

Organic nitrogen in aerosols and precipitation at Barbados and Miami: Implications regarding sources, transport and deposition to the western subtropical North Atlantic

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[1] The deposition of anthropogenic nitrogen (N) species is believed to have a significant impact on the oligotrophic North Atlantic, but the magnitude of ecological effects remains uncertain because the deposition of water soluble organic N (WSON) is poorly quantified. Here we present measurements of water soluble inorganic N (WSIN) and WSON in aerosol and rain at two subtropical North Atlantic time series sites: Barbados and Miami. WSON total deposition rates ranged from 17.9 mmol m⁻² yr⁻¹ to 49.6 mmol m⁻² yr⁻¹, contributing on average only 6–14% of total N deposition, less than half the poorly constrained global average which is typically cited as 30%. On an event basis, biomass burning and dust events yielded the largest concentrations of WSON. However, biomass burning was relatively infrequent and highly variable in composition, and much of the organic N associated with dust appeared to be externally adsorbed from pollution sources. Conversely, in Miami pollution made relatively small contributions of WSON on an event basis, but impacts were relatively frequent, making pollution one of the largest sources of WSON during the year. The largest contributor to WSON was volatile basic organic N (VBON) species, which were present at concentrations 1–2 times higher than particulate WSON. Despite VBON inputs, samples associated with pollution-source trajectories yielded much more inorganic N than WSON. Consequently, we would expect that in the future as anthropogenic N emissions increase, inorganic nitrogen will remain the dominant form of N that is deposited to the western North Atlantic.

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1. Introduction

[2] Atmospheric nitrogen deposition to the ocean has doubled since the mid-1800s due to anthropogenic activity [Dentener *et al.*, 2006], and could result in enhanced new production and net air/sea CO₂ exchange, increased N₂O emissions from the ocean to the atmosphere, and phosphorus stress in surface waters due to the high N:P ratios in deposition [Duce *et al.*, 2008; Krishnamurthy *et al.*, 2009, 2010, 2007; Zamora *et al.*, 2010]. Anthropogenically derived N deposition consists of inorganic species, such as NO₃⁻ and NH₄⁺, and a poorly characterized organic N fraction, which is by far the least understood component of atmospheric N in deposition. Although numerous studies show that WSON is largely bioavailable [Boulart *et al.*, 2006; Paerl *et al.*, 1999; Peierls and Paerl, 1997; Seitzinger and Sanders, 1999],

there are relatively few measurements of the organic fraction and these yield estimates that range between 5 and 88% of total soluble nitrogen (TSN) in wet deposition [Cornell *et al.*, 2003], with a mean value estimated at 30% [Duce *et al.*, 2008; Jickells, 2006; Zhang *et al.*, 2008]. Thus, the effects of anthropogenic N on the surface ocean are unclear due to the large uncertainty in the sources and magnitudes of organic N in deposition.

[3] Organic nitrogen deposition in the subtropical North Atlantic is of particular interest because the basin is closely surrounded by the landmasses of Africa, Europe, and North America, and thus it receives higher levels of anthropogenic N than other major ocean basins [Dentener *et al.*, 2006]. Also, the subtropical North Atlantic is highly oligotrophic, with nanomolar inorganic nutrient concentrations at the surface [Li and Hansell, 2008; Sohm and Capone, 2006; Wu *et al.*, 2000]. Therefore, the effect of increasing atmospheric nitrogen deposition on upper ocean biogeochemistry may be exacerbated relative to other non-high nutrient low chlorophyll ocean regions [Okin *et al.*, 2011].

[4] In order to better constrain the importance of organic N to total N deposition in the subtropical North Atlantic, we measured inorganic and organic N in rain and aerosols

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collected at two time series sites in the subtropical North Atlantic: Barbados (an island site) and Miami (a coastal site bordering the subtropical North Atlantic). On the basis of aerosol chemical characteristics, back trajectories, and satellite data, we relate our measurements to possible aerosol source regions and source types. In this way we identify which aerosol sources had the greatest impact on WSON concentrations and broadly estimate the anthropogenic contribution to WSON deposition in the subtropical North Atlantic.

2. Methods

2.1. Environmental Setting

[5] Atmospheric WSON was sampled at two sites subtropical North Atlantic sites: the island of Barbados, West Indies (13°N, 59°W), and the coastal city Miami, Florida, USA (25°N, 83°W).

2.1.1. Barbados

[6] Barbados, the easternmost of the Windward Islands, is under the influence of the Trade Winds during much of the year, with easterly winds blowing across the island >95% of the time. Aerosol studies on Barbados began in 1965 [Prospero and Lamb, 2003] and show that mineral dust is the dominant aerosol during spring, summer and fall [Li *et al.*, 1996; Prospero and Lamb, 2003], transported from sources in North Africa, 4500 km to the east [Prospero *et al.*, 1970; Prospero and Carlson, 1972; Prospero *et al.*, 1981]. The transit across the Atlantic requires 5–7 days to Barbados and somewhat longer to Miami. The concentrations of dust events are highly variable, ranging from <1 $\mu\text{g dust m}^{-3}$ to several hundred $\mu\text{g dust m}^{-3}$ [Li *et al.*, 1996]. Sea salt aerosol is always present and is dominant at higher wind speeds. A third common aerosol source type impacting Barbados is biomass burning associated with transport from sub-Saharan Africa or possibly South America.

[7] Samples were collected at the University of Miami's atmospheric chemistry sampling site at Ragged Point, Barbados. Aerosol and precipitation sampling were carried out at the top of a 17 m tower, located on a 30 m bluff on the easternmost (windward) coast of the island. To avoid local contamination, aerosols were sampled under computer control only during onshore winds in the easterly sector between 335° to 130° when winds exceeded 1 m s⁻¹ except during rain events. The many previous studies performed at this site, including trace metals [Arimoto *et al.*, 1995] and microorganisms [Prospero *et al.*, 2005] show no impacts from local sources. At Barbados and Miami, some aerosol samples, identified in the text, were collected without sector control in order to capture fresh terrestrially influenced air for comparison purposes. Rain sampling was not sector-controlled; consequently, given the complex wind fields associated with rain events, it is possible that local sources had an impact. But because of the relatively remote location of our site and the absence of major local pollution sources on Barbados, we do not think that this is a major concern. Additionally, although there is considerable ship traffic in the North Atlantic, local ships do not generally pass directly upwind of our sampling site as the port is on the western (opposite) side of the island.

2.1.2. Miami

[8] Bulk aerosol samples were gathered at Virginia Key on the roof of a Rosenstiel School of Marine and Atmospheric Sciences (RSMAS) building (~20 m above ground/sea level). The sampling site is at the water's edge about 4 km from the mainland, with the residential island of Key Biscayne being the only land standing between the site and the ocean. Similarly to Barbados, aerosols were sampled under computer control when wind was arriving from over the ocean within the sector 45°–204°. Non-sectored samples were also collected as noted in the text.

[9] During the summer, Miami lies in the Trade Wind regime and winds have a predominantly marine origin. Aerosol studies, begun there in 1974, show that dust is the dominant aerosol constituent in summer [Prospero, 1999]. Based on the multiple-day timescale of dust episodes in Miami, the persistence of trade-wind flow, back trajectories, and satellite depictions of aerosol distributions, we would expect that the summertime aerosol composition in Miami is similar to that of a large area of the western subtropical Atlantic region [Prospero, 1999; Trapp *et al.*, 2010]. However, on an annual basis, Miami receives about a third to a half of the dust received on Barbados due to lower dust concentrations and a shorter dust transport season [Prospero, 1999].

[10] When dust is not present, easterly winds generally deliver relatively clean marine air. However, local impacts are much more likely than at Barbados. In addition to passing over Key Biscayne, marine air masses sometimes pass over the Bahamas or Cuba before reaching Miami. Also there is a possibility of impacts from coastal sites because of air mass recirculation during the sea-breeze/land-breeze cycle.

[11] In winter and spring, especially with the passage of cold fronts, winds carry pollution and terrestrially influenced aerosols either directly to Miami [Prospero, 1999] or indirectly from the northeastern North America in air masses that are carried out to the Atlantic and subsequently retroflected to the southeast after 2–7 days over the ocean (Figure 1). During the time these terrestrially derived aerosols spend over the ocean, they may be diluted, rained out, and/or chemically modified [Li *et al.*, 1996]. In the spring dry season, smoke from the mid-Atlantic coast of North America sometimes is transported eastward over the ocean and then to the south, sometimes reaching Miami. Additionally, Miami is periodically affected by biomass burning events in Florida and the local Caribbean.

2.2. Sample Collection

[12] Total suspended particles (i.e., bulk aerosols) were collected using high-volume, 24-h bulk aerosol samplers. On Barbados, bulk aerosol samples were collected during two field campaigns (25 August–24 September 2007 and 8 August–6 September 2008). In Miami, samples were collected from 11 May 2007 to 31 July 2009. Miami samples were often collected over multiple days because aerosol filters were not exchanged on weekends, during rain/lightning events, or during high winds. Bulk aerosol samples were initially collected on pre-combusted (500°C) Pall A/E glass fiber filters and subsequently on Whatman QMA quartz fiber filters. Starting in Miami on 9 August 2007, a secondary cellulose filter impregnated with citric acid [Norwegian Institute for Air Research, 2001] was placed behind the top

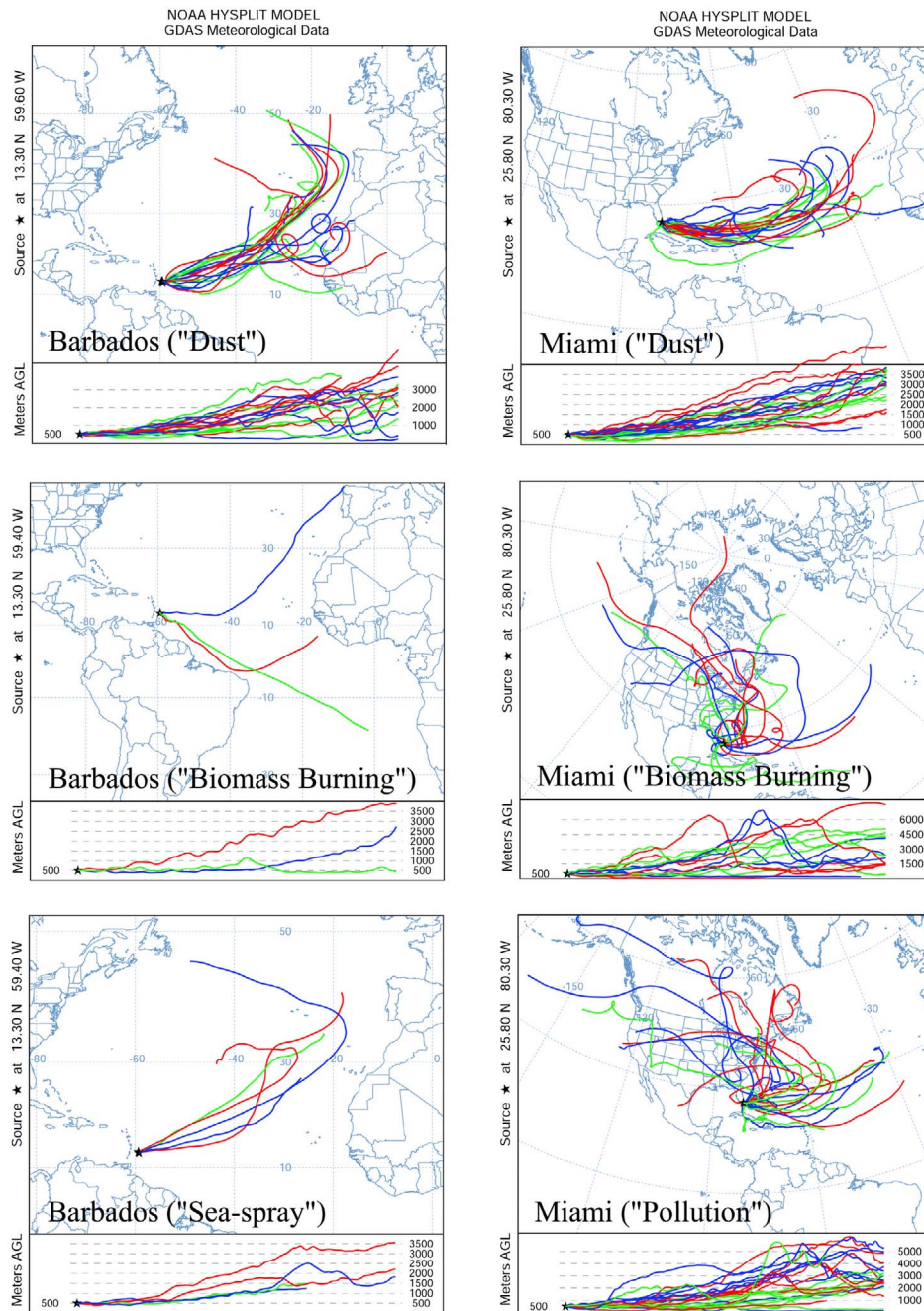


Figure 1. Sampling locations and HYSPLIT 10-day back trajectories illustrating typical air mass flows to Miami and Barbados during the study period. Trajectories are grouped by dominant aerosol sources on a given day (including dust, marine, biomass burning, and pollution aerosols). All trajectories shown here end at 0500 UTC and at 500 m (mid-MBL).

filter to capture gaseous ammonia and ammonium volatilized from the top filter. We combine ammonium measurements from the top filter and ammonia measurements from the back filter for a combined NH_x measurement ($\text{NH}_x = \text{NH}_3 + \text{NH}_4$).

[13] Size-segregated samples were collected in Barbados during the second campaign using a Sierra high-volume cascade impactor. To ensure detectable concentrations, the size-segregated aerosols were sampled for ~ 3 – 4 days. Impactor filter changes were generally timed to coincide with

the arrival of new air masses and aerosol source types based on synoptic conditions, HYSPLIT forecast trajectories, and satellite images. Size-segregated samples were also periodically collected on the RSMAS roof in Miami during individual dust, biomass burning, and pollution events in 2008 and 2009.

[14] Similarly to *Spokes et al.* [2000] and *Lesworth et al.* [2010], W-41 cellulose filters were used as the collection substrate for most of the size segregated samples except

Table 1. Filter Blank Values and Detection Limits for Aerosols and Wet Deposition

	Filter Blanks ($\mu\text{mol filter}^{-1}$)				Filter Detection Limits ^a (nmol m^{-3})				Rain Blanks (μM)	Rain Detection Limits ^b (μM)
	Quartz (n = 7)	Glass (n = 26)	Citric Acid (n = 22)	Cascade Impactor (n = 10)	Quartz	Glass	Citric Acid	Cascade Impactor	(n = 12)	
$\text{NO}_3^- + \text{NO}_2^-$	0.2 ± 0.2	0.2 ± 0.2	0.0 ± 0.0	0.0 ± 0.0	0.6	0.7	0	0.1	0.1 ± 0.2	0.60
NH_4^+	0.0 ± 0.0	0.1 ± 0.2	0.4 ± 0.2	0.1 ± 0.1	0.0	0.4	0.5	0.3	0.1 ± 0.4	1
WSON	0.0 ± 0.2	0.0 ± 0.3	0.2 ± 0.3	0.1 ± 0.0	0.6	0.9	0.8	0.1	0.0 ± 0.4	1

^aAerosol detection limits are determined as 3σ of the blank multiplied by an air volume of 1000 m^3 .

^bRain detection limits are determined as 3σ of the blank.

during June and July 2009, when quartz fiber filter substrates were used in combination with a citric acid impregnated cellulose back-up filter. Most cascade impactor collections were set up to yield three size fractions: <1 , $1\text{--}2.5$, and $>2.5 \mu\text{m}$ diameter. Field and lab blanks were determined for all filter types and subtracted from sample values (Table 1). For samples with N-species concentrations above detection limits (Table 1), blanks for glass/quartz filters and cellulose filters were on average $<10\%$ of sample $\text{NO}_3^- + \text{NO}_2^-$, NH_4^+ , and WSON_A concentrations.

[15] After collection, aerosol samples were folded in pre-combusted Al foil sheets using stainless steel forceps, placed in individual plastic Ziploc bags, and frozen at $\sim -17^\circ\text{C}$ until analysis. Filter blanks (Table 1) were determined for all filter types and were subtracted from sample values. Aerosol filter portions were extracted into 45 ml deionized water buffered at pH ~ 8 with 2.5 mmol NaHCO_3 to approximate seawater pH (similarly to *Aminot and Andrieux* [1996]). Samples were vigorously shaken and left in solution for ~ 12 h to allow complete desorption. Rain and aerosol extracts were filtered through $0.2 \mu\text{m}$ Supor[®] filters and either immediately analyzed or stored frozen until analysis.

[16] Rain samples in Barbados were gathered during the two field campaigns. Miami rain samples were collected from 22 March 2007 to 3 August 2009. Wet deposition in Miami and Barbados was captured using automatic samplers similar to those in the National Atmospheric Deposition Network (<http://nadp.sws.uiuc.edu/NADP/>) that opened during rain events.

[17] In an effort to reduce rain carbon blanks, the sampling protocol evolved over the duration of the sampling program. Initially, a polyethylene bucket was used to capture rain deposition; starting in April 2008, stainless steel buckets were used. Water soluble organic N in rain (WSON_R) blank concentrations were not affected by bucket type (with measured TSN blanks changing from 0.0 ± 0.2 to $0.0 \pm 0.1 \mu\text{M}$). Rainwater samples were retrieved as soon as practical after the rain event, but always within 24 h after collector deployment. Samples were immediately filtered using $0.2 \mu\text{m}$ Supor[®] filters and frozen until analysis. Field blanks were below the detection limits.

2.3. Sample Analyses

[18] Aerosol extracts and rain samples were analyzed for $\text{NO}_3^- + \text{NO}_2^-$ and NH_4^+ by continuous flow colorimetry using the methods described by *Zhang et al.* [1997, also Method 349.0: Determination of ammonia in estuarine and coastal waters by gas segmented continuous flow colorimetric analysis, http://www.epa.gov/nerlcwww/m349_0.pdf]. TSN

and water soluble organic carbon (WSOC) were analyzed with a Shimadzu TOC-V total carbon analyzer combined with a TNM-1 total N analyzer. We follow the practice of operationally defining WSON [*Spokes et al.*, 2000] as the difference between TSN and water soluble inorganic nitrogen (WSIN) under the assumption that inorganic N is comprised solely of $\text{NO}_3^- + \text{NO}_2^-$ and NH_4^+ . Non-sea-salt sulfate (nss-SO_4^{2-}), and the Cl^- , Na^+ , K^+ ions were determined using flame photometry and ion chromatographic techniques, and dust (ash) content was determined gravimetrically [*Savoie et al.*, 2002].

[19] Because WSIN concentrations are generally much higher than WSON concentrations, WSON was subject to relatively large and variable analytical uncertainties. This was a particular problem for samples with WSON concentrations below the WSON method detection limit (MDL) of $1.7 \mu\text{M}$. Others have dealt with this problem by assigning such data a zero value or a value of half of the MDL [e.g., *Mace et al.*, 2003a]. Others have excluded data with high relative uncertainties [e.g., *Lesworth et al.*, 2010]. To avoid introducing positive bias into sample statistics, we included all WSON values below the MDL as they were determined (similarly to *Keene et al.* [2002]) (Table 2). Dealing with the data in this way does not introduce a positive bias, but it does yield data with a lower analytical confidence. To take into account this inherent data analysis limitation, we chiefly concentrate on the statistical central tendencies of the WSON data rather than on individual datum.

2.4. Determination of Aerosol Sources

[20] Air mass characteristics and aerosol sources were determined using a combination of chemical characteristics of the aerosol, meteorological observations, satellite observations, and back trajectories. We assigned a “marine” classification to samples collected when winds were onshore (see section 2.1 for sector information) and when the air masses had spent >1 week over the ocean based on HYSPLIT back trajectories (R. Draxler and G. D. Rolph, HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) Model access via NOAA ARL READY Website, 2011, <http://ready.arl.noaa.gov/HYSPLIT.php>) computed for a starting altitude of 500 m, i.e., within the nominal marine boundary layer (MBL). “Local marine” days were assigned to Miami samples that qualified for the “marine” classification but which, based on HYSPLIT back trajectories, had either recently passed over regional islands (e.g., Cuba) or had lingered over coastal waters where onshore offshore mixing was likely. A “terrestrial” classification indicated trajectories that had contacted continental landmasses in the prior 5 days.

Table 2. Criteria Used for Classification of Dominant Aerosol Source Types^a

Data Source Type	Dust	Sea-Spray	Biomass Burning	Pollution
<i>Chemical Criteria</i>				
Dust ($\mu\text{g m}^{-3}$)	>11.2 (B: 44% M: 18%)	No	No	<3.5 (B: 72% M: 48%)
Sea salt ($\mu\text{g m}^{-3}$)	No	>8.3 (B: 80% M: 40%)	No	No
nss-nc K ⁺ (nmol m ⁻³)	No	No	>0.94 (B: 18% M: 29%)	No
nss SO ₄ ²⁻ (nmol m ⁻³)	No	No	No	>11.4 (B: 44% M: 86%)
Dust:nss-nc K ⁺ ratio ($\mu\text{g/nmol}$)	>22.6 (B: 57% M: 33%)	No	<1.86 (B: 13% M: 28%)	No
Dust:Seasalt ratio ($\mu\text{g}/\mu\text{g}$)	>0.58 (B: 60% M: 47%)	<0.58 (B: 40% M: 53%)	No	No
Dust:nss SO ₄ ²⁻ ratio ($\mu\text{g/nmol}$)	>0.09 (B: 99% M: 66%)	No	No	<0.48 (B: 28% M: 74%)
Seasalt:nss-nc K ⁺ ratio ($\mu\text{g/nmol}$)	No	>15.1 (B: 46% M: 17%)	<15.1 (B: 44% M: 51%)	No
Seasalt:nss SO ₄ ²⁻ ratio ($\mu\text{g/nmol}$)	No	>0.29 (B: 96% M: 67%)	No	<0.90 (B: 58% M: 14%)
nss SO ₄ ²⁻ :nss-nc K ⁺ ratio (nmol/nmol)	No	No	No	>15.3 (B: 68% M: 78%)
<i>Meteorological Criteria</i>				
Winds ocean-sectored >50% of time	No	Yes	No	No
Presence of SAL indicated from sounding data	If available	No	No	No
Model back trajectories:	“Marine”	“Marine,” non-“Local Marine”	No	No
<i>Satellite Criteria</i>				
MODIS, SeaWiFS, CALIPSO, GOES data indicate source:	Yes	No	Yes	Yes: no upwind biomass burning
<i>Qualitative Criteria</i>				
Filter coloration	No	No	No	Grey
Ground-based LIDAR	Yes, avail. in Barbados	No	No	No

^aThe percentage of viable samples that met each criterion is indicated for Barbados (B) and Miami (M).

[21] Samples were further categorized when possible by dominant aerosol source (i.e., dust, sea-spray, biomass burning, and pollution). As indicated in Table 2, source categorizations were primarily determined from the respective contents of mineral dust, sea salt, non-sea salt/non-crustal K⁺ (nss-nc K⁺) [Andreae, 1983], and non-sea salt SO₄²⁻ (nss-SO₄²⁻). Note that marine methano-sulfuric acid (MSA) production may be a significant source of nss-SO₄²⁻ at our sites (Savoie *et al.*, 2002). Therefore, as indicated in Table 2, the nss-SO₄²⁻ data were supplemented by other criteria, including a gray filter coloration (indicating the presence of black carbon).

[22] To obtain a “Dust,” “Sea-spray,” or “Biomass Burning” classification, the respective concentrations of mineral dust, sea salt, and nss-nc K⁺ had to be in the upper quartile of values for all samples, independent of site (Table 2). Due to the uncertainty in natural sources of nss-SO₄²⁻, to obtain a “Pollution” classification, nss-SO₄²⁻ only had to be above the lower quartile range of values. We excluded days containing multiple strong aerosol sources (e.g., dust mixed with biomass burning) by using the ratios of each primary chemical source indicator to each other indicator (e.g., mineral dust, sea salt, nss-nc K⁺, and nss-SO₄²⁻) (Table 2).

[23] Additional criteria for source categorizations are shown in Table 2. Note that nss-nc K⁺ data were not available for all samples (as was the case in Miami during local Everglades fires). If nss-nc K⁺ data were unavailable, a “Biomass Burning” categorization was only assigned if there was a detectable (by human olfactory senses) scent of burning at the sampling site. Such a smell indicated particularly strong and fresh sources of biomass burning, and so in order to fully sample these events, the wind-sector control condition was bypassed so that westerly winds carrying the smoke could be sampled. Also note that under our classifi-

cation system, we cannot assess how much pollution might have influenced biomass burning samples.

3. Results and Discussion

3.1. Composition of Aerosol N

3.1.1. Bulk Concentrations of Aerosol N

[24] Bulk WSON_A concentrations measured at Barbados and Miami are shown in Figure 2. The concentrations of bulk aerosol WSIN (WSIN_A) and WSON_A were more than two times higher in Miami than in Barbados (Table 3). The difference in WSIN was observed even under “Dust” conditions (Figure 2), providing clear evidence of continental influence in our results despite our efforts to minimize the impact of local sources by sampling only onshore winds. Our results exemplify the difficulties in trying to estimate end-member source values for aerosols, i.e., to estimate the N contribution from a specific aerosol source such as dust. As noted by Russell *et al.* [2003], continental and ocean air mix in the coastal zone, even when the direction of synoptic-scale airflows are mainly from marine sources. Therefore, the values presented in Figure 2 as natural source “end member” values are probably elevated in N with respect to the true end-member values, particularly in Miami. Nonetheless, there are clear differences in WSON_A levels that can be linked to the dominant aerosol source type. From these differences, it is possible to identify trends in end-member aerosol nitrogen sources to the subtropical North Atlantic.

[25] The highest WSON_A concentrations were obtained in Miami during “Biomass Burning” events (Figure 2). However, the various biomass burning events measured in Miami yielded a wide range of concentrations. The May 2007 Bugaboo scrubland fire in north Florida and southern Georgia was one of the largest fires ever recorded in the southeast United States [MODIS Rapid Response Team,

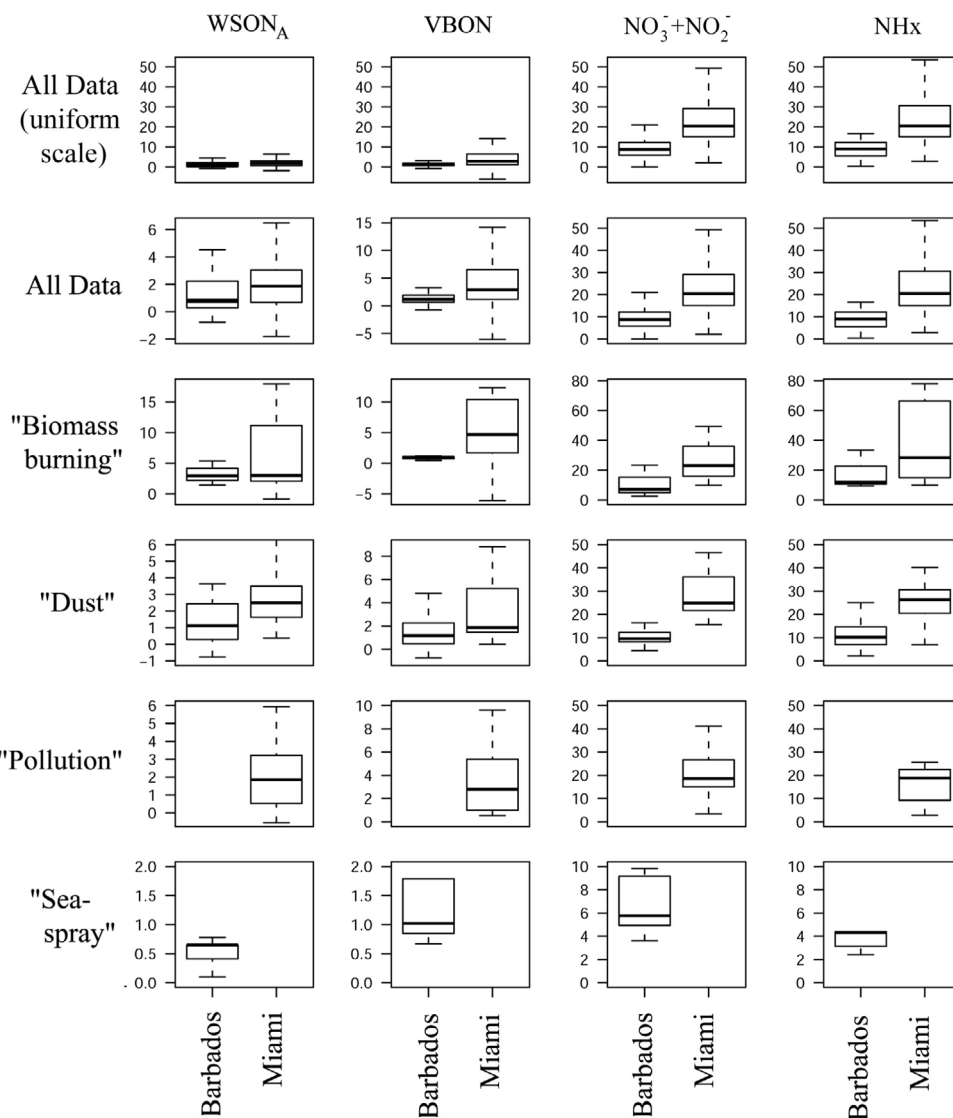


Figure 2. Bulk aerosol N concentrations in Barbados and Miami (nmol N m^{-3}). Data presented include all data at each site, as well as the concentrations in samples classified according to the dominant source: “Dust,” “Biomass Burning,” “Pollution,” and “Sea-spray.” For classification criteria, see section 2.5. Box plots illustrate the median (bold line), the 25th and 75th percentiles of the concentrations (box), and the range of the data not including outliers (whiskers). Outliers, which are determined as data exceeding 1.5 times the value of the interquartile range, are not shown.

2007]. In samples collected during this fire, WSO_{N_A} from the top filter ($14.3 \pm 3.8 \text{ nmol N m}^{-3}$, $n = 5$) yielded about 5 times the average Miami WSO_{N_A} concentrations, values that were comparable to concurrently sampled $\text{NO}_3^- + \text{NO}_2^-$ and NH_4^+ concentrations. The following summer, two biomass burning events (a May Everglades swamp fire and a June peat fire from North Carolina) yielded much lower WSO_{N_A} concentrations, with respective mean WSO_{N_A} concentrations of $2.2 \pm 1.0 \text{ nmol N m}^{-3}$ ($n = 4$) and 2.7 ± 1.1 ($n = 3$). Concentrations of WSO_{N_A} from the 2008 biomass burning events were comparable to concentrations typically observed in Miami in the absence of biomass burning ($2.2 \pm 2.2 \text{ nmol N m}^{-3}$). Also, there were clear differences between the ratios of $\text{WSO}_{\text{N}_A}:\text{NO}_3^-$ and $\text{WSO}_{\text{N}_A}:\text{WSOC}$, indicating compositional differences in the smoke. In 2007, WSO_{N_A} concentrations were approximately equal to $\text{NO}_3^- + \text{NO}_2^-$

concentrations. In 2008, $\text{NO}_3^- + \text{NO}_2^-$ concentrations in smoke were 7–44 times higher. $\text{WSO}_{\text{N}_A}:\text{WSOC}$ ratios in the 2007 Bugaboo fire smoke were $\sim 1:21$; ratios in the summer 2008 smoke samples were 1:60 and 1:20. We speculate that the composition of biomass being burned and atmospheric oxidation and processing during transport have a large effect on the concentrations of WSO_{N_A} in smoke aerosols.

[26] WSO_{N_A} in Barbados was also linked on certain days with biomass burning aerosols from Africa and (and possibly on occasions South America) (Figure 2). These samples were collected in summer, when burning was concentrated in central Africa in the southern hemisphere, over 10,000 km distant. Consequently, we would expect that the impact of burning would be at a minimum at this time of year in this region of the Atlantic. The range in concentrations of “Biomass Burning” WSO_{N_A} at Barbados were smaller than at

Table 3. Bulk Aerosol N Concentrations in Barbados and Miami (nmol N m^{-3})

	n	$\text{NO}_3^- + \text{NO}_2^-$		NH_x		WSO_{N_A}			VBO_{N}		
		av.	s.d.	av.	s.d.	av.	s.d.	n > MDL	av.	s.d.	n > MDL
<i>Barbados</i>											
Dust	20	10.3	4.0	11.4	6.6	1.4	1.3	7	1.7	2.1	6
Sea-spray	5	6.7	2.7	4.2	1.7	0.5	0.3	0	1.7	1.4	2
Biomass burning	3	11.0	10.9	18.3	13.2	3.3	2.0	2	0.9	0.4	0
All data	57	9.8	5.9	10.1	6.5	1.3	1.5	18	1.6	1.7	17
<i>Miami</i>											
Dust	25	28.3	9.4	25.6	9.9	3.0	2.0	18	3.6	3.1	13
Biomass burning	15	28.1	15.7	47.5	47.9	6.2	6.4	13	5.0	6.2	6
Pollution	32	21.6	10.5	23.2	24.3	2.1	2.0	18	3.7	2.8	12
All data	189	24.4	15.7	26.1	21.0	2.4	3.1	101	4.9	6.6	87

Miami, possibly due to dilution of the aerosols during transport and washout by rain over the very long transit from central Africa. Nevertheless, the concentration of WSO_{N_A} during “Biomass Burning” days was slightly higher than those measured on other source-type days, indicating that even in the summer months, biomass burning aerosols have a non-negligible impact on the composition of Barbados aerosols and presumably on that of aerosols over a large area of the tropical Atlantic. *Lesworth et al.* [2010] on several cruises throughout the Atlantic obtained some samples with WSO_{N_A} which they associated with biomass burning. Their median concentrations were $\sim 6.9 \text{ nmol N m}^{-3}$ as compared to a median concentration of $3.0 \text{ nmol N m}^{-3}$ measured at both Miami and Barbados.

[27] High WSO_{N_A} concentrations in dust-laden aerosol samples have been reported previously. During three Atlantic cruises, *Lesworth et al.* [2010] observed the highest concentrations of WSO_{N_A} on days associated with dust aerosols. Also, the highest concentrations of WSO_{N_R} measured on a mountain-top site in Puerto Rico were obtained on days associated with dusty air masses [*Gioda et al.*, 2011]. It is difficult to determine whether the high levels of WSO_{N_A} that we observed on dusty aerosols was due to compounds directly associated with dust as emitted from the source region or whether it was due to pollutants that became associated with dusty air masses during transit, as proposed by *Mace et al.* [2003b]. However, while over Africa, the dust carried to Barbados is likely mixed with predominantly European pollution [*Lelieveld et al.*, 2002; *Savoie et al.*, 2002], as evidenced by slightly higher NH_x and $\text{NO}_3^- + \text{NO}_2^-$ concentrations in “Dust” days relative to “Sea-spray” days in Barbados (Figure 2).

[28] “Pollution” dominated days were only conclusively identified in Miami, and these yielded relatively low WSO_{N_A} concentrations on an event basis ($2.1 \text{ nmol N m}^{-3}$). To put these values into the larger perspective of the North Atlantic, WSO_{N_A} measured at Mace Head, on the west coast of Ireland, on days categorized as relatively polluted (easterly flow) were $\sim 114\text{--}139 \text{ nmol N m}^{-3}$ [*Spokes et al.*, 2000], about 60 times higher than the value in Miami. As we restricted sampling to air masses coming from the ocean-sector, the majority of the “Pollution” samples we analyzed

had spent some time over the ocean (Figure 1), at least five days based on HYSPLIT back trajectories for most samples. During this time the air masses most likely became diluted, and the aerosols chemically altered or potentially rained out. As such, the concentrations observed in Miami are likely representative of those present over the greater subtropical North Atlantic region during pollution events.

[29] Despite low concentrations, however, we observed a high frequency of “Pollution” days at the Miami site. Over the May 2007–May 2009 sampling period, 20% of all days satisfied the criteria for “Pollution” days, as opposed to 5% for “Dust” and 7% for “Biomass Burning.” Thus, despite the relatively low concentrations measured in events, pollution was nonetheless one of the largest sources of WSO_{N_A} in Miami due to its frequency of occurrence.

[30] Samples collected on Barbados should be less impacted by anthropogenic sources. It is difficult to detect a relationship between sea salt and WSO_{N_A} in “Sea-spray” days in Barbados because of the relatively high uncertainty associated with low WSO_{N_A} concentrations. On average on Barbados, WSO_{N_A} on “Sea-spray” days was $0.5 \pm 0.3 \text{ nmol N m}^{-3}$ ($n = 5$) (Figure 2). Other studies have also indicated a marine source of WSO_{N_A} [e.g., *Cornell et al.*, 2001]. *Facchini et al.* [2008] observed an oceanic source of dimethyl- and diethyl-amine that would contribute up to $0.6 \text{ nmol N m}^{-3}$ WSO_{N_A} in the North Sea, which they hypothesize to be related to secondary biogenic formation rather than a direct sea spray source. *Miyazaki et al.* [2010] observed WSO_{N_A} at $\sim 57 \text{ nmol N m}^{-3}$ in the North Pacific in an area most likely heavily impacted by Asian pollution sources. Although they indicated that natural sources may have contributed based on chemical tracers and isotopic ratios of the aerosol, the total was most likely small. For example, the concentrations of diethylamine, proposed by *Facchini et al.* [2008] to have a marine source, was only $0.12 \text{ nmol N m}^{-3}$. The North Atlantic is well traveled by ships, whose emissions are often poorly regulated [*Corbett et al.*, 1999]. Barbados itself is a popular port, and so we cannot discount the possibility that some of the WSO_{N_A} signal that we observed is due to ship emissions; as previously stated, though, ship traffic is almost entirely confined to the Caribbean side of the island, away from the sampling site.

3.1.2. WSO_{N_A} Size Distribution

[31] Size-segregated aerosol N data are shown in Figure 3 (Barbados) and Figure 4 (Miami). In the “Pollution” samples from Miami, the size cutoff was changed from $1 \mu\text{m}$ to $0.7 \mu\text{m}$ for the 2009 samples. This change did not appear to affect the overall trend in WSO_{N_A} size distribution in Miami, with $\sim 86\%$ of WSO_{N_A} being present in the “fine” size fraction for both years.

[32] Because Barbados is the least polluted site in this study, aerosols sampled there are most representative of dust aerosols present over the western subtropical North Atlantic. Nearly all the size-segregated samples were highly influenced by dust at this site. During “Dust” days, $56 \pm 6\%$ of the WSO_{N_A} was present in the submicron size fraction (Figure 3). On days when biomass burning aerosols were mixed with dust, a comparable fraction ($61 \pm 40\%$) of WSO_{N_A} was present in the submicron size fraction. Comparison of Miami and Barbados “Dust” WSO_{N_A} concentrations suggests that WSO_{N_A} may be adsorbed or be deposited

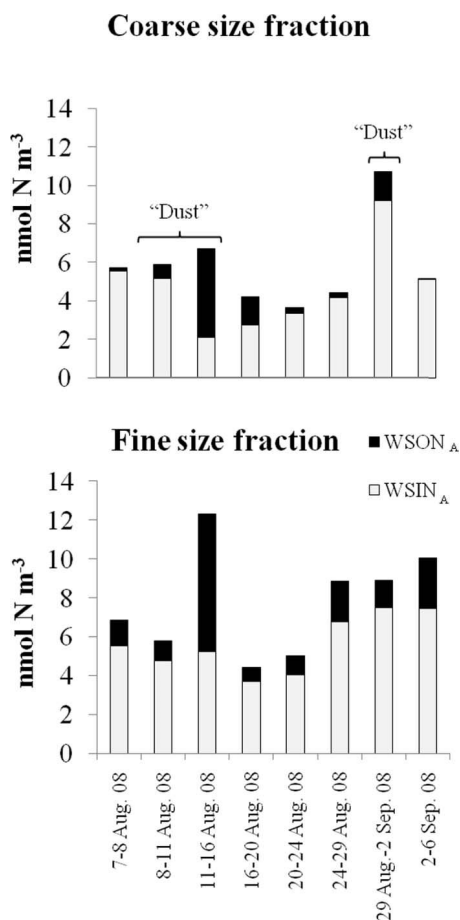


Figure 3. Barbados fine ($<1 \mu\text{m}$) and coarse ($>1 \mu\text{m}$) inorganic nitrogen and WSON_A concentrations (nmol N m^{-3}) in aerosols sampled August 7, 2008–September 6, 2008. Days influenced by biomass burning, and dust aerosol sources are indicated (sources are the same for the top and bottom panels). Unlabelled days indicate days with a mix of aerosol sources.

from the fine-aerosol phase onto dust particles. The statement hinges on two observations. The first is that most of the WSON_A associated with “Dust” days in Miami is attributable to pollution aerosols mixed with the dust. We believe this is the case because WSON_A concentrations on “Dust” days were on average 2 times higher in Miami than in Barbados (10.9 ± 7.7 versus $5.5 \pm 5.4 \text{ nmol m}^{-3}$, respectively, Figures 3 and 4), even though actual dust concentrations were comparable (27.0 ± 6.8 versus $25.2 \pm 2.7 \mu\text{g m}^{-3}$, respectively). The second observation is that even though most of the WSON_A on “Dust” days in Miami is probably derived from pollution sources, the majority (78%) of “Dust” WSON_A observed in our sampling period was associated with larger size fractions (i.e., with the dust particles), suggesting that dust serves as a depositional surface for pollutant WSON_A . In contrast, on “Pollution” days in the absence of dust WSON_A is primarily (86%) associated with the submicron fraction. Mace *et al.* [2003b] presented evidence that over the Mediterranean WSON_A adsorption to dust particles might take place and Lesworth *et al.* [2010] suggested that the dust they observed off the coast of Africa was strongly influenced by pollution

from Europe. However, ours is the first direct evidence that WSON_A is indeed depositing onto dust particles.

[33] The cascade impactor data also demonstrate the variability of the WSON_A properties of biomass burning aerosols. During the first major biomass burning event in Miami 2008 (Everglades swampland fires), WSON_A was approximately evenly distributed between the super and sub-micron size fractions. In the aged North Carolina peat smoke samples, the second biomass burning event of 2008, WSON_A was primarily in the “coarse” size fraction ($>0.5 \mu\text{m}$). We interpret this difference to the changes in the size distribution that took place during transit over the ocean from North Carolina over the period of 3–14 days.

3.1.3. Volatile Basic Organic N (VBON) in Aerosols

[34] Similar to the generally accepted operational definition of WSON in the bulk aerosol as the difference between TSN and WSIN , we define the difference between TSN and WSIN on the back-up filter as Volatile Basic Organic Nitrogen (VBON). In doing so, we leave open the possibility that an unknown inorganic compound may be contributing. In Barbados, VBON concentrations were comparable to WSON_A concentrations ($1.6 \pm 1.7 \text{ nmol N m}^{-3}$ VBON compared to $1.3 \pm 1.5 \text{ nmol N m}^{-3}$ WSON_A). In Miami, VBON concentrations ($4.9 \pm 6.9 \text{ nmol N m}^{-3}$) were approximately twice the top filter WSON_A concentrations ($2.4 \pm 3.1 \text{ nmol N m}^{-3}$).

[35] The concentrations of VBON measured in this study are compared to the concentrations of individual relatively volatile organic species that might conceivably be candidate species (Table 4). The concentration of VBON that we measured is on the high end of most measured values except in unusual locations (e.g., cattle lots). Thus, we considered the possibility that the observed VBON signal was a sampling artifact. We explored several possible sources of artifact. 1) We tested and ruled out the possibility that the concentrations of citric acid used on the filters may cause a reduced analytical recovery of NH_4^+ or an enhanced recovery of TSN by making standard additions to a sample with a citric acid filter blank. 2) The VBON signal was not present on the field and laboratory blanks, which suggests that it accumulated during sampling. 3) It is unlikely that the observations can be explained by particles penetrating the top filter or between the sides of the gaskets of the sampling device because there were no visible particles on the back filter and because concentrations of VBON on the back filter in Miami were twice as high as WSON_A concentrations on the top filter.

[36] Furthermore, we observed a statistically significant reduction in VBON concentrations during rainy conditions ($p < 0.05$, permutation test, see auxiliary material) (Table 5 and Figure 5).¹ As would be expected from rainfall scavenging, concentrations of aerosol $\text{NO}_3^- + \text{NO}_2^-$, WSOC , and other measured atmospheric species at our sites were also reduced as determined by the same statistical tests (Table 5). We also observed an enhancement of VBON in samples with “terrestrial” back trajectories in Miami as opposed to “marine” back trajectories ($p < 0.05$, permutation test) (Figure 5). Within terrestrial, non-“Biomass Burning” samples, changes in NH_x (which has a strong pollution source)

¹Auxiliary materials are available in the HTML. doi:10.1029/2011JD015660.

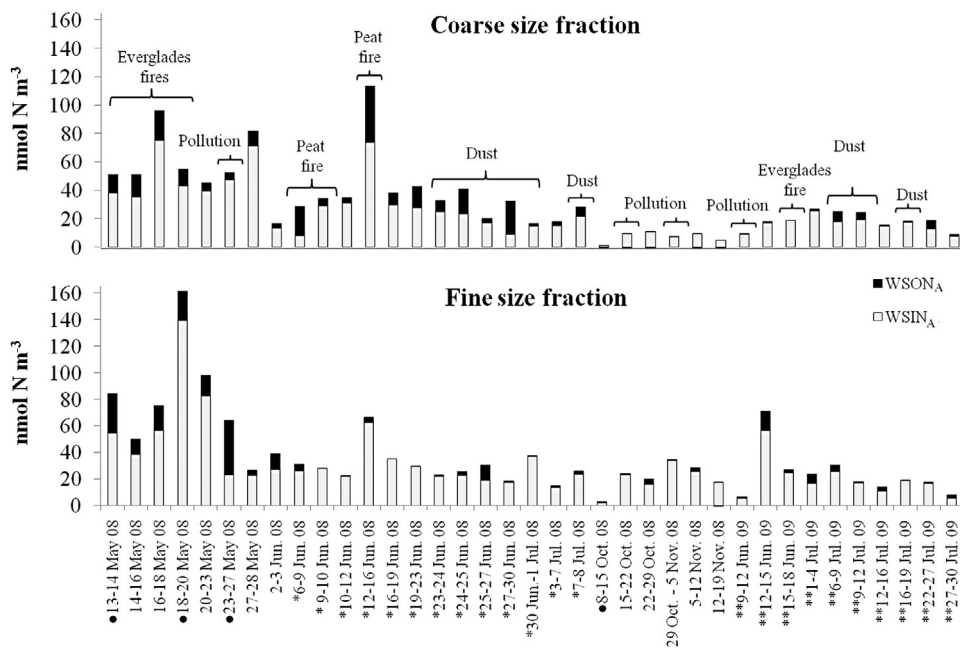


Figure 4. Miami size-resolved $WSIN_A$ and $WSON_A$ concentrations (nmol N m^{-3}) in aerosols periodically sampled between May 13, 2008 and July 30, 2009. The cutoff between coarse and fine aerosols varied due to a change in sampling protocol, so that unmarked days had a cutoff of $1 \mu\text{m}$, samples marked by a single asterisk had a cutoff of $0.5 \mu\text{m}$, and samples marked by a double asterisk had a cutoff of $0.7 \mu\text{m}$. Samples collected out-of-sector are marked by a solid dot. Days influenced by biomass burning, pollution, and dust aerosol sources are indicated.

Table 4. Concentrations of Potential Organic VBON Compounds in Aerosol and Gas Phases as Determined in This Study and Published Elsewhere^a

Compound	Concentration (nmol N m^{-3})			Reference ^c
	Marine/Coastal Sites	Rural/Urban Sites	Unusual Sites ^b	
	<i>Gas Phase^d</i>			
Methylamine	0.011–0.200	0.409–0.645	0–4908	[1]
Dimethylamine	0.039–0.196	0.02–0.074	0–5358	[1]
Trimethylamine	0.001–0.39	0.213–1.677	0–4949	[1]
Diethylamine	n.d.	0.057–0.07	n.d.	[1]
Triethylamine	n.d.	<0.02–0.029	n.d.	[1]
	<i>Aerosol Phase</i>			
Urea	0.2–17.7	~18	n.d.	[2,3]
Arginine	0–0.72	0.021	<1–170	[1,4,5]
Lysine	n.d.	0.011	n.d.	[1]
Methylamine	0–0.099	<0.002–1.755	3.863	[1,8]
Dimethylamine	0.008–0.688	<0.222	n.d.	[1,8–10]
Trimethylamine	0–0.004	n.d.	n.d.	[1]
Ethylamine	0.069	0.029–<0.464	n.d.	[1]
Diethylamine	0.003–0.344	<1.094	n.d.	[1,9,11,12]
Triethylamine	n.d.	<0.138	n.d.	[8]
Ethanolamine	0.027–0.049	0.005–0.236	n.d.	[1]
Ornithine	n.d.	0.236	n.d.	[1]
Total amine N	0.129–0.286	n.d.	10–345	[1]
	<i>Gas+Aerosol Phase</i>			
33 amine compounds	n.d.	0.21–0.56	n.d.	[13]
VBON	4.5 ± 8.6 (Miami)	n.d.	n.d.	<i>This study</i>
VBON	1.9 ± 2.4 (Barbados)	n.d.	n.d.	<i>This study</i>

^aHere n.d. indicates no data.

^bSamples gathered from unusual sites include a fish meal plant, a smog chamber, an agricultural area, a landfill, a livestock farm, a feedlot, a biomass burning site, and an urban area near an incinerator, a waste collection area, and a sewage treatment plant.

^cReferences are as follows: 1- *Ge et al.* [2011, and references therein]; 2- *Bo et al.* [2009]; 3- *Cornell et al.* [2003]; 4- *Mace et al.* [2003b]; 5- *Mace et al.* [2003c]; 6- *Mace et al.* [2003a]; 7- *Mace and Duce* [2002]; 8- *VandenBoer et al.* [2011]; 9- *Facchini et al.* [2008]; 10- *Calderón et al.* [2007]; 11- *Miyazaki et al.* [2010]; 12- *Miyazaki et al.* [2011]; 13- *Akyüz* [2007].

^dValues have been converted from parts per unit volume assuming sampling conditions of 25°C and 1 atm.

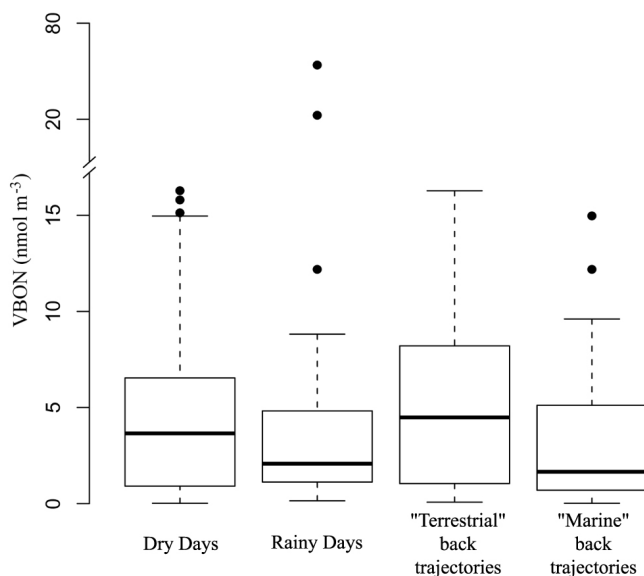


Figure 5. VBON concentrations (nmol m^{-3}) in Miami sampled on days with and without rain and on days designated as having “terrestrial” and “marine” back trajectories. Miami days with rain had significantly lower VBON concentrations than on days without rain. Days with “terrestrial” back trajectories had significantly higher VBON concentrations than days with “marine” back trajectories. Box plots illustrate the median (bold line), the 25th and 75th percentiles of the concentrations (box), the range of the data not including outliers (whiskers), and outliers (circles), which are determined as data exceeding 1.5 times the value of the interquartile range.

and VBON were related ($r^2 = 0.57$, $p < 0.05$). In Barbados, there was no observed reduction in VBON concentrations on rainy days or on “terrestrial” days. However, it would be difficult to find an association of VBON with rain or back trajectory considering the strong marine influence on air masses arriving at this site and the smaller sample sizes and higher analytical errors associated with lower VBON concentrations.

[37] A reduction in VBON concentrations on days with rain is evidence that VBON was related to a real atmospheric constituent removed by rain. If the VBON signal was a sampling artifact linked to the sampling protocol, there should be no difference with respect to the air mass

Table 5. Miami Atmospheric Constituent Concentrations on Days With and Without Rain

Atmospheric Constituent	Mean (Rain)	Mean (No Rain)	Significant Difference? ^a
$\text{NO}_3^- + \text{NO}_2^-$ (nmol m^{-3})	25.7	21.7	yes, $p > 0.05$
NH_x (nmol m^{-3})	26.3	25.8	no
O_3^b (ppm)	0.027	0.025	no
NO_x^b (ppm)	4.3	3.9	no
WSO_A (nmol m^{-3})	2.5 (44% ^c)	2.3 (46% ^c)	no
VBON (nmol m^{-3})	5.6 (63% ^c)	3.3 (66% ^c)	yes, $p > 0.05$
WSOC (nmol m^{-3})	56.2	39.0	yes, $p > 0.05$

^aUsing the parametric method.

^bFlorida Department of the Environment, unpublished data, 2008.

^cPercent of organic N samples above the MDL.

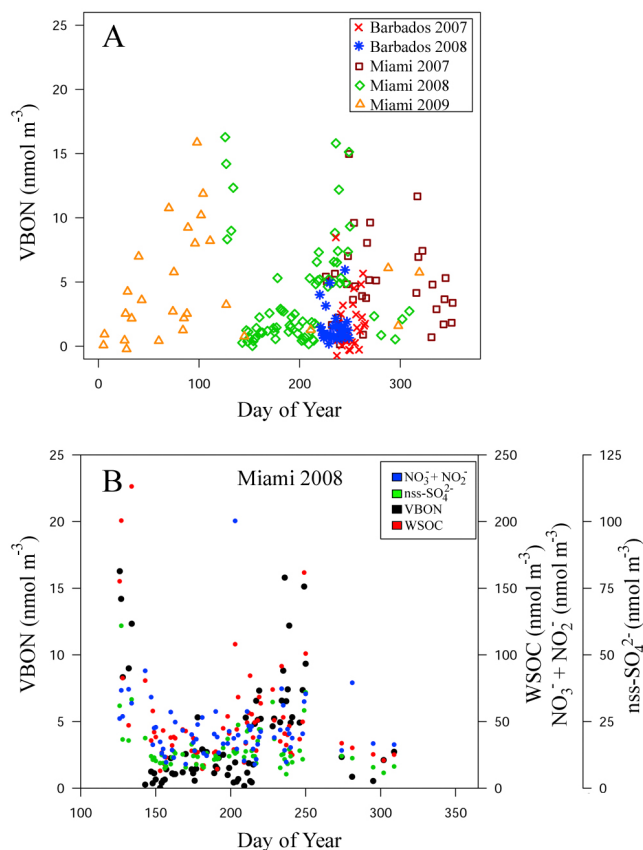


Figure 6. VBON (nmol N m^{-3}) as a function of day of year. (a) All VBON measurements in Miami (excluding the 2009 data gathered using a different protocol (i.e., behind a cascade impactor) and Barbados. (b) Only Miami 2008 data; also shown are concurrently sampled nss-SO_4^{2-} , $\text{NO}_3^- + \text{NO}_2^-$, and WSOC data.

source on any given day unless the artifact is derived from other species in the sample (such as WSO_A). Finally, local contamination specific to any one site is an unlikely cause for the VBON signal because it was observed in both Miami and Barbados at relatively high concentrations compared to literature reports of VBON candidate organic compound concentrations (Table 4). VBON concentrations were lower in Barbados than in Miami, consistent with VBON having a pollution source (Figure 2).

[38] Perhaps the strongest evidence that VBON represents a real atmospheric constituent is the seasonal cycle in VBON concentrations in Miami and Barbados (Figure 6a). The Miami measurements were made over a three year period, 2007 to 2009. The Barbados measurements were made over two one-month summer field programs in 2007 and 2008. In Figure 6a, these data are combined and plotted over one annual cycle. The Miami data show VBON concentrations increasing over the spring and then dropping sharply during April–May to uniformly low values (ca. $1.4 \pm 1.0 \text{ nmol N m}^{-3}$) over the summer. The Barbados measurements, made mostly over the months of July and August, closely match those made in Miami over the same time period. In Miami, concentrations increase in August, matching values in the spring. At Barbados, values also increased sporadically in August and more consistently in September. The temporally coher-

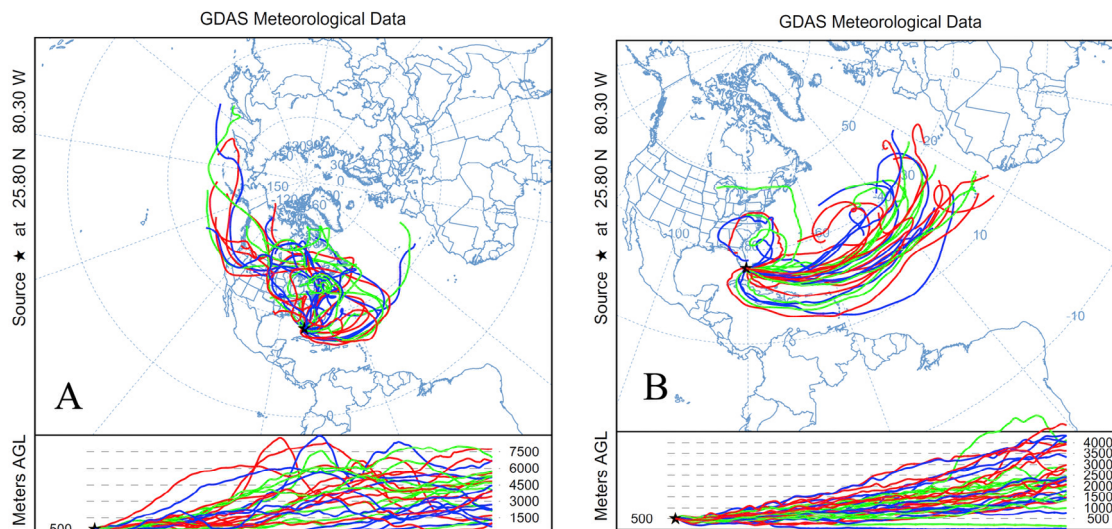


Figure 7. Back trajectories of all days in Miami during the period of (a) 4–30 April 2008 (before the transition into low VBON) and (b) 6 June–9 July 2008 (during the period of low VBON).

ent character of these measurements made at these two locations separated by 15 degrees of latitude suggests that concentrations are being controlled by large-scale processes linked to a seasonal cycle.

[39] This same seasonal cycle is observed in the Miami measurements of $\text{NO}_3^- + \text{NO}_2^-$, nss-SO_4^{2-} and WSOC (Figure 6b). Focusing only on Miami data over the summer of 2008, it becomes clear that the observed reduction in VBON concentrations occurred during an air mass regime change. The high values from 6 to 14 May 2008 (days 126–134) represent the “Biomass Burning” samples from May 2008 (Figure 6b). By 26 May (day 146), wind patterns had completely switched so that they were no longer blowing from the southwest (carrying smoke) but rather were blowing from the east bringing in marine air. The changes in air masses are clearly indicated by a drop in nss-SO_4^{2-} , $\text{NO}_3^- + \text{NO}_2^-$, and WSOC concentrations (all species associated with continental - pollution dominated - air masses). There is a concurrent drop in VBON at the same time (Figure 6b). Concentrations of all species remain relatively low throughout the summer, as easterly wind patterns prevailed. Around August 8 (day 220), wind patterns shifted again so that winds were coming from the west bringing with them an increase in nss-SO_4^{2-} , $\text{NO}_3^- + \text{NO}_2^-$, WSOC, and VBON concentrations.

[40] Linking the sharp seasonal change in VBON concentrations in the spring to air mass changes is supported by a comparison of Miami HYSPLIT back trajectories for the months of April and June 2008 (Figure 7). April trajectories show a very mixed pattern with flow predominantly from the mid and high latitudes over North America. In contrast, those from June show a consistent transport pattern from the east over the tropical Atlantic. The character of the trajectories is also quite different. As a group in April many trajectories sink from substantially higher altitudes (maximum altitudes about 8000m) than those in June, which top out at about 4000m. Also, the June trajectories show a rather regular pattern of subsidence consistent with the tropical meteorology over this region in this season; in contrast the

April trajectories are much more erratic, a pattern consistent with the vigorous weather systems that pass through the midlatitudes at this time.

[41] We therefore conclude that the observed VBON signal is most likely caused by an actual atmospheric constituent, either from WSO_{N_A} volatilized from the top filter or from gaseous VBON compounds in the atmosphere. While the glass filters were observed to preferentially volatilize aerosol NH_4^+ with respect to quartz filters (see section 2.4.2), no statistically significant differences in VBON concentrations were observed from glass or quartz filter substrates sampled at the same time (paired t-test) (Table S1, auxiliary material). This result could either indicate that the VBON signal was caused by gaseous VBON or that a large fraction of WSO_{N_A} was more basic than NH_3 (as is the case for some amines), and thus more likely to volatilize for both glass and quartz filters. Although we are not aware of documented WSO_{N_A} volatilization, organic carbon volatilization is a well-known sampling artifact [Turpin *et al.*, 2000]. Because of this uncertainty, we present the VBON data along with the WSO_{N_A} values throughout the figures in this paper.

[42] In Table 4 measurements of VBON in Miami and Barbados are compared with previously reported data for specific VBON species. Our VBON values are quite high compared to those of individual VBON species (Table 4). Urea has been measured in diverse environments, with some at relatively high concentrations (Table 4). Urea is basic and may be volatile under the conditions present at some sampling sites [Cornell *et al.*, 1998]. Volatile basic amine species such as methylamine, dimethylamine, trimethylamine, diethylamine, and ethanolamine have been observed before in aerosols and gases dominated by marine air mass sources, with their sums ranging from 0.2 to 2.0 nmol N m^{-3} (Table 4). Based on the observed concentrations in marine and coastal locations, these previously measured amine compounds are unlikely to fully explain the full VBON signal in Miami (Table 4), unless urea contributed some portion of the signal. Selected aerosol samples with high VBON levels were analyzed for urea, and the concentrations

Table 6. Volume Weighted N Species Concentrations in Miami and Barbados Rain (μM)

	n	$\text{NO}_3^- + \text{NO}_2^-$			NH_4^+			WSON_R			n > MDL
		av.	Median	s.d.	av.	Median	s.d.	av.	Median	s.d.	
Barbados	18	4.1	3.1	1.9	3.0	2.1	2.0	0.8	0.2	1.1	8
Miami	62	10.0	7.1	5.5	7.7	6.7	4.8	1.3	1.0	1.6	42

of urea found were not high enough to explain the VBON signal (D. McDonald, personal communication, 2010). All urea concentrations were below the analytical detection limit, with the highest observed urea concentration equivalent to 0.3 nmol m^{-3} , a value which, if correct, would have supplied 2% of the VBON signal for that sample. Additionally, several of the samples with the highest VBON concentrations were analyzed for amine content by Fourier Transform Infrared (FTIR) spectroscopy, but amines alone were not observed in sufficiently high concentrations to account for the VBON signal (A. Wozniak and H. Abdullah, personal communication, 2010).

[43] If the VBON signal is not the product of an unknown sampling artifact, then it may be formed of the many organic nitrogen compounds in the atmosphere that have not yet been measured or identified. In southern Scotland, *González-Benítez et al.* [2010] found that gaseous WSON compounds accounted for a substantial portion (~75%) of total atmospheric WSON, although agricultural inputs of NH_x and potentially other atmospheric species were much higher than at our sites. *Altieri et al.* [2009] found >400 WSON_R compounds in four New Jersey rain samples, ~70% of which were reduced CHNO^+ compounds. Their finding could indicate a large contribution from urea, amino acids, and/or or alkyl amines, any of which could be basic. *Özel et al.* [2009] found that the majority of organic N compounds measured in 23 urban aerosol samples were from nitriles, amines, and amides. However, it is uncertain how many of these compounds would be volatile under our sampling conditions. Simple CHN-containing compounds, such as the previously observed types of amines listed in Table 4, comprised only 2% of the observed WSON_R signal in the *Altieri et al.* [2009] study. Microbial action on the filters may be a possible source of VBON, considering that some of the samples were collected over several days. However, average VBON concentrations were not significantly different between samples collected on one day versus multiple days (permutation test, $p > 0.05$).

[44] The strong seasonal cycle of VBON observed at Miami and the association of this cycle with trajectories from the midlatitudes and often from high altitudes suggests that VBON is associated with upper-atmospheric transport. Other pollutants, such as peroxyacetyl nitrate (PAN) and its homologues, have a similar seasonality and trajectory character. PAN itself is not basic and its derivatives are not likely to account for a source of VBON. However, VBON reaction chemistry might be altered in the presence of NO_x formed from decomposed PAN. NO_x , for example, can participate in the atmospheric transformation of amines to amides, some of which are volatile and basic [*Schade and Crutzen*, 1995; *Malloy et al.*, 2009; *Murphy et al.*, 2007]. Future studies investigating the role of WSON in pollution

should take the VBON pool into account and could benefit from a deeper exploration of the sources and speciation of VBON.

3.1.4. Concentrations of WSIN_R and WSON_R in Precipitation

[45] Concentrations of all N species ($\text{NO}_3^- + \text{NO}_2^-$, NH_4^+ , WSON_R) were each about twice as high in Miami rain compared to Barbados rain (Table 6). In addition, rainfall rates in Miami (149 cm y^{-1}) (M. D. Winsburg, Precipitation data: Miami, 2009, Florida Climate Center, http://coaps.fsu.edu/climate_center/data/precip_miami.shtml) are somewhat greater than those in coastal Barbados ($110\text{--}125 \text{ cm y}^{-1}$) [*Rouse*, 1962]. These two factors imply a substantially greater wet deposition N flux in Miami, as discussed more fully in section 3.2. The large increase in both WSIN_R and WSON_R concentrations in Miami is probably due to the greater influence of North American pollution sources. Nonetheless, at both sites, WSON_R comprised only a small percentage of the total N wet deposition flux, accounting for just 8% of TSN in Miami and Barbados.

3.2. Deposition of Atmospheric Soluble N

[46] The atmospheric N deposition fluxes in Miami and Barbados are estimated in Table 7 and Figure 8. Dry deposition flux (F_{dry}) was estimated from:

$$F_{\text{dry}} = C V_d \quad (1)$$

where C is the atmospheric N concentration (nmol N m^{-3}) and V_d is the dry deposition velocity (m s^{-1}). The wet deposition flux (F_{wet}) was determined from:

$$F_{\text{wet}} = C R \quad (2)$$

where C is the concentration of WSON_R ($\mu\text{mol N L}^{-1}$) and R is the amount of rainfall (in mm) for each event.

[47] The deposition velocity of aerosol N was calculated using the size-segregated aerosol data collected in Miami and Barbados (Figures 3 and 4) and following the assumptions used by *Duce et al.* [1991]. Most $\text{NO}_3^- + \text{NO}_2^-$ was present in the coarse size fraction, most likely due to the sea salt displacement reaction with nitric acid to form coarse-mode sodium nitrate. Therefore, the deposition velocity of $\text{NO}_3^- + \text{NO}_2^-$ was estimated at 0.02 m s^{-1} [*Duce et al.*, 1991]. The majority of NH_4^+ was in the fine fraction, and so the deposition velocity of NH_4^+ was estimated at 0.006 m s^{-1} [*Spokes et al.*, 2000]. WSON_A was found to be present in both the coarse and fine fractions although its size distribution appeared to be influenced by source (see section 3.1.3), as also found by *Lesworth et al.* [2010]. Based on these data and on the precedent of *Spokes et al.* [2000], we assume that WSON_A has an average deposition velocity of about 0.012 m s^{-1} . Deposition velocity of VBON is roughly estimated at 0.006 m s^{-1} (similar to NH_4^+) because VBON is at least semi-volatile and may be gaseous, and thus it should be more subject to removal processes that affect small particles, such as Brownian diffusion, than to processes that affect larger particles, such as gravitational settling.

[48] It should be noted that actual V_d values are poorly quantified in marine environments where deposition is a strong function of aerosol size, wind speed, aerosol hygroscopicity, and relative humidity [*Prospero and Arimoto*,

Table 7. Estimated Wet and Dry WSON Deposition to Miami and Barbados^a

	Annual Rainfall ^b (cm yr ⁻¹)	Wet NO ₃ ⁻ + NO ₂ ⁻ Flux		Wet NH ₄ ⁺ Flux		WSON _R Flux		% WSON _R /TSN		Wet TSN Flux	
		av.	Sensitivity Range	av.	Sensitivity Range	av.	Sensitivity Range	av.	Sensitivity Range	av.	Sensitivity Range
Barbados	118	13.3 ± 6.1		9.7 ± 6.5		2.6 ± 3.6		10%		30.2 ± 16.8	
Miami	149	40.8 ± 22.5		31.4 ± 19.6		5.3 ± 6.5		7%		81.8 ± 48.4	
		Dry NO ₃ ⁻ + NO ₂ ⁻ Flux		Dry NH _x Flux		Dry WSON _A Flux		Dry VBON Flux ^c		Dry TSN Flux	
		av.	Sensitivity Range	av.	Sensitivity Range	av.	Sensitivity Range	av.	Sensitivity Range	av.	Sensitivity Range
<i>Barbados</i>											
Dust		17.8 ± 7.0	6–53	5.9 ± 3.4	2–18	1.4 ± 1.3	0–4	0.9 ± 1.1	0–3	26.0 ± 10.2	9–78
Sea-spray		11.5 ± 4.7	4–35	2.2 ± 0.9	1–7	0.5 ± 0.3	0–2	0.9 ± 0.7	0–3	15.1 ± 5.0	5–45
Biomass burning		19.0 ± 18.9	6–57	9.5 ± 6.7	3–28	3.4 ± 2.1	1–10	0.5 ± 0.2	0–1	32.3 ± 24.0	11–97
All data		16.9 ± 10.2	6–51	5.2 ± 3.4	2–26	1.3 ± 1.6	0–4	0.9 ± 0.9	0–3	24.3 ± 12.9	8–73
<i>Miami</i>											
Dust		0.21 ± 0.15	16–147	13.3 ± 5.1	4–40	3.1 ± 2.1	1–9	1.8 ± 1.6	1–6	67.4 ± 20.4	22–202
Biomass burning		0.22 ± 0.08	16–146	24.6 ± 24.8	8–74	6.4 ± 6.6	2–19	2.6 ± 3.2	1–8	81.7 ± 48.9	27–245
Pollution		0.12 ± 0.14	13–112	12.0 ± 12.6	4–36	2.1 ± 2.0	1–7	1.9 ± 1.5	1–6	50.0 ± 21.0	7–150
All data		0.08 ± 0.31	14–126	13.5 ± 10.9	5–41	2.5 ± 3.2	1–7	2.5 ± 3.4	1–8	60.2 ± 37.8	20–181

^aDry deposition values are calculated by mean aerosol concentration and deposition velocities of 0.02, 0.012 and 0.006 m s⁻¹ for NO₃⁻ + NO₂⁻, WSON_A and NH_x and VBON, respectively. Dry deposition “sensitivity range” indicates the effect of a factor of three uncertainty in deposition velocity values for the average dry deposition flux.

^bAverage annual rainfall from Winsburg [2009] and Rouse [1962].

2009]. Following Duce *et al.* [1991], for the deposition velocity for most non-sea salt particles we use plus/minus a factor of three for the error range estimate [Duce *et al.*, 1991]. The deposition rates shown in Table 7 and Figure 8 include this range along with the means. It is possible that a larger error estimate would be more realistic, in part because errors in deposition velocities increase rapidly with increasing wind speeds [Prospero and Arimoto, 2009]. Also note that due to our assumption of a constant V_d , we cannot resolve seasonal or spatial changes in estimated dry deposition. Thus, our wet N deposition estimates are much more reliable than those for dry deposition.

[49] The Miami WSIN_R data were very similar to WSIN_R concentrations measured in the nearby Florida Everglades by the National Atmospheric Deposition Program (Table 8). Given these collective WSIN_R deposition rates and the WSON_R, WSIN_A, and WSON_A deposition rates measured in Miami, it appears that Florida experienced higher WSIN and WSON deposition fluxes than Barbados (Table 7 and Figure 8). However, the Miami and Barbados data are not directly comparable because the Barbados data were only gathered during the summer. Nonetheless, we expect to measure greater N deposition in Florida both because it is more frequently impacted by polluted air masses than Barbados and because it has greater annual rainfall.

[50] In both wet and dry deposition, the ratio of WSON to TSN was relatively low. While deposition velocity assumptions directly affect WSON dry deposition values, wet deposition is not affected by these assumptions. In the rain samples, WSON_R also contributed a relatively low percent-

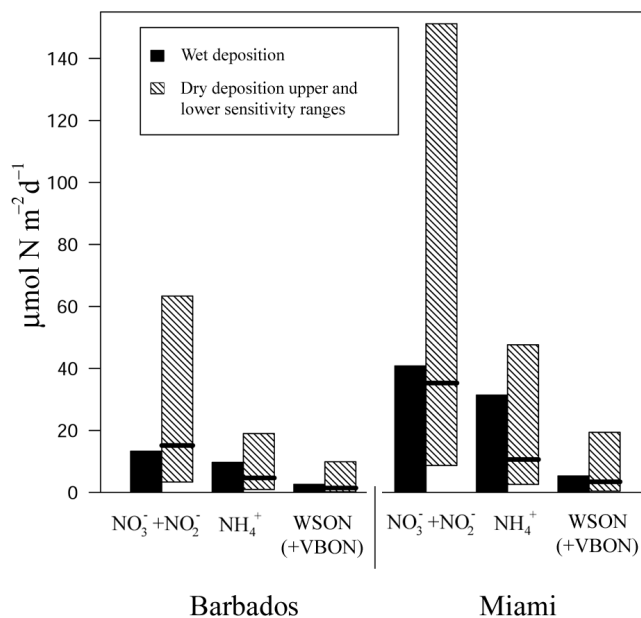


Figure 8. Estimated wet and dry deposition to Barbados and Miami. The “sensitivity range” for dry deposition incorporates the upper and lower quantile values of deposition flux expected given a factor of three error in assumed deposition velocities. Median estimated dry deposition flux is indicated by a bold line.

Table 8. WSON_R Wet Deposition Fluxes ($\mu\text{mol m}^{-2}\text{d}^{-1}$) at Coastal and Marine Locations^a

Location	n	Wet Deposition Rate (cm yr ⁻¹)	NO ₃ ⁻ + NO ₂	NH ₄ ⁺	WSON _R	WSON _R (%)	Reference
<i>North Atlantic Sites</i>							
Belgium (over air masses)	179	42	141	128	45	14%	<i>Benics et al.</i> [2009]
Belgium (Atlantic/UK/Channel)	91	42	232	185	16	4%	<i>Benics et al.</i> [2009]
Belgium (continental)	46	42	53	84	136	50%	<i>Benics et al.</i> [2009]
Belgium (North Sea)	42	42	40	52	3	3%	<i>Benics et al.</i> [2009]
Tampa Bay, FL	11	133	151 ± 141	48 ± 22	17 ± 10	8%	<i>Calderón et al.</i> [2007]
Bermuda	18	133	-	-	58 ± 26	59%	<i>Cornell et al.</i> [1995]
Bermuda	5	133	12 ± 5	16 ± 12	20 ± 11	42%	<i>Cornell et al.</i> [1998]
Mace Head, Ireland	7	120	14 ± 10	4 ± 4	11 ± 10	37%	<i>Cornell et al.</i> [1998]
La Selva, Costa Rica	107	208	23	34	41	41%	<i>Eklund et al.</i> [1997]
Luquillo, Puerto Rico	21	104	15 ± 12	11 ± 7	20 ± 6	44%	<i>Giada et al.</i> [2011]
Southeast Scotland	27	124	-	-	18	55%	<i>González Benítez et al.</i> [2009]
Charlottesville, VA	83	139	94	76	12	6%	<i>Keene et al.</i> [2002]
Newark, DE	50	114	88	65	13	8%	<i>Keene et al.</i> [2002]
New Castle, NH	12	140	54	91	2	2%	<i>Keene et al.</i> [2002]
Wilmington, NC	129	132	42 ± 4	35 ± 5	17 ± 5	21%	<i>Kieber et al.</i> [2005]
Long Island Sound, NY	730 ^b	122	36 ± 35	30 ± 38	14 ± 14	17%	<i>Luo et al.</i> [2002]
Everglades National Park, FL	9855 ^b	133	30 ± 6	22 ± 9	-	-	NADP data archive
Morehead City, NC	42	155	-	-	23 ± 26	26%	<i>Peierls and Paerl</i> [1997]
North Sea	54	77	115	78	13	6%	<i>Rendell et al.</i> [1993]
Lewes, DE (coastal site)	60	114	67	42	19	15%	<i>Russell et al.</i> [1998]
Lewes, DE (coastal site)	37	114	62	33	28	23%	<i>Scudlark et al.</i> [1998]
New Brunswick, NJ	11	122	85 ± 8	76 ± 9	29 ± 3	15%	<i>Seitzinger et al.</i> [2003]
Mace Head, Ireland	62 ^b	120	75	84	99	27%	<i>Spokes et al.</i> [2000]
Miami, FL	62	149 ^c	41 ± 23	31 ± 20	5 ± 7	7%	This study
Barbados	18	118 ^c	13 ± 6	10 ± 7	3 ± 4	10%	This study
Average North Atlantic						23 ± 18%	
<i>Other Worldwide Sites</i>							
Hawaii, HI	>2190 ^a	78	3	2	1	14%	<i>Carrillo et al.</i> [2002]
Tahiti	8	162	19 ± 13	6 ± 5	15 ± 14	37%	<i>Cornell et al.</i> [1998]
Kilauea, HI	20	131	10 ± 16	7 ± 10	23 ± 22	62%	<i>Cornell et al.</i> [2001]
Oahu, HI	17	78	25 ± 25	8 ± 16	6 ± 8	19%	<i>Cornell et al.</i> [2001]
Singapore	12	173	~646 ± 646	~67 ± 67	~409 ± 646	36%	<i>Karthikeyan et al.</i> [2009]
Cape Grim, Australia	6	89	33 ± 20	40 ± 35	18 ± 13	19%	<i>Mace et al.</i> [2003b]
Erdemli, Turkey	18	36	32 ± 21	40 ± 32	15 ± 31	17%	<i>Mace et al.</i> [2003c]
Eastern Mediterranean	74	55	26.3	18.4	13.2	23%	<i>Violaki et al.</i> [2010]
Dalian, China	330 ^b	60	~220	~220	~310	39%	<i>Zhang et al.</i> [2008]
Qingdao, China	300 ^b	70	~147	~254	~248	38%	<i>Zhang et al.</i> [2008]
Fenghua, China	300 ^b	167	~251	~548	~639	44%	<i>Zhang et al.</i> [2008]

^aWet deposition fluxes are calculated from deposition rates (estimated by *Adler et al.* [2003]) and rain N concentrations.

^bValues correspond to period over which samples were gathered, rather than exact sample numbers

^cAverage annual rainfall from M. D. Winsburg (Precipitation data: Miami, 2009, Florida Climate Center, http://coaps.fsu.edu/climate_center/data/precip_miami.shtml) and *Rouse* [1962].

age of TSN deposition (~8% of TSN in Miami and 10% at Barbados) (Table 7 and Figure 8). Again we note that on Barbados, rain was only sampled in the summer rainy season; consequently, these values may not accurately represent annual deposition values.

[51] The mean WSON_R contributions to TSN in rain measured at Miami and Barbados, 7% and 10% respectively, are much smaller than the 30% reported for ocean regions other than the North Atlantic. They are also somewhat lower than the ~22% reported within the North Atlantic (Table 8), although the WSON_R contribution to TSN in rain in the North Atlantic is quite variable, ranging between 3 and 70% of TSN. A recent comprehensive study of aerosols in the eastern Atlantic by *Lesworth et al.* [2010] found a higher contribution (25%) of WSON_A to the TSN pool than we did, with the highest percentages associated with dust aerosols. In contrast, WSON_A contributed only 5–7% of the TSN pool in Miami and Barbados on dusty days.

[52] There are several possible explanations for the low contributions of WSON_A to the TSN pool that we observed

compared to *Lesworth et al.* [2010]. Procedural differences may contribute; *Lesworth et al.* [2010] excluded data with an uncertainty of >100%, which excluded most data where WSON_A levels were lowest. This method improved their analytical certainty but removed values with a low proportion of organic N relative to inorganic N. If data were not excluded, WSON_A contributed 17% of TSN in all of their data (based on their Table 2). Also, they used sonication to extract their samples while we used passive desorption, a less aggressive method. Problems with sonication may include breaking apart particles and lysing cells, while problems with passive desorption may include incomplete desorption or bacterial activity. Alternatively, if procedural differences were minor, seasonal differences may account for part of the discrepancy. We sampled during the summer in Barbados, when biomass burning impacts are most likely at a seasonal minimum and dust is a major aerosol source. *Lesworth et al.* [2010] sampled over the ocean during the fall, when biomass burning (a major source of WSON_A) is prevalent. A third possibility is that WSON_A concentrations

might change during transport from the east to the west. Their samples were mostly gathered in the eastern Atlantic, and were less aged than the dust samples gathered in Barbados and Miami. Finally, there is some uncertainty in the degree of sampling artifacts on our individual WSO_{NA} measurements (see sections 2.4 and 3.1.4). Including VBON with WSO_{NA} in Miami and Barbados would raise the potential contribution of WSO_{NA} to aerosols from 4 to 8% to 8–11%, and in dusty samples from 5 to 7% to 8–10%. Clearly, the contribution of WSON to the TSN pool was fairly uniform and relatively low at our sites, a conclusion that is supported by the wet deposition data.

[53] A caveat to the data presented here is that HNO_3 was not measured, even though it can be important to overall N deposition at some other sites [e.g., Luo *et al.*, 2002; Russell *et al.*, 2003]. Literature data collected at coastal locations in the North Atlantic indicate that the deposition of HNO_3 may range between 2 and 60 $\mu\text{mol m}^{-2} \text{d}^{-1}$, depending on the degree of continental versus marine influence [Russell *et al.*, 2003; Fischer *et al.*, 2006; Bencs *et al.*, 2009; Luo *et al.*, 2002]. At our study locations, we expect HNO_3 to be on the low side of these estimates, due to the reaction of HNO_3 with sea salt aerosol and dust [e.g., Finlayson-Pitts, 2009]. We observed that the majority of NO_3^- was associated with coarse mode particles, a result that we would expect if HNO_3 had reacted with sea salt and mineral dust. Also, in Barbados, the size distribution of NO_3^- has previously been observed to overlap with the peak in sea salt aerosol and to be identical to that of mineral dust [Li-Jones and Prospero, 1998]. Based on airplane measurements gathered at 152 m near Bermuda, Hastie *et al.* [1990] reported median HNO_3 concentrations of about 3 nmol m^{-3} . Based on these concentrations and assuming a V_d of 0.76 cm s^{-1} [Russell *et al.*, 2003], we expect at minimum a HNO_3 dry deposition flux of around 2 $\mu\text{mol m}^{-2} \text{d}^{-1}$ from open ocean air masses.

[54] Total estimated N deposition to Barbados and Miami was 50 and 138 $\mu\text{mol m}^{-2} \text{d}^{-1}$, respectively. The results of the WSIN deposition model presented by Dentener *et al.* [2006] compare moderately well with our observations; it predicts atmospheric WSIN deposition of ~23 and 101 $\mu\text{mol m}^{-2} \text{d}^{-1}$ in Barbados and Miami, as compared to our observed 45 and 127 $\mu\text{mol m}^{-2} \text{d}^{-1}$ WSIN deposition observed. Again we caution that our results might be biased because the Barbados data were collected in the summer only.

4. Conclusions

[55] The data presented here provide a comprehensive picture of temporal and spatial trends in end-member WSO_{NA} in the atmosphere over the western subtropical North Atlantic. Our results show that WSO_{NA} concentrations are largely linked to transport from continental sources. The highest concentrations were associated with biomass burning and with African dust. Because biomass burning events are relatively infrequent at our sampling sites, their significance to the bulk WSON deposition is reduced to a minor role. Additionally, while biomass burning can produce high concentrations of WSO_{NA} (as previously observed by Mace *et al.* [2003a] and Baker *et al.* [2006]), our study shows that the composition and magnitude of biomass burning N is quite variable. This result suggests that the effects of biomass burning on the ocean deposition should also be quite vari-

able, and that these effects depend on the type of biomass being burned, and subsequently on chemical processing during atmospheric transport.

[56] It is difficult to distinguish between the relative impact of natural and anthropogenic sources of WSO_{NA} . Based on the changes in size distributions of organic N in samples collected during polluted and dusty days in Barbados and Miami, we surmise that much of the dust-associated WSO_{NA} in the western subtropical North Atlantic is very likely derived from deposition to the dust surface during transport. Based on the WSO_{NA} measured on Barbados on “Sea-spray” days, we conclude that the ocean is a relatively minor source, contributing 0.5 nmol N m^{-3} on average. However, it is not clear how much of the WSO_{NA} measured during “clean” marine air conditions might actually be due to pollution emissions from ships or other distant pollution sources.

[57] The most consistent source of WSON in Miami samples was pollution. Although these samples were considerably influenced by pollution aerosols, WSO_{NA} contributed only a very small portion of TSN (6% without VBON, 10% including VBON) on “Pollution” days. We also find that WSO_{NA} contributes much less than the 30% generally cited in literature estimates to TSN deposition. This result held true for all four N source types identified in our study: i.e., samples categorized as “Sea-spray,” “Dust,” “Biomass Burning,” and “Pollution.” Thus, if N pollution emissions aerosols continue to increase as predicted [Dentener *et al.*, 2006], we expect that WSIN will continue to be the most important source of TSN to the subtropical North Atlantic. Therefore, while anthropogenic activity is increasing total N inputs to the ocean, the increases in WSON to the western subtropical North Atlantic may be smaller than previously thought.

[58] Finally, our measurements show for the first time that a major portion of soluble organic N in polluted air is in the form of operationally defined VBON, present either as gases in the atmosphere or as volatilizable aerosols. The composition of the VBON pool is uncertain, particularly because the magnitude of the VBON pool cannot be explained by amines alone or by the expected concentrations of individual VBON species measured in other marine locations. However, our data provide evidence that VBON concentrations in Miami are significant (about twice the size of the WSO_{NA} compounds captured in Miami), and that VBON has a terrestrial source, perhaps associated with pollution. The strong seasonal cycle in VBON concentrations measured at Miami suggest transport from the midlatitudes and the upper troposphere. WSO_{NA} associated with polluted air masses in Miami is present mainly in the fine size aerosol fraction, suggesting that if VBON is semi-volatile, it can interact with these smaller particles. Questions remain regarding the sources and composition of VBON, and the role it has in N deposition to the ocean.

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