Short communication

Isotopic composition of nitrate in sequential Hurricane Irene precipitation samples: Implications for changing NOX sources

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Highlights

- NO3− isotopic composition of sequential hurricane rain samples are presented.
- Changing NO3 source contributions to hurricane rain NO3− are investigated.
- Soil, lightning and fossil fuel emissions contributed to hurricane rain NO3−.

Abstract

Previous studies have concentrated on adverse ecosystem effects resulting from nitrogen (N) loading from runoff and increased N2O emissions due to hurricane activity but little focus has been placed on N inputs delivered by hurricane precipitation. Understanding these N inputs during extreme rain events is increasingly important since global climate change may alter hurricane activity. In this study, ten sequential Hurricane Irene rain samples were analyzed for isotopic composition of nitrate (NO3−) to investigate NOX (≡NO + NO2) sources contributing to NO3− deposited by a hurricane. The samples were divided into three groups (I, II, III) by k-means clustering using rain event back trajectories, δ15N-NO3− values, and NO3− concentrations. Chemical, physical and isotopic analyses, including δ15N- and δ18O-NO3−, anions, cations, H+H2O2, DOC, acetaldehyde, ethanol and rainfall intensity, were then used to explore similarities in geographic origins and potential relationships with NOx and other emission sources. While it is possible that all samples had contributions from various NOx sources, group I samples had marine back trajectories and a mean δ15N-NO3− value (0.7 ± 1.9‰) suggesting primarily lightning-sourced NOx contributions to NO3− deposition. As the hurricane made landfall, Group II samples transitioned to reflect more of a terrestrial signature with a higher mean δ15N−NO3− value (+11.0 ± 0.5‰) indicating NOx emission contributions from vehicles and power plants sources. As the hurricane continued to move inland, Group III δ15N−NO3− values (5.5 and 5.7‰) reflect the potential mixing of biogenic soil NOx emissions with vehicle and power plant sources. Higher concentrations of ethanol, acetaldehyde, NH4+ and carbohydrates in Group III samples support the influence of biogenic sources.

The isotopic composition of NO3− in hurricane rain can aid in discerning varying NOx sources contributing to nitrate concentrations in extreme rain events. This knowledge can in turn further our understanding of how forthcoming hurricane events may alter the N cycle of an ecosystem.

1. Introduction

Hurricanes impact the nitrogen (N) cycle by increasing N runoff, producing N-rich organic debris, and inducing enhanced soil N2O emissions (Erickson and Ayala, 2004; Zhang et al., 2009). For example, Zhang et al. (2009), determined that N runoff to the Biscayne Bay, FL, USA, five days after Hurricane Katrina, caused a 5.2-fold increase in nitrate (NO3−) concentrations that did not return to pre-hurricane levels for three months. Other studies have reported increases in N inputs to surface waters following hurricanes as a consequence of N runoff from agricultural operations, wastewater
operations, urban impermeable surfaces, and leaching of plant material or organic-rich sediments (Burkholder et al., 2004; Mcdowell et al., 1996; Novak et al., 2012; Schaefer et al., 2000). In addition to increased N inputs to water bodies, hurricanes can induce increases in N2O emissions to the atmosphere for sustained periods of time due to an increase in N availability from N-rich labile litter (Erickson and Ayala, 2004). Erickson and Ayala (2004) reported N2O emissions five times higher than pre-hurricane fluxes for up to seven months following Hurricane Georges in Puerto Rico. Additionally, a 15-fold increase in N2O emissions was observed one month following Hurricane Hugo and emissions were still above pre-hurricane levels seven months post-hurricane (Steudler et al., 2013). While studies have focused on adverse ecosystem effects resulting from N loading from runoff and increased N2O emissions due to hurricane activity, little focus has been placed on N inputs delivered by hurricane precipitation. The dynamics of these inputs during extreme rain events is increasingly important since global climate change may alter hurricane activity (Emanuel, 2005; Webster et al., 2005).

Large coastal rain events can play a significant role in N contribution, as wet deposited N from all rain event types can be responsible for up to 30% of total N delivered annually to estuarine systems (Castro et al., 2003). Hurricane activity produces large amounts of rainwater and therefore can deliver large amounts of dilute N in wet deposition to coastal ecosystems. To gain further understanding of the dynamics of NO3− deposition during a hurricane event, Hurricane Irene (26–27 August 2011) precipitation was sequentially sampled at a coastal North Carolina site. While hurricane NO3− concentration data has been investigated at this location (Miller et al., 2008; Mullah et al., 2012), this study analyzes sequential samples for isotopic composition of NO3−, along with rainwater chemistry, to investigate dynamic variations in NO3− source contributions during the hurricane.

2. Methods

2.1. Sample collection, ancillary analyte analyses, and mapping methods

(Supplementary information 1.1).

2.2. Nitrate and nitrite analysis

(Supplementary information 1.2).

2.3. Nitrate isotope analyses

(Supplementary information 1.3).

3. Results and discussion

3.1. Nitrate concentration, correlations, and δ15N and δ18O of NO3− (Table 1)

The range in NO3− concentrations in Hurricane Irene samples was 0.014–0.28 mg/L, with a volume weighted average of 0.059 mg/L. This average is similar to average NO3− concentrations (0.11 and 0.10 mg/L) of previous hurricane rainwater collected at this location (Miller et al., 2008; Willey et al., 2000) and to non-hurricane marine rains collected at this site (Mullah et al., 2012). Nitrate concentrations of precipitation during Hurricane Irene were lower than average rain (0.40 mg/L) from this site during non-hurricane marine rains. Total rainfall was 16% of total annual rainfall volume during Hurricane Irene corresponding to an annual NO3− in wet deposition at this location of 1.5% (Mullah et al., 2012).

δ15N–NO3− values ranged from −5.7 to +11.3‰ with an average normalized to volume and concentration of +3.2 ± 2.2‰. δ15N–NO3− values were negatively correlated with rain intensity (R = 0.60, p < 0.05), δ18O–NO3− (R = 0.67, p < 0.05) and [H+] (R = 0.57, p < 0.05). The negative correlation with rain intensity suggests a possible rainout effect where during intense rain, the rainout process is not as selective for NO3− enriched in the heavier 15N atom. While this rainout effect may be possible, rain intensity would also be expected to correlate with δ18O–NO3− values, but it doesn’t (R = 0.31, p = 0.35). The negative correlation between [H+] and δ15N–NO3− is opposite to what is observed in continental rainwater (Elliott et al., 2007) but is similar to what is reported in an ice core by Geng et al. (2014). The negative correlation between δ18O–NO3− and δ15N–NO3− is opposite that reported in a continental rainwater study (n = 883) (Elliott et al., in prep), thus speaking to the uniqueness of this extreme weather event.

The range of δ18O–NO3− was +32.2 to +68.7‰ with an average normalized to volume and concentration of +47.9 ± 15.3‰. δ18O–NO3− values were negatively correlated with [H+] (p < 0.05) and positively correlated with H2O2 (p < 0.05). The correlation between δ18O and H2O2 suggests atmospheric oxidation chemistry possibly drives δ18O values as NO3− is oxidized via hydroxyl radical. The correlation also suggests NO3− oxidation occurring via H2O2 and laboratory experiments demonstrate H2O2 can oxidize NO3− in rainwater at environmentally relevant concentrations of H1+, H2O2, and NO3− (Kieber et al., 1999). The δ18O values are relatively low compared to the reported range (~63‰ to ~94‰) of ~150 precipitation sites (n = 883) across the U.S. (Kendall et al., 2007) but were similar to low values reported by the only other intra-rain event study reporting δ18O–NO3− values (Buda and DeWalle, 2009).

3.2. NOx sources during Hurricane Irene

Hurricane samples were divided into 3 groups (Groups I, II, and III) by XLSTAT k-means clustering (iterations = 500, convergence = 0.00001) using the variables NO3− concentration, δ15N and rain event back trajectory type (Fig. 1). Fig. 2 presents sample δ15N–NO3− values compared to δ15N–NO3− source ranges.

3.2.1. Group I

Back trajectories of Group I samples (A through E) are primarily marine. The principal NO3− source in back trajectories of these samples is likely lightning as lightning is estimated to contribute 70% of the NO3− below 500 mbar over the North Atlantic in summer (Levy et al., 1996). Reported lightning δ15N–NO3− range is ~0.5 to +1.4‰ (Hoering, 1957), a range close to the range observed in samples A through E (~3.2 to +0.5‰). The mean δ15N–NO3− value of samples A through E (~0.7 ± 1.9‰) is comparable to a study in Bermuda (~1.8 ± 1.7‰) in which warm season NO3− in rain was
attributed to lightning NOx (Hastings, 2003). While $\delta^{15}$N-NO$_3^-$ values do suggest lightning as a source, the final portion of the samples’ back trajectories are over land therefore vehicles, power plants, and soil emissions may have also contributed to NO$_3^-$ concentrations.

3.2.2. Group II

Back trajectories of Group II samples (G through I) are mixed marine and terrestrial. Lightning sourced NOx is not likely as prominent a source in these samples because there were no lightning strikes reported in the terrestrial portion of the hurricane back trajectories (NOAA, 2013). As the back trajectories become more terrestrial, primary NOx emission sources are likely to be electric generating units (EGUs) and vehicles. The reported vehicle $\delta^{15}$N-NOx range is $+$3.4 to $+$17‰ (Ammann et al., 1999; Moore, 1977; Felix and Elliott, 2014) with one study reporting much lower values ($-$49 to $-$20‰) (Felix and Elliott, 2013, 2014; Li and Wang, 2008). There were also no lightning strikes reported in the terrestrial portion of the back trajectories (NOAA, 2013). Thus, vehicles/EGUs and precipitation induced soil NOx emissions are likely the primary sources of NOx to these samples. Hurricane activity induces an increase in soil N$_2$O emissions (Erickson and Ayala, 2004; Steudler et al., 2013) therefore there is also an increase in NOx is representative of these two fossil fuel combustion related sources. The $\delta^{15}$N-NO$_3^-$ values in these samples represents a change from a marine back trajectory and lightning-sourced NOx to terrestrially-sourced NOx likely resulting from fossil fuel combustion. This period of rain also denotes a conversion from a NO$_3^-$ rainout process into terrestrial recharge process. Samples A through F represent a rainout of possibly lightning sourced NO$_3^-$ followed by an increase in NO$_3^-$ concentration via terrestrial recharge beginning with sample G (Fig. 3).

3.2.3. Group III

Back trajectories of Group III samples (J and K) are mixed marine and terrestrial. These samples have lower $\delta^{15}$N-NO$_3^-$ values ($-$5.7 to $-$5.5‰) than the previous mixed trajectory samples (G – I) which suggests that soil NOx emissions were a contributing source to these samples because soil NOx emissions have low $\delta^{15}$N-NO$_3^-$ values ($-$49 to $-$20‰) (Felix and Elliott, 2013, 2014; Li and Wang, 2008). There were also no lightning strikes reported in the terrestrial portion of the back trajectories (NOAA, 2013). Thus, vehicles/EGUs and precipitation induced soil NOx emissions are likely the primary sources of NOx to these samples. Hurricane activity induces an increase in soil N$_2$O emissions (Erickson and Ayala, 2004; Steudler et al., 2013) therefore there is also an increase in NOx.

Fig. 1. Rain event back trajectories are plotted as sequential dots (Group I yellow (A–E), Group II red (G–I), Group III green (J–K)). Each line of sequential dots is labeled with a letter representing the rain event sample. EGU NOx emissions (kg) from the days of the rain event are represented by proportional blue circles to provide reference for trajectories that directly pass over EGU emissions. Annual county level 2008 biogenic NOx emissions (kg/km²/yr) are represented by graduated colors to provide a reference for areas of increasing biogenic emissions. “X” marks the location of the rain collection site. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
emissions since NOx is a byproduct of the same nitrification and denitrification processes that produce N2O emissions.

To further corroborate a biogenic NOx source to samples J and K, acetaldehyde and ethanol, both of which are primarily biogenically sourced (Kirstine and Galbally, 2012; Millet et al., 2010), reach a maximum in these group III samples. NH4 concentrations also peak in these samples, which in prior studies indicates an agricultural NH4 source at this location (Kieber et al., 2005). The agricultural NH4 source suggests a possible soil biogenic NOx source from denitrification and nitrification occurring in fertilized fields. Carbohydrate concentrations were also highest in samples J and K indicating an increasing biogenic plant source (Mullaugh et al., 2014).

4. Conclusion

Dual isotopic analysis was utilized to investigate variable NO3 sources and fluxes in wet deposition during a hurricane. While it is possible that multiple NOx sources contributed to NO3 concentrations in each sample, observed δ15N–NO3 values suggest NO3 is initially from lightning sourced NOx whereas onshore movement of air masses later in the rain event suggests NO3 is attributed to terrestrial source recharge from fossil fuel combustion and soil NO3 sources. The δ15N–NO3 values suggest a majority of the NO3 deposited during the hurricane are lightning and fossil fuel combustion sourced and given that lightning and fossil fuel combustion produce ‘new’ nitrogen, a majority of the NO3 delivered by the hurricane is from ‘new’ NOx as opposed to the ‘recycled’ NOx produced by soil microbes. While lightning is predicted to contribute ~5% to global and U.S. inventory NOx (Delmas et al., 1997; Zhang et al., 2003), the observed data in group I samples suggests that lightning produced NOx can be a greater contributor to nitrate deposition in marine-based large rain events. The lightning NOx source during this event represents a significant NOx input produced over the open ocean that is subsequently transported and deposited as reactive nitrogen to a terrestrial system. This is important since significant correlations between NO3, H+, and SO4 in long term rainwater collection study at this site suggest common anthropogenic sources as the primary source of NO3 to rain (Kieber et al., 2005). Understanding the shifting NOx sources contributing to extreme precipitation event NO3 concentrations will aid in understanding how future hurricane events may alter the N cycle of a coastal ecosystem in the future.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2015.01.075.

References


Fig. 2. Sample δ15N–NO3 values (black diamonds) and δ15N–NO3 source ranges represented by shaded boxes. (Ammann et al., 1999; Felix et al., 2012; Felix and Elliott, 2013; Felix and Elliott, 2014; Heaton, 1990; Hoering, 1957; Li and Wang, 2008; Moore, 1977). It is important to note the graph does not include δ15N–NO3 data from one study that observed lower vehicle emissions since NOx is a byproduct of the same nitrification and denitrification processes that produce NO2 emissions.

Fig. 3. NO3 concentration vs. total rainfall. The rainout process is represented by the left box and the terrestrial recharge process is represented by the right box.
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