportional stream water export of impervious NO$_3$$_{\text{Atm}}$(deposition) for the mechanism (i.e., direct routing of rainfall NO$_3$$_{\text{Atm}}$ to streams) that generates increased NO$_3$$_{\text{Atm}}$ export in more developed watersheds, which thus expands on previous research demonstrating that more developed watersheds export relatively more NO$_3$$_{\text{Atm}}$(Buda and DeWalle, 2009; Burns et al., 2009; Kaushal et al., 2011; Bostic et al., 2021).

Our study collected samples across the storm hydrograph and measured $\Delta^{17}$O of NO$_3$ which provided more accurate load estimates of, and insights into, storm NO$_3$$_{\text{Atm}}$ export than $\delta^{18}$O of NO$_3$. For example, estimates of daily NO$_3$$_{\text{Atm}}$ loads were biased by a median absolute value of 36 % using standard methods (i.e., daily average discharge multiplied by NO$_3$$_{\text{Atm}}$ concentration, estimated using $\Delta^{17}$O, of a single grab sample; Tsunogai et al., 2014; Rose et al., 2015; Nakagawa et al., 2018) when compared to true daily loads calculated using samples collected across the storm hydrograph from two events that encompassed a full day. Additionally, use of $\Delta^{17}$O generally provides more certain estimates of NO$_3$$_{\text{Atm}}$ fractions and concentrations than $\delta^{18}$O because biological processing (e.g., assimilation, denitrification) can change $\delta^{18}$O of NO$_3$ and generate large uncertainty ($\pm$30%o, Kendall et al., 2007) in the $\delta^{18}$O-NO$_3$ end-member and ultimately estimates of NO$_3$$_{\text{Atm}}$(Tsunogai et al., 2016). $\Delta^{17}$O of NO$_3$, due to its mass-independent fractionation origin, is not subject to the same variability associated with biological processing as $\delta^{18}$O, thereby decreasing uncertainty in NO$_3$$_{\text{Atm}}$ estimates (Young et al., 2002; Michalski et al., 2004; Kendall et al., 2007). Indeed, average event NO$_3$$_{\text{Atm}}$ fractions (i.e., NO$_3$$_{\text{Atm}}$/NO$_3$$_{\text{Total}}$) would have been underestimated by an average of 3 % (range = 0 %–7 %) at both sites when using $\delta^{18}$O-NO$_3$ only (Fig. S4) but with a greater effect at the more developed site (GWN). An average underestimate of 3 % may appear minor, but it is notable considering that event NO$_3$$_{\text{Atm}}$ fractions averaged 2 % and 10 % in the less and more developed watersheds, respectively. Increased accuracy of NO$_3$$_{\text{Atm}}$ export during storm events combined with the DF conceptual framework (Fig. 2) provides a relatively simple means of assessing whether storm events or baseflow have an outsized impact on NO$_3$ source export. More accurate estimates of NO$_3$$_{\text{Atm}}$ export also allow for more quantitative investigations into the role of impervious surfaces in routing event rainfall NO$_3$$_{\text{Atm}}$ to streams.

Impervious areas in the developed watershed are effective conduits of NO$_3$$_{\text{Atm}}$ to surface waters, as demonstrated by
the approximately proportional relationship between event stream water NO$_3^{-}$Atn export and event NO$_3^{-}$Atn deposition on impervious surfaces (Fig. 6). This relationship provides evidence, in addition to higher event-water fractions (Fig. 4), for the mechanism of impervious surfaces enhancing the export of NO$_3^{-}$Atn during storm events. The 1:1 correspondence of this relationship is surprising, however. For 100% of rainfall NO$_3^{-}$Atn on impervious surfaces to be exported as stream water during a given event (i.e., a 1:1 relationship), all impervious areas in the watershed would have to be hydrologically connected to surface waters (i.e., effective impervious areas; Shuster et al., 2005). In a mesoscale (84 km$^2$) and heterogeneous watershed such as GWN, the total impervious area is not equivalent to the effective impervious area. Rather, many impervious surfaces drain onto pervious surfaces or are “ineffective” at directly routing precipitation to channels (Walesh, 1989), but we note that certain pervious surfaces, such as reclaimed mine lands, effectively function as impervious (Negley and Eshleman, 2006). It is likely that the observed 1:1 relationship (Fig. 6) is additionally affected by flushing of dry NO$_3^{-}$Atn deposition from effective impervious areas. Dry NO$_3^{-}$ deposition, similar to wet deposition, inherits positive $\Delta^{17}O$ values ($\sim$ 15% e–30% e; Nelson et al., 2018) and is generally higher in urban relative to rural areas both locally (Lovett et al., 2000; Bettez and Groffman, 2013) and globally (Decina et al., 2019). Thus, flushing of dry NO$_3^{-}$ deposition residing on impervious surfaces (on surfaces such as leaves that can wash onto impervious surfaces) during storm events could contribute to the 1:1 relationship observed in the more developed watershed (green circles in Fig. 6).

$\Delta^{17}O$ of NO$_3^{-}$ can additionally be used to “correct” $\delta^{15}N$ and $\delta^{18}O$ values (Eqs. 7 and 8) to better indicate isotope values of terrestrial NO$_3^{-}$ sources (Dejwakh et al., 2012). Values of both $\delta^{15}N_{\text{Terr}}$ and $\delta^{18}O$-NO$_3^{-}$$_{\text{Terr}}$ during storm events fall within the range of values that are typical of natural “soil” and fertilizer (Kendall et al., 2007), but interestingly, NO$_3^{-}$$_{\text{Terr}}$ isotope values decreased during storm events relative to baseflow in both watersheds (though not significantly for $\delta^{15}N$ in GUN; Fig. 3). This shift to lower $\delta^{15}N_{\text{Terr}}$ and $\delta^{18}O$-NO$_3^{-}$$_{\text{Terr}}$ values during storm events may reflect the flushing of less “processed” NO$_3^{-}$ sources from upper soil horizons (Creed et al., 1996), as processing (e.g., denitrification) generally leaves the remaining NO$_3^{-}$ with more positive $\delta^{15}N$ and $\delta^{18}O$ values due to biologically mediated fractionation (Denk et al., 2017). Lower $\delta^{15}N_{\text{Terr}}$ during storm events relative to baseflow was not statistically significant in the mixed agricultural–forested watershed (GUN), but this was due to a single event in which $\delta^{15}N_{\text{Terr}}$ increased from baseflow to storm flow. Impervious surfaces in the developed watershed likely reduce flushing of this lower $\delta^{18}O$-NO$_3^{-}$$_{\text{Terr}}$ by restricting infiltration, but 30% of this watershed is not “developed” (and a higher percentage contains pervious surfaces), which likely contributes to the similarity in NO$_3^{-}$$_{\text{Terr}}$ isotope patterns between study watersheds. Additionally, relatively lower NO$_3^{-}$$_{\text{Terr}}$ isotope values in storm events could be due to reduced in-stream NO$_3^{-}$ uptake (e.g., assimilation, denitrification) during periods of elevated discharge (Grimm et al., 2005). Biological NO$_3^{-}$ uptake generally fractionates against heavier isotopes, which increases isotope ratios of the remaining NO$_3^{-}$ (Kendall et al., 2007). If in-stream NO$_3^{-}$ uptake rates are reduced during high flows, the resulting effect could contribute to the lower NO$_3^{-}$$_{\text{Terr}}$ isotope values during storm events. Relatively lower $\delta^{18}O$-NO$_3^{-}$$_{\text{Terr}}$ values during storm events relative to baseflow and associated insights into watershed-scale N biogeochemistry were only realized by using $\Delta^{17}O$ to “correct” $\delta^{18}O$ values. Without this correction, $\delta^{18}O$-NO$_3^{-}$$_{\text{Terr}}$ during storm events is strongly influenced by the elevated $\delta^{18}O$ of NO$_3^{-}$Atn, as shown by the similar patterns between $\Delta^{17}O$ and “uncorrected” $\delta^{18}O$ in the more developed watershed (Fig. 3).

Large inputs and stores of N associated with agricultural activity likely contribute to baseflow and storm events having similar impacts on NO$_3^{-}$$_{\text{Terr}}$ and NO$_3^{-}$Atn export in the mixed agricultural–forested watershed (GUN). DFs of both NO$_3^{-}$$_{\text{Terr}}$ and NO$_3^{-}$Atn were approximately 1, indicating that loads are primarily explained by changes in discharge. Nutrients, including NO$_3^{-}$, showing similar patterns (loads explained primarily by discharge) over annual timescales have been attributed to large stores of NO$_3^{-}$ associated with agricultural inputs (Basu et al., 2010; Thompson et al., 2011). With significant agricultural land use, both currently (41.3% in 2016; Table 1) and historically (58% in 1960; O’Bryan and McAvoy, 1966), and consistently high NO$_3^{-}$ concentrations in stream water, GUN likely has large stores of NO$_3^{-}$ in soil and groundwater. Interestingly, our results demonstrate
the control of discharge on NO$_3$-Terr and NO$_3$-Atm loads over storm event timescales, suggesting that large reservoirs of NO$_3$ contribute to stream water export of nutrients across varied flow conditions and not just baseflow.

The combination of our results with projections of increasing frequency of intense precipitation events (Najjar et al., 2010; Walsh et al., 2014) and increasing urban and suburban sprawl (Jantz et al., 2005; Seto et al., 2012) suggests that NO$_3$-Atm may become a relatively more important NO$_3^-$ source to downstream waters, assuming no change in NO$_3^-$ deposition rates. This assumption may not be valid everywhere; however, for example, NO$_3^-$ deposition is declining locally (i.e., mid-Atlantic USA; Li et al., 2016) but increasing across many regions (i.e., East Asia; Liu et al., 2013). In our more developed watershed, the positive correlation between rainfall and the fraction of deposited NO$_3^-$ exported in stream water (Fig. 5) suggests that large storm events may export proportionally greater fractions of rainfall NO$_3$-Atm in urbanizing catchments and increased loads of NO$_3$-Atm to downstream waters. Best management practices in developed watersheds (e.g., storm water control measures) can mitigate these potential impacts by increasing infiltration of rainfall (and NO$_3^-$ dissolved in rainfall) and reducing hydrologic connectivity of overland flow paths (i.e., decrease effective impervious areas; Lee and Heaney, 2003; Walsh et al., 2009), both of which may reduce the load of NO$_3$-Atm and the proportion of “event” water in streams during storm events. Such practices may additionally reduce NO$_3$-Terr loads by stimulating denitrification (Bettez and Groffman, 2012) but could also increase the importance of baseflow in NO$_3^-$ export due to increased infiltration. Thus, monitoring of both baseflow and storm events is necessary to quantify potential changes and make targeted water quality management decisions. Finally, best management practices intended to reduce NO$_3$-Atm loads in developed watersheds via increased infiltration may provide numerous co-benefits, including reduced runoff (Hood et al., 2007) and higher baseflow (Fletcher et al., 2013), both of which could help restore aquatic ecosystems impacted by urbanization (Walsh et al., 2005).

5 Conclusions

We found that storm flow has a disproportionately large impact on NO$_3$-Atm export, whereas baseflow has a disproportionately small impact on NO$_3$-Terr export in a moderately developed watershed. In contrast, neither storm flow nor baseflow has an outsized impact on NO$_3$-Atm or NO$_3$-Terr export in a mixed land-use watershed with significant agriculture. Hydrologic connectivity of overland flow paths associated with impervious surfaces likely promotes rapid transport of NO$_3$-Atm to streams during storm events in the more developed watershed, with higher rainfall storms exporting a greater fraction of deposited NO$_3^-$ than lower rainfall events and event NO$_3$-Atm stream water export approximately equaling rainfall NO$_3$-Atm on impervious surfaces. Large reserves of new and/or legacy agriculturally associated nitrogen in soils in the mixed land-use watershed likely influenced the similar responses of NO$_3$-Atm or NO$_3$-Terr to storm flow and baseflow.

Data availability. Complete data are presented in Tables S4 and S5.

Supplement. The supplement related to this article is available online at: https://doi.org/10.5194/bg-20-2485-2023-supplement.

Author contributions. DMN and KNE: conceptualization, methodology, writing (review and editing), supervision, funding acquisition. JTB: conceptualization, methodology, investigation, formal analysis, writing (original draft), writing (review and editing), visualization, funding acquisition.

Competing interests. The contact author has declared that none of the authors has any competing interests.

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Acknowledgements. Thanks to Pavithra Pitumpe Arachchige and Jim Garlitz for NO$_3^-$ concentration analysis. Robert Hirsch of the US Geological Survey provided guidance on WRTDS-K and R scripts for estimating NO$_3$-Total uncertainty. Any opinions, findings, conclusions, and recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the National Science Foundation. Thanks for helpful comments from two anonymous reviewers that improved the manuscript.

Financial support. David M. Nelson, Keith N. Eshleman, and Joel T. Bostic received support from Maryland Sea Grant under award NA14OAR4170090 R/WS-3 from the National Oceanic and Atmospheric Administration, U.S. Department of Commerce. Joel T. Bostic received support from Maryland Sea Grant under award SA75281900-A from the National Oceanic and Atmospheric Administration, U.S. Department of Commerce. This material is based upon work supported by the National Science Foundation Graduate Research Fellowship (to Joel T. Bostic) under grant no. 1840380.

Review statement. This paper was edited by Perran Cook and reviewed by two anonymous referees.
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