Chemistry of fog waters in California’s Central Valley—Part 3: concentrations and speciation of organic and inorganic nitrogen

Qi Zhang, Cort Anastasio*

Atmospheric Science Program, Department of Land, Air, and Water Resources, University of California, One Shields Avenue, Davis, CA 95616-8627, USA

Received 22 January 2001; accepted 12 June 2001

Abstract

Although organic nitrogen (ON) has been found to be a ubiquitous and significant component in wet and dry deposition, almost nothing is known about its concentration or composition in fog waters. To address this gap, we have investigated the concentration and composition of ON in fog waters collected in Davis, in California’s Central Valley. Significant quantities of dissolved organic nitrogen (DON) were found in these samples, with a median concentration of 303 μM N (range = 120–1630 μM N). DON typically represented approximately 16% of the total dissolved nitrogen (inorganic + organic) in Davis fog waters. The median concentration of nitrogen in free amino acids and alkyl amines was 16 μM N (range = 3.8–120 μM N), which accounted for 3.4% of the DON in Davis fogs. Thus, although the absolute concentrations of free amino compounds were significant, they were only a minor component of the DON pool. Combined amino nitrogen (e.g., proteins and peptides) was present at higher concentrations and accounted for 6.1–29% (median = 16%) of DON. Overall, free and combined amino compounds typically accounted for a median value of 22% of DON in the fog waters.

The high concentrations of DON found, and the fact that amino and other N-containing organic compounds can serve as nitrogen sources for microorganisms and plants, indicate that atmospheric ON compounds likely play an important role in nitrogen cycling in the Central Valley. In addition, due to the basicity of some N functional groups, ON compounds likely contribute to the previously observed acid buffering capacity of Central Valley fog waters. Finally, a comparison of fog waters with fine particles (PM$_{2.5}$) collected from the same site during the same period of time indicated that the median concentrations (mol N m$^{-3}$-air) of total water-soluble ON, free amino nitrogen and total amino nitrogen were very similar in the fog water and PM$_{2.5}$. Given the high water solubility of many organic N compounds, this result suggests that ON might contribute to the hygroscopic properties of atmospheric particles.

Keywords: Fog chemistry; Nitrogen cycling; Amino compounds; PM$_{2.5}$; Organic carbon

1. Introduction

Intense radiation fog events are common in the Central Valley (CV) of California during winter. These fogs usually form late at night and dissipate 3 or 4 h after sunrise, although they can persist for several days without fully breaking up (Sagebiel and Seiber, 1993). In foggy regions such as the CV, fog events may strongly influence atmospheric chemistry and air quality. For example, fog formation can significantly increase the removal rates of atmospheric particles, accelerate gas to particle partitioning, and lead to reactions in the...
aqueous phase and at the gas–liquid interface (Blando and Turpin, 2000; Collett et al., 1999a; Fuzzi et al., 1997; Gustafsson and Gschwend, 1999; Hoag et al., 1999; Laj et al., 1997; Lillis et al., 1999; Seinfeld and Pandis, 1998). In addition, since the deposition of fog water can be an important source of water, nutrients, and pollutants, fogs can also play crucial roles in the maintenance and decline of ecosystems, especially in coastal and mountain regions (Finlayson-Pitts and Pitts, 2000; Weathers, 1999).

Understanding the effects of fogs on atmospheric chemistry and ecological health requires detailed information on their chemical composition. While inorganic compounds have been studied extensively in fog waters, relatively little is known about the organic constituents. As shown by previous studies, the concentrations of organic carbon in fog waters can be quite high (Collett et al., 1999b; Facchini et al., 1999; McGregor, 2000). For example, reported levels in samples from the CV range from 420 to 9250 \( \mu \)M C (Collett et al., 1999b; McGregor, 2000). The presence of high concentrations of organic compounds may significantly affect the chemistry and toxicity of fog waters (Blando and Turpin, 2000; Collett et al., 1999a,b; Facchini et al., 1999; Glotfelty et al., 1987, 1990; Lo and Lee, 1997; Sagebiel and Seiber, 1993; Schomburg et al., 1991; Suzuki et al., 1998). For example, organic compounds likely contribute considerably to the buffering capacity recently identified in CV fog waters (Collett et al., 1999a). Also, organic species are undoubtedly involved in the chemical reactions that occur in foggy or cloudy atmospheres (Anastasio et al., 1997; Anastasio and McGregor, 2000, 2001; Blando and Turpin, 2000; McGregor and Anastasio, 2001). In addition, the occurrence of surface-active organic materials can cause substantial enrichment of hydrophobic toxic substances, such as pesticides, in fog waters (Glotfelty et al., 1987, 1990; Sagebiel and Seiber, 1993; Schomburg et al., 1991).

Past studies have found that measured individual organic compounds can only account for a small fraction of the total organic carbon (TOC) in fog waters. For example, in samples from the CV identified low molecular weight carboxylic acids and carbonyl compounds typically accounted for less than 20% of TOC (Collett et al., 1999a,b). A complementary approach to studies of individual organic compounds is classification of organic carbon based on functional groups, polarity, or molecular weight (e.g. Anastasio et al., 1997; Deecesari et al., 2000; Facchini et al., 1999; Grosjean and Wright, 1983). While this latter approach is more general than compound-specific studies, it typically accounts for a larger fraction of organic carbon and can have important implications for the bulk properties of organic compounds in atmospheric waters. For instance, Facchini et al. (1999) found that \( \sim 40\% \), on average, of water-soluble organic carbon in Po Valley fog waters was in macromolecular compounds (> 500 Da), but analysis for 120 individual organic compounds could only account for less than 5%, on average, of the total dissolved organic carbon.

One broad class of organic compounds that has not been examined yet in fog waters is nitrogen-containing organic compounds. Based on measurements of dry and wet deposition, organic nitrogen (ON) is widespread in atmospheric condensed phases and usually represents a significant portion of the total nitrogen (Anastasio and McGregor, 2000; Cornell et al., 1995, 1998, 2001; Jassby et al., 1994; Russell et al., 1998; Scudlark et al., 1998; Tipperley et al., 1985). In addition, a number of other studies have shown that amino compounds are also common in atmospheric deposition (McGregor and Anastasio, 2001, and references therein), although the contribution of amino compounds to ON in atmospheric particles or drops has not been previously determined. Based on the chemical and physical properties of amino compounds and other ON functional groups, these compounds could significantly affect the formation and chemistry of fog drops if present in sufficient concentrations.

The overall goal of this study was to quantify and speciate the organic and inorganic nitrogen in fog waters collected from Davis, California. We report here the major results from this study, including: (1) the concentrations and relative amounts of dissolved inorganic and organic nitrogen in fog waters and (2) the contribution of free and combined amino compounds to the pool of ON in the fog waters. Finally, we compare nitrogen data in fog waters with those in colocated PM\(_{2.5}\) samples to explore the potential importance of ON compounds in fog and aerosol processing.

2. Experimental methods

2.1. Sample collection and processing

Fog water samples (see Table 1) were collected in Davis, CA, during winters from 1997 to 2001 using a Caltech Active Strand Cloudwater Collector (CASC2; Demoz et al., 1996). Fog waters were collected directly into high density polyethylene (HDPE) bottles and were filtered (0.45 \( \mu \)m Teflon; MSI Tefsep) right after collection. Filtered samples were stored frozen (\(-20^\circ\)C) until analysis. Two cloud waters from Tenerife (Canary Islands) were also studied. To minimize contamination, the collection surfaces of the CASC2, and all supplies used with the samples, were cleaned using procedures described by McGregor (2000). Powder-free gloves were worn during all sample collection and processing steps.
As a check on possible contamination, collector rinse waters (Milli-Q water that was sprayed into the CASCC2 and collected as a sample) were collected prior to fog sampling events, and were treated and analyzed in the same way as fog samples. Additional details of the Davis site and the procedures used for sample collection and processing are given in Anastasio and McGregor (2001).

Samples of fine particles (PM$_{2.5}$; i.e., particles with aerodynamic diameters $\leq 2.5 \mu m$) were collected using Zefluor filters (3 $\mu m$ pore, Gelman Sciences) in an Interagency Monitoring for Protected Visual Environments (IMPROVE) sampler (Malm et al., 1994). Samples were typically collected for 48 h at a flow rate of $\sim 23 l/min$ and were stored in the refrigerator prior to extraction. Water-soluble nitrogen compounds were extracted from the PM$_{2.5}$ into Milli-Q water by sonication (1 h at 0°C). The extracts were then filtered (0.22 $\mu m$ Teflon; Cameo 13F syringe filter) and stored frozen in HDPE bottles. Concentrations of total inorganic nitrogen in PM$_{2.5}$ samples were adjusted to account for the loss of ammonium nitrate during sampling (estimated as 30% based on a study by Ashbaugh et al. (1998) for winter PM$_{2.5}$ samples collected in Sacramento, CA, 15 miles east of Davis).

2.2. Chemical analysis

All chemicals used were reagent grade or better and were used as received. Amino acids, alkyl amines, pyridine, and urea (all $\geq 98\%$ purity) and cytochrome c (95%) were received from Sigma or Aldrich. Data for other chemicals used are listed below. Purified water (“Milli-Q water”) was from a Milli-Q Plus system ($\geq 18.2 M\Omega cm$, Millipore).

2.2.1. Dissolved inorganic nitrogen (DIN: $NH_4^+$, NO$_3^-$, and NO$_2^-$)

Concentrations of NH$_4^+$, NO$_3^-$, and NO$_2^-$ were determined using a Dionex DX-120 Ion Chromatograph equipped with a DS4-1 conductivity detector, 25$\mu l$ injection loop, and either (i) for anion analysis, an AS14 analytical column (4 $\times$ 250 mm), AG14 guard column (4 $\times$ 50 mm), and ASRS-II 4-mm suppressor, or (ii) for cation analysis, a CS12 analytical column (4 $\times$ 250 mm) with corresponding guard column and a CSRS-ULTRA 4-mm suppressor. Method detection limits for ions were typically $0.07$–$0.12 \mu M$. Recoveries of known additions in samples were within 95–105%. Relative percent differences for replicate analyses were always within $\pm 7\%$, and were usually less than $\pm 5\%$. Results from

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Date collected</th>
<th>Time collected</th>
<th>Duration of collection (min)</th>
<th>Volume of air sampled (m$^3$)</th>
<th>LWC$^a$ (g m$^{-3}$-air)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fog waters from Davis, CA</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DA97-01F</td>
<td>1/30/97</td>
<td>01:52–03:55</td>
<td>123</td>
<td>618</td>
<td>0.10</td>
</tr>
<tr>
<td>DA97-05F</td>
<td>2/3/97</td>
<td>05:45–08:37</td>
<td>122</td>
<td>613</td>
<td>0.10</td>
</tr>
<tr>
<td>DA98-05F</td>
<td>1/22–23/98</td>
<td>22:15–01:15</td>
<td>180</td>
<td>904</td>
<td>0.076</td>
</tr>
<tr>
<td>DA98-09F</td>
<td>1/25/98</td>
<td>01:25–04:55</td>
<td>210</td>
<td>1055</td>
<td>0.081</td>
</tr>
<tr>
<td>DA98-12F</td>
<td>1/26/98</td>
<td>05:00–10:30</td>
<td>330</td>
<td>1657</td>
<td>0.009</td>
</tr>
<tr>
<td>DA98-13F</td>
<td>2/13/98</td>
<td>04:35–07:00</td>
<td>145</td>
<td>728</td>
<td>0.094</td>
</tr>
<tr>
<td>DA98-16F</td>
<td>12/18/98</td>
<td>03:22–08:30</td>
<td>308</td>
<td>1547</td>
<td>0.15</td>
</tr>
<tr>
<td>DA98-17F</td>
<td>12/18/98</td>
<td>08:30–11:20</td>
<td>170</td>
<td>854</td>
<td>0.14</td>
</tr>
<tr>
<td>DA99-01F</td>
<td>1/4–5/99</td>
<td>22:15–03:07</td>
<td>292</td>
<td>1467</td>
<td>0.10</td>
</tr>
<tr>
<td>DA99-02F</td>
<td>1/5/99</td>
<td>03:08–08:27</td>
<td>319</td>
<td>1602</td>
<td>0.11</td>
</tr>
<tr>
<td>DA99-04F</td>
<td>1/9/99</td>
<td>03:00–10:36</td>
<td>456</td>
<td>2290</td>
<td>0.058</td>
</tr>
<tr>
<td>DA99-05F</td>
<td>1/10/99</td>
<td>04:00–10:07</td>
<td>367</td>
<td>1843</td>
<td>0.030</td>
</tr>
<tr>
<td>DA99-06F</td>
<td>1/11/99</td>
<td>00:00–10:06</td>
<td>606</td>
<td>3044</td>
<td>0.045</td>
</tr>
<tr>
<td>DA99-07F</td>
<td>1/11–12/99</td>
<td>23:00–10:00</td>
<td>660</td>
<td>3315</td>
<td>0.040</td>
</tr>
<tr>
<td>DA99-08F</td>
<td>1/13/99</td>
<td>05:40–09:17</td>
<td>217</td>
<td>1090</td>
<td>0.027</td>
</tr>
<tr>
<td>DA01-01F</td>
<td>1/2–3/01</td>
<td>23:30–08:00</td>
<td>510</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

Cloud waters from Tenerife, Canary Islands

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Date collected</th>
<th>Time collected</th>
<th>Duration of collection (min)</th>
<th>Volume of air sampled (m$^3$)</th>
<th>LWC$^a$ (g m$^{-3}$-air)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO97-AS1</td>
<td>7/8/97</td>
<td>00:00–02:00</td>
<td>120</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>CO97-AS2</td>
<td>7/9/97</td>
<td>00:00–02:00</td>
<td>120</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

$^a$ Liquid water content, units of g-H$_2$O m$^{-3}$-air.
external check standard of all ions of interest (Dionex and Spex CertiPrep) were always within ±10% of certified values.

2.2.2. Dissolved organic nitrogen and carbon (DON, DOC)

DON was converted to DIN by a UV photooxidation method (Cornell and Jickells, 1999; Scudlark et al., 1998) and then calculated as the difference in DIN values before and after photolysis. Photooxidation was carried out using a cylindrical reactor (RPR-100; Southern New England Ultraviolet Company, Inc.) equipped with 16 mercury lamps (RPR-2537, 25 W). Samples (fog waters and PM2.5 extracts) were held in quartz tubes (GE021 quartz, 2.5 ml capacity, ID=0.8 cm) in a circular array evenly spaced along the inner wall of the reaction chamber, 1.5 in from the lamps. Each quartz tube was loaded with 1 ml of sample and was tightly stoppered with a Teflon PTFE plug. Samples were illuminated for 24 h and were kept below ~50°C during illumination by a built-in cooling fan. For samples where DON was measured several times after different lengths of storage in the freezer, reported values are for the first measurement.

To ensure complete conversion of DON to DIN, prior to photooxidation fog and cloud samples were diluted with Milli-Q to keep the inorganic nitrogen concentration in the range of 20–60 μM (Cornell and Jickells, 1999). Samples were also acidified with sulfuric acid (Optima grade; Fisher) to pH ≈ 3 prior to photooxidation in order to more efficiently convert organic N to inorganic forms. For example, in the case of urea, which is relatively recalcitrant to UV oxidation (Cornell and Jickells, 1999), we found less than 50% recovery of the M N from 2 alkyl amines, 55 m M N urea and 10 μM N pyridine. The inorganic nitrogen standard was composed of 30 μM each of NO3- and NH4+. The photo-oxidation efficiency for the standard organic and inorganic nitrogen solutions, and their mixtures, ranged from 90% to 107%. Procedural blanks (photo-lyzed Milli-Q) typically contained 0.2–0.9 μM N, mainly as NH4+. In view of the facts that ON was determined by difference, and that analytical uncertainties for NH4+ and NO3− will propagate, the detection limit for DON was estimated to be ~1 μM N.

DOC was measured by a Shimadzu TOC 5050 carbon analyzer using a high temperature combustion method, as described by McGregor (2000).

2.2.3. Dissolved free amino nitrogen (DFAN)

In this study DFAN was determined by summing the concentrations of N in 19 primary amino acids (alanine, arginine, asparagine, aspartic acid, glutamic acid, glycine, histidine, iso-leucine, leucine, lysine, methionine, methionine sulfoxide, ornithine, phenylalanine, serine, threonine, tryptophan, tyrosine, and valine) and 2 alkyl amines (ethanolamine and methylvamine). Samples were derivatized with an o-phthalaldehyde/mercaptoethanol reagent and analyzed by gradient high performance liquid chromatography (HPLC) with fluorescence detection (Gorzelska et al., 1992; Jones et al., 1981).

Identities of amino compounds were determined by comparison of retention times of analytes in the samples with those in the standard solution, and were confirmed by standard additions into the samples. The average relative standard deviation of the retention time of individual amino compounds during an analytical day (typically 14 h) was less than 2%. In this method, three pairs of compounds coeluted with no separation between the two compounds in each pair: glycine/threonine, serine/glutamine, and aspartic acid/cysteine-sulfonic acid. In order to quantify these compounds, we assigned any of these three peaks exclusively to the first compound in each pair. Uncertainties introduced by this assumption did not affect the DFAN results significantly because each compound in a given pair had a similar response factor and because none of these compounds were the dominant amino species.

Total free amino nitrogen concentrations in procedural blanks (derivatized Milli-Q water) ranged from 6 to 45 nM N (mean = 24 nM N). These blank levels were negligible compared to sample values (range = 3.8–117 μM N; mean = 16.3 μM N). The relative percent difference of DFAN measured in replicate injections was ≤15%. Recoveries of individual amino compounds from standard additions were 80–120%. Although we were not able to identify all peaks in the sample chromatograms, the sum of the unidentified peak heights typically accounted for less than 15% of the total peak height. Thus, the unidentified peaks led to only small underestimates for DFAN in the samples.

2.2.4. Dissolved combined amino nitrogen (DCAN)

Samples were treated with a vapor-phase acid hydrolysis method (Keil and Kirchman, 1991; Tsugita et al., 1987) to liberate combined amino acids (e.g., in proteins and peptides). The resulting free amino acids were quantified by the HPLC technique described in Section 2.2.3 and total dissolved amino nitrogen (TDAN) was determined as the sum of nitrogen in individual compounds in the hydrolyzed sample. DCAN was then determined as the difference between TDAN and DFAN (i.e., DCAN = TDAN−DFAN).
As a procedural blank, Milli-Q water was hydrolyzed and analyzed with the samples. The average total amino N in hydrolyzed Milli-Q water was 73 nM N, which was <0.1% of the mean value in fog samples. As a check standard, Cytochrome c was also processed with the hydrolysis method and then analyzed. The resulting amino acid composition was in good agreement with literature sequence values (Tsugita et al., 1987) and the recovery of total amino N in the standard was 92%, indicating good procedural efficiency.

### 3. Results and discussion

#### 3.1. Controls

As a check for possible contamination introduced during sample collection and processing, collector rinse waters were collected and analyzed (see Section 2.1). For cations and anions, concentrations in the rinse waters were all less than 10% of the median values in the bulk fog waters (Table 1). Concentrations of DOC in rinse waters ranged from 100 to 400 μM C, except for one rinse water where the aliquot for analysis was apparently contaminated (Anastasio and McGregor, 2001). Excluding this one value, the average concentration of DOC in rinse waters (220 μM C) was less than 12% of the median fog value. DON was measured in two rinse waters while DFAN and DCAN were measured in one rinse water. The concentrations of DON, DFAN, and DCAN in the rinse waters were ≤2% of the corresponding median fog values. In addition, the rinse waters showed no significant light absorption at wavelengths above 290 nm (Anastasio and McGregor, 2001). Based on all of these data, it appears that the collection and filtration processes did not introduce significant levels of contaminants into the fog samples. However, it should be noted that a few sample values were below the limit of quantification (defined here as 3 times the average value of the analyte in rinse waters) and therefore should not be treated quantitatively. These sample values are flagged as such in the data tables.

Our original attempts at DON quantification using a persulfate oxidation method were unsatisfactory because of high background N in reagents and low reproducibility for duplicate analyses. During the time required to change from this method, samples were stored in the freezer (−20 °C) for at least six months (~200 days for 60% of the fog samples) prior to initial analysis of DON by the UV photooxidation method. To test the possible influence of this storage, we examined DON concentrations as a function of storage time after this initial analysis. Over half of the fog water samples showed little change in DON concentration during storage, but several suffered losses of DON (Fig. 1). We set out to collect additional fogs during the winter of 2000–2001 in order to better characterize the effects of storage on

![Graph](https://example.com/graph.png)

**Fig. 1.** Change in dissolved organic nitrogen concentrations in filtered (0.45 μm) Davis fog waters during low temperature (−20 °C) storage.
DON levels, but we only were able to collect one sample during this period. In this one sample (DA01-01F) there was no difference in DON concentration measured immediately after collection and after one month of storage in the freezer (Fig. 1). While we cannot know with certainty whether there were significant DON losses between the times of collection and initial analysis for the samples that showed declining DON concentrations during storage, linearly extrapolating the trends in Fig. 1 suggests that reported DON values might be underestimated by 20–40% in these samples. Amines in the samples should have been stable during storage, based on previous results in filtered, frozen rain samples stored for up to 3 months (Gorzelska et al., 1992) and our observations that frozen amino acid standards stored for a year were stable.

There was little variation (<5%) in NH$_4^+$ or NO$_3^-$ concentrations during sample storage, indicating that DON was not decomposing to form dissolved inorganic N species. Our sample processing and storage protocols (i.e., filtration and low temperature storage) suggest that microorganisms were not responsible for the observed DON losses. In addition, preliminary results based on analysis of sample splits stored in different types of containers indicate that post-collection losses of DON in precipitation from physical sorption onto HDPE surfaces are probably insignificant (W. Keene, personal communication). Scudlark et al. (1998), using unfiltered Delaware rain samples left outside during summer, also found significant losses of DON but little accompanying change in DIN. They suggested that microbial uptake was not the primary cause for the DON loss, but that the formation of volatile products from ON precursors might be. A similar mechanism might have been responsible for the observed DON losses in our frozen Davis fog samples, but this hypothesis needs further testing.

### 3.2. General characteristics of Davis fog waters

A total of 16 samples collected during 14 fog events in the winters of 1997–2001 were investigated in this study (Table 1). As shown in Table 2, the Davis fog waters were characterized by: (1) near-neutral pH values (median = 6.71), largely because of ammonia inputs; (2) high light absorption coefficients (e.g., $\alpha_{313} = 0.111 \pm 0.009 \text{ cm}^{-1} \ (\text{mean} \pm 1\sigma)$), indicating significant potential for sunlight-initiated reactions; (3) minor inputs of marine air (i.e., generally low concentrations of Cl$^-$ and Na$^+$); (4) very high levels of total dissolved nitrogen (median = 2370 $\mu$M N), and (5) high concentrations of DOC (median = 1850 $\mu$M C). In addition, DOC concentrations and light absorption in these samples were positively correlated ($R^2 = 0.90$), as seen in a previous study of Davis fog waters (McGregor, 2000). These results are similar to those from previous fogs collected in Davis and at several sites in the San Joaquin Valley (SJV), in the southern portion of California’s CV (Anastasio, 1994; Collett et al., 1999a, b). Though local emissions can also affect composition, our Davis results provide additional evidence that fog water composition is similar throughout much of the CV (Collett et al., 1999b). In addition, our measured concentrations of species such as nitrate, ammonium, and sulfate in Davis fog waters were typically 100–200 times higher than corresponding concentrations in wintertime rain at this site (NADP, 2001). Given the significant sedimentation velocities of fog drops (Hoag et al., 1999), these concentrations indicate that deposition of fog drops can be an important source of soluble species to ecosystems in the CV.

The compositions of the two Tenerife (Canary Islands) cloud samples were characteristic of polluted marine air masses, and were quite different from the Davis fogs. For example, the Tenerife samples were much more acidic (median pH = 3.55), contained much larger amounts of Cl$^-$, Na$^+$ and non-sea-salt SO$_4^{2-}$, and demonstrated significantly weaker sunlight absorption (Table 2). Concentrations of DOC in the Tenerife cloud waters were also much lower than those in the Davis fog samples.

Despite their high concentrations, NO$_3^-$ and NO$_2^-$ accounted for only a small portion of light absorption by the fog and cloud waters (e.g., typically <10% at 313 nm), as seen previously (Anastasio and McGregor, 2001; McGregor, 2000). In conjunction with the high DOC concentrations, this suggests that organic carbon was largely responsible for the light absorption in both the Davis and Tenerife samples. Given that DOC is a photochemical source of organic triplet excited states, singlet molecular oxygen, and peroxides in aqueous phases (Anastasio et al., 1994, 1997; Faust et al., 1993; Schwarzenbach et al., 1993), optically active organic compounds might be important initiators of aqueous reactions in CV fogs.

### 3.3. Inorganic and organic nitrogen

As mentioned above, one characteristic of Davis fog waters is the high concentration of total dissolved nitrogen (Table 2). Similar observations, although based exclusively on dissolved inorganic nitrogen, have been reported for fog waters from the SJV (Collett et al., 1999a, b) and in a previous study in Davis (McGregor, 2000).

#### 3.3.1. Dissolved inorganic nitrogen

\[ \text{DIN} = \text{NH}_4^+ + \text{NO}_3^- + \text{NO}_2^- \]

In the Davis fog waters, dissolved inorganic nitrogen represented the majority of the total dissolved nitrogen (TDN) (range = 72–96%, median = 84%; Table 3). Ammonium and nitrate were the dominant ions...
measured, and were the major components of DIN, typically representing approximately 60% and 40%, respectively, of the inorganic N (Table 3). The median concentrations of these two species were 1200 and 790 \( \mu M \), respectively. Similar observations have been reported in previous studies of CV fogs (Anastasio, 1994; Anastasio and McGregor, 2001; Collett et al., 1999a, b; McGregor, 2000). The presence of large amounts of \( \text{NH}_4^+ \) in the CV fogs is likely associated with intensive agricultural activities in the valley (Coe et al., 1998). Although concentrations of \( \text{NO}_2^- \) were much lower than \( \text{NH}_4^+ \) and \( \text{NO}_3^- \) (Table 3), nitrite is often the dominant precursor of photochemically produced hydroxyl radical in Davis fog waters (Anastasio and McGregor, 2001).

In the Tenerife cloud waters, the median DIN concentration (470 \( \mu M \)) was almost four times lower than the median fog water value (Table 3). In addition, although \( \text{NH}_4^+ \) and \( \text{NO}_3^- \) were still important components in the Tenerife samples, they were no longer the most abundant ions; concentrations of Na\(^+\) were comparable to those of \( \text{NH}_4^+ \), while concentrations of \( \text{Cl}^- \) and \( \text{SO}_4^{2-} \) were significantly greater than those of \( \text{NO}_3^- \) (Table 3).

### 3.3.2. Dissolved organic nitrogen (DON) and the organic C:N ratio

Concentrations of DON in Davis fog waters were quite high, ranging from 120 to 1630 \( \mu M \) N (median = 303 \( \mu M \) N; Table 3). These values are

---

**Table 2**

Characteristics of fog and cloud waters

<table>
<thead>
<tr>
<th>Sample name</th>
<th>pH</th>
<th>( z_{313} ) (cm(^{-1} ))</th>
<th>Concentration (( \mu M ))</th>
<th>( \text{Cl}^- )</th>
<th>( \text{Br}^- )</th>
<th>( \text{SO}_4^{2-} )</th>
<th>( \text{Na}^+ )</th>
<th>( \text{K}^+ )</th>
<th>DOC(^b)</th>
<th>TDN(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Fog waters from Davis, CA</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DA97-01F</td>
<td>6.74</td>
<td>0.054</td>
<td>24.4</td>
<td>&lt;0.1</td>
<td>16.4</td>
<td>10.8</td>
<td>6.4</td>
<td>930</td>
<td>730</td>
<td></td>
</tr>
<tr>
<td>DA97-05F</td>
<td>7.04</td>
<td>0.100</td>
<td>19.9</td>
<td>&lt;0.1</td>
<td>19.2</td>
<td>12.6</td>
<td>8.7</td>
<td>2490</td>
<td>1000</td>
<td></td>
</tr>
<tr>
<td>DA98-05F</td>
<td>6.87</td>
<td>0.091</td>
<td>81.6</td>
<td>&lt;0.1</td>
<td>135</td>
<td>13.1</td>
<td>14.3</td>
<td>1670</td>
<td>2730</td>
<td></td>
</tr>
<tr>
<td>DA98-09F</td>
<td>6.71</td>
<td>0.121</td>
<td>18.6</td>
<td>&lt;0.1</td>
<td>63.6</td>
<td>4.1</td>
<td>3.2</td>
<td>3140</td>
<td>2490</td>
<td></td>
</tr>
<tr>
<td>DA98-12F</td>
<td>5.58</td>
<td>0.319</td>
<td>271</td>
<td>1.9</td>
<td>3210</td>
<td>169</td>
<td>39.7</td>
<td>9250</td>
<td>35,550</td>
<td></td>
</tr>
<tr>
<td>DA98-13F</td>
<td>6.82</td>
<td>0.014</td>
<td>27.9</td>
<td>&lt;0.1</td>
<td>66.2</td>
<td>31.5</td>
<td>[1.1]</td>
<td>[420]</td>
<td>1480</td>
<td></td>
</tr>
<tr>
<td>DA98-16F</td>
<td>7.50</td>
<td>0.054</td>
<td>8.3</td>
<td>&lt;0.1</td>
<td>13.6</td>
<td>63.9</td>
<td>5.3</td>
<td>2070</td>
<td>1340</td>
<td></td>
</tr>
<tr>
<td>DA98-17F</td>
<td>6.75</td>
<td>0.050</td>
<td>8.0</td>
<td>&lt;0.1</td>
<td>19.7</td>
<td>56.9</td>
<td>2.0</td>
<td>1310</td>
<td>1340</td>
<td></td>
</tr>
<tr>
<td>DA99-01F</td>
<td>6.62</td>
<td>0.021</td>
<td>5.3</td>
<td>&lt;0.1</td>
<td>14.0</td>
<td>5.5</td>
<td>5.1</td>
<td>840</td>
<td>1080</td>
<td></td>
</tr>
<tr>
<td>DA99-02F</td>
<td>6.80</td>
<td>0.035</td>
<td>6.8</td>
<td>&lt;0.1</td>
<td>17.9</td>
<td>6.0</td>
<td>2.6</td>
<td>960</td>
<td>1020</td>
<td></td>
</tr>
<tr>
<td>DA99-04F</td>
<td>6.37</td>
<td>0.115</td>
<td>32.1</td>
<td>3.0</td>
<td>135</td>
<td>10.3</td>
<td>6.9</td>
<td>3160</td>
<td>6070</td>
<td></td>
</tr>
<tr>
<td>DA99-05F</td>
<td>5.87</td>
<td>0.247</td>
<td>82.4</td>
<td>&lt;0.1</td>
<td>191</td>
<td>25.9</td>
<td>3.0</td>
<td>6340</td>
<td>10,090</td>
<td></td>
</tr>
<tr>
<td>DA99-06F</td>
<td>6.04</td>
<td>0.084</td>
<td>24.4</td>
<td>3.3</td>
<td>32.3</td>
<td>6.5</td>
<td>[1.5]</td>
<td>1680</td>
<td>2650</td>
<td></td>
</tr>
<tr>
<td>DA99-07F</td>
<td>5.74</td>
<td>0.087</td>
<td>19.4</td>
<td>&lt;0.1</td>
<td>41.8</td>
<td>44.6</td>
<td>4.5</td>
<td>1850</td>
<td>2250</td>
<td></td>
</tr>
<tr>
<td>DA99-08F</td>
<td>6.19</td>
<td>0.267</td>
<td>201</td>
<td>&lt;0.1</td>
<td>465</td>
<td>95.2</td>
<td>20.1</td>
<td>4570</td>
<td>7310</td>
<td></td>
</tr>
<tr>
<td>DA01-01F</td>
<td>5.87</td>
<td>0.118</td>
<td>39.0</td>
<td>&lt;0.1</td>
<td>81.2</td>
<td>120.5</td>
<td>8.5</td>
<td>—</td>
<td>3138</td>
<td></td>
</tr>
</tbody>
</table>

| **Cloud waters from Tenerife, Canary Islands** |        |                             |                             |                 |                 |                 |               |             |        |        |
| CO97-AS1    | 3.68   | 0.011                       | 329                          | <0.1            | 263             | 289             | 11.2          | [380]       | 470    |        |
| CO97-AS2    | 3.42   | 0.013                       | 527                          | 0.4             | 378             | 453             | 11.3          | [440]       | 590    |        |

**Statistics for Davis fog waters**

- Min: 5.58, 0.014, 5.3, <0.1, 13.6, 4.1, [1.1], [420], 730
- Max: 7.50, 0.319, 271, 3.3, 3210, 169, 39.7, 9250, 35,550
- Median: 6.71, 0.087, 24.4, <0.1, 52.7, 19.5, 5.2, 1850, 2370
- Mean: 6.51, 0.111, 54.4, 0.6, 282.4, 42.3, 8.3, 2710, 5020
- SD: 0.53, 0.093, 75.7, 1.1, 787.8, 48.5, 9.7, 2390, 8560

\(^a\) Values in square brackets were above the method detection limit but below the limit of quantification, defined here as three times the average value of an analyte in the rinse waters. Average rinse water values (\( \mu M \)) were: \( \text{Cl}^- = 1.6 \), \( \text{Br}^- < 0.1 \), \( \text{SO}_4^{2-} = 0.7 \), \( \text{Na}^+ = 1.2 \), \( \text{K}^+ = 0.6 \), DOC = 220 \( \mu mol \text{C l}^{-1} \), TDN = 47 \( \mu mol \text{N l}^{-1} \).

\(^b\) Dissolved organic carbon, units of \( \mu mol \text{C l}^{-1} \).

\(^c\) Total dissolved nitrogen, units of \( \mu mol \text{N l}^{-1} \).
Table 3  
Concentrations of inorganic and organic nitrogen (units of μmol N l⁻¹)  

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Inorganic nitrogen</th>
<th>Organic nitrogen</th>
<th>C:N</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DIN % of TDN</td>
<td>NH₄⁺ % of DIN</td>
<td>DON % of TDN</td>
</tr>
<tr>
<td>Fog waters from Davis, CA</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DA97-01F</td>
<td>613 84</td>
<td>447 73</td>
<td>12.3 2.0</td>
</tr>
<tr>
<td>DA97-05F</td>
<td>788 79</td>
<td>473 60</td>
<td>75.0 9.5</td>
</tr>
<tr>
<td>DA98-05F</td>
<td>2410 88</td>
<td>1440 60</td>
<td>29.3 1.2</td>
</tr>
<tr>
<td>DA98-09F</td>
<td>2190 88</td>
<td>1290 59</td>
<td>21.5 1.0</td>
</tr>
<tr>
<td>DA98-12F</td>
<td>34100 96</td>
<td>19900 58</td>
<td>0.4 0.0</td>
</tr>
<tr>
<td>DA98-13F</td>
<td>1200 82</td>
<td>719 60</td>
<td>6.1 0.5</td>
</tr>
<tr>
<td>DA98-16F</td>
<td>1060 79</td>
<td>643 60</td>
<td>13.0 1.2</td>
</tr>
<tr>
<td>DA98-17F</td>
<td>1220 91</td>
<td>783 64</td>
<td>63.1 5.2</td>
</tr>
<tr>
<td>DA99-01F</td>
<td>783 72</td>
<td>514 66</td>
<td>10.5 1.3</td>
</tr>
<tr>
<td>DA99-02F</td>
<td>794 78</td>
<td>539 68</td>
<td>13.7 1.7</td>
</tr>
<tr>
<td>DA99-04F</td>
<td>5330 88</td>
<td>3150 59</td>
<td>80.6 1.5</td>
</tr>
<tr>
<td>DA99-05F</td>
<td>8570 85</td>
<td>4680 55</td>
<td>49.9 0.6</td>
</tr>
<tr>
<td>DA99-06F</td>
<td>2250 85</td>
<td>1290 57</td>
<td>16.6 0.7</td>
</tr>
<tr>
<td>DA99-07F</td>
<td>1860 83</td>
<td>1130 61</td>
<td>31.7 1.7</td>
</tr>
<tr>
<td>DA99-08F</td>
<td>5680 78</td>
<td>3670 65</td>
<td>69.9 1.2</td>
</tr>
<tr>
<td>DA99-09F</td>
<td>2880 92</td>
<td>1730 60</td>
<td>56.8 2.0</td>
</tr>
<tr>
<td>Cloud waters from Tenerife, Canary Islands</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO97-AS1</td>
<td>420 89</td>
<td>348 83</td>
<td>&lt;0.1 0.0</td>
</tr>
<tr>
<td>CO97-AS2</td>
<td>520 88</td>
<td>383 74</td>
<td>&lt;0.1 0.0</td>
</tr>
<tr>
<td>Statistics for Davis fog waters</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Min</td>
<td>613 72</td>
<td>447 55</td>
<td>&lt;0.1 0.0</td>
</tr>
<tr>
<td>Max</td>
<td>34100 96</td>
<td>19900 73</td>
<td>80.6 9.5</td>
</tr>
<tr>
<td>Median</td>
<td>2020 84</td>
<td>1200 60</td>
<td>25.4 1.3</td>
</tr>
<tr>
<td>Mean</td>
<td>4490 84</td>
<td>2710 62</td>
<td>34.4 2.0</td>
</tr>
<tr>
<td>Std Dev</td>
<td>8210 6.2</td>
<td>4770 4.5</td>
<td>27.1 2.3</td>
</tr>
</tbody>
</table>

a Values in italics represent the percent of the specified nitrogen pool represented by a given compound or compound class. All values were above limits of quantification, defined here as three times the average value of an analyte in the rinse waters. Average rinse water values (μmol N l⁻¹) were: DIN = 15, NH₄⁺ = 14, NO₂⁻ = 0.1, NO₃⁻ = 1.0, DON = 4.3, DFAN = 0.18, DCAN = 1.20.

b DIN = dissolved inorganic nitrogen = NH₄⁺ + NO₂⁻ + NO₃⁻; TDN = total dissolved nitrogen = DIN + DON.
c DON = dissolved organic nitrogen; DFAN = dissolved free amino nitrogen; DCAN = dissolved combined amino nitrogen.
d Ratio of number of C and N atoms in organic compounds, determined as [DON]/[DOC].
approximately 10 times higher than previously reported DON concentrations in precipitation (Michalzik et al., 1997; Scudlark et al., 1998). Organic forms accounted for 3.9–28% (median = 16%) of the TDN in the Davis fog waters (Table 3). DON concentrations in the two Tenerife cloud waters were 53 and 74 μM N, accounting for 11–12% of the TDN. Thus, despite the large differences in composition between the Davis and Tenerife samples, organic forms were a significant component of the nitrogen budget in each. As noted in Section 3.1, organic N values might be underestimated in some of our samples, and thus the contribution of DON to TDN would also be underestimated.

We have also calculated the bulk C:N ratio of the organic compounds in the Davis and Tenerife samples (i.e., the ratio [DOC]/[DON] in a given sample). For the Davis fog waters, these values ranged from 1.6 to 12, with a median value of 4.7 (Table 3). Values for the Tenerife cloud samples (7.1 and 6.0) were slightly higher. In a recent study, Michalzik et al. (1997) reported a wide range of organic C:N ratios (4.8–47) in bulk precipitation collected in German forests. Their data showed an inverse correlation between the total N content and the organic C:N ratio. Samples with high concentrations of total nitrogen had substantially lower organic C:N ratios (4.8–8.3) than those with lower N contents, where C:N ratios were typically > 20 (Michalzik et al., 1997). Such a trend was not observed in the Davis fog samples. In fact, there was essentially no correlation ($R = -0.053$) between the TDN concentration and C:N ratio.

The C:N ratio of organic matter plays an important role in determining the assimilation pathways and the mineralization products formed during microbial uptake of ON (Antia et al., 1991; Bushaw et al., 1996). It is also often used as an indicator for the biological availability of N-containing organic matter. Humic substances, for example, often have high C:N ratios (averaging approximately 50) and are generally biologically refractory (Thurman, 1985). In view of this, the organic compounds in Davis fog waters appear to be rich in N and thus this organic N should be relatively bioavailable. This is consistent with past studies at coastal and oceanic sites, which have shown that ON in atmospheric deposition is largely bioavailable to aquatic microorganisms (Peierls and Paerl, 1997; Seitzinger and Sanders, 1997, 1999; Timperley et al., 1985).

### 3.3.3. Free and combined amino compounds

As shown in Table 3, concentrations of DFAN in Davis fog waters ranged from 3.8 to 120 μM N, with a median value of 16 μM N. Nitrogen in free amino compounds typically represented 3–4% of the total organic N (Table 3). Among the 11 samples analyzed for DFAN, 7 were also analyzed for combined amino compounds (DCAN, i.e. proteins, peptides, and other forms). On a nitrogen basis, combined amino compounds were approximately 4–5 times more important than free amino forms, accounting for 6.1–29% (median = 16%) of DON (Table 3). Overall, total (free and combined) amino nitrogen accounted for 7.3–34% (median = 20%) of DON.

Fig. 2 shows the nitrogen budget for a typical Davis fog water sample. As shown in this figure, DON represented 17% of the total N in this sample and amino acids, especially in combined forms, represented a significant portion (22%) of this DON. However, the bulk of the ON in this sample (as in all of the samples studied here) was unidentified.

While not measured in this study, a wide variety of ON compounds have been identified in the atmosphere, and could have contributed to DON in our samples. These compounds include amides such as urea (Cornell et al., 1998; Timperley et al., 1985), organic nitrates (Buhr et al., 1990; Nielsen et al., 1995), nitrogen
heterocycles (Burnett, 1969; Pellizzari et al., 1976), nitroaromatics (Ciccioli et al., 1995; Hachimi et al., 1996), humic substances (Havers et al., 1998a, b), nitrogenated soot (Novakov et al., 1972), as well as a host of others (Graedel et al., 1986). Recent mass spectrometric analyses have revealed that most of the organic N compounds in rainwater from New Jersey had molecular weights less than 300 Da (Mazurek et al., 2000); based on molecular ion masses, this study tentatively identified several DON compounds including allyl urea, dibutylamine, and quinoline. At several sites in the Pacific (New Zealand, Japan, Hawaii, and Tahiti) urea accounted for approximately half of the ON in wet deposition and aerosol particles (Timperley et al., 1985; Cornell et al., 1998, 2001). However, urea was a much smaller component (typically <10%) of water-soluble ON in rain water and aerosol particles collected from marine sites in the Atlantic and from continental sites in the UK (Cornell et al., 1998).

3.4. Comparison of nitrogen composition in fog waters and PM$_{2.5}$

Atmospheric particles and fog droplets can interconvert through the processes of fog formation and evaporation (Blando and Turpin, 2000; Finlayson-Pitts and Pitts, 2000; Hoag et al., 1999; Lillis et al., 1999). In foggy atmospheres, hydrophilic compounds, especially those that contribute significantly to the hygroscopic properties of particles, are expected to be present in both fog waters and fog condensation nuclei. To examine the possible influences of water-soluble nitrogen species on particle hygroscopicity, we have compared water-soluble nitrogen concentrations in fog waters and PM$_{2.5}$ samples collected during December 1997 to March 1998.

As shown in Fig. 3, the median atmospheric concentrations (nmol N m$^{-3}$-air) of condensed phase total amino N and ON were essentially the same in the fog waters and PM$_{2.5}$. Since nucleation scavenging usually is the dominant mechanism for the introduction of particulate water-soluble compounds into fog drops (Facchini et al., 1999), the presence of similar amounts of water-soluble ON in fog and PM$_{2.5}$ suggests that this group of compounds contributes to the hygroscopic properties of atmospheric fine particles.

While the median value of free amino N in fog waters was approximately 60% higher than that in PM$_{2.5}$ (Fig. 3), the mean value was only ~10% higher (1.19 nmol N m$^{-3}$-air in fog waters compared to 1.04 nmol N m$^{-3}$-air in PM$_{2.5}$). Since atmospheric amino acids will exist almost exclusively in condensed phases (Saxena and Hildemann, 1996), the generally higher concentrations of free amino compounds in fog drops might be due to faster hydrolysis of combined amino compounds (to form DFAN) in aqueous drops (Gorzelska and Galloway, 1990; Mopper and Zika, 1987).

The median atmospheric concentration of inorganic nitrogen was ~2 times higher in the fog waters compared to in PM$_{2.5}$ (Fig. 3). This observation is consistent with model predictions where the presence of fog increased concentrations of condensed phase nitrate.

---

Fig. 3. Median atmospheric concentrations (±1 S.D.) of nitrogen species in 4 fog and 13 PM$_{2.5}$ samples collected during December 1997 to March 1998. Concentrations of water-soluble N in the PM$_{2.5}$ (units of nmol N m$^{-3}$-air) were as follows (range; median): free amino N (0.34–3.32; 0.68), total amino N (4.48–4.93; 4.82), total organic nitrogen (4.77–52.8; 26.3), total inorganic nitrogen (89.6; 15.8–27.2).
and ammonium by a factor of ~2 because of enhanced
gas-to-drop partitioning (Hoag et al., 1999).

3.5. Possible sources of organic N in tropospheric
condensed phases

Despite its widespread nature and significant concentra-
tions, little is quantitatively known about the individual
compounds, or even compound classes, that make up tropospheric ON. While this makes it difficult
to assess the sources of tropospheric organic N, some
speculations about sources can be made. For example,
there is some evidence to suggest that atmospheric ON is
largely from continental sources, based on higher
concentrations of DON in continental rains compared
to marine rains, and on δ15N values of DON in
rainwater (Cornell et al., 1995, 2001; Russell et al.,
1998).

More generally, atmospheric ON can be from natural
and anthropogenic sources, and can be either primary
(i.e., directly emitted to the atmosphere) or secondary
(forming in the atmosphere). We first consider here
potential natural primary sources of ON. One important
class of biogenic primary ON compounds in the
atmosphere is proteinaceous matter either emitted from
plants (e.g., spores and pollens), derived from plant
and animal debris, or associated with bacteria, yeast,
and molds (e.g., Fuzzi et al., 1997; Gorzelska et al.,
1992; Milne and Zika, 1993). Another potentially important
group of natural primary ON compounds is humic and
fulvic substances from soil dust or surface waters. These
compounds can be an important component of organic
carbon in atmospheric condensed phases (Facchini et al.,
1999; Havers et al., 1998a,b), and they contain
numerous ON functional groups including amines, N
heterocycles, and nitriles (Schulten and Schnitzer, 1998).
In addition, urea and uric acids from soil, birds, or
animals (Timperley et al., 1985; Cornell et al., 1998) can
also be significant natural primary sources of ON to
atmospheric condensed phases.

Primary anthropogenic sources of ON compounds to
the atmosphere include agricultural activities (e.g. use
of urea fertilizer and N-containing pesticides and herbici-
cides; Cornell et al., 1998; Giot-féty et al., 1987, 1990;
Schomburg et al., 1991; Timperley et al., 1985) and
combustion processes. Examples of ON from combus-
tion sources include nitro-polycyclic aromatic com-
ounds from vehicles and N heterocycles and nitriles
from biomass combustion (Graedel et al., 1986; Mast
et al., 1984).

There are also a number of secondary sources of ON
involving reactions of inorganic nitrogen species in the
gas phase or in/on condensed phases. For example, gas
phase reactions involving NOx and organic compounds
can form nitroaromatics and organonitrates such as
peroxyacetyl nitrate (PAN) and larger peroxyacetyl
nitrates (Finlayson-Pitts and Pitts, 2000; Graedel et al.,
1986). Reactions involving gaseous nitrogen species and
particulate matter, such as the reactions of NO or NH3
on soot at elevated temperatures (Chang and Novakov,
1975), can also produce secondary ON. Secondary ON
is also formed from reactions occurring within aqueous
drops, such as the formation of nitrophenols from the
reaction of phenol with NO3 in the presence of NO2
(Barletta et al., 2000 and references therein). After
formation, the partitioning of secondary ON comp-
pounds between the gas phase and condensed phase
(particles and/or aqueous drops) will depend upon the
properties of the compounds (e.g., vapor pressure and
water solubility) as well as the amount and properties of
the condensed phases (Seinfeld and Pandis, 1998).

In addition to chemical reactions, it is likely that
biological processes in atmospheric drops and particles
also form secondary ON compounds. Recent reports
have shown that bacteria and yeast can grow in fog and
cloud drops, even if supercooled (Fuzzi et al., 1997;
Sattler et al., 2001). This suggests that microorganisms
in cloud or fog drops form secondary ON compounds
such as proteins and peptides from inorganic N
precursors such as ammonium and nitrate. In turn, it
is likely that these proteinaceous compounds are a
secondary source of atmospheric free amino compounds
via enzymatic and photocatalytic hydrolysis (Gorzelska
et al., 1992; Milne and Zika, 1993; Mopper and Zika,
1987).

3.6. Implications

Previous studies have demonstrated that organic
compounds have a large influence on the chemistry of
fog waters in California’s CV (Anastasio et al., 1997;
Anastasio and McGregor, 2000, 2001; Collett et al.,
1999a,b; Hoag et al., 1999; McGregor and Anastasio,
2001). The results presented here suggest that nitrogen-
containing organics contribute significantly to this
chemistry. For example, ON compounds probably
contribute to the unexplained acid buffering capacity
of CV fog waters identified recently (Collett et al.,
1999a). There are a number of nitrogen functional groups
that could contribute to this buffering, including N hetero-
cycles (e.g., pyridine, imidazole, and quinoline), aromatic
amines (e.g., aniline) and imines. These and other
organic N groups have pKa values in the range of 4–7
(Lide, 1992), which is the pH range where Collett et al.
(1999a) found significant unexplained buffering in CV
fog waters. ON compounds probably also influence the
light absorption properties, and thus the photochemical
reactivity, of fog waters through reactions of nitrogen
chromophores such as nitro- and nitroso- groups.

ON might also affect the toxicity of fog waters. For
example, the presence of surface-active DON com-
pounds, such as proteins and peptides, could be at least
partially responsible for the fact that California fog waters are sometimes enriched, relative to Henry’s law, in hydrophobic organic compounds such as pesticides and their oxidation products (Glotfelty et al., 1987, 1990). In addition, a number of toxic N-containing organic compounds, such as aromatic nitro compounds and nitrosamines, have been measured in the atmosphere or in emission sources to the atmosphere (Graedel et al., 1986), suggesting that some portion of fog water ON is toxic.

Finally, past studies have shown that a significant portion of atmospheric ON is bioavailable to aquatic microorganisms (Peierls and Paerl, 1997; Seitzinger and Sanders, 1997, 1999; Timperley et al., 1985) and that amino acids can be an important source of N for plants (Yu et al., 2001). These studies, in conjunction with our current results showing that organic compounds represent a significant component of the total dissolved N in fog waters, suggest that deposition of ON can be an important source of fixed nitrogen to water bodies and vegetation in California’s CV, as well as in other areas. Indeed, in another study of atmospheric organic N in California, ON represented, on average, 24% and 76% of the total N in wet and dry deposition, respectively, deposited to Lake Tahoe (Jassby et al., 1994).

4. Conclusions

We measured considerable amounts of TDN in wintertime fog waters collected in Davis, California. While inorganic nitrogen species, primarily NH₄⁺ and NO₃⁻, accounted for the bulk (72–96%) of this fog water nitrogen, DON, measured here for the first time in fog waters, was also a significant component. Concentrations of DON ranged from 120 to 1630 μM N and accounted for 3.9–28% (median = 16%) of TDN. Ratios of C : N in the fog water dissolved organic compounds ranged from 1.6 to 12, with a median value of 4.7. The fact that the organic compounds in the Davis fog waters are quite nitrogen rich suggests that this ON is relatively bioavailable and, therefore, that it is an important source of nitrogen to aquatic and terrestrial ecosystems in the region.

Total (free and combined) dissolved amino compounds typically represented ~20% of the DON in fog waters on a nitrogen atom basis. Combined amino compounds (e.g., proteins and peptides) were the dominant component of the fog amino compounds (typically 16% of fog DON), while free amino acids and alkyl amines were a smaller component (typically 3–4% of DON). Thus while amino compounds were an important class of DON in our samples, the identities of the bulk of the ON compounds are unknown.

The observation that similar amounts of ON were present in PM₂.₅ and fog waters collected in Davis during the same period indicates that water-soluble ON might significantly contribute to the hygroscopic properties of atmospheric fine particles. In addition, due to the basicity of a number of N-containing organic functional groups, ON compounds likely contribute significantly to the acid buffering capacity of CV fog waters. Similarly, ON compounds likely affect other aspects of fog water chemistry. Given these important roles, more work needs to be done to further identify the ON compounds present in atmospheric condensed phases.

Acknowledgements

The authors thank Keith McGregor (UC Davis) for TOC analysis and assistance with fog sampling, Mike Jimenez-Cruz (UC Davis) for assistance with fog sampling, Zengshou Yu (UC Davis) for assistance with sample hydrolysis, Eli Sherman and Jeff Collett Jr. (Colorado State University) for the Tenerife cloud samples, and Tony Andreoni and Dean Bloudoff (California Air Resources Board) for loan of the CASCC2. This work was supported by the U.S. EPA (R819658 and R825433) Center for Ecological Health Research at the University of California at Davis. Although the information in this document has been funded in part by the United States Environmental Protection Agency, it may not necessarily reflect the views of the Agency and no official endorsement should be inferred. Additional funding for this work was provided by a graduate traineeship from the University of California Toxic Substances Research and Teaching Program (Ecotoxicology component), the California Agricultural Experiment Station (Project CA-D*LAW-6403-RR), and by a Jastro-Shields Graduate Research Award from the University of California at Davis.

References


Anastasio, C., Faust, B.C., Rao, C.J., 1997. Aromatic carbonyl compounds as aqueous-phase photochemical sources of


