

Composition of Dissolved Organic Nitrogen in Continental Precipitation Investigated by Ultra-High Resolution FT-ICR Mass Spectrometry

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*Received March 13, 2009. Revised manuscript received
June 22, 2009. Accepted July 14, 2009.*

The atmospheric transport of fixed nitrogen (N) is a critical component of the global N cycle that has been heavily impacted by human activities. It has been shown that organic N is an important contributor to atmospheric N, but its sources and composition are largely unknown. Rainwater samples collected in New Jersey were analyzed by negative and positive ion ultrahigh-resolution electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS). Elemental compositions of 402 N-containing compounds were determined and five main groups of compound classes were identified: compounds containing carbon, hydrogen, oxygen, and N detected as positive ions (CHON⁺), compounds containing CHON detected as negative ions (CHON⁻), compounds containing CHN detected as positive ions (CHN⁺), and CHON compounds that contain sulfur (S) detected as both positive and negative ions (CHONS⁺, CHONS⁻, respectively). The CHON⁺ compound class has the largest number of compounds detected (i.e., 281), with the majority, i.e., 207, containing only one N atom. The elemental ratios of these compounds and their detection in the positive ion mode suggest that they are compounds with reduced N functionality. Known contributors to secondary organic aerosol with anthropogenic sources were also identified including organonitrate compounds and nitrooxy organosulfates.

Introduction

The atmospheric transport and deposition of reactive N are important components of the perturbed global N cycle (1). The cycling of reactive N in the atmosphere is usually measured in terms of inorganic N species (reduced NH₃, NH₄⁺, and oxidized NO_x, HNO₃, N₂O, NO₃⁻); though it is now recognized that organic nitrogen is also an important component of atmospheric N (2, 3). Atmospheric dissolved

organic nitrogen (DON) is likely a complex mixture of compounds with a wide range of sources. Some sources and components of DON have been recognized and quantified. For example, organic nitrates exist in both polluted and pristine regions of the atmosphere and form during gas phase reactions of NO_x and volatile organic carbons (VOCs) (4, 5). Reduced forms of N, including urea and amino acids, exist in the atmosphere and are emitted directly from biomass burning and agricultural areas (6–9). Recently, smog chamber experiments simulating secondary organic aerosol (SOA) formation in the presence of ammonium sulfate have led to the formation of imidazoles (10).

Amino acids are one of the few DON compound classes quantified in rainwater (9, 11, 12), fogwater (13), and aerosols (14). Dissolved free amino nitrogen (DFAN) is typically quantified by an HPLC derivatization technique that is based on a comparison of the retention times of amino acids in a standard mix. Dissolved combined amino nitrogen is quantified by an acid hydrolysis method used to liberate the amino acids in proteins and peptides, then quantified by the same HPLC derivatization technique used for DFAN. Based on these measurements, free and combined amino acids account for 2–25% of the DON in rainwater, fogwater, and aerosols (2). Together, the sum of quantified DON constituents accounts for less than 50% of atmospheric DON. Thus, attributing the sources and assessing the impacts of DON is difficult.

The coupling of electrospray ionization (ESI) inlet systems to mass spectrometers of various resolutions has greatly improved our ability to chemically characterize polar dissolved organic compounds at the molecular level in aqueous environmental samples (15). The most significant advances have been made with ultrahigh-resolution ESI Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS), which allows the identification and separation of thousands of compounds in a sample. For each mass detected, the exact elemental composition (C_aH_bN_cO_dP_eS_f), the double bond equivalent (DBE; number of rings plus double bonds), and elemental ratios (H:C, O:C, N:C) can be calculated. Compounds with primarily acidic functional groups (e.g., organonitrate, carboxylic acids) are transferred to the detector as negative ions and those with primarily basic functional groups (e.g., N heterocycles, amines, alcohols) are transferred as positive ions, making it an ideal tool for characterizing a complex mixture such as DON.

Previous studies have attempted to identify the sources and potential importance of rainwater DON by focusing on comparing the bulk concentrations of inorganic and organic nitrogen species across various spatial and temporal scales (16–18). Since DON is a subset of the complex dissolved organic carbon (DOC) in the atmosphere, it is likely that DON, like DOC, is a dilute complex mixture of compounds with varying individual sources and concentrations. Analysis of organic matter in 11 rainwater samples by unit mass resolution ESI-MS over the mass range 50–500 Da led to the identification of 305 unique masses in the positive and negative ion modes combined (19). However, with unit mass resolution ESI-MS it is not possible to discern if there are multiple compounds within a unit mass bin and what elements (e.g., oxygen, nitrogen, sulfur) are present on the compounds that are detected. The goal in this study was to use ultrahigh-resolution FT-ICR MS to investigate DON on a molecular level by identifying the total number of masses that contribute to DON in the rainwater samples and by assessing to what extent the N has reduced or oxidized functionalities. By addressing these questions we attempt to link groups of DON compounds to potential primary and

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TABLE 1. Bulk Properties of Rainwater Samples Collected in New Jersey

date collected	storm trajectory	rainfall amount (cm)	temp (°C)	pH	NO ₃ ⁻ (μM)	NH ₄ ⁺ (μM)	DON (μM)	DOC (μM)	PO ₄ ³⁻ (μM)
14 May 2002 Camden	SW	3.0	15	4.0	32	44	29	259	0.1
5 October 2002 Camden ^a	W	0.4	21	4.1	44	94	33	263	0.5
20 July 2002 Pinelands	WNW	2.1	22	3.7	59	42	38	224	0.2
10 July 2002 Pinelands ^b	WNW	1.2	22	3.8	53	28	35	253	0.1

^a Negative ion data only. ^b Positive ion data only.

TABLE 2. Number of Compounds in Each Compound Class and the Average (Arithmetic Mean ± Standard Deviation) Elemental Ratios for Each Compound Class (Compounds That Do Not Contain N in Their Elemental Formulas Are Not Included)

type	no. of compounds	% of total	H:C	O:C	N:C	O:N	MW	OM:OC
CHON+	281	70	1.8 ± 0.4	0.38 ± 0.2	0.16 ± 0.1	3 ± 1.8	204 ± 46	1.8 ± 0.3
CHON-	72	18	1.9 ± 0.9	1.6 ± 1.5	0.34 ± 0.3	5 ± 2.4	191 ± 67	3.7 ± 2.3
CHN+	7	2	1.4 ± 0.7		0.26 ± 0.2		92 ± 39	1.4 ± 0.2
CHONS+	14	3	1.6 ± 1.2	0.8 ± 0.5	0.4 ± 0.3	2.5 ± 2	176 ± 39	3.3 ± 1.2
CHONS-	28	7	1.8 ± 1.6	1.7 ± 0.9	2.7 ± 1.9	7.5 ± 3.3	271 ± 60	4.2 ± 1.5

secondary sources, and to provide the chemical insight needed to predict the behavior and fate of atmospheric DON.

Experimental Section

Precipitation was collected from two sites in the northeastern United States, as described in detail by Altieri et al. (20). Additional sample collection and analysis information can be found in the Supporting Information. Briefly, the urban site Camden, NJ (Latitude 39° 56' 57.45" N; Longitude 75° 7' 16.60" W; elevation 11 m) is a city directly across the Delaware River from Philadelphia, PA. The rural site Pinelands, NJ is located in the Lebanon State Forest (Latitude 39° 56' 43.61" N; Longitude 74° 37' 1.52" W; elevation 1 m) and is influenced by regional transport. Two samples were collected from the Camden, NJ site, one in spring and one in fall. Two summer time samples were collected from the Pinelands, NJ site (Table 1). The samples were collected using wet-dry deposition collectors (Aerochem Metrics Model 301, Bushnell, FL) according to regulations outlined by the National Atmospheric Deposition Program (21).

Analyses were performed on the four precipitation samples with a 7-T ESI FT-ICR MS (Thermo-Finnigan LTQ-XL, Woods Hole Oceanographic Institute Mass Spectrometer Facility) operated in both the negative and positive ion mode. The spectra were mass calibrated with standard ions using an external calibrant (G2421A Agilent "tuning mix") and the residual root-mean-square error after calibration was 1.1–1.6 ppm. The mass lists were processed and exported using Xcalibur v 2.0 SR2 (ThermoFisher Scientific). Midas Formula Calculator Software (v1.1) was used to calculate all mathematically possible formulas for all ions with a signal-to-noise ratio ≥ 10 using a mass tolerance of ± 1 ppm.

Results and Discussion

The four rainwater samples analyzed were collected from two locations over different seasons in New Jersey, yet they are similar in bulk properties and storm trajectories (Table 1). The inorganic N concentrations in these samples are consistent with those of other continental precipitation samples (2, 22–25). The DON concentration is also consistent with concentrations reported for continental precipitation collected in the United States (29–38 μM), as is the contribution of DON to TDN (19–30%) (2, 12, 17, 26–28).

Sample Comparison. In the discussion that follows, as in Altieri et al. (20), we have combined the elemental formulas for each of the samples due to the high percentage of overlap. The majority of the N-containing elemental formulas detected in the positive ion mode were found in all three rainwater samples (i.e., <25% unique in each sample), and this similarity across samples was also found for compounds detected as negative ions (20). As an example, all of the N-containing elemental formulas determined in the July 20, 2002 sample are listed with their corresponding *m/z* (Table S-1). We consider the combined data representative of N-containing organic compounds in rainwater collected from an urban impacted (i.e., downwind of a major city) location in New Jersey.

DON Composition. There were 100 masses detected in the negative ion mode over the mass range 50–500 Da that had elemental formula assignments containing N, and 302 N-containing elemental formulas assigned to masses in the positive ion mode over the mass range 50–300 Da (Table 2, Figure 1). For each elemental composition assigned to a mass there are multiple structural isomers possible, and thus this is likely an underestimate of the total number of compounds contributing to the DON in these rainwater samples. The large number of elemental formulas determined in these mass ranges highlights the complexity of this mixture of compounds. It should also be noted that the advanced mass spectrometric methods used are nonquantitative, and thus the quantitative contribution of each compound or each compound class is unknown. To quantify all of the >400 DON compounds detected, authentic standards of each compound would be needed, and that is beyond the scope of this study.

The elemental formulas determined fall into five main compound classes: carbon, hydrogen, oxygen, and nitrogen only, detected in the negative ion mode (CHON-), CHON compounds detected in the positive ion mode (CHON+), compounds containing only CHN detected in the positive ion mode (CHN+), sulfur (S)-containing CHONS compounds detected in the negative ion mode (CHONS-), and CHONS compounds detected in the positive ion mode (CHONS+).

Though the positive ion mode was scanned over a smaller mass range than the negative ion mode (50–300 Da vs 50–500 Da, respectively), the CHON+ compound class has the largest number of elemental formulas, representing 70% of the total number of N-containing compounds (Figure 1). The CHON-

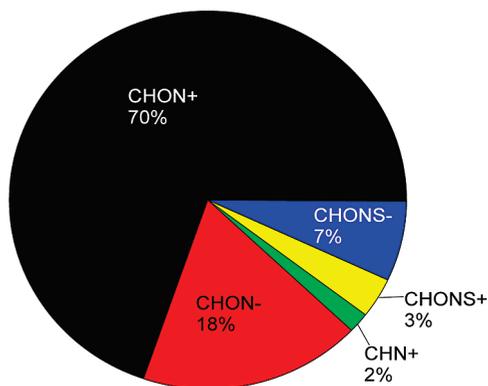


FIGURE 1. Number of each type of elemental formula detected in the rainwater samples that contained N (positive ion mode $+m/z$ 50–300 and negative ion mode $-m/z$ 50–500). There were 402 N-containing compounds detected.

group had the second largest number of elemental formulas, contributing 18% to the total. The CHONS– compounds contribute 7% to the total, with the CHONS+ and CHN+ compounds contributing 3% and 2% to the total, respectively. In the following sections, we discuss in detail the compounds found in each compound class focusing on the CHON+ compounds because of their dominance in total number detected.

Amino Acids and Reduced N Compounds. There were eight CHON+ elemental formulas in the rainwater that are consistent with amino acids commonly measured in precipitation as dissolved free amino acids: valine, leucine (or isoleucine), glutamic acid, phenylalanine, tyrosine, lysine, histidine, and arginine (9, 11, 12, 23, 29). Of the 281 CHON+ elemental formulas, 207 contain only one N atom, 60 have two N atoms, and the remaining 14 compounds have >3 N atoms. The CHON+ compound class has lower oxygen to carbon (O:C), lower organic molecular weight to organic carbon weight (OM:OC), and lower oxygen to nitrogen (O:N) average (arithmetic mean) ratios than all of the other oxygen-containing compound classes (Table 2).

In the CHON+ class, there were 184 elemental masses containing one N atom and at least two O atoms on the molecule. This composition is typical for amino acids, but the molecular weights of many of these compounds are higher than those of known amino acids (up to 240 Da). The oxygen content of these compounds varies from 2–9 O atoms, and the DBE ranges from 0–12. Amino acids can contribute up to 20% of the DON in rain and fog waters (2, 13). They are reactive, and can be oxidized in the atmosphere, and have recently been reported to act as catalysts in atmospheric condensed phase reactions (30). Given the complexity that can result from atmospheric condensed phase (e.g., in aerosols and clouds) reactions (e.g., oligomerization), it is possible that condensed phase reactions involving amino acids could lead to the formation of many compounds that would not be detected by traditional analytical techniques. For example, ~54 compounds in the oligomer series' formed from the aqueous photooxidation of methylglyoxal were detected by FT-ICR MS, but were not detected by traditional HPLC techniques (31). The large number of compounds with 1 N atom on the molecule and varying CHO compositions suggests that whatever atmospheric reactions are forming these compounds they are not impacting the N functionality of the molecule, and are only altering the carbon and oxygen composition. The amino acids may contribute a fairly small percentage to the total DON, but their oxidation products and/or oligomerization products might be numerous and would be detected in the CHON+ compound class, thus their quantitative contribution to DON may be higher than an estimate based on amino acids alone.

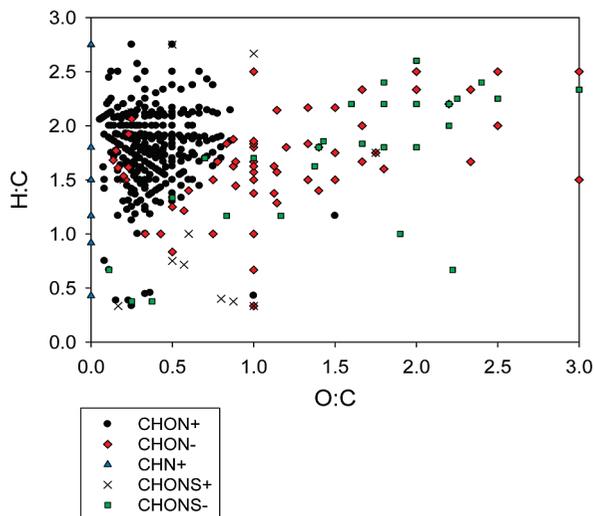


FIGURE 2. Elemental ratios of the N-containing compounds (positive and negative ion mode) detected in the rainwater.

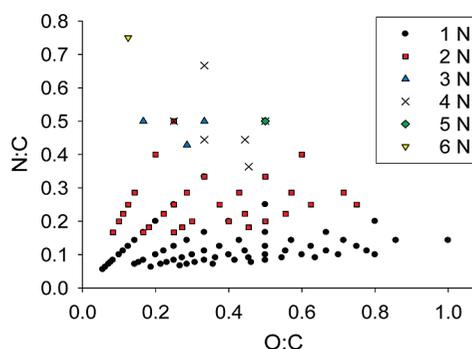


FIGURE 3. Elemental ratios of only the CHON+ compounds detected in the rainwater. The legend denotes the number of N atoms on the molecule.

One way to identify oligomerization products is the van Krevelen diagram, which plots the hydrogen to carbon (H:C) ratio as a function of the O:C ratio. The van Krevelen can be used to display compositional characteristics, to compare the elemental ratios of each compound in a compound class, and to identify groups of compounds related by regular mass differences (32). The CHON+ compounds have H:C ratios comparable to the other compound classes, but lower O:C ratios (black circles, Figure 2). The low O:C, O:N, and OM:OC average ratios, and the grouping of the compounds on the van Krevelen diagram indicate that the CHON+ compounds do not have organic nitrate functionality, and are likely compounds with reduced N functional groups.

In the traditional van Krevelen diagram (H:C vs O:C), the CHON+ compounds are grouped very close together and it is difficult to discern patterns. The van Krevelen was modified to focus on the N component of the CHON+ compounds, and the nitrogen to carbon (N:C) ratio was plotted as a function of the O:C ratio (Figure 3). In this N-based van Krevelen diagram, certain patterns become evident. For example, there is a series of compounds that contain 1 N atom, and differ by CH_2O units (Table 3). The DBE does not increase with the addition of CH_2O meaning the number of rings and double bonds does not change on the molecule and the addition of CH_2O is through single bonds only. A plot of the DBE values as a function of molecular weight also highlights regular differences in the CHON+ compounds (Figure S-1). The patterns in the van Krevelen and the relationships between series of compounds suggest that some of the CHON+ compounds could be formed through oligomerization reactions in the atmosphere.

TABLE 3. Series of CHON+ Compounds That Differ by CH₂O Identified in the Modified N-Based van Krevelen (Figure 3)

⁺ <i>m/z</i> (measured)	formula [M + H] ⁺	DBE	H:C	N:C	O:C
162.07607	C ₆ H ₁₂ N ₁ O ₄	2	1.83	0.17	0.67
192.08666	C ₇ H ₁₄ N ₁ O ₅	2	1.86	0.14	0.71
222.09721	C ₈ H ₁₆ N ₁ O ₆	2	1.88	0.13	0.75
252.10777	C ₉ H ₁₈ N ₁ O ₇	2	1.89	0.11	0.75
282.11832	C ₁₀ H ₂₀ N ₁ O ₈	2	1.90	0.10	0.80

Organonitrates. There were 72 CHON[−] masses in the mass range 50–500 Da. Similar to the CHON⁺ compounds, the majority (i.e., 59) of the CHON[−] compounds have only one N atom. Eight compounds have two N atoms, four compounds have 3 N atoms, and one compound has 4 N atoms. The average H:C ratio of the CHON[−] compound class is comparable to that of the CHON⁺ compounds, however, the average O:C, N:C, O:N, and OM:OC ratios are all much higher in the CHON[−] compound class than in the CHON⁺ compound class (Table 2). The CHON[−] compounds group to the right of the CHON⁺ compounds on the van Krevelen diagram (Figure 2), indicating a higher degree of oxidation. When the mass-to-charge ratios are plotted together differences in the CHON⁺ and CHON[−] compounds are also apparent (Figure S-2). The higher O:C, O:N, OM:OC ratios, and the placement on the van Krevelen diagram are consistent with the N in these compounds being an organic nitrate (ONO₂) group. The nitrate ion is detected in the negative ion mode, and organonitrates, if present, are also expected to be seen in the negative ion mode. There were 61 CHON[−] compounds with O:N ratios of 3–9, which allows all 61 compounds to potentially have organic nitrate functionalities.

Elemental formulas consistent with common C₁–C₁₅ alkyl nitrates frequently measured in the gas phase (33) were not detected; this is consistent with the low solubility of alkyl nitrates. The CHON[−] compounds in the rainwater have higher O:C and O:N ratios than simple alkyl nitrates, which might explain why these organonitrate compounds are more water-soluble. It is possible that oxidation of alkyl nitrates and other VOC and NO_x reactions are the sources of these rainwater CHON[−] compounds.

Sulfur- and Nitrogen-Containing Compounds. There were 42 elemental formulas assigned that contained CHONS: 14 masses detected in the positive ion mode, and 28 masses detected in the negative ion mode. The 28 CHONS[−] compounds have been discussed previously (20). The elemental ratios, oxygen content, placement on the van Krevelen diagram (Figure 2), and comparison with other elemental formulas documented in atmospheric samples all suggest that these components are nitrooxy organosulfates. Nitrooxy organosulfates are formed in the atmosphere from organic precursors in the presence of high-acidity sulfate-containing aerosols under high NO_x conditions (34).

The 14 compounds containing CHONS detected in the positive ion mode have comparable average H:C ratios, but lower average O:C, N:C, OM:OC, and O:N ratios than the CHONS[−] compound class (Table 2). The molecular weight range (130–257 Da), and the average molecular weight (176 Da) of the CHONS⁺ compounds are lower than those of the CHONS[−] compounds (i.e., 176–493 and 271 Da, respectively). Note that different mass ranges were scanned (*m/z*⁺ 50–300, *m/z*[−] 50–500); however, there are only 5 CHONS[−] compounds detected above *m/z* 300. The CHONS⁺ compounds group to the left of the CHONS[−] compounds on the van Krevelen diagram (Figure 2), indicating a lower degree of oxidation. Taken as a whole, this indicates that the CHONS⁺ compounds do not have a combination of nitrate and sulfate functionalities, and are not nitrooxy organosul-

fates like the CHONS[−] compounds. These observations, the low oxygen content of these compounds, and their detection in the positive ion mode suggest that the N and/or S is present in a ring. The DBE values were higher in this group than the others, ranging from 0–8 with an average of 4, which also supports the presence of N and S in a ring structure. However, without further chemical analysis (e.g., tandem MS-MS, LC-MS) it is not possible to positively identify these compounds.

Carbon, Hydrogen, and Nitrogen Compounds. There were seven masses detected in the positive ion mode that were assigned elemental formulas containing only CHN. There are also other compounds with primary sources that the ESI process would have difficulty ionizing including PAHs, and soot derived material, thus it is possible that the low number of masses detected in this compound class is an underestimate of the actual number of CHN compounds in the rainwater. The average H:C ratio was comparable to that of the other compound classes, though the average molecular weight and OM:OC ratios were lower than in the other compound classes. Because the compounds were detected in the positive ion mode the N functionality is likely as an amine or as a N heterocycle. Similar to the CHONS⁺ compounds, the DBE values were high in this group and ranged from 0 to 8 with an average of 4, allowing the compounds to be ring structures or to have multiple double bonds. There are many structures and structural isomers possible for the detected CHN⁺ formulas including diethylamine (C₄H₁₁N), methylimidazole (C₄H₇N₂), tetrahydropyridine (C₅H₁₀N), aniline (C₆H₇N), and diphenylamine (C₁₂H₁₂N). Two of the CHN⁺ compounds, C₄H₇N₂ and C₄H₁₂N, have the same elemental formula as compounds identified with biomass burning aerosols. Though it is not possible to positively identify any of these compounds without further analysis, the likely possibilities include primary compounds with anthropogenic and/or biomass burning sources (35).

Impacts. The large number of elemental formulas with reduced N functionality and the amino acids in the CHON⁺ compound class likely contribute to the bioavailability of atmospheric DON deposition. There is evidence that atmospheric DON can be a bioavailable source of N to coastal systems and can be utilized for primary production (36–38). Though the amino acids are likely from primary emissions, many of the other >200 CHON⁺ compounds are likely formed through secondary processing in the atmosphere of alkyl amines or amino acids. This is contrary to previous assessments of atmospheric DON which have assumed that reduced N compounds could not be produced in situ under the oxidizing conditions of the atmosphere (39). In addition to being bioavailable, amino acids, and in theory the amino acid like compounds, can act as efficient ice nuclei and could be surface active (14).

The complexity in the number and type of elemental formulas determined in the rainwater helps explain why traditional analytical techniques have not been able to characterize the full suite of N-containing organic compounds. Many of these compounds are multifunctional and some are highly oxygenated, thus they likely contribute to the fraction of atmospheric organic matter that is considered humic like substances (HULIS). Some of these compounds (e.g., nitrooxy organosulfates) are known contributors to SOA, which suggests that SOA formed in the presence of nitrogen could be contributing to the complexity in rainwater DON. This provides motivation for continuing to include nitrogen in experiments on SOA formation mechanisms, but also for detailed product identification in those experiments to identify the formation of organic N-containing compounds (e.g., 10, 34).

The majority of the compounds that were detected by FT-ICR MS are likely to have secondary sources. For example, CHONS[−] compounds are formed from secondary reactions

in the atmosphere in the presence of anthropogenic NO_x, sulfate, and reactive organics. CHON⁻ compounds are likely formed from atmospheric reactions of VOCs and NO_x. As discussed above, the CHON⁺ compounds could be from secondary processing of amines or amino acids in the atmosphere. Though the reactive organics (e.g., VOCs, amino acids) could potentially be from biogenic sources, the oxidants (e.g., ozone, NO_x) are mostly anthropogenic making them secondary anthropogenic compounds. The bulk of the DON being formed in the atmosphere from secondary reactions is also supported by the similarity in N-containing compounds across the different samples. The large contribution of compounds formed through atmospheric reactions that involve anthropogenic oxidants suggests that anthropogenic secondary sources contribute significantly to atmospheric DON. This work provides motivation to expand studies of atmospheric DON to remote locations to determine the potential for deposition of secondary anthropogenic compounds in remote ecosystems. It is important that we continue to improve our understanding of the extent to which the perturbed atmospheric N cycle is impacting air quality and receiving ecosystems.

Acknowledgments

We acknowledge Dr. Melissa Soule, Dr. Elizabeth Kujawinski, and the funding sources of the WHOI FT-MS Users' Facility (National Science Foundation OCE-0619608 and the Gordon and Betty Moore Foundation). Travel support for K.E.A. to the WHOI FT-MS Facility was provided by the WHOI Director's discretionary funds. Graduate student support for K.E.A. was provided by the National Center for Environmental Research, U.S. Environmental Protection Agency's Science to Achieve Results (STAR) Program R833751.

Supporting Information Available

Additional information on Sample Collection and Analysis, a table listing all of the measured *m/z*'s and calculated elemental formulas for one rainwater sample, and two additional figures. This information is available free of charge via the Internet at <http://pubs.acs.org/>.

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ES9007849