During the Southern Hemispheric spring of 2000 (during the months of November and early December), rain, bulk and size-separated aerosol samples were collected at the Cape Grim Baseline Air Pollution Station located on the island of Tasmania, Australia and analyzed for total organic nitrogen (N), urea, and dissolved free amino acids. Rain and bulk aerosol samples contained organic N at concentrations representing, on average, between 19 and 25% of total N. Urea was not detected in the six rain samples analyzed. However, urea represented ~24% of the organic N contained in nonbaseline aerosol samples, and ~2% of the organic N contained within baseline samples. Trajectory analysis combined with meteorological data indicated that high concentrations of urea within aerosols were mainly due to Tasmanian sources, likely animal emissions, although the application of urea fertilizers cannot be dismissed as a source. In nonbaseline samples the highest concentrations of urea were associated with the coarse mode aerosol (>1 μm), although urea was also found in the fine mode aerosol (<1 μm), potentially indicating gas-to-particle conversion of urea. Aerosol samples collected in marine air masses contained urea within an intermediate fraction centered at ~1 μm suggesting the sea surface microlayer as a source. Dissolved free amino acids contributed ~53% of the organic N in rain, but were not a significant proportion of the total organic N fraction in either nonbaseline or baseline aerosol samples. Due to their presence in rain, amino acids likely exist in aerosols as unhydrolyzed proteins. In cascade impactor samples highly influenced by marine sources, profiles for amino N were inversely related to urea N, possibly indicating live species and the sea surface microlayer as a source for organic N.

Index Terms: 0312 Atmospheric Composition and Structure: Air/sea constituent fluxes (3339, 4504); 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 1615 Global Change: Biogeochemical processes (4805); Keywords: water-soluble nitrogen, nitrogen cycling, sea surface microlayer, aerosols, rain, organic nitrogen


1. Introduction

Nitrogen, a limiting nutrient for many coastal and oligotrophic oceanic ecosystems, can either be helpful or harmful depending on its delivery route, species composition, and abundance [Antia et al., 1991; Donaghay et al., 1992; Kroese and Seitzinger, 1998; Pael et al., 2000]. The atmosphere can have a substantial impact on nitrogen (N) delivery to coastal ecosystems worldwide. In these areas, the average atmospheric flux for inorganic N represents ~30% of total N delivery, although it can range from 10 to 70% of the total N delivered as “new” N [Duce, 1998; Pael et al., 2000]. Most current estimates of total N delivered to oceanic ecosystems from atmospheric deposition only include the inorganic N species ammonium (NH₄⁺) and nitrate (NO₃⁻). The organic N proportion of total N is usually not included in atmospheric deposition studies. Therefore current atmospheric deposition approximations generally under-
estimate total N entering oceanic ecosystems via the atmosphere [Cornell et al., 1995].

[1] In a recent assessment of organic N in rainwater, Cornell et al. [2001] indicated that organic N represents ~29, ~26, and ~62% of the total N entering continental, coastal, and remote oceanic areas worldwide, respectively, in wet deposition. Adding organic N to atmospheric deposition measurements of inorganic N increases N totals. For example, in the aforementioned study of Duce [1998], including organic N (by an addition of 26% to atmospheric N values) would increase the percentage of atmospheric N as total N from ~30 to ~40% for coastal areas worldwide. An increased supply of fixed N in atmospheric deposition is expected in the coming decades, as humans fix more nitrogen for food and fuel, causing increases in atmospheric deposition. Adding organic N to atmospheric deposition has significant implications for coastal, and remote oceanic areas worldwide, respectively, thus far indicate a large proportion of organic N within the Southern Ocean.

[2] Organic N, as defined in this manuscript, is not the same as total organic N (Norg), which includes organic N (by an addition of 26% to atmospheric N values) would increase the percentage of atmospheric N as total N from ~30 to ~40% for coastal areas worldwide. An increased supply of fixed N in atmospheric deposition is expected in the coming decades, as humans fix more nitrogen for food and fuel, causing increases in atmospheric deposition. Adding organic N to atmospheric deposition has significant implications for coastal, and remote oceanic areas worldwide, respectively, thus far indicate a large proportion of organic N within the Southern Ocean.

An increased supply of fixed N in atmospheric deposition is expected in the coming decades, as humans fix more nitrogen for food and fuel, causing increases in atmospheric deposition. Adding organic N to atmospheric deposition has significant implications for coastal, and remote oceanic areas worldwide, respectively, thus far indicate a large proportion of organic N within the Southern Ocean.

[3] To date, sampling in the marine atmosphere has been sparse for individual organic compounds potentially contributing to the bulk organic N fraction. A few studies have been conducted in the last two decades as the reliability of analytical methods for organic N improved. Mopper and Ziska [1987] reported dissolved free amino acid concentrations in marine rains that equaled or exceeded concentrations of inorganic N (NH$_4^+$ and NO$_3^-$) in samples collected from the Gulf of Mexico (amino acids ~1$\mu$M, NH$_4^+$ ~6$\mu$M, and NO$_3^-$ ~9$\mu$M in rain) and the northwest Atlantic Ocean (amino acids ~5$\mu$M, NH$_4^+$ ~12$\mu$M, and NO$_3^-$ ~32$\mu$M in rain). While such a finding could suggest that dissolved free amino acids are a significant proportion of organic N in rains in marine areas, other studies such as those of Gorzelka and Galloway [1990] have indicated a limited role for amino acids. Urea has also been investigated recently in a few marine areas. Cornell et al. [2001, 1998] reported large contributions of urea in rains collected from sites in Hawaii (urea was ~50% of the organic N in rain) and Tahiti (urea was ~40% of the organic N in rain), respectively. Timperely et al. [1985] also reported large quantities of urea within rains collected in Japan (urea was ~50% of the organic N in rain) and New Zealand (urea was ~33% of the organic N in rain), possibly suggesting high concentrations of urea for samples influenced by marine sources. However, in other areas the concentration of urea has been found to be below detection or very low in concentration. For example, Cornell et al. [1998] reported urea at concentrations below detection in rain samples collected at Bermuda and at Mace Head, Ireland.

[4] Given the findings listed above it is clear that the present data for total organic N and individual organic N species such as urea and amino acids contribute to a complicated scientific scenario regarding the sources for organic N within the marine atmosphere, the source(s) and abundance of amino acids in the atmospheric samples collected from these areas, and the source(s) of urea reported to date. In order to understand nutrient limitations and the impact of the atmosphere on oceanic ecosystems in future decades, the sources and species comprising the organic N fraction must be elucidated.

[5] To add further information concerning the origins of organic N and the relationship of the previously examined organic N species urea and dissolved free amino acids to organic N totals, a study was conducted at Cape Grim Baseline Air Pollution Station (CGBAPS). Determining the variation of the total organic N fraction between remote oceanic areas in the Northern and Southern Hemispheres was also a main objective (since the majority of N fixation occurs in the Northern Hemisphere and since the majority of recent remote marine organic N sampling campaigns have been undertaken in these areas). The station, operated by the Australian Bureau of Meteorology, is located on the north-west corner of the island of Tasmania, south of mainland Australia (40.41°S, 144.41°E) (Figure 1). The station sits at ~94 m on a cliff at the end of Cape Grim, which extends into oceanic waters near an area where the Bass Strait meets the Southern Ocean.

[6] The air sampling at CGBAPS was conducted during November and early December of 2000. During this time period, rain and high-volume bulk and size-separated aerosols were collected and investigated for total inorganic N, total organic N, dissolved free amino acids, and urea. Aerosol collections were conducted during periods when CGBAPS was collecting simultaneous meteorological measurements for wind speed, wind direction, and condensation nucleus (CN) counts (described in further detail in subsequent sections). The origin of the air sampled was described by air mass back trajectory plots, obtained through the US National Oceanic and Atmospheric Administration’s (NOAA), Climate Monitoring and Diagnostics Laboratory (CMDL).

[7] In this manuscript total organic N, hereinafter referred to as “organic N,” is defined as the total N from inorganic ion analysis (from NH$_4^+$, nitrite (NO$_2^-$), and NO$_3^-$) following a 2-hour UV irradiation, minus inorganic ions (NH$_4^+$, NO$_2^-$ and NO$_3^-$) measured prior to UV analysis. The term “amino N” is used to define the total N from 17 individual amino acids including aspartic acid, glutamic acid, serine, threonine, glycine, alanine, arginine, proline, valine, methionine, isoleucine, leucine, phenylalanine, cystine, lysine, histidine, and tyrosine. The term “urea N” is used to define the total N determined from urea. Analytical techniques are discussed in section 2.2.

2. Sample Collection and Analysis

2.1. Sample Collection

[5] Rain and bulk and size-separated aerosols were collected on the roof deck at CGBAPS. Rain samples were collected with 30 cm diameter polyethylene funnels fitted to 500 ml polyethylene bottles. Both funnels and bottles were first soaked in detergent for 24 hours to remove organic impurities from the plastic, then soaked in a 20% hydrochloric acid (HCl) water bath for at least 30 min, and finally rinsed at least six times with purified water (>17.7 MΩ cm) prior to deployment. Each day at ~1000 hours LT (Australian Eastern Standard Time, AEST) a clean bottle and a clean funnel were attached to a post above the roof deck in
anticipation of rain. If no rain was collected during a 24-hour collection period the sample container was discarded and a new container was installed. If rain was collected, it was filtered through 0.45 μm Nuclepore polycarbonate filter and frozen at −20°C until analysis. The filter was rinsed with approximately 10 ml of the sample to be analyzed to insure no contamination of N compounds eluted from the filter. A series of rain procedural blanks was also collected each day by pouring ~50 ml of purified water (>17.7 MΩ cm) through the clean funnel-bottle assembly. Procedural blanks were treated as rain samples and also frozen at −20°C until analysis. The data presented have been cor-

Figure 1. Sample Cape Grim back trajectory plots for (a) a 24-aerosol sample collected during nonbaseline conditions (8 November 2000), and (b) a sample collected during baseline conditions (23–24 November 2000, on the sector control system). Solid lines represent calculated trajectories beginning at 0000 hours UT. Dashed lines represent calculated trajectories beginning at 1200 hours UT. Numbers shown on trajectory plots represent the location of air masses on specific days before reaching CGO (Cape Grim). The elevation (ELEV) for the air masses is also shown at the bottom of each trajectory diagram.
rected for these blanks (analytical blanks are discussed in section 2.2).

[10] Bulk and size-separated cascade impactor aerosol samples were also collected on the roof deck at CGBPAS. For this collection, the bulk aerosol collector and the cascade impactor heads were mounted on a mast above the roof deck, ~2 m above the surface of the roof deck. The samplers were elevated above the surface of the roof deck to minimize contamination from soil-influenced aerosols coming from the slope of the cliff [Andreae, 1982], as the station sits at the top of a steep cliff. Pumps and controllers for the systems were placed at roof deck level to limit the influence of impurities from the pumps, and a 2-inch diameter hose was connected between the pumps and the heads of the bulk collector and the cascade impactor. Bulk and size-separated aerosol samples were collected for ~24 hours on precombusted (4 hours at 450°C in a muffle furnace) glass-fiber filters using a high-volume collection system and a high-volume modified Sierra cascade impactor (Thermo Andersen, Smyrna, GA, USA), respectively, sampling at a rate of ~45 m³ of air per hour. Prior to analysis, 1/4 of bulk filters and 1/2 of cascade impactor filters were extracted in ~30 ml of purified water (> 17.7 MΩ cm), and sonicated for 30 min in an ambient water bath. Extracts were then filtered, as were the rain samples, through a 0.45-µm nuclepore polycarbonate filter prior to analysis. Deployment blanks were also obtained by placing precombusted filters in line for 24 hours on idle systems (i.e., no airflow through the filters). Deployment blanks were processed as other aerosol sample types (1/4 of a sample was extracted for bulk aerosol deployment blanks and 1/2 of a sample was extracted for cascade impactor deployment blanks). The data presented have been corrected for these blanks (analytical blanks are discussed in section 2.2).

2.2. Sample Analysis

[11] Rain and aerosol extracts were analyzed first for the inorganic N species, NH₄⁺ NO₃⁻ and NO₂⁻. For these ion analyses, a Dionex (Sunnyvale, CA, USA) DX 300 ion chromatography equipped with a Rheodyne (Cotati, CA, USA) 9126 rear-loading valve and Dionex AI450 chromatography software was utilized. Ammonium ion analysis was accomplished using a Dionex CS12A cation exchange column guarded with a Dionex CG12A guard column in autosuppression mode. Due to the high amount of sodium ion (Na⁺) in the rain and aerosol samples (from sea salt), the standard Dionex cation exchange method was adjusted for high Na⁺ by slowing the flow rate and altering the eluent to 10 mM of methanesulfonic acid (MSA). This modification allowed for low-level detection of NH₄⁺ (at a level of ~10 ppb NH₄⁺ using a 100-µl loop) in the presence of high sodium. The precision of the NH₄⁺ ion analysis was ±6%. Nitrite and NO₃⁻ analysis was accomplished using a Dionex AS12A anion exchange column guarded with a Dionex AG12A guard column. The separation was performed according to the standard method provided for the column: an isotropic elution with a solution of sodium bicarbonate and sodium carbonate. The precision of the NO₂⁻ and NO₃⁻ ion analyses was ±3%. Due to low concentrations obtained for NO₂⁻ (less than 1% of total N in all samples), NO₂⁻ concentrations have not been reported in section 3.

[12] Organic N (as total N - inorganic N) was determined following UV photo-oxidation using a Metrohm 705 UV digestor (Metrohm, Switzerland). For the UV analysis, filtered rain or aerosol extracts were diluted to an appropriate level in a total volume of 12 ml and exposed to UV light for 2 hours at a temperature of 85°C. Following the UV analysis, samples were treated as inorganic N samples and injected onto the appropriate columns without further treatment. Blanks for the total N (post-UV) rain analysis represented ~5% of total N (mean of 1.7 µM N, standard deviation of 0.09 µM N). Blanks for the total N (post-UV) for bulk aerosol analyses represented ~4% of total N (mean of 6.0 µM N, standard deviation of 3.9 µM N). Cascade impactor blanks represented ~15% of total N (at 6.0 µM N) in individual stages. All data reported in the manuscript have been corrected for deployment blanks.

[13] Due to the analytical variability associated with UV total N methods [Cornell and Jickells, 1999; Mace and Duce, 2002a], a study was conducted to determine the precision of the total N analysis. For this analysis, the bulk glass-fiber aerosol filter sample collected on 1 November 2000 was sectioned into equal quarters and analyzed for total inorganic and total organic N. As a result of the analytical variability of inorganic ion analyses both predigestion and postdigestion, the variability associated with the extraction procedure, the variability associated with aerosol collections using high-volume samplers, and the variability associated with deployment blanks, organic N concentrations in duplicate analyses can only be expected to agree within 30% (Table 1).

[14] Urea was analyzed in rain and aerosols using a new ion chromatography method developed in the laboratory at Texas A&M University [Mace and Duce, 2002b]. The method utilizes a Dionex CS12 cation exchange column, a CG12 guard column, an eluent consisting of 20 mM of MSA, and UV detection at 190 nm. A UV/Vis spectrophotometer (a part of the DX 300 ion chromatograph) provided the means for quantitative determination. For analysis, filtered rain or aerosol extracts (pretreatment procedure described in section 2.1) were injected onto the column without further preparation. A liquid urea standard purchased from Sigma (St. Louis, MO, USA, product 535-30) was utilized for the quantitative determination of urea within samples.

[15] Amino acids were analyzed using a modified 4-dimethylaminoazobenzene-4'-sulfonyl chloride (DABS-Cl) method [Stocchi et al., 1992]. Prior to analysis, 10 ml of filtered sample were dried in a Savant speed-vac concentrator (Thermo Savant, Holbrook, NY, USA) and derivatized.
Table 2. Time Degradation Results*

<table>
<thead>
<tr>
<th>Description</th>
<th>NO\textsubscript{3} N</th>
<th>NH\textsubscript{4} N</th>
<th>Total N</th>
<th>Urea N</th>
<th>Amino N</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1\textsuperscript{b}</td>
<td>2\textsuperscript{c}</td>
<td>1</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>Bulk filter, Nov. 8, 2000</td>
<td>0.2</td>
<td>0.3</td>
<td>0.01</td>
<td>0.1</td>
<td>0.5</td>
</tr>
<tr>
<td>CI Nov. 17, 2000, stage 1</td>
<td>0.3</td>
<td>0.8</td>
<td>0.02</td>
<td>0.004</td>
<td>1.9</td>
</tr>
<tr>
<td>CI Nov. 17, 2000, stage 2</td>
<td>0.5</td>
<td>0.6</td>
<td>0.02</td>
<td>0.006</td>
<td>0.6</td>
</tr>
<tr>
<td>CI Nov. 17, 2000, stage 3</td>
<td>0.6</td>
<td>0.7</td>
<td>0.02</td>
<td>0.001</td>
<td>0.9</td>
</tr>
<tr>
<td>CI Nov. 17, 2000, stage 4</td>
<td>0.8</td>
<td>1.0</td>
<td>0.02</td>
<td>0.004</td>
<td>1.9</td>
</tr>
<tr>
<td>CI Nov. 17, 2000, stage 5</td>
<td>0.5</td>
<td>0.6</td>
<td>0.02</td>
<td>0.004</td>
<td>1.9</td>
</tr>
<tr>
<td>CI Nov. 17, 2000, stage 6</td>
<td>0.1</td>
<td>b.d.\textsuperscript{d}</td>
<td>0.02</td>
<td>0.006</td>
<td>b.d.</td>
</tr>
<tr>
<td>P Value</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bulk aerosol</td>
<td>0.91</td>
<td>0.69</td>
<td>0.87</td>
<td>0.72</td>
<td>0.61</td>
</tr>
<tr>
<td>Cascade</td>
<td>0.34</td>
<td>0.50</td>
<td>0.18</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Units are nmol N/m\textsuperscript{3} for all species.
\textsuperscript{b}Number 1 denotes the first analysis.
\textsuperscript{c}Number 2 denotes the second analysis.
\textsuperscript{d}Letters b.d. denote samples where species were below detection.

with DABS-Cl. An LC-DABS 15 cm × 4.6 mm, 3 μm particle column, guarded with an LC-18-T guard column (Supelco, Bellefonte, PA, USA), and a gradient of chromatography grade acetonitrile:methanol and a pH neutral 25 mM potassium phosphate dibasic solution provided the means for amino acid separation. The DX 300 ion chromatograph, fitted with a Teflon switching valve and set to record absorbance at 436 nm using the UV/vis detector, was a suitable system for this analysis. A liquid amino acid standard purchased from Sigma (product AA-S-18), containing the 17 amino acids listed in section 1, was utilized for quantitative determinations of amino acids within samples.

### 2.3. Time Degradation Study of Aerosol Samples

Due to the ability of organic compounds to degrade and the potential impact as a sampling artifact, we conducted a time degradation study using ten bulk aerosol and cascade impactor samples collected during the sampling campaign. Samples used in the study were analyzed on-site at Cape Grim and then again at Texas A&M University, 6 months later. Samples were kept frozen and in the dark at −20°C at CGBAPS, and then transported still frozen, by express courier, from Cape Grim to Texas A&M. Samples were processed as described above and the values obtained at Cape Grim were compared, by way of \textit{t} test, to values obtained at Texas A&M 6 months later. No statistically significant differences were found between the two groups (Table 2) suggesting that organic N compounds collected in atmospheric aerosols are relatively stable under conditions that limit thermal, photochemical, or biological breakdown. Since all rain samples were analyzed on site and could not be transported to the United States due to customs restrictions, a similar study could not be conducted on filtered rain samples or filtered aerosol extracts.

### 2.4. Meteorological Conditions During the Field Campaign

During the sampling most of the wind flow to CGBAPS was nonbaseline (Figure 2). Baseline conditions were defined as a CN count of ≤600 CN/cm\textsuperscript{3} and winds between 198° and 280°. Winds were mainly nonbaseline, easterly as seen in Figures 1a and 2, with high concentrations of CN/cm\textsuperscript{3} (Figure 2). Nonbaseline conditions also included southerly winds across Tasmania. A total of thirteen 24 hour bulk and cascade impactor samples were collected under nonbaseline conditions from 1–20 November 2000. From 21 November to 7 December 2000 samplers were placed on a baseline sector control system at CGBAPS in order to obtain clean marine air mass samples. Only two 24 hour samples were collected under baseline conditions, mainly due to the high CN counts that persisted (Figure 2). Baseline conditions required westerly winds with CN counts at a level of ≤600 CN/cm\textsuperscript{3}, as described above, and are the result of clean marine air from the Southern Ocean (Figure 1b). All aerosol samples collected under nonbaseline and baseline conditions were analyzed as described above.

### 3. Results and Discussion

#### 3.1. Organic Nitrogen in Rain

Six rain samples of sufficient volume were collected for analysis. In Table 3, average concentrations obtained for individual N species as well as average percentages for organic components are presented. As seen in Table 3, organic N represented approximately 19% of total N. While urea has been reported as a component of rain in other oceanic atmospheric sampling campaigns [Cornell et al., 2001; 1998; Timperley et al., 1985], urea was not detected in any of the rain samples analyzed. However, other unknown urea-like compounds (compounds containing an amino group) were detected by the new urea method (described in section 2.2). Since the urea diacetylmonoxime method [see Cornell et al., 1998] most commonly utilized by researchers is capable of identifying other compounds (i.e., allantoin, allantoic acid, citrulline, and uric acid) as urea [Price and Harrison, 1987; Mace and Duce, 2002b], and because this method is also prone to chemical failure...
when aldehydes and phenols are present [Zuoguo et al., 1986], other urea-like compounds such as allantoic acid and allantoin may have contributed to the high urea values reported in other studies [i.e., Cornell et al., 2001, 1998; Timperely et al., 1985]. While many mammals excrete most of their unused N as urea, a variety of mammals, and most birds, reptiles, and insects excrete unused N as uric acid or allantoin derivatives [Webb, 2001; Groot Koerkamp et al., 1998]. These chemicals (commonly known as purine derivatives by plant physiologists) are also present in the leaf tissues and the xylem of higher plants [Thomas and Schrader, 1981]. However, the absence of urea in the rain samples collected may be due to other factors. Rain samples were collected on dates of low urea concentrations within aerosols: 1, 8, 9, 10, 15, 20 November (discussed in section 3.2.), so any aerosol scavenging of urea would produce rain samples with low urea concentrations. We suggest that any urea within rain samples at Cape Grim: (1) was decomposed
Table 3. Nitrogen in Rain

<table>
<thead>
<tr>
<th>Date</th>
<th>NO3</th>
<th>NH4</th>
<th>Organic N</th>
<th>S, Organic N</th>
<th>Amino N</th>
<th>S, Amino N</th>
<th>Urea N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oct. 1</td>
<td>8.9</td>
<td>6.5</td>
<td>b.d.</td>
<td>0.1</td>
<td>no value</td>
<td>2.5</td>
<td>b.d.</td>
</tr>
<tr>
<td>Oct. 2</td>
<td>13.7</td>
<td>12.5</td>
<td>2.8</td>
<td>0.5</td>
<td>1.4</td>
<td>2.8 x 10^2</td>
<td>b.d.</td>
</tr>
<tr>
<td>Nov. 9</td>
<td>29.4</td>
<td>45.0</td>
<td>11.5</td>
<td>5.7 x 10^2</td>
<td>1.4</td>
<td>5.5 x 10^4</td>
<td>b.d.</td>
</tr>
<tr>
<td>Nov. 11</td>
<td>8.1</td>
<td>15.0</td>
<td>7.2</td>
<td>0.5</td>
<td>6.4</td>
<td>5.0 x 10^4</td>
<td>b.d.</td>
</tr>
<tr>
<td>Nov. 15</td>
<td>13.1</td>
<td>13.2</td>
<td>16.5</td>
<td>1.4</td>
<td>9.2</td>
<td>8.6 x 10^4</td>
<td>b.d.</td>
</tr>
<tr>
<td>Nov. 20</td>
<td>8.1</td>
<td>15.0</td>
<td>7.2</td>
<td>0.5</td>
<td>0.5</td>
<td>2.5 x 10^4</td>
<td>b.d.</td>
</tr>
<tr>
<td>Average</td>
<td>7.4</td>
<td>6.2</td>
<td>5.2</td>
<td>2.9 x 10^3</td>
<td>3.8</td>
<td>2.8 x 10^4</td>
<td>b.d.</td>
</tr>
<tr>
<td>SD</td>
<td>13.4</td>
<td>16.4</td>
<td>7.2</td>
<td>4.1 x 10^3</td>
<td>2.8</td>
<td>2.3 x 10^4</td>
<td>b.d.</td>
</tr>
</tbody>
</table>

Average organic N as % of total N

Average urea N as % of organic N 0
Average amino acid N as % of organic N 53
Unknown organic N 47

*Units are μmol N/l for all species. The letter S indicates the calculated scavenging ratio for the species identified.
*Negative values that arise for organic N as a result of analytical uncertainty and urea N samples where urea concentrations were not found have been designated as below the detection limit. For calculation of the average, these samples have been designated as 0.
*When negative values were found for organic N in rain or aerosol, the computed scavenging ratio is designated as 0.
*Organic N percentages calculated by using NO3, NH4, NO2 and organic N averages.

by thermal, photochemical, or biochemical means and/or (2) escaped to the vapor phase during the time of rain collection, or (3) was below the detection limit of the method (0.3 μM N as urea) for rainwater.

While urea was not detected in any of the rain samples analyzed, dissolved free amino acids made up a considerable proportion of the total organic N, ~53% as seen in Table 3. The remainder, ~47% of the organic N, was uncharacterized. We suggest that the high proportion of free amino acids is due to the decomposition of proteins (peptides) within rain samples prior to collection because dissolved free amino acids were low in concentration within bulk aerosols (discussed in section 3.3). Since rain samples at Cape Grim were collected during the spring, the degradation of pollen is a likely source for the large amino acid concentrations determined in rain samples. As recently indicated by Scheller [2001], pollen grains were responsible for high concentrations of amino acids in dew collected in the spring in Germany.

Unidentified compounds containing amino groups, absorbing at the same wavelength (190 nm) as urea were detected by the new urea method, suggesting that at least some proportion of the remaining organic N compounds may be by-products of protein or nucleic acid decomposition, or possibly unhydrolyzed organic N compounds capable of passing through the 0.45-μm filter. For example, the degradation of nucleic acids (in DNA and RNA) produces a variety of organic N compounds [Salway, 1999]. Ammonia produced from nucleic and amino acid decomposition may also be recycled by live species to produce organic N compounds used for metabolic energy, DNA/RNA synthesis, and/or protein synthesis. Due to the persistence of bacteria and viruses in the natural environment (e.g., in the surface ocean waters, in concentrations of ~10^3/l and ~10^10/l, respectively [Fuhrman, 1999]), and the production of film and jet drops from the sea surface microlayer (see Clark and Zika [2000] and Liss and Duce [1997] for droplet production mechanisms and the role of the sea surface microlayer) the concentrations of bacteria and viruses can be even more concentrated in entrained drops in oceanic areas [Cincinelli et al., 2001 and references therein]. The presence of bacteria in rain has been previously documented [Milne and Zika, 1993 and references therein]. Therefore it would be advantageous in the near term to examine bacterial production rates in rainwater samples using current methods (i.e., 3H-leucine incorporation, Smith and Azam [1992] and Kirchman [1993]) in order to ascertain the presence of live species capable of metabolizing organic N compounds, such as urea, free dissolved amino acids, and/or peptides, within rainwater. Due to the potential problems associated with cooling rain samples with dry ice (such as the trapping of gas-phase species, Cornell et al. [2001]) to stabilize organic N compounds within solution, we suggest that the measurement of bacterial production rates combined with the collection of rain samples in opaque containers would provide the best current solution for organic N rain collection analysis. In future, automated samplers for the simultaneous collection and analysis of rainwater are necessary.

Due to the amount of time required to collect a rain sample of sufficient volume for all analytical procedures, it is possible that organic N compounds within rainwater underwent thermal or photochemical decomposition, as mentioned previously. McGregor and Anastasio [2001] have recently discussed the photochemical decomposition of amino acids within fog waters (concentrated solutions). Their results indicate that reactions of amino acids with hydroxyl radical (•OH) are capable of transforming peptides (yielding free amino acids) or free amino acids (yielding simpler N compounds). Calculations for the scavenging ratio for free amino acids in samples collected at Cape Grim point to such postdepositional changes for free amino acids. The scavenging ratio (S), a calculation for the removal of particles or gases during wet precipitation, is defined by the following equation:

\[ S(\text{dimensionless}) = \frac{C_p}{C_w}, \]

where \( C_p \) is the concentration in rain in μmol N/kg, \( C_w \) is the concentration in air in μmol N/m\(^3\), and \( \rho \) is the density of air at 20°C and 1013 hPa, 1.2 kg/m\(^3\).
For free amino acids at Cape Grim, a calculation of this type yields an average scavenging ratio of $S = 2.8 \times 10^4$, a value suggesting the scavenging of highly soluble gas-phase species, since aerosol phase scavenging typically yields values for $S$ ranging from 200 to 2000 [Duce et al., 1991]. However, since amino acids are known to have large Henry’s law constants (from $2.0 \times 10^5 - 1.0 \times 10^{11}$ (mol/m$^3$ Pa)) [Saxena and Hildemann, 1996] (see also a compilation of Henry’s law constants for inorganic and organic species of potential importance in environmental chemistry [1999], available http://www.mpchmainz.mpg.de/~sander/res/henry.html) at amino acids from the gas phase can likely

![Figure 3. Amino acids in (a) rain ($N = 5$), (b) bulk nonbaseline aerosols ($N = 5$), and (c) bulk baseline aerosols ($N = 2$). The average percent contribution for individual amino acids to amino N totals are also presented.](image-url)
be excluded as important contributors for the dissolved amino acid fraction within rainwater samples. Therefore the increased presence of dissolved free amino acids in rainwater solutions suggests enzymatic cleavage of combined amino acids causing the release of free amino acids, or the formation of free amino acids within solutions postdeposition due to thermal or photochemical decomposition.

As seen in Figure 3a, all amino acids analyzed were found to contribute to amino N totals. Arginine was the greatest contributor to amino N due to its structure that contains four N atoms. It is also possible that the increased presence of arginine in rainwater is due to its presence in the urea cycle as a precursor to urea production [Salway, 1999].

As discussed by McGregor and Anastasio [2001] methionine is a highly reactive molecule that decays rapidly in the presence of simulated sunlight. In Cape Grim rain samples methionine was present in a few samples at low concentration, but was generally found to be below the concentration of other amino acids containing a single N atom of similar molecular weight (the molecular weight of methionine is 149.2) (i.e., aspartic acid, MW = 133; glutamic acid, MW = 147.1; isoleucine, MW = 131.2; leucine, MW = 131.2), even though the DABS-Cl amino acid method utilized is capable of detecting methionine at concentrations at or below the concentration of the other 16 amino acids analyzed. The quantities of other amino acids within rain are not easily explained given the knowledge of molecular structure for individual amino acids or the current knowledge for the photochemistry of amino acids. More research is needed to determine the atmospheric transformation of amino acids.

### 3.2. Organic Nitrogen in Bulk Aerosols

As mentioned above, 13 bulk aerosol samples were collected during nonbaseline conditions and two bulk samples were collected during baseline conditions. In general, the concentrations of organic N components in nonbaseline samples were elevated under conditions when the wind was southerly across Tasmania and under conditions when CN counts were elevated (samples from 2, 4, 11, 12, and 19 November), indicating the influence of local sources on bulk aerosol organic N components under these conditions. Aerosol samples collected during periods when winds were easterly typically contained lower quan-

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**Table 4. Nitrogen in Bulk Aerosols**

<table>
<thead>
<tr>
<th>Date: Nov. 1, 2000</th>
<th>NO(_3)</th>
<th>NH(_4)</th>
<th>Organic N</th>
<th>Amino N</th>
<th>Urea N</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4.5</td>
<td>0.5</td>
<td>5.4</td>
<td>no analysis</td>
<td>b.d.</td>
</tr>
<tr>
<td>Nov. 2, 2000</td>
<td>16.7</td>
<td>3.3</td>
<td>12.4</td>
<td>no analysis</td>
<td>7.6</td>
</tr>
<tr>
<td>Nov. 4, 2000</td>
<td>6</td>
<td>1.2</td>
<td>18.8</td>
<td>0.04</td>
<td>b.d.</td>
</tr>
<tr>
<td>Nov. 8, 2000</td>
<td>14.5</td>
<td>2.8</td>
<td>b.d.</td>
<td>0.06</td>
<td>1.0</td>
</tr>
<tr>
<td>Nov. 9, 2000</td>
<td>29.8</td>
<td>1.1</td>
<td>2.4</td>
<td>0.14</td>
<td>0.9</td>
</tr>
<tr>
<td>Nov. 10, 2000</td>
<td>11.9</td>
<td>8.7</td>
<td>b.d.</td>
<td>no analysis</td>
<td>no analysis</td>
</tr>
<tr>
<td>Nov. 11, 2000</td>
<td>15.2</td>
<td>9.4</td>
<td>b.d.</td>
<td>0.22</td>
<td>0.4</td>
</tr>
<tr>
<td>Nov. 12, 2000</td>
<td>3.7</td>
<td>0.7</td>
<td>1.6</td>
<td>no analysis</td>
<td>b.d.</td>
</tr>
<tr>
<td>Nov. 15, 2000</td>
<td>7.4</td>
<td>15.2</td>
<td>1.9</td>
<td>no analysis</td>
<td>0.7</td>
</tr>
<tr>
<td>Nov. 16, 2000</td>
<td>8.4</td>
<td>1.7</td>
<td>2.3</td>
<td>no analysis</td>
<td>b.d.</td>
</tr>
<tr>
<td>Nov. 17, 2000</td>
<td>4.1</td>
<td>0.3</td>
<td>0.5</td>
<td>no analysis</td>
<td>b.d.</td>
</tr>
<tr>
<td>Nov. 18, 2000</td>
<td>5.1</td>
<td>1.2</td>
<td>2.1</td>
<td>no analysis</td>
<td>b.d.</td>
</tr>
<tr>
<td>Nov. 19, 2000</td>
<td>11.9</td>
<td>1.8</td>
<td>b.d.</td>
<td>0.02</td>
<td>b.d.</td>
</tr>
<tr>
<td>Average</td>
<td>10.7</td>
<td>2.6</td>
<td>3.6</td>
<td>0.1</td>
<td>0.9</td>
</tr>
<tr>
<td>SD</td>
<td>7.3</td>
<td>3.0</td>
<td>5.7</td>
<td>0.09</td>
<td>2.2</td>
</tr>
</tbody>
</table>

**Baseline Samples**

<table>
<thead>
<tr>
<th>Sample: Baseline 1</th>
<th>NO(_3)</th>
<th>NH(_4)</th>
<th>Organic N</th>
<th>Amino N</th>
<th>Urea N</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4.6</td>
<td>0.57</td>
<td>1.6</td>
<td>0.2</td>
<td>0.03</td>
</tr>
<tr>
<td>Baseline 2</td>
<td>0.2</td>
<td>0</td>
<td>0.26</td>
<td>0.03</td>
<td>b.d.</td>
</tr>
<tr>
<td>Average</td>
<td>2.5</td>
<td>0.28</td>
<td>0.93</td>
<td>0.11</td>
<td>0.02</td>
</tr>
<tr>
<td>SD</td>
<td>3.2</td>
<td>0.4</td>
<td>0.95</td>
<td>0.12</td>
<td>0.02</td>
</tr>
</tbody>
</table>

**Percentage**

- Average organic N as % of total N: ~21%
- Average urea N as % of organic N: ~24%
- Average amino acid N as % of organic N: ~3%
- Unknown organic N: ~73%

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**Notes:**

- Units are nmol N/m³ for all species.
- Negative values that arise for organic N as a result of analytical uncertainty and urea N samples where urea concentrations were not found have been designated as below the detection limit (b.d.). For calculation of the average, these samples have been designated as 0.
- Organic N percentages calculated by using NO\(_3\), NH\(_4\), NO\(_2\), and organic N averages.
- Baseline samples were collected on the baseline sector control system (see Figure 2 for baseline criteria). Due to filter breakage during sampling, a third sample collected from November 25 to 30, 2000 was discarded and not analyzed. Baseline sample 1 was collected on the sector control system from Nov. 21–24, 2000. Baseline sample 2 was collected on the sector control system from Dec. 1–7, 2000.
tities of organic N and urea. In Figure 1a, an example of an aerosol sample collected under easterly flow on 8 November 2000 is presented. Correlations with meteorological conditions were indicated using a Pearson Product Moment correlation that showed statistically significant relationships between (1) NO$_3^-$ and CN/cm$^3$ concentrations, $P = 0.04$, (2) organic N and wind direction, $P = 0.03$, and (3) urea N and wind direction, $P = 0.04$ for all samples collected between 1 and 19 November 2000. (No other statistically significant correlations were evident from the data.)

In the nonbaseline samples collected, organic N represented $\sim 21\%$ of total N (Table 4). Baseline samples contained a similar proportion of organic N, $\sim 25\%$, although the concentration of organic N in nonbaseline samples was higher (an average of 3.6 nmol N/m$^3$) than in baseline samples (an average of 0.93 nmol N/m$^3$) (Table 4) likely due to local continental sources, as discussed above. The scavenging ratio calculated for organic N at Cape Grim ($S = \sim 2900$, Table 3) was similar to the value that can be calculated from the data of Cornell et al. [2001] for rain and aerosol samples collected in Hawaii, USA ($S = \sim 1000$), possibly suggesting that aerosol scavenging is largely responsible for the organic N fraction at this location, although gas-phase species cannot be excluded as a source for some of the organic N.

One of the goals of this work (as stated in section 1) was to determine the difference in organic N concentrations between the remote marine atmosphere in the Northern Hemisphere (Hawaii) and the Southern Hemisphere (Cape Grim). Due to unfavorable meteorological conditions, we were only able to measure organic N in two baseline aerosol samples at Cape Grim. A comparison of baseline samples from both Hawaii and Cape Grim seems to indicate a higher concentration of organic N in clean marine, remote Northern Hemispheric aerosols ($\sim 3.3$ nmol N/m$^3$ (interquartile range 2.1--3.7 nmol N/m$^3$), in the study by Cornell et al. [2001] in Hawaii) than in aerosols collected during our sampling of baseline samples at Cape Grim ($\sim 0.93$ nmol N/m$^3$ (actual values 0.26 and 1.6 nmol N/m$^3$, Table 4). However, further study is needed in the remote Southern Hemisphere atmosphere to confirm or deny differences in remote oceanic...
organic N concentrations, possibly indicating an anthropogenic signal for organic N.

[27] Unlike rain samples that contained no detectable urea, nonbaseline aerosol samples contained urea in concentrations representing ~24% of total organic N (even though 7 of the 12 bulk aerosol samples collected under easterly wind flow and analyzed contained no detectable urea). The percentage of urea within nonbaseline samples was substantially higher than the content of urea within baseline samples, ~2% of total organic N (Table 4). The disproportionate proportion of urea within aerosols collected under nonbaseline samples versus baseline samples indicates the influence of local Tasmanian sources on urea N totals, potentially explained by animal or other agricultural emissions. The Australian Bureau of Statistics [1998] indicates that the island of Tasmania contains ~3.8 million sheep and ~500,000 cattle. A significant proportion of these animals in Tasmania graze on land in the largely agricultural Circular Head region, to the south and southeast, up-wind of Cape Grim; the direction of the winds that contained the greatest concentration of urea within aerosols. While grazing animals are a probable source for the large urea concentrations observed during conditions of southerly wind flow, high urea concentrations could also be released from the application of urea fertilizer in crop areas in Tasmania. The continent of Australia consumes ~5.5 Tg of urea fertilizer each year for agricultural use [Food and Agricultural Organization Statistical Database (FAOSTAT), 2001].

[28] Due to the influence of Tasmanian sources, bulk aerosol samples contained ~4 times as much organic N as baseline samples (3.6 nmol N/m³ in nonbaseline samples as compared to 0.9 nmol N/m³ in baseline samples, Table 4). While urea contributed significantly to nonbaseline organic N totals (~24% in these samples) dissolved free amino acids were not a considerable proportion of either nonbaseline (~3%) or baseline (~12%) organic N (Table 4). Also, amino N was not statistically related to other variables (e.g., wind speed, wind direction), suggesting complex sources and atmospheric processing (currently not fully understood) for amino N within aerosols. As seen in Figures 3b and 3c, nonbaseline and baseline samples contained similar proportions of individual amino acids.

3.3. Organic Nitrogen in Cascade Impactor Aerosols

[29] The majority of organic N was found in the coarse mode aerosol (>1 μm) fraction within nonbaseline samples possibly indicating the presence of organic material entrained from nearby soils or sea salt particles, as previously suggested by Cornell et al. [2001]. As for NH₄⁺ organic N was also found within the submicrometer (<1 μm) fraction of the atmospheric aerosol in nonbaseline samples (Figure 4) suggesting gas-to-particle conversion for the fine mode of organic N as suggested by Cornell et al. [2001] and Mylonas et al. [1991]; or the concentration of organic matter produced by the ocean in fine mode aerosol as suggested by Oppo et al. [1999] and Cincinelli et al. [2001]. Baseline samples exhibited similar profiles for organic N (Figure 4). Urea N and amino N were also found within the coarse and fine modes in both baseline and nonbaseline aerosols (Figure 4). Baseline samples contained more urea N and amino N within the fine mode relative to the coarse mode aerosol.

Figure 5. Organic N in baseline cascade impactor aerosol samples from this work compared to data for total PAHs in cascade impactor aerosol samples as reported by Cincinelli et al. [2001].

[30] An unexpected finding was the presence of organic N in an intermediate mode centered at ~1.0 μm in baseline (Figure 5) and in some nonbaseline samples. Higher concentrations for this intermediate fraction were found in baseline samples relative to nonbaseline samples, suggesting an oceanic influence. As outlined by Ellison et al. [1999], marine aerosols ejected from the ocean’s surface acquire a coating of organic surfactants. These surfactants are often hydrophobic in nature and lead to the formation of an inverted micelle, containing a hydrophobic outer layer and a water-soluble inner layer of high ionic strength. According to the Spray Drop Adsorption Model (SDAM) of Oppo et al. [1999] the presence of organic surfactants in marine aerosols leads to the production of fine mode (<1 μm) aerosols highly enriched in organics while larger particles remain mainly inorganic. In their work, Cincinelli et al. [2001] found agreement for the SDAM of Oppo et al. [1999] when they measured surface fluorescent organic matter and compounds such as polyaromatic hydrocarbons (PAHs) that can interact with the organic matter in surface waters. Our results for the size distribution of organic N in baseline aerosols are similar to the work of Cincinelli et al.
[2001] for total PAHs in cascade impactors (Figure 5) suggesting a role for the sea surface microlayer as a source for some of the organic N measured in marine areas. An influence from the sea surface microlayer is not surprising, since the sea surface microlayer is known to contain large concentrations of bacteria and viruses as well as organic N compounds containing hydrophilic side chains such as humics [Ellison et al., 1999], and large quantities of amino acids and associated enzymes [Milne and Zika, 1993; Carlucci et al., 1992; Kuznetsova and Lee, 2001].

A comparison between nonbaseline cascade impactor samples collected under conditions of differing wind direction also suggested the influence of the ocean’s surface on the intermediate fraction centered at ~1 µm (see Figure 5). As seen in Figure 6, urea N was found to be elevated in the intermediate fraction at ~ 1 µm in samples collected during periods when winds were easterly (samples from 1, 8, 9, 10, 15, 16, 17, and 18 November 2000), and largely influenced by marine sources in the Bass Strait during the period of a 24-hour aerosol collection, as seen in Figure 1a. An inverse linear relationship was also found for urea N and amino N concentrations in easterly samples ($R^2 = 0.42$ for all six stages and $R^2 = 0.91$ excluding stage 6, where gas-phase urea N may bias any amino N/urea N relationship). The inverse relationship for amino and urea N within easterly samples possibly suggests the release of urea N from live species, such as bacteria, living at the sea surface. Live species are known to be highly enriched within the sea surface microlayer compared with the waters 10 cm below the surface [Carlucci et al., 1992]. (Large concentrations of dissolved free amino acids and diminished concentrations of urea may indicate the decay of live species).

Figure 6. Urea and amino N concentrations in nonbaseline cascade impactor samples during differing wind directions. Average values are shown. Easterly values represent averages of cascade impactor samples from 1, 8, 9, 10, 15, 16, 17, and 18 November 2000. Southerly values represent averages of cascade impactor samples from 2, 4, 11, 12, and 19 November 2000.
4. Conclusions

[32] Samples collected during times when winds were southerly (samples from 2, 4, 11, 12, and 19 November 2000) did not show trends similar to those for easterly samples (Figure 6). Southerly samples contained urea N and amino N in a bimodal distribution, in the coarse and fine modes, as expected in continental regions, suggesting the influence of soils and gas-to-particle conversion, respectively, for organic N in aerosol samples influenced by the island. The presence of dissolved free amino acids in the coarse mode aerosol (>1 μm) in these samples is likely the result of bacterial processing of amino acids within soils, since it is known that terrestrially derived mineral particles contain amino N [Milne and Zika, 1993]. The presence of amino acids within the fine mode aerosol in these samples is not easily explained, due to the apparent lack of gas-phase amino acids, although Spitz [1990] also found amino acids within the fine aerosol mode and suggested a terrestrial source. Due to unanswered questions regarding the presence of organic N species in individual cascade impactor stages, we suggest that further size-separated aerosol sampling campaigns be conducted in areas where clean marine aerosols can be obtained and studied for organic N compounds.

[33] Rain samples at Cape Grim contained large quantities of dissolved free amino acids and urea N concentrations below detection. The percentage of organic N within rain samples was similar to values obtained in previous studies for coastal areas [Cornell et al., 2001]. The presence of large quantities of dissolved free amino acids in rain suggests the catabolism of peptides within rain samples, since aerosol samples contained low concentrations of dissolved free amino acids and since amino acids apparently have no known gas-phase longevity. The lack of urea within rain is either due to the degradation or loss of urea within rain samples, or concentrations of urea in rain below the limit of detection for the analytical method utilized. Aerosol samples collected simultaneously with rain samples contained little urea N, so any aerosol scavenging of urea would result in low concentrations of urea within rain.

[34] Concentrations of organic and urea N within aerosols were correlated with wind direction. Samples collected when the wind was southerly (across Tasmania) contained higher concentrations of organic and urea N, indicating the influence of local sources, likely animal emissions from the numerous cattle and sheep on the island of Tasmania, although urea fertilizer emissions cannot be dismissed as a potential source. Cascade impactor samples collected during the same periods of southerly wind flow (across Tasmania) contained both organic and urea N within the coarse (>1 μm) and fine mode (<1 μm) fraction of aerosols, indicating possible contributions from soils and the gas-to-particle conversion of organic and urea N. Amino N was also found in the coarse and fine mode aerosol in these samples. Coarse mode amino N is likely from the processing of proteins in soils in southerly aerosol samples. Amino N in fine mode aerosol could either be due to bioaerosols (that range in size from 0.005 to 2 μm, Matthias-Maser and Jaenicke [1995]), the sea surface, or another unknown source.

[35] Aerosol samples collected under conditions when the wind flow was easterly and highly influenced by marine sources (from along the north coast of Tasmania and the Bass Strait) contained lower concentrations of organic and urea N. In these samples organic and urea N was found in the intermediate mode at ~1 μm possibly indicating the presence of bioaerosols and the sea surface microlayer as a source. Our results for organic N are similar to the work of Cincinelli et al. [2001] for total PAHs in marine aerosols, suggesting that the sea surface microlayer is a source of organic N. Amino N in marine influenced samples was low in cascade impactor stages when urea N concentrations were high (in the same stage) possibly suggesting the presence of live species that were utilizing N, since it is known that bacteria are highly concentrated in the sea surface microlayer [Carlucci et al., 1992].

[36] Due to the unresolved issues associated with the presence or absence of amino acids within rain and aerosols collected during the campaign, it would be advantageous in the near term to examine both dissolved and combined (unhydrolyzed) forms of amino N in rain, bulk and size-separated aerosols in marine areas. Since the presence of organic, urea, and amino N within our samples suggests the influence of a marine source in samples collected near coastal areas and the influence of soil organic matter derived from local anthropogenic sources, it would be beneficial to examine bacterial numbers and growth within rain and aerosol samples collected in marine areas. Also, since forms of organic N exhibited relationships to one another in samples (i.e., simultaneously elevated or inversely correlated), and since other unknown amino compounds were detected (using the new urea method) in the samples we investigated, it is possible that other natural N compounds, compounds resulting from the catabolism of nitrogenous organics within biological samples, contribute significantly to the organic N fraction in nonurban areas. Given the present knowledge of the sea surface microlayer and its influence on aerosol composition and size distributions, it is likely that it is a source of some the organic N collected in the remote marine atmosphere. Its influence on organic N totals should be investigated further.

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