Water-soluble organic nitrogen in atmospheric fine particles (PM$_{2.5}$) from northern California

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[1] Recent studies have suggested that organic nitrogen (ON) is a ubiquitous and significant component of atmospheric dry and wet deposition, but very little is known about the concentrations and speciation of organic nitrogen in aerosol particles. In addition, while amino compounds also appear to be ubiquitous in atmospheric condensed phases, their contribution to organic nitrogen has not been previously quantified. To address these issues, we have characterized the water-soluble organic nitrogen and amino compounds in fine particles (PM$_{2.5}$) collected in Davis, California, over a period of 1 year. Concentrations of water-soluble organic nitrogen (WSON) ranged from 3.1–57.8 nmol N m$^{-3}$ air, peaking during winter and early spring, and typically accounted for ~20% of total nitrogen in Davis PM$_{2.5}$. Assuming an average N-normalized molecular weight of 100 Da per N atom for WSON, particulate organic nitrogen had a median mass concentration of 1.6 µg m$^{-3}$ air, and typically represented 18% of the total fine particle mass. The average mass of water-soluble ON in Davis PM$_{2.5}$ was comparable to that of sulfate during the summer, but was significantly higher in winter. Total amino compounds (free plus combined forms) made up a significant portion of particulate organic nitrogen (median value equal to 23%), primarily due to the presence of combined amino compounds such as proteins and peptides. Total amino compounds had a median mass concentration of 290 ng m$^{-3}$ air, and typically accounted for 3.3% of the total fine particle mass. These results indicate that organic nitrogen is a significant component of fine particles in northern California, and suggest that this group of compounds might play an important role in the ecological, radiative, and potential health effects of atmospheric fine particles in this region.

INDEX TERMS: 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); KEYWORDS: amino compounds, amino acids, proteins, aerosol composition, organic carbon

1. Introduction

[2] Atmospheric fine particles (PM$_{2.5}$, i.e., particulate matter with aerodynamic equivalent diameters ≤2.5 µm) have important effects on visibility and climate [Finlayson-Pitts and Pitts, 2000], and there is growing evidence that they also significantly affect human health [e.g., Samet, 2000]. Because atmospheric particles typically have high concentrations of nitrogen (N), they can also be an important source of fixed nitrogen to the environment [Peters and Brucknerschatt, 1995; Sievering et al., 1996; Sorteberg et al., 1998] and thereby cause significant adverse impacts to terrestrial and aquatic ecosystems. For example, prolonged nitrogen deposition to terrestrial ecosystems can eventually lead to nitrogen saturation, which can cause soil acidification, mobilization of toxic metals, and an increase in forest mortality [Aber et al., 1989; Fenn et al., 1998; Foster et al., 1997, 1996]. Aquatic ecosystems, especially oligotrophic systems, are also susceptible to excessive nitrogen deposition and its accompanying effects such as acidification, eutrophication, and decreased water quality [Fenn et al., 1998]. Prominent examples of these impacts in California include the nitrogen saturation of forests in southern California [Bytnerowicz and Fenn, 1996] and the shift in nutrient response, from nitrogen to phosphorus limitation, of Lake Tahoe in northern California [Jassby et al., 1994].

[3] To date, most studies of fixed nitrogen in atmospheric condensed phases have focused on inorganic species (NO$_3^-$, NO$_2^-$, and NH$_4^+$), and thus relatively little is known about organic nitrogen in the troposphere. However, based on available data, organic nitrogen appears to be a ubiquitous and significant component of dry and wet deposition [e.g., Cornell et al., 1995; Jassby et al., 1994; Knap et al., 1986; Russell et al., 1998; Scudlark et al., 1998; Timperley et al., 1985]. As summarized by Anastasio and McGregor [2000], in the United States typically 20 to 80% of the N in atmospheric deposition is in organic form. The only published measurements of atmospheric organic nitrogen in California indicate that organic forms typically account for 24% and 77% of the total N in wet and dry deposition, respectively, received by Lake Tahoe [Jassby et al., 1994]. Taken together, these data suggest that organic species represent a considerable portion of atmospheric particulate nitrogen and therefore that organic nitrogen might have significant ecological effects.

[4] These data also suggest that organic nitrogen compounds might play significant roles in the effects of PM$_{2.5}$ on visibility, climate, and human health. For example, water-soluble organic carbon compounds can affect the hygroscopicity of atmospheric particulate matter and therefore alter the climate- and visibility-related impacts of particles [e.g., Andreae and Crutzen, 1997; Ellison et al., 1999; Facchini et al., 1999a; Novakov and Penner, 1993; Saxena et al., 1995; Saxena and Hildebrand, 1996]. Given the high water solubility of several nitrogen functional groups (e.g., amines and nitrates), organic nitrogen compounds might represent an important component of water-soluble organic carbon [e.g.,...
Saxena and Hildemann, 1996]. In addition, since the health effects of particulate matter are likely related to their composition [e.g., Samet, 2000], organic nitrogen compounds might influence the toxicity and health effects of PM if they are significant components of atmospheric particles. However, to our knowledge, few studies have examined total organic nitrogen in atmospheric particles [Cornell and Jickells, 1999; Cornell et al., 2001].

[5] A wide variety of organic nitrogen compounds have been measured, or hypothesized to exist, in the atmosphere. These include amino compounds [Gorzelska et al., 1992; Milne and Zika, 1993; Mopper and Zika, 1987], urea [Cornell et al., 1998; Tipperley et al., 1985], organic nitrates [Buhr et al., 1990; Nielsen et al., 1995], nitrogen heterocycles [Burnett, 1969; Pellizzari et al., 1976; Rogge et al., 1993a, 1993b], nitro-aromatics [Ciccioli et al., 1995; Dimashti et al., 2000], humic substances [Havers et al., 1998a, 1998b], nitrogenated soot [Novakov et al., 1972], as well as a host of others [Graedel et al., 1986]. Of these classes, amino compounds have been studied extensively in the atmospheric environment [Gorzelska and Galloway, 1990; Gorzelska et al., 1992, 1994; McGregor and Anastasio, 2001; Milne and Zika, 1993; Mopper and Zika, 1987]. Amino compounds are of interest because of their potential effects on particle hygroscopicity [Saxena and Hildemann, 1996] and atmospheric chemistry [McGregor, 2000; McGregor and Anastasio, 2001; Milne and Zika, 1993]. They are also a source of bioavailable nitrogen to ecosystems [Antia et al., 1991; Thomas, 1997]. While amino compounds appear to be ubiquitous in atmospheric condensed phases, there are no published reports of simultaneous measurements of amino compounds and total organic nitrogen in atmospheric samples, and therefore it is unclear how important this class of compounds is as a constituent of atmospheric organic nitrogen.

[6] The overall goal of this present study was to quantify the concentrations of water-soluble amino compounds and total organic nitrogen in PM$_{2.5}$. Because of the importance of nitrogen deposition in California, and the paucity of atmospheric organic nitrogen data in the western United States, our focus here is on PM$_{2.5}$ samples collected over a 1-year period in Davis, California. We report here the major results from this study, including (1) the concentrations and seasonal variations of water-soluble organic nitrogen, free amino N, and total amino N in PM$_{2.5}$; (2) the importance of free and combined amino compounds in the PM$_{2.5}$ organic nitrogen pool; and (3) the contribution of amino compounds (free and total) and N-containing organic compounds to the total mass of PM$_{2.5}$.

2. Experimental Methods

2.1. Reagents, Samples, and Sample Processing

[7] All chemicals used were reagent grade or better and were used as received. Amino acids, alkyl amines, pyridine, and urea were ≥98% purity and 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 (≥18.2 MΩ cm, Millipore). All glassware and other items used for sample processing and analysis were cleaned using procedures described by McGregor [2000].

[8] Fine particles were sampled during August 1997 to July 1998 at the National Atmospheric Deposition Program site (CA98) at the University of California at Davis, 2 miles southwest of the center of the city Davis (population ~55,000). Meteorological data were collected simultaneously at the adjacent university weather station. Davis is in the Sacramento Valley of Northern California, a region with hot and dry summers and mild and wet winters. During the sampling year of this study, over 80% of the precipitation events occurred between November and March. Air quality in Davis is affected by emissions from the surrounding agricultural areas, urban emissions (e.g., Sacramento 15 miles to the northeast and the San Francisco Bay area 70 miles to the southwest), and transportation emissions (e.g., Interstate-80 runs along the southern edge of the town).

[9] PM$_{2.5}$ samples were collected onto Teflon filters (Zefluor, 25 mm diameter, 3 μm pore, Pall-Gelman) using an Interagency Monitoring for Protected Visual Environments (IMPROVE) sampler [Mailm et al., 1994] at a flow rate of ~23 L min$^{-1}$. Generally, two 48-hour samples were collected each week, typically during Saturday–Sunday and then Tuesday–Thursday. Approximately every other week’s samples were analyzed for this study. The median volume of air sampled per filter was 67 m$^3$.

[10] The mass of PM$_{2.5}$ collected for each sample was determined using a Cahn 28 electromicrobalance (calibrated with a 200-mg class 1.1 standard weight). Measured sample masses were adjusted to account for the evaporation of particulate ammonium nitrate from samples during collection. On the basis of data from Ashbaugh et al. [1998] for PM$_{2.5}$ samples collected in Sacramento, California (15 miles east of Davis), we estimated PM$_{2.5}$ mass losses of 2, 10, 10, and 18% for our summer, fall, spring, and winter samples, respectively. After weighing, filters were stored individually in cleaned, sealed Petri dishes (Falcon tight-fit lid (fish, 50 × 9 mm) kept in a sealed plastic bag at ~4°C in the dark. Prior to analysis, each sampled filter was cut into halves, and one half was extracted by sonication (Fisher FS30) in 8.0 or 9.0 mL of Milli-Q water for 60 min at 0–4°C. The other half was immediately put back into storage. After extraction, sonication extracts were filtered (0.22 μm Teflon; Cameo 13F syringe filter) and stored frozen (~20°C) until analysis.

2.2. Sample Analysis

[11] Concentrations of inorganic anions and cations were measured with a Dionex DX-120 ion chromatograph described elsewhere [Zhang and Anastasio, 2001]. Water-soluble organic nitrogen (WSON) was determined by a UV-photolysis method [Cornell and Jickells, 1999; Scudlark et al., 1998]. For this method the concentration of inorganic nitrogen was first measured in the sample, the sample was then illuminated to convert WSON to inorganic nitrogen (24 hours of 254 nm illumination), and finally the concentration of inorganic N was measured after illumination. The concentration of WSON was calculated as the difference in inorganic nitrogen concentrations before and after illumination.

[12] Water-soluble total nitrogen (WSTN) in each sample was determined as the sum of WSON and water-soluble inorganic N (WSIN = NH$_4^+$, NO$_2^-$, and NO$_3^-$). These latter values were adjusted to account for estimated evaporative losses of ammonium nitrate during sampling. On the basis of the analysis of Ashbaugh et al. [1998], and our own sampling during October 2000, we estimated that ~30% of NH$_4$NO$_3$ evaporated from our PM$_{2.5}$ samples during winter, and approximately 50% evaporated during spring and fall. Because of larger uncertainties in NH$_4$NO$_3$ losses during summer, we have not used or reported values for WSIN or WSTN in summer samples.

[13] Primary amino acids and alkyl amines were analyzed by high-performance liquid chromatography (HPLC) in conjunction with precolumn o-phthalialdehyde/2-mercaptoethanol fluorescence derivatization [Gorzelska et al., 1992; Jones et al., 1981]. Water-soluble free amino nitrogen (WSFAN) reported in this study was the sum of the nitrogen concentrations of 18 primary amino acids (alanine, arginine, aspartic acid, glutamic acid, glycine, histidine, isoleucine, leucine, lysine, methionine, methionine sulfone, ornithine, phenylalanine, serine, threonine, tryptophan, tyrosine, and valine) and 2 alkyl amines (ethanolamine and methylamine) that were quantified in aqueous extracts of PM$_{2.5}$. Water-soluble total amino nitrogen (WSTAN) was determined by hydrolyzing the samples to liberate combined amino acids (e.g., those in proteins and peptides) [Keil and Kirchman, 1991; Tsugita et al., 1987] and then quantifying the concentrations of the resulting free amino compounds with the HPLC method described above. Water-soluble combined amino nitrogen (WSCAN) was calculated.
2.3. Quality Control

The difference between WSTAN and WSFAN, i.e., WSCAN = WSTAN − WSFAN. Additional details of our analytical procedures are given by Zhang and Anastasio [2001].

2.4. Statistical Analysis

Concentrations of WSON and WSFAN in PM$_{2.5}$ extracts were fit (using Microsoft Excel) to a lognormal distribution using a probability density function [Georgopoulos and Seinfeld, 1982]

$$P_L(c) = \frac{1}{c \ln \sigma_g (2\pi)^{0.5}} \exp[-(\ln c - \ln \mu_g)^2/2(\ln \sigma_g)^2)]$$

where $c$ is the concentration of analyte of interest, $\mu_g$ is the geometric mean, and $\sigma_g$ is the standard geometric deviation.

3. Results and Discussion

3.1. Concentrations of Organic Nitrogen and Amino Compounds

Concentrations of water-soluble organic nitrogen (WSON) and water-soluble free amino nitrogen (WSFAN) in PM$_{2.5}$ were approximately lognormally distributed, as shown in Figure 1. Concentrations of particulate WSON ranged from 3.1 to 57.8 nmol N m$^{-3}$ air, with a median value of 15.6 nmol N m$^{-3}$ air, while WSFAN concentrations ranged from 0.08 to 3.32 nmol N m$^{-3}$ air (median equal to 0.42 nmol N m$^{-3}$ air, Table 1). Similar amounts of WSFAN have been reported for particles collected from over the North Atlantic Ocean (<0.001 to 1.61 nmol N m$^{-3}$ air) [Gorzelska and Galloway, 1990] and in particles (<8 µm diameter) collected by airplane over Canada (0.004 to 6.7 nmol N m$^{-3}$ air; calculated from data of Gorzelska et al. [1994]). Atmospheric concentrations of WSFAN in coarse particles (diameters $\geq$2.5 µm) in Davis are likely higher than those in PM$_{2.5}$, given that biogenic materials such as plant debris, pollen, and bacteria are probably enriched in the coarse particles [Milne and Zika, 1993].

A comparison of WSFAN concentrations with the corresponding WSON values reveals that free amino compounds
typically represented 2–4% (≤10% in all but two samples) of the
organic N (Table 1), indicating that WSFAN was generally a minor
component of the water-soluble fine particulate organic N in the
Davis region. Because no previous studies on atmospheric samples
have reported concentrations of free amino compounds and total
organic N simultaneously, the fraction of particulate organic N
accounted for by amino N in other regions cannot be assessed.
However, our results are similar to the WSFAN/WSON values
estimated for marine aerosols over the North Atlantic Ocean (2–
17% [Gorzelska and Galloway, 1990]).

[21] Water-soluble combined amino nitrogen (WSCAN, i.e.,
proteins, peptides, and other forms) were analyzed in 9 of the 41
PM$_{2.5}$ samples studied. On a nitrogen basis, combined amino
compounds were more important than the free amino compounds,
and concentrations of WSCAN were typically 4 times higher than
those of WSFAN. Together, free and combined amino compounds
(WSTAN) accounted for a significant portion of organic nitrogen
in PM$_{2.5}$ (range equal to 8.5–71%, median equal to 23%; Table 1),
primarily because of the combined amino compounds. To the best
of our knowledge, there are no other published reports of simulta-
neous measurements of total amino compounds and total organic N
in atmospheric particles or deposition, and thus the ratio of
WSTAN/WSFAN in other regions cannot be assessed.

[22] In individual samples the relative contribution of WSTAN
to WSON generally decreased with increasing concentration of
WSON (Figure 2a). For example, in the two PM$_{2.5}$ samples with
the lowest WSON concentrations, amino compounds were the
dominant organic nitrogen species (representing 64 and 71% of
WSON), while in the sample with the highest measured WSON
concentration total amino compounds accounted for only 8.5% of
WSON. The ratio WSFAN/WSON showed a similar dependence
on WSON concentration (Figure 2b). While most of the samples
with high WSON concentrations (>30 nmol N m$^{-3}$ air) and
correspondingly low WSFAN/WSON ratios represented winter
samples, no such seasonal segregation existed for the rest of the
data. These observations, in conjunction with the fact that the
concentrations of WSTAN were relatively uniform throughout the
year (Table 1), suggest that water-soluble organic nitrogen in Davis
PM$_{2.5}$ consists of a background level of amino nitrogen, upon
which other organic nitrogen compounds are added. There was no
correlation between WSON and either WSTAN or WSFAN
($R^2 < 0.10$), suggesting that the amino compounds and the other
organic nitrogen species in PM$_{2.5}$ have different sources and/or
atmospheric lifetimes.

[23] In addition to organic nitrogen compounds, we also mea-
ured water-soluble inorganic N (WSON = NH$_4^+$ + NO$_3^-$ + NO$_2^-$)
in order to determine water-soluble total nitrogen (WSTN) in our
samples. During winter the median concentration of WSTN in
PM$_{2.5}$ was 140 nmol N m$^{-3}$ air (range equal to 21–230), and
organic nitrogen (WSON) typically accounted for 23% (range
equal to 6–48%) of the total particulate N. This is similar to the

situation in Davis winter fog waters, where total dissolved nitrogen
concentrations ranged from 72 to 349 nmol N m$^{-3}$ air and organic
forms typically contributed 16% (range equal to 4–28% [Zhang
and Anastasio, 2001]). Total water-soluble N concentrations in
PM$_{2.5}$ during fall and spring (median values of 50–60 nmol N m$^{-3}$
air) were generally lower than in winter, but the contribution from
organic N was similar in all three seasons (typically 16–22% during
during fall and spring; range equal to 5–44%). Because of larger
uncertainties in inorganic N sampling losses during the summer
(see section 2.2), we have not calculated values for WSON/WSTN
in our summer PM$_{2.5}$ samples. Nonetheless, our results indicate
that organic nitrogen typically represented ~20% of the water-
soluble nitrogen in PM$_{2.5}$ for at least 9 months during the sampling
year. The contributions of organic nitrogen to total N in Davis
PM$_{2.5}$ and fog waters are at the lower end of the range of
previously reported values for organic nitrogen in wet and dry
deposition samples in the United States (~20–80% [Anastasio and
McGregor, 2000]).

3.2. Seasonal Trends in WSON, WSFAN, WSTAN,
and SO$_4^{2-}$

[24] As shown in Figure 3a, concentrations of water-soluble
organic nitrogen peaked during late fall and winter (November to
February). Water-soluble free amino compounds (WSFAN)
exhibited a seasonal pattern similar to that of WSON, though peak
concentrations appeared somewhat later (Figure 3b); concentra-
tions of WSFAN varied by a factor of ~40 between the minimum
and maximum values (Table 1). Concentrations of water-soluble
total amino nitrogen (WSTAN) had a similar, though less pro-
nounced, seasonal trend, with a peak in February–March and only
a factor of ~4 difference in the minimum and maximum values
(Figure 3b and Table 1).

[25] Possible reasons for these seasonal trends include varia-
tions in emissions, deposition, boundary layer height, temper-
ature, relative humidity, and/or chemistry. Because the identities
of the majority of the organic nitrogen compounds are unknown,
it is difficult to speculate on why WSON exhibits the observed
seasonal trend. We have examined the data for possible correla-
tions between concentrations of organic and amino N and
meteorological variables such as relative humidity, precipitation
amounts, temperature, and wind direction. (Meteorological data
are compiled in Table A1 of the supplementary material.)

WSON, WSFAN, and WSTAN concentrations were all positively

| Table 1. Budget of Water-Soluble Organic Nitrogen in PM$_{2.5}$
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<td>Minimum</td>
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<td>Median</td>
<td>Mean</td>
<td>Standard Deviation</td>
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<td></td>
<td>Concentrations, $^b$nmol N m$^{-3}$air</td>
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<tr>
<td>WSFAN</td>
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<td>3.32</td>
<td>0.42</td>
<td>0.58</td>
<td>0.59</td>
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<tr>
<td>WSCAN</td>
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<td>4.57</td>
<td>2.60</td>
<td>2.53</td>
<td>2.08</td>
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<tr>
<td>WSTAN</td>
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<td>4.93</td>
<td>3.12</td>
<td>3.23</td>
<td>1.28</td>
</tr>
<tr>
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<td>15.6</td>
<td>18.9</td>
<td>13.6</td>
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<tr>
<td>WSFAN/WSON</td>
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<td>24</td>
<td>2.4</td>
<td>4.0</td>
<td>4.2</td>
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<tr>
<td>WSTAN/WSON</td>
<td>8.5</td>
<td>71</td>
<td>23</td>
<td>32</td>
<td>24</td>
</tr>
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$^a$Forty-one samples were characterized for each category except for WSTAN ($N = 9$). Typical relative standard deviations for sample
concentrations were WSFAN (+14%, −19%), WSTAN and WSCAN (+17%, −16%), and WSON (+27%, −8%).

$^b$WSFAN, water-soluble free amino nitrogen; WSCAN, water-soluble combined amino nitrogen; WSTAN, water-soluble total amino nitrogen;
WSON, water-soluble organic nitrogen.
correlated with relative humidity, but only weakly so ($R^2 = 0.28$, 0.26, and 0.13, respectively). Correlations with the other meteorological variables were even weaker. The positive correlation between relative humidity and organic nitrogen concentration might be an indication that more WSON partitions to particles in the presence of liquid water. This would be expected, for example, with WSON that exhibited acid-base chemistry. The higher concentrations of WSTAN and WSFAN in late winter and spring are probably due, at least in part, to increased releases of pollens and spores during this time. The higher concentrations of particulate free amino compounds during winter and spring (when relative humidities were generally higher) might also have been influenced by increased hydrolysis of combined amino compounds (to form WSFAN) in the presence of liquid water [Gorzelska and Galloway, 1990; Mopper and Zika, 1987]. Finally, the higher concentrations of particulate organic nitrogen observed during winter were likely also a result of lower boundary layer heights during this time.

Concentrations of sulfate were higher during summer and lower during winter (Figure 3c), a pattern that is the reverse of the seasonal trends in WSON, WSTAN, and WSTAN. This sulfate trend could be due to greater SO$_2$ emissions, or a greater rate of SO$_2$ oxidation to sulfate, during summer compared to winter. Given the lack of atmospheric liquid water during summer in the Central Valley, this trend suggests that the summertime oxidation of SO$_2$ via gas-phase reaction with hydroxyl radicals is more important on an annual basis than oxidation in liquid drops during winter.

3.3. Mass Budgets of Amino Compounds, Organic Nitrogen, and Sulfate

Mass concentrations of WSTAN and WSFAN in Davis PM$_{2.5}$ ranged from 0.15 to 0.43 $\mu$g m$^{-3}$ air (median equal to 0.29 $\mu$g m$^{-3}$ air) and 0.007 to 0.28 $\mu$g m$^{-3}$ air (median equal to 0.033 $\mu$g m$^{-3}$ air), respectively (Table 2). Total amino compounds were responsible for 1.6 to 14% of the PM$_{2.5}$ mass (median equal to 3.3%, Table 2), while free amino compounds typically accounted for <1%. Therefore, although free amino compounds contributed negligibly to the total mass of Davis fine particles, combined amino compounds were more important and in some cases contributed significantly to the total PM$_{2.5}$ mass. The mass concentrations of both WSTAN and WSFAN were generally highest during winter and spring. These mass trends mirror the seasonal trends in N concentrations (Figure 3b) because the N-atom-normalized average molecular weights (±1σ) for total and free amino compounds were relatively constant in the PM$_{2.5}$ samples (94 ± 6 and 82 ± 4 Da per N atom, respectively).

To estimate the contribution of organic nitrogen to fine particle mass, we assumed that WSON compounds had an average N-normalized molecular weight of 100 Da per N atom, based on a C:N ratio of ~5 (median value measured in Davis fog waters by Zhang and Anastasio [2001]) and assuming a 1:1:6 molar ratio for nitrogen, oxygen, and hydrogen. This value of 100 Da/N is close to the average N-normalized molecular weight of WSTAN discussed above (94 ± 6 Da per N atom), and is similar to values for individual N-containing compounds previously reported in atmospheric particles (e.g., pyrrole (67.1 Da/N), pyridine (79.0), aniline (93.1), isoquinoline (129.2), nitrophenol (140), and 1,2-dimethoxy-4-nitrobenzene (183.1)). On the basis of this estimated N-normalized molecular weight the median WSON mass in PM$_{2.5}$ was 1.6 $\mu$g m$^{-3}$ air, and WSON typically represented 18% of the total mass of PM$_{2.5}$ (range equal to 6–76%; Table 2). As seen for the N concentration data discussed earlier (Figure 3), calculated mass concentrations of WSON were also highest during the winter (median values: 3.6 $\mu$g m$^{-3}$ and 31% of PM$_{2.5}$ mass).

The actual mass of WSON in individual samples could be significantly higher or lower than the values estimated here, depending on the actual average N-normalized molecular weight.
weight of WSON in each sample. For example, if samples contained significant amounts of soil humic substances, which typically have N-normalized molecular weights of \(~400\) Da per N atom (calculated from data of Gieseking [1975]), our estimates of WSON mass would likely be underestimated. Conversely, significant amounts of particulate urea (30 Da per N atom) in our samples would reduce the average N-normalized molecular weight of WSON and cause us to overestimate WSON mass. This specific latter possibility seems less likely, given that Cornell et al. [1998] found that urea accounted for less than 1% of particulate WSON in a rural area with relatively high urea emissions. Despite these uncertainties, the mass contribution of WSON to PM$_{2.5}$ certainly appears to be significant.

3.4. Implications of Results

[31] Our finding that organic nitrogen accounts for a significant portion of total N in atmospheric fine particles in northern California suggests that the deposition of atmospheric organic nitrogen has important effects on terrestrial and aquatic ecosystems in the region. Because a significant portion of atmospheric organic nitrogen is bioavailable to aquatic microorganisms [Peierls and Paerl, 1997; Seitzinger and Sanders, 1999; Timperley et al., 1985], deposition of organic nitrogen will likely be an important source of fixed nitrogen to water bodies in California’s Central Valley and the Sierra Nevada mountains. This has already been shown for Lake Tahoe, where atmospheric nitrogen (including significant amounts of organic forms) accounts for over half of the N input to the lake, and algal growth has shifted from a nitrogen-limited to a nitrogen- and phosphorous-colimited regime [Jassby et al., 1994].
identify these components. A number of organic N compounds, was unidentified, and clearly more work needs to be done to containing functional groups.

the fine particulate organic carbon compounds in the Central Valley comparison suggests that, at least during winter, a large fraction of fine particle mass during winter [34]. Indeed, we found that combined amino compounds, including proteins and peptides, typically represented 1999].

ing proteins and peptides, typically represented [32]. The significant contribution (~20%) of water-soluble organic nitrogen compounds to total PM$_{2.5}$ mass suggests that this group of compounds might also play a role in the effects of fine particles on visibility and climate. The effect of particulate WSON on visibility might be even greater than is suggested by its mass contribution since much of the organic nitrogen measured here is hygroscopic (based on our aqueous extraction method) and since water uptake by fine particles can cause large increases in their light scattering [Finlayson-Pitts and Pitts, 2000]. In a similar vein, organic nitrogen might also have a significant effect on the ability of particles to act as cloud condensation nuclei, and therefore might influence the indirect climate forcing of aerosols. The presence of surface-active organic nitrogen compounds, such as proteins and peptides, will lower the surface tension of wetted aerosol particles and thereby enhance their activation and growth into cloud or fog drops [Facchinini et al., 2000, 1999b; Oppo et al., 1999; Rodhe, 1999]. Indeed, we found that combined amino compounds, including proteins and peptides, typically represented ~3% of the PM$_{2.5}$ mass in Davis. Of course, evaluating the influence of particulate organic nitrogen on visibility reduction and cloud or fog drop formation will require more specific studies than what we report here, including measurements of WSON and WSTAN as a function of particle size.

In addition to the effects on hygroscopicity discussed above, organic nitrogen components might also affect the acid-neutralizing capacity of particles (since several nitrogen functional groups are basic) as well as their light absorption properties (due to nitrogen chromophores such as nitro groups). Organic nitrogen might also play an important role in the adverse human health effects that appear to be associated with fine particles since a number of organic nitrogen compounds are mutagenic, carcinogenic, or otherwise toxic [Graedel et al., 1986]. Finally, it is interesting to compare our WSON mass results (where watersoluble organic N represented ~20% of the PM$_{2.5}$ mass in Davis) with previous observations in the San Joaquin Valley which indicated that organic carbon typically accounted for 20–50% of fine particle mass during winter [Schauer and Cass, 2000]. This comparison suggests that, at least during winter, a large fraction of the fine particulate organic carbon compounds in the Central Valley contain nitrogen. Thus the chemical, physical, and biological properties of these organic particles are likely influenced by N-containing functional groups.

While free and combined amino compounds typically accounted for a significant portion (~20%) of water-soluble organic nitrogen in PM$_{2.5}$ from Davis (Table 2), the bulk of WSON was unidentified, and clearly more work needs to be done to identify these components. A number of organic N compounds, including urea, nitro-phenols, and N-containing aromatics such as methoxyypyridine, isoquinoline, and 1,2-dimethoxy-4-nitrobenzene, have been detected in atmospheric particles, but their concentrations are typically very low [Cornell et al., 1998, and references therein; Lutte et al., 1997, and references therein; Schauer et al., 1996, and references therein]. This suggests that particulate organic nitrogen is composed of a wide range of compounds and that compound-specific studies should be complemented by more general characterizations based on functional groups, polarity, or other bulk properties.

Although past work on atmospheric amino compounds has focused on the free forms, our finding that combined forms were much more abundant indicates that future research in this area should include measurements of total (i.e., free and combined) amino compounds. In addition, the identities and concentrations of less soluble organic nitrogen compounds should also be examined. Any less soluble organic nitrogen in the particles we collected would not have been properly accounted for in our measurement of organic nitrogen because of the aqueous extraction method used. Overall, a better understanding of the influence of organic nitrogen compounds on the chemical, physical, and biological properties of atmospheric particles and aqueous drops will require better characterization of their identities.

4. Conclusions

We have found that water-soluble organic nitrogen was an important component of the total nitrogen and total mass of atmospheric fine particles in Davis, California. Typically, organic forms represented ~20% of the total water-soluble particulate nitrogen and an estimated 18% of the total fine particle mass (assuming an average N-normalized molecular weight of 100 Da per nitrogen atom). Total amino compounds typically represented 23% of the water-soluble organic nitrogen in PM$_{2.5}$, primarily due to combined amines such as proteins and peptides. Concentrations of particulate organic and amino nitrogen both peaked between November and March, possibly because of increased amounts of atmospheric liquid water, lower mixing heights, and increased emissions of pollen and spores.

Overall, these results indicate that organic nitrogen is an important component of atmospheric particles in northern California. After deposition, this particulate organic nitrogen likely has significant effects on aquatic (and perhaps terrestrial) ecosystems in this region. In addition, because of its abundance, organic nitrogen might also significantly influence the effects of fine particulate matter on visibility, climate, and human health in this region. Past measurements of organic nitrogen in wet and dry

Table 2. Mass Concentrations and Percent of Total PM$_{2.5}$ Mass (in Parentheses) for Organic Nitrogen Species and Sulfate$^a$

<table>
<thead>
<tr>
<th>Species</th>
<th>Minimum</th>
<th>Maximum</th>
<th>Median</th>
<th>Mean</th>
<th>s.d.</th>
</tr>
</thead>
<tbody>
<tr>
<td>WSFAN</td>
<td>0.007</td>
<td>0.28</td>
<td>0.033</td>
<td>0.047</td>
<td>0.049</td>
</tr>
<tr>
<td>WSTAN</td>
<td>0.071</td>
<td>2.39</td>
<td>0.30</td>
<td>0.65</td>
<td>0.41</td>
</tr>
<tr>
<td>WSON$^a$</td>
<td>0.31</td>
<td>5.32</td>
<td>1.60</td>
<td>3.93</td>
<td>3.81</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>0.077</td>
<td>2.3</td>
<td>0.72</td>
<td>0.93</td>
<td>0.59</td>
</tr>
<tr>
<td>Total PM$_{2.5}$ mass</td>
<td>3.1</td>
<td>26.3</td>
<td>7.1</td>
<td>8.4</td>
<td>4.4</td>
</tr>
</tbody>
</table>

$^a$Data are based on 41 samples except for WSTAN (nine samples). For a given entry the values for mass concentration and percent of total mass do not necessarily correspond to the same sample; e.g., the median WSON values represent the median mass concentration, and the median percent of total mass (not the median mass concentration and its percent of total mass). Typical relative standard deviation (s.d.) values for WSFAN and WSTAN are the same as in Table 1; values for SO$_4^{2-}$ and total mass were approximately (+12%, −8%) and ±10%, respectively. On the basis of known errors the RSD for WSON was (+27%, −8%), but this does not take into account possible errors in the assumed N-normalized molecular weight of WSON.

$^b$Mass was estimated assuming an average molecular weight of 100 Da per N atom for WSON; see section 3.3.
deposition from a widespread set of locations suggest that the effects of organic N compounds are important in many other regions and on larger spatial scales as well.

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