PERGAMON

AE International – North America

Atmospheric Environment 37 (2003) 2247–2258

ATMOSPHERIC ENVIRONMENT

www.elsevier.com/locate/atmosenv

Free and combined amino compounds in atmospheric fine particles ($PM_{2.5}$) and fog waters from Northern California

Qi Zhang[1], Cort Anastasio*

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

Received 5 October 2002; accepted 10 February 2003

Abstract

Atmospheric fine particles ($PM_{2.5}$) collected during August 1997–July 1998 and wintertime fog waters collected during 1997–1999 at Davis, California were analyzed for free and combined amino compounds. In both $PM_{2.5}$ and fog waters, the average concentrations of combined amino compounds (CAC, e.g., proteins and peptides) were generally 4–5 times higher than those of free amino compounds (FAC, i.e., amino acids and alkyl amines). Concentrations of total amino compounds (TAC = FAC + CAC) ranged from 1260 to 3650 pmol m^{-3} air in $PM_{2.5}$, and from 1620 to 5880 pmol m^{-3} air in fog waters. Average values ($\pm 1\sigma$) were 2500 ± 879 and 3400 ± 1430 pmol m^{-3} air, respectively. Concentrations of amino compounds in $PM_{2.5}$ varied seasonally, with a peak during late winter and early spring. Ornithine was a major FAC component in both $PM_{2.5}$ and fog waters (typically accounting for $\sim 20\%$ of FAC), but these sample types otherwise had fairly different FAC distributions. FAC in $PM_{2.5}$ were enriched in protein-type amino species such as glycine/threonine, serine and alanine, while fog water FAC had significantly higher levels of non-protein species such as methylamine, γ-aminobutyric acid and ethanolamine. The compositions of CAC in $PM_{2.5}$ and fogs were fairly similar and were mainly protein-type. Mass concentrations of TAC in $PM_{2.5}$ and fog waters were, on average, 302 and 399 ng m^{-3} air, respectively. Amino compounds were an important component of the organic carbon pool for both fog and particles, with TAC accounting for an average of 13% of the dissolved organic carbon in fog waters and $\sim 10\%$ of the water-soluble organic carbon in $PM_{2.5}$. At these levels amino compounds likely play important roles in the chemistry of fog drops and fine particles, for example by influencing their buffering capacity and basicity.
© 2003 Elsevier Science Ltd. All rights reserved.

Keywords: Organic nitrogen; Amino acids; Proteins; Buffering capacity; Organic carbon

1. Introduction

Recent studies have demonstrated that organic nitrogen typically represents 20–80% of the total nitrogen in deposition, atmospheric drops, and airborne particles (Anastasio and McGregor, 2000; Cornell et al., 2001; Weathers et al., 2000; Zhang and Anastasio, 2001; Zhang et al., 2002a, b). These results suggest that organic nitrogen compounds might contribute to the nutrient budgets of ecosystems and influence atmospheric chemistry and air quality. Although detailed information on the chemical forms of organic N is required to understand its effects, currently very little is known about the composition and chemistry of this group of compounds in the atmosphere.

One class of organic N compounds that has been measured extensively in the atmosphere is amino

*Corresponding author. Tel.: +1-530-754-6095; fax: +1-530-752-1552.

E-mail address: canastasio@ucdavis.edu (C. Anastasio).

[1] Now at Cooperative Institute for Research in Environmental Sciences (CIRES), University of Colorado, 216 UCB, Boulder, CO 80309-0216, USA.

1352-2310/03/$ - see front matter © 2003 Elsevier Science Ltd. All rights reserved.
doi:10.1016/S1352-2310(03)00127-4

compounds. Significant amounts of amino acids and alkyl amines have been found in the gas phase (Neste et al., 1987), particles (Gorzelska and Galloway, 1990; Gorzelska et al., 1994; Milne and Zika, 1993; Spitzy, 1990; Zhang et al., 2002a), precipitation (Gorzelska et al., 1992; Mopper and Zika, 1987), dew waters (Scheller, 2001) and fog drops (Saxena, 1983; Zhang and Anastasio, 2001). Proteinaceous matter, including plant debris, pollen, algae, and bacteria, has also been frequently detected in the atmosphere (Ankilov et al., 1999; Artaxo et al., 1988, 1990; Fuzzi et al., 1997; Sattler et al., 2001; Tong and Lighthart, 2000), accounting for as much as 55–95% of particulate mass over the Amazon Basin (Artaxo et al., 1988, 1990) and approximately 3% of $PM_{2.5}$ mass in Northern California (Zhang et al., 2002a).

Interest in amino compounds in the atmosphere is driven in part by the bioavailability of these compounds in deposition and their potential roles in ecological processes and plant nutrition. Free and combined amino acids, for example, can be utilizable sources of N for plants and microorganisms (e.g., Rice, 1999; Rosenstock and Simon, 1993; Yu et al., 2002) and can stimulate the growth of biomass (e.g., Barak et al., 1990). The physical–chemical traits of amino compounds are another reason that this group is an interesting subject in atmospheric science. For example, some bacteria and amino acids, such as L-leucine, are efficient ice nuclei (Szyrmer and Zawadzki, 1997). Amino compounds might also be involved in cloud formation, as suggested by the consistent presence of proteinaceous matter in cloud waters (Saxena, 1983), and their surface active properties (Facchini et al., 1999b; Zhang and Anastasio, 2001). Thus, amino compounds could affect the atmospheric water cycle, the atmospheric radiation balance, and the scavenging of air pollutants. In addition, several amino acids, such as methionine and tryptophan, are rapidly transformed in water drops and particles during exposure to ozone and sunlight (McGregor and Anastasio, 2001). Such reactions likely influence atmospheric chemistry and physics. For example, the oxidation of methionine has been hypothesized to produce ultra-fine particles in the remote summer Arctic (Leck and Bigg, 1999), although this has not been examined in detail.

The overall goal of this present study was to characterize free and combined amino compounds (CAC) in $PM_{2.5}$ and fog waters from Northern California in order to better understand their chemistry. We report here the major results from this study, including the concentrations, seasonal variations and distributions of free and CAC in fog waters and $PM_{2.5}$ (particles with aerodynamic diameters $\leqslant 2.5\,\mu m$) and the contribution of these compounds to the organic carbon (OC) pool in $PM_{2.5}$ and fog waters.

2. Experimental methods

2.1. Sample collection and processing

$PM_{2.5}$ samples were collected from August 1997 to July 1998 at the NADP site in Davis, California. Water-soluble components were extracted into Milli-Q water by sonication at 0–4°C, followed by filtration (0.22 μm Teflon) and frozen (−20°C) storage in HDPE bottles. Fog waters were collected at the same site during winters of 1997–1999 and were filtered (0.45 μm Teflon) and stored frozen (−20°C) immediately after collection. Detailed information on sample collection and processing has been reported elsewhere (Zhang and Anastasio, 2001; Zhang et al., 2002a).

2.2. Sample analyses

2.2.1. Free amino compounds (FAC)

A total of 22 primary amino acids and alkyl amines (Table 1) were analyzed by high performance liquid chromatography (HPLC) using a method adapted from Jones et al. (1981) and Gorzelska et al. (1992). Sigma AA-S-18 amino acid standard solution and individual amino compounds were used to make aqueous standard solutions. *O*-phthaldialdehyde/mercaptoethanol (OPA) derivatization reagent was made from 50 mg *o*-phthaldialdehyde, 50 μl mercaptoethanol, 1.25 ml methanol and 11.2 ml of 0.4 M sodium borate buffer (pH 9.5 ± 0.1). All solutions were prepared in Milli-Q water ($\geqslant 18.2\,M\Omega\,cm$).

Generally, a mix of 200 μl aliquot of standard or sample and 20 μl of 2% sodium dodecyl sulfate (to increase sensitivity for Orn and Lys) were derivatized with 30 μl of OPA, shaken for 1.0 min, neutralized with 10 μl of 10% acetic acid and injected into the HPLC system. The HPLC consisted of a C-18 analytical column (Keystone BetaBasic-18, 5 μm bead, 3.0×250 mm) with accompanying guard column, two Shimadzu pumps (LC-10AT), and a Shimadzu RF-551 fluorescence detector ($\lambda_{excitation} = 330$ nm and $\lambda_{emission} = 420$ nm).

Derivatized amino acids and alkyl amines were eluted at a flow rate of 0.44 ml/min using a gradient program with two eluents: eluent A (20:80 by volume of methanol and 0.05 M sodium acetate buffer (pH 6.1 ± 0.1)) and eluent B (80:19:1 by volume of methanol, 0.04 M sodium acetate buffer (pH 6.1 ± 0.1) and tetrahydrofuran). The gradient program was (% eluent B after specified time): start 15% B; 2-min 45% B; 8-min 47% B; 12-min 55% B; 16-min 55% B; 20-min 59% B; 24-min 80% B; 25-min 80% B; 35-min 100% B; and 39-min end. Because glycine and threonine coeluted and had similar response factors (Yu et al., 2002), they are reported as a total Gly/Thr concentration here.

Table 1
Average concentrations (pmol m^{-3} air) of individual free and combined amino compounds in $PM_{2.5}$ and fog waters

Compound	Abbr.[b]	Chemical formula	MW (g mol^{-1})	Acidity or basicity[c]	Average concentrations ± 1σ (pmol m^{-3} air)[a]							
					Free amino compounds				Combined amino compounds			
					$PM_{2.5}$ ($n = 41$)		Fog ($n = 11$)		$PM_{2.5}$ ($n = 9$)		Fog ($n = 7$)	
					Avg.	1σ	Avg.	1σ	Avg.	1σ	Avg.	1σ
Protein type												
Alanine	Ala	$C_3H_7NO_2$	89.0	N	24	18	32	30	170	85	269	146
Arginine	Arg	$C_6H_{14}N_4O_2$	174.2	B	5.2	7.3	5.7	4.1	59	40	129	149
Asparagine	Asn	$C_4H_8N_2O_3$	134.1	N	NA[d]	NA[d]	7.6	7.5	27	17	38	36
Aspartic acid	Asp	$C_4H_7NO_4$	133.1	A	10	7.8	22	21	107	64	199	140
Glutamic acid	Glu	$C_5H_9NO_4$	147.1	A	5.2	4.1	10	9.7	117	62	185	113
Glycine[e]	Gly	$C_2H_5NO_2$	75.1	N	101	74	38	26	183	104	435	292
Histidine	His*	$C_6H_9N_3O_2$	155.2	N	3.8	5.6	14	9.5	2.4	3.4	26	24
Iso-leucine	Ile	$C_6H_{13}NO_2$	131.2	N	6.0	5.0	17	19	59	32	84	78
Leucine	Leu	$C_6H_{13}NO_2$	131.2	N	9.0	8.9	33	35	72	36	181	152
Lysine	Lys	$C_6H_{14}N_2O_2$	146.2	B	5.6	6.6	22	14	81	35	95	66
Methionine	Met	$C_5H_{11}NO_2S$	149.2	N	<0.1	<0.1	0.9	1.9	41	43	22	21
Phenylalanine	Phe*	$C_9H_{11}NO_2$	165.2	N	2.4	4.2	16	11	55	29	145	209
Threonine[e]	Thr	$C_4H_9NO_3$	119.1	N	—	—	—	—	—	—	—	—
Tryptophan	Trp*	$C_{11}H_{12}N_2O_2$	204.2	N	<0.6	<0.6	11	22	44	26	44	37
Tyrosine	Tyr*	$C_9H_{11}NO_3$	181.2	N	6.5	4.7	14	11	56	31	117	87
Serine	Ser	$C_3H_7NO_3$	105.1	N	56	50	64	61	562	365	429	431
Valine	Val	$C_5H_{11}NO_2$	117.2	N	7.6	5.8	21	16	66	33	107	93
Non-protein type												
Ethanolamine	2AE	C_2H_7NO	61.0	B	6.0	7.4	27	29	62	55	110	99
γ-aminobutyric acid	GABA	$C_4H_9NO_2$	103.1	N	4.0	6.0	47	98	42	34	60	48
Methionine sulfoxide	MetSO	$C_5H_{11}NO_3S$	165.2	N	<0.2	<0.2	2.4	1.6	4.1	4.5	27	52
Methylamine	MA	CH_5N	32.0	B	56	52	166	115	90	147	130	163
Ornithine	Orn	$C_5H_{12}N_2O_2$	168.6	B	118	203	145	69	149	149	7.8	13

[a] Calculated using 0.5 times the method detection limit for any value below detection limit.
[b] Aromatic amino compounds are marked with an asterisk.
[c] Classified based on the pH at which the net charge on a molecule is zero, i.e., pI (Lide, 1992). A: acidic (pI < 5); B: basic (pI > 9); N: neutral (pI = 5–9).
[d] Free Asn was not analyzed in $PM_{2.5}$.
[e] Because Gly and Thr co-eluted on the HPLC (Section 2.3) listed concentrations of Gly are the sum of Gly + Thr.

2.2.2. Combined amino compounds (CAC)

These compounds (e.g., proteins and peptides) were first hydrolyzed (Tsugita et al., 1987) and then analyzed with the HPLC technique described in Section 2.2.1. The hydrolysis procedure consisted of: drying a mix of 100 μl of sample and 10 μl of ascorbic acid (20 mg/ml in water) in a test tube by lyophilization; placing the test tube in a 10 ml ampoule (Kontes) containing 170 μl of acid hydrolysis mixture (7 M HCl, 10% trifluoroacetic acid, and 0.1% phenol); sealing the ampoule under mild vacuum (⩽160 mm Hg of Ar); heating the ampoule in an oil bath (158°C) for 30 min; and extracting the hydrolyzed product with 500 μl of Milli-Q water. Concentrations of CAC were calculated as the difference in FAC measured after and before hydrolysis. Additional details on the hydrolysis method are reported in Yu et al. (2002).

It should be noted that the terms used here (FAC, CAC and TAC) encompass those used in two preceding papers (Zhang and Anastasio, 2001; Zhang et al., 2002a). For example, FAC here is used to refer both to dissolved free amino nitrogen (DFAN) compounds in fog waters as well as water-soluble free amino nitrogen (WSFAN) compounds in $PM_{2.5}$.

2.3. Quality control

Each analysis was evaluated and monitored in terms of the reproducibility of peak retention times, peak heights and the linearity of the calibration curve. In general at least one replicate injection was made after every ten sample runs. The average relative percent difference (RPD) in measurements of individual amino compounds between replicate injections was 9.4%. The

method detection limit (MDL; Greenberg et al., 1991) for individual amino compounds ranged from 1.3 to 18.9 nM (mean = 5.3 nM). During each analytical period at least one procedural blank (Milli-Q water taken through the entire analytical procedure) was analyzed. Concentrations of individual amino compounds in procedural blanks were always less than detection limits. Extraction efficiencies of individual amino compounds, determined from two successive extractions of the same sample filter, ranged from 84% to 100% with an average value of 92%. Since the values of amino compounds in aerosols reported in this study were all derived from measurements in the first extracts they might be somewhat underestimated.

In order to check for possible contamination, we collected, processed and analyzed corresponding sample blanks: i.e., Milli-Q water that was sprayed into the fog sampler or clean Zefluor filters that were taken through the sampling process. Average concentrations of individual FAC in sample blanks were typically $<2\%$ and 7%, respectively, of the average fog and $PM_{2.5}$ values, while those of CAC were typically $<3\%$ and 15%, respectively, of the average fog and $PM_{2.5}$ values. Limits of quantification (LOQ) in samples were defined as three times the average sample blank value (Zhang and Anastasio, 2001) or 2.5 times the MDL (Greenberg et al., 1991), whichever was higher. Values for the MDL and LOQ are listed in Supplementary Tables 1 and 2.

Cytochrome *c* was hydrolyzed and analyzed to test the hydrolysis efficiency for combined amino acids. The recovery of amino N from the protein was 92% of theoretical value; the average relative difference between theoretical and measured amounts of individual compounds was 9.0%. The average concentration of total amino acids in Milli-Q water taken through the hydrolysis procedure was $<0.1\%$ of the mean value in the fog samples.

3. Results and discussions

3.1. Concentrations and speciation of amino compounds

3.1.1. Free amino compounds in $PM_{2.5}$

Levels of FAC in $PM_{2.5}$ ranged from 63 to 1720 pmol m^{-3} air, with a mean value ($\pm 1\sigma$) of 427 ± 358 pmol m^{-3} air (Table 2). Similar amounts of FAC have been reported for particles collected over the North Atlantic Ocean (below detection limit to 1610 pmol m^{-3} air; Gorzelska and Galloway, 1990) and over Canada (4–6700 pmol m^{-3} air; calculated from data of Gorzelska et al., 1994). Ornithine typically was the most abundant FAC in $PM_{2.5}$ sample with a mean ($\pm 1\sigma$) concentration of 118 ± 203 pmol m^{-3} air (Table 1). On average, Orn accounted for $23 \pm 14\%$ of the FAC pool in $PM_{2.5}$ (Fig. 1a). Glycine (Gly) and/or threonine (Thr) were the other most abundant FAC species in $PM_{2.5}$, with an average combined concentration of 101 ± 74 pmol m^{-3} air and an average contribution of $26 \pm 8\%$ to the FAC pool (Table 1, Fig. 1a). Serine (Ser), methylamine (MA), and alanine (Ala) also contributed significantly, accounting for an average of $13 \pm 7\%$, $13 \pm 6\%$ and $6 \pm 2\%$, respectively, of the FAC pool in $PM_{2.5}$ (Fig. 1a). This is similar to a past measurement of FAC in marine air where Gly, Thr, Ser, and Ala were the dominant FAC species, together accounting for more than 50% of the total FAC pool (Mopper and Zika, 1987). In contrast, Orn was only a minor component in this marine air sample, accounting for $\sim 4\%$ of the FAC.

We have also examined the relative amounts of protein-type (i.e., species used in protein biosynthesis) and non-protein-type (e.g., amines and Orn) amino compounds (Table 1). In $PM_{2.5}$, protein-type FAC were typically nearly twice as abundant as non-protein-type compounds (Table 2).

3.1.2. FAC in fog waters

The mean concentration of FAC in fog waters was roughly 70% greater than that in $PM_{2.5}$ (Table 2). Atmospheric concentrations of FAC in fog waters ranged from 239 to 1540 pmol m^{-3} air (mean $\pm 1\sigma = 714 \pm 375$ pmol m^{-3} air). Aqueous concentrations of FAC in our Davis fog waters (2.6–99 μM; mean $\pm 1\sigma = 20 \pm 27$ μM) were similar to those measured in dew samples from Germany, where concentrations ranged from 0.5 to 110 μM (average = 22.5 μM; calculated from data of Scheller, 2001). In comparison, previously reported FAC values in rainwaters are much lower. For example, the average concentration of total FAC in continental rain samples was ~ 0.4 μM (calculated from Gorzelska et al., 1992) and was 6.5 μM in marine rains (Mopper and Zika, 1987).

As in $PM_{2.5}$, Orn was also the main FAC component in fog waters, accounting for an average of $22 \pm 6.6\%$ of the FAC pool (Fig. 1b). However, the distribution of the other FAC was fairly different in fog waters compared to $PM_{2.5}$. Fog waters contained 3–4 times more MA and 2AE than $PM_{2.5}$ (Table 1) and had considerably larger amounts of GABA, which accounted for 7% of the fog FAC but only $\sim 1\%$ of the $PM_{2.5}$ FAC (Fig. 1a and b). In addition, Met, MetSO, and Trp were never detected in $PM_{2.5}$ but were frequently observed in fog waters. Average fog water concentrations of free Met and MetSO were approximately 1–2 pmol m^{-3} air, while that of Trp was 11 pmol m^{-3} air (Table 1). In general, the fog FAC pool had a larger contribution from non-protein species (an average $55 \pm 9.2\%$ of the total FAC pool) compared to $PM_{2.5}$ ($39 \pm 15\%$; Table 2).

Past measurements have shown that FAC distributions in precipitation vary significantly among different locations. For example, the FAC pool in rain samples

Table 2
Concentrations, and percent contributions to the total pool, for amino compounds in $PM_{2.5}$ and fog waters

	Concentration (pmol m^{-3} air)			% of FAC or CAC pool	
	Non-protein type	Protein type	Total	Non-protein type	Protein type
Free amino compounds (FAC)					
$PM_{2.5}$ (*n=41*)					
Minimum	15	49	63	14	22
Maximum	1360	807	1720	78	86
Median	131	163	283	34	66
Average	184	243	427	39	61
1σ	235	180	358	15	15
Fog waters (*n=11*)					
Minimum	123	116	239	41	25
Maximum	750	794	1540	75	59
Median	348	329	691	52	48
Average	387	327	714	55	45
1σ	197	201	375	9.2	9.2
Combined amino compounds (CAC)					
$PM_{2.5}$ (*n=9*)					
Minimum	77	943	1020	7.0	60
Maximum	820	2730	3210	40	93
Median	270	1480	1870	14	86
Average	347	1700	2050	16	84
1σ	267	609	726	11	11
Fog waters (*n=7*)					
Minimum	75	1220	1370	3.1	78
Maximum	870	4930	5110	22	97
Median	184	2140	2500	11	89
Average	335	2510	2840	12	88
1σ	294	1190	1250	8.2	8.2

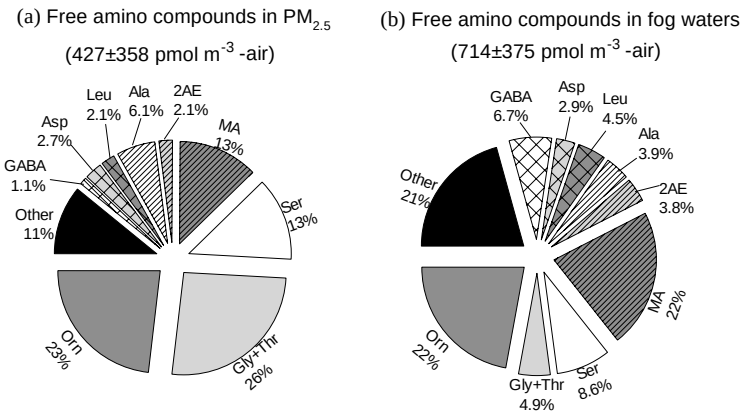

Fig. 1. Average contributions of individual compounds to the free amino compound (FAC) pool in (a) $PM_{2.5}$ (41 samples) and (b) fog waters (11 samples). The category "other" for $PM_{2.5}$ includes Lys (1.1%), Arg (1.4%), His (0.8%), Ile (1.8%), Val (2.0%), Glu (1.6%), Tyr (1.7%), and Phe (0.6%). "Other" for the fog waters includes Lys (3.2%), Arg (0.9%), His (2.3%), Ile (2.2%), Val (2.5%), Glu (1.7%), Tyr (2.5%), Phe (2.1%), Asn (1.0%), MetSO (0.3%), Trp (1.9%), and Met (0.1%). Values in parentheses represent the average percent contribution to the corresponding FAC pool.

collected over the Atlantic Ocean was dominated by Gly, Ser, Ala and acidic amino acids (Mopper and Zika, 1987), while in rain samples collected over rural Virginia, the major FAC species were Arg, Asn, Gln, MA, Ser and Ala (Gorzelska et al., 1992). Arg, proline and Gln/Glu, however, were the predominant FAC species in dew samples collected from rural Germany (Scheller, 2001). Orn was only measured in the marine rain samples (Mopper and Zika, 1987) and was only a minor component (1.0–9.4%) of the FAC pool. However, it might have been present at significant levels in the rural rain and dew because of the occurrence of high concentrations of Arg in these samples (Gorzelska et al., 1992; Scheller, 2001) and the fact that Orn is a metabolite of arginine in the urea cycle (Armstrong, 1989).

3.1.3. Combined amino compounds in $PM_{2.5}$

Concentrations of CAC were approximately 5 times greater than those of free species in $PM_{2.5}$, with an average concentration of $2050 \pm 730\,\text{pmol}\,\text{m}^{-3}$ air (Table 2). In contrast to the free species, the CAC pool in $PM_{2.5}$ was more evenly distributed among a larger number of individual compounds (Fig. 2a). Although never detected as free species in $PM_{2.5}$, Met, MetSO, and Trp were present at low concentrations in combined forms in $PM_{2.5}$ (Table 1). This is not surprising since Met and Trp are often present at low levels in proteins (Block, 1956). The presence of trace amounts of MetSO might be due to oxidation of combined Met during the hydrolysis procedure. The fact that protein-type species on average accounted for $84 \pm 11\%$ (i.e., $1700 \pm 609\,\text{pmol}\,\text{m}^{-3}$ air) of the CAC pool in $PM_{2.5}$ (Table 2) suggests that most of the CAC were present in proteinaceous species although other combined forms, such as amino acid-humic complexes (Tarr et al., 2001; Thorn et al., 1996), might also have been significant.

3.1.4. CAC in fog waters

As seen for $PM_{2.5}$, concentrations of CAC in fog drops were $\sim$ 4 times greater than those of FAC with an average atmospheric concentration of $2840 \pm 1250\,\text{pmol}\,\text{m}^{-3}$ air (Table 2). Corresponding aqueous concentrations of CAC in individual fog water samples ranged from 14 to 237 μM and had a mean value ($\pm 1\sigma$) of 78 ± 75 μM (Supplementary Table 2). Ser and Gly/Thr were the most abundant combined amino species (each contributing $\sim$15% to the fog CAC pool), followed by Ala, Glu, Asp, and Leu (Fig. 2b). Orn and MA were minor components in the fog CAC pool, in contrast to their dominance in the fog FAC pool (Table 1, Figs. 1b and 2b). The distribution of CAC in fog waters was generally similar to that in $PM_{2.5}$ (Fig. 2). In addition, as for the case of $PM_{2.5}$, most of the CAC in fog waters were protein type (average $\pm 1\sigma = 88 \pm 8.2\%$; Table 2).

3.2. Seasonal trends of amino compounds

Concentrations of FAC in $PM_{2.5}$ varied by a factor of $\sim$30 during the year, with higher values occurring during the period from late fall to early spring (Fig. 3, Table 2). Ornithine in $PM_{2.5}$ showed the strongest seasonal variation, with an average wintertime concentration $\sim$4 times higher than that in summer (Supplementary Table 1). In contrast, concentrations of Gly/Thr were more consistent throughout the year, varying by a factor of approximately 2. The other amino species

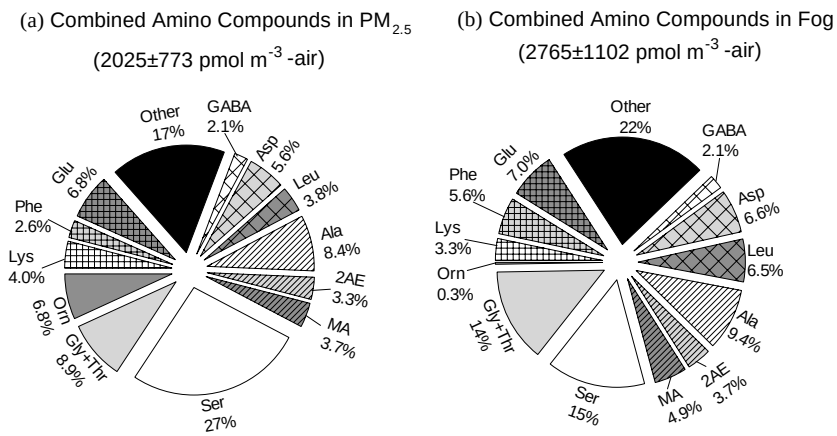

Fig. 2. Average contributions of individual compounds to the combined amino compound (CAC) pool in (a) $PM_{2.5}$ (9 samples) and (b) fog waters (7 samples). "Other" for $PM_{2.5}$ includes Phe (2.6%), Asn (1.2%), His (0.2%), MetSO (0.3%), Tyr (2.7%), Trp (2.2%), Met (1.9%), Val (3.3%), and Ile (3.0%). "Other" for the fog waters includes Phe (5.6%), Asn (1.5%), His (1.0%), MetSO (0.8%), Tyr (3.9%), Trp (2.0%), Met (0.8%), Val (3.5%), and Ile (3.0%). Values in parentheses represent the average percent contribution to the corresponding CAC pool.

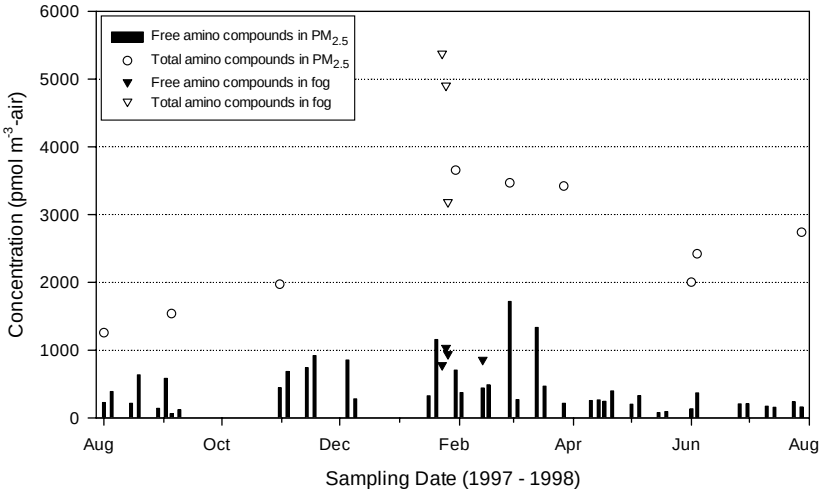

Fig. 3. Seasonal trends in concentrations of free and total (free + combined) amino compounds in $PM_{2.5}$ and fog waters collected from Davis, California.

were also relatively consistent throughout the year. Concentrations of total amino compounds (TAC) had a seasonal trend similar to FAC, but less pronounced, with a peak between January and March (Fig. 3). Concentrations of FAC in fog waters were similar to those in $PM_{2.5}$ during the same period but those of CAC were somewhat larger in fogs. In addition, the average concentrations of FAC and CAC in fog waters varied by a factor of 2–3 between the 1997 and 1999 collection seasons (Fig. 3).

The distribution of FAC in $PM_{2.5}$ was fairly consistent seasonally although the relative importance of individual species varied slightly throughout the year. Orn and Gly/Thr were always the most abundant FAC, with greater average contributions from Orn in winter and spring and more Gly/Thr in summer and fall. The average distribution of CAC in $PM_{2.5}$ also exhibited little change between different seasons. Similarly, FAC and CAC distributions in winter fog waters from different years showed only small differences.

3.3. Mass concentrations and apparent molecular weights and formulae of amino compounds

The average mass concentrations of both free and CAC were significantly higher ($\sim$30%, Fig. 4) in fog waters than in $PM_{2.5}$. The total masses of amino compounds in fog and $PM_{2.5}$ were 399 ± 162 and $302 \pm 108\,ng\,m^{-3}$ air, respectively (Fig. 4). Interestingly, these numbers are very close to the concentration of proteins (mean $\pm 1\sigma = 390 \pm 210\,ng\,m^{-3}$ air) measured in bulk aerosol particles from Southwestern Siberia (Ankilov et al., 1999). CAC accounted for a major portion of the mass of amino compounds in both fog waters and $PM_{2.5}$ (84 ± 4% and 83 ± 14% of the total, respectively; Supplementary Tables 1 and 2). As discussed previously, TAC typically accounted for $\sim$3% of the measured $PM_{2.5}$ mass (Zhang et al., 2002a).

We have calculated the concentration-weighted apparent molecular weight (AMW) for bulk amino compounds in each fog and $PM_{2.5}$ sample using $\Sigma(MW_i \times C_i)/\Sigma(C_i)$, where MW_i and C_i are the molecular weight and concentration of amino compound i, respectively. The average AMWs of FAC and CAC were 107 ± 12 and 121 ± 4.9 g/mol, respectively, in $PM_{2.5}$ and were 113 ± 10 and 120 ± 11 g/mol, respectively, in fog waters. Note that the AMW of the CAC refers to the hydrolyzed (free) forms, not the combined molecules that were originally present in samples. When treated as a whole, the AMW of TAC (i.e., the sum of free and combined) were very similar in $PM_{2.5}$ and fog waters, with values of 121 ± 4.5 and 118 ± 9.1 g/mol, respectively. In addition, the apparent chemical formulae for bulk TAC were very similar in both types of samples: $C_{4.2\pm0.2}H_{8.9\pm0.4}N_{1.3\pm0.1}O_{2.4\pm0.2}$ in $PM_{2.5}$ and $C_{4.6\pm0.6}H_{8.9\pm0.8}N_{1.3\pm0.2}O_{2.3\pm0.1}$ in fog waters, where the subscripts represent the average number $\pm 1\sigma$ of the corresponding atom.

3.4. Acid/base chemistry of amino compounds

At the typical pH values of atmospheric cloud and fog drops the carboxylic acid group(s) on a given amino acid is deprotonated and bears a negative charge while the amino group(s) is protonated and carries a positive charge. The pH at which the net charge on a molecule is zero, i.e., the isoelectric point (pI), can be used to classify amino compounds as acidic (pI < 5), basic (pI > 9) or neutral (pI = 5–9; Table 1). Of the 22 FAC identified in this study, 5 were basic (Orn, Lys, MA, 2AE, and Arg),

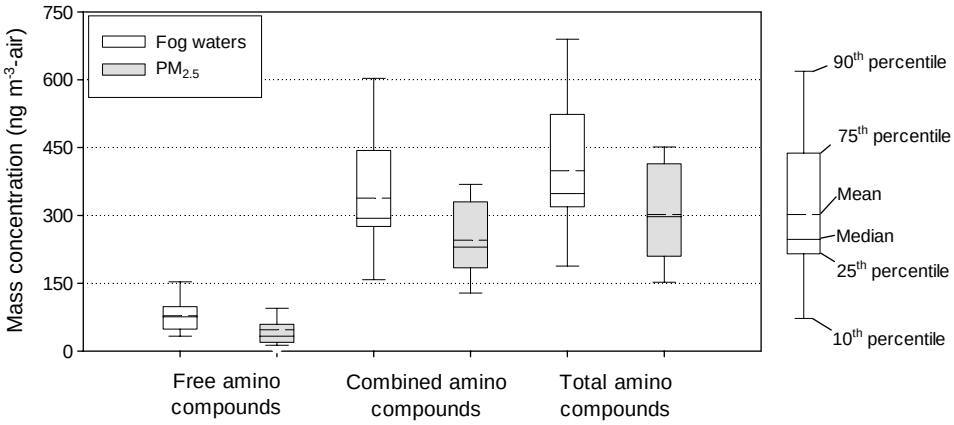

Fig. 4. Mass concentrations of amino compounds in $PM_{2.5}$ and fog waters collected from Davis, California. The legend on the right describes the components of each box and whisker plot. The number of samples in each category is listed in Table 2.

15 were neutral, and only two (aspartic acid and glutamic acid) were acidic (Table 1). While $PM_{2.5}$ contained relatively more neutral free amino species, fog waters contained more basic ones (Fig. 5). The difference was largely due to the fact that alkyl amines (MA and 2AE) accounted for a greater fraction of FAC in fog waters (26%) than they did in $PM_{2.5}$ (15%; Fig. 1), which likely resulted from greater amounts of partitioning of these gas phase species into fog drops.

The total (free + combined) amino pool in both fog and $PM_{2.5}$ samples were dominated by neutral compounds and contained significantly more basic species than acidic ones. This observation indicates that amino compounds are, overall, a source of basicity to atmospheric condensed phases. However, it should be noted that ammonia is by far the dominant base in Central Valley air: NH_4^+ concentrations are typically 10–40 times higher than the amino compound concentrations described here (Zhang and Anastasio, 2001; Zhang et al., 2002a). In areas where NH_3/NH_4^+ concentrations are lower, the basicity contribution from amino compounds could be more significant. In addition, amino compounds with side chains that have pK_a values around 4–7, such as Asp, GABA, Glu and His, might contribute to the buffering capacity of atmospheric condensed phases at pH values lower than where NH_4^+ ($pK_a = 9.25$; Lide, 1992) will be important. The average concentration of these four amino compounds (free + combined) in Davis fog waters was approximately 13 μM, which could account for ~10% of the unexplained acid buffering capacity reported previously for fog waters from California's Central Valley (mean $\pm 1\sigma = 119 \pm 74$ μM, range = 27–246 μM; Collett et al., 1999a).

3.5. Contribution of amino compounds to the OC pool

Mean concentrations of carbon in FAC and CAC in fog waters were 10–392 and 56–1440 μM C, respectively, corresponding to 0.8–7.8% and 5.4–20%, respectively, of the dissolved organic carbon (DOC) in the fog drops (Table 3). Together, free and combined amino compounds (TAC) accounted for 6.2–23% (average $\pm 1\sigma = 13 \pm 6.5\%$) of the DOC in fog waters (Table 3). This contribution from amino compounds is significant, especially given the fact that the most abundant identified individual organic species (including formaldehyde, formate, and acetate) together generally account for ~ 20% or less of the DOC in atmospheric water drops (Collett et al., 1999b; Facchini et al., 1999a). The average ($\pm 1\sigma$) carbon content of TAC in $PM_{2.5}$ was 126 ± 42 ng C m^{-3} air. Although not measured in our $PM_{2.5}$ samples, based on measurements of organic carbon OC in Davis $PM_{1.8}$ during winter (8.5 ± 4.4 μg m^{-3} air; M. Kleeman, unpublished data), and assuming a water-soluble (WSOC)/OC ratio of 0.20 (Saxena and Hildemann, 1996), the average WSOC concentration in wintertime Davis $PM_{2.5}$ was estimated to be ~1.7 μg C m^{-3} air. Given that the average amino C content in our winter samples was 175 ng C m^{-3} air, amino compounds appear to account for approximately 10% of WSOC in $PM_{2.5}$ at Davis during winter.

4. Implications and summary

Previous studies have demonstrated that amino acids, proteins and protein–tannin complexes are sources of available nitrogen to a wide range of plants (Yu et al., 2002) and aquatic microorganisms (Rice, 1999; Rosenstock and Simon, 1993). Our measurements of considerable amounts of free and combined amino compounds in atmospheric fine particles and fog drops clearly indicate that significant amounts of these compounds are delivered to ecosystems through atmospheric deposition. Given the importance of nitrogen in deposition, atmospheric

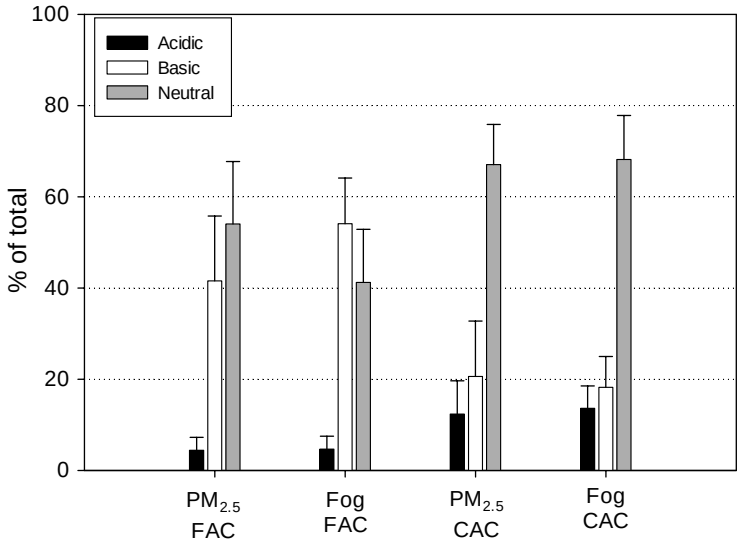

Fig. 5. Acidity/basicity distribution of free and combined amino compounds in $PM_{2.5}$ and fog waters. Bars represent average values with error bars of one standard deviation.

Table 3
Contribution of free and combined amino compounds to the dissolved organic carbon pool in fog waters

	Concentration (μM C)				% of DOC pool		
	DOC[a] ($n = 9$)	FAC ($n = 9$)	CAC ($n = 7$)	TAC ($n = 7$)	FAC ($n = 9$)	CAC ($n = 7$)	TAC ($n = 7$)
Min	425	10	56	66	0.8	5.4	6.2
Max	9250	392	1440	1750	7.8	20	23
Median	2490	44	268	310	2.4	13	15
Average	3150	77	392	465	2.7	11	13
Std Dev	2670	107	475	580	2.0	5.6	6.5

[a] Calculated from values reported in Zhang and Anastasio (2001).

amino compounds might therefore significantly influence ecological issues such as plant nutrition, ecosystem functions, and aquatic productivity.

Amino compounds might also significantly impact the physical, chemical and biological properties of atmospheric particles and water drops. For example, Saxena and Hildemann (1996) suggested amino acids as a potentially important class of hygroscopic compounds based on thermodynamic considerations (e.g., high water solubility and low vapor pressure). Our findings that amino compounds are common constituents of atmospheric condensed phases, and that they are a significant component of the hydrophilic organic carbon pool, provide additional evidence that these compounds likely play important roles in the process of particle activation and uptake of water.

Amino acids might also have an impact on the chemistry of transition metals such as iron and copper in atmospheric drops and particles. A number of amino acids form strong complexes with these metals (Martell and Smith, 1974), suggesting that FAC (and perhaps CAC) could influence the ability of Fe and Cu to participate in reactions such as the formation and destruction of oxidants. For example, a number of amino acid complexes of Cu absorb sunlight much more strongly than the uncomplexed components and undergo direct photoreactions to form products such as $^{\bullet}O_2^-$ and HOOH (Hayase and Zepp, 1991).

Several amino acids, such as tryptophan and tyrosine, can directly absorb sunlight ($\lambda > 290$ nm) and sensitize the oxidation of other compounds, including amino acids (Creed, 1984; Walrant and Santus, 1974). They also react rapidly with ozone to form products such as ammonium, organic acids, nitro or nitroso compounds and hydroxylamines (Berger et al., 1999; McGregor and Anastasio, 2001; Milne and Zika, 1993; Suzuki et al., 1985). Reactions such as these will change the composition of condensed phase organic compounds in the atmosphere and influence the properties of atmospheric particles and water drops.

FAC can be either directly emitted from plants and animals or be released from CAC through enzymatic

and photocatalytic hydrolysis (Gorzelska et al., 1992; Milne and Zika, 1993). The later mechanism is supported by a recent study from Tarr et al. (2001), who demonstrated the release of free amino acids from dissolved fulvic acids and colloidal matter in natural waters during sunlight illumination. Given that atmospheric aging and the extent of protein hydrolysis are likely positively correlated, the ratio of the concentrations of free and combined protein-type amino compounds might provide a measure for the "age" of particles. The ratios of protein-type FAC/CAC in our $PM_{2.5}$ samples and fog waters were typically in the same range (0.13–0.16), suggesting that residence times for amino compounds are similar in Davis $PM_{2.5}$ and fog drops. Mopper and Zika (1987) made a similar argument, i.e., that atmospheric aging might increase the FAC/CAC ratio, based on their observation that this ratio was ~5–10 times higher in marine rain samples compared to terrestrial rain samples. They suggested that this was a result of long-distance transport of terrestrial particles to the ocean (Mopper and Zika, 1987).

It is very interesting that there were relatively high concentrations of Orn in our samples since this is not an essential amino acid for protein synthesis. The commonly known biological sources of ornithine are hydrolysis of peptides with Orn residues and metabolism of Arg during the urea cycle (Armstrong, 1989). However, these two pathways do not appear to be the major sources of Orn in our samples since concentrations of free and combined Arg, as well as combined Orn, were all quite low. According to a recent study, Orn is also produced by bacteria associated with poultry (Geornaras et al., 1995), which might explain our results given the agricultural nature of our sampling area. If this is the case, Orn might be a useful tracer of emissions from some livestock operations (Armstrong, 1989; Geornaras et al., 1995; Mopper and Zika, 1987).

Overall, our results clearly indicate that there are significant concentrations of airborne amino compounds in Northern California. It is especially interesting that these compounds represented a significant portion of the hydrophilic organic carbon (OC) pool. As discussed above, amino compounds likely play noteworthy roles in the region, possibly affecting atmosphere–biosphere nutrient cycling, atmospheric chemistry and air quality. Given the apparent ubiquity of atmospheric amino compounds over continental and marine areas (Milne and Zika, 1993), these effects are likely widespread.

Acknowledgements

The authors thank Keith McGregor, Mike Jimenez-Cruz and Zengshou Yu (UC Davis) for experimental assistance; Dr. Michael Kleeman and Jorn Herner (UC Davis) for providing particulate organic carbon data; and Tony Andreoni and Dean Bloudoff (California Air Resources Board) for the CASCC2. This work was supported by the US 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 fellowship 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 UC Davis.

References

Anastasio, C., McGregor, K.G., 2000. Photodestruction of dissolved organic nitrogen species in fog waters. Aerosol Science and Technology 32 (2), 106–119.

Ankilov, A.N., Baklanov, A.M., Borodudin, A.I., Buryak, G.A., Malyshkin, S.B., Ol'kin, S.E., P'yankov, O.V., P'yankova, O.G., Safatov, A.S., Sergeev, A.N., 1999. Estimate of the biological component of the atmospheric aerosol in Southwestern Siberia. Atmospheric Oceanic Optics 12 (6), 488–492.

Armstrong, F.B., 1989. Biochemistry, Oxford University Press, New York, p. 675.

Artaxo, P., Storms, H., Bruynseels, F., Grieken, R.V., 1988. Composition and sources of aerosols from the Amazon Basin. Journal of Geophysical Research 33 (D2), 1605–1615.

Artaxo, P., Maenhaut, W., Storms, H., Vangrieken, R., 1990. Aerosol characteristics and sources for the Amazon Basin during the wet season. Journal of Geophysical Research-Atmospheres 95 (D10), 16971–16985.

Barak, P., Molina, J.A.E., Hadas, A., Clapp, C.E., 1990. Mineralization of amino acids and evidence of direct assimilation of organic nitrogen. Soil Science Society of America Journal 54 (3), 769–774.

Berger, P., Leitner, N.K.V., Dore, M., Legube, B., 1999. Ozone and hydroxyl radicals induced oxidation of glycine. Water Research 33 (2), 433–441.

Block, R.J., 1956. Amino Acid Handbook; Methods and Results of Protein Analysis. Thomas, Springfield Ill, p. 386.

Collett, J.L., Hoag, K.J., Rao, X., 1999aa. Internal acid buffering in San Joaquin valley fog drops and its influence on aerosol processing. Atmospheric Environment 33 (29), 4833–4847.

Collett, J.L., Hoag, K.J., Sherman, D.E., Bator, A., Richards, L.W., 1999bb. Spatial and temporal variations in San Joaquin valley fog chemistry. Atmospheric Environment 33 (1), 129–140.

Cornell, S., Mace, K., Coeppicus, S., Duce, R., Huebert, B., Jickells, T., Zhuang, L.Z., 2001. Organic nitrogen in

Hawaiian rain and aerosol. Journal of Geophysical Research-Atmospheres 106 (D8), 7973–7983.

Creed, D., 1984. The photophysics and photochemistry of the near-UV absorbing amino acids—I. Tryptophan and its simple derivatives. Photochemistry and Photobiology 39 (4), 537–562.

Facchini, M.C., Fuzzi, S., Zappoli, S., Andracchio, A., Gelencser, A., Kiss, G., Krivacsy, Z., Meszaros, E., Hansson, H.C., Alsberg, T., Zebuhr, Y., 1999aa. Partitioning of the organic aerosol component between fog droplets and interstitial air. Journal of Geophysical Research-Atmospheres 104 (D21), 26821–26832.

Facchini, M.C., Mircea, M., Fuzzi, S., Charlson, R.J., 1999bb. Cloud albedo enhancement by surface-active organic solutes in growing droplets. Nature 401 (6750), 257–259.

Fuzzi, S., Mandrioli, P., Perfetto, A., 1997. Fog droplets—an atmospheric source of secondary biological aerosol particles. Atmospheric Environment 31 (2), 287–290.

Geornaras, I., Dykes, G.A., Vonholy, A., 1995. Biogenic amine formation by poultry-associated spoilage and pathogenic bacteria. Letters in Applied Microbiology 21 (3), 164–166.

Gorzelska, K., Galloway, J.N., 1990. Amine nitrogen in the atmospheric environment over the North Atlantic Ocean. Global Biogeochemical Cycles 4 (3), 309–333.

Gorzelska, K., Galloway, J.N., Watterson, K., Keene, W.C., 1992. Water-soluble primary amine compounds in rural continental precipitation. Atmospheric Environment 26 (6), 1005–1018.

Gorzelska, K., Talbot, R.W., Klemm, K., Lefer, B., Klemm, O., Gregory, G.L., Anderson, B., Barrie, L.A., 1994. Chemical composition of the atmospheric aerosol in the troposphere over the Hudson Bay lowlands and Quebec-Labrador regions of Canada. Journal of Geophysical Research-Atmospheres 99 (D1), 1763–1779.

Greenberg, A.E., Eaton, A.D., Clesceri, L.S., American Public Health Association, American Water Works Association and Water Pollution Control Federation, 1991. Standard Methods for the Examination of Water and Wastewater: 1991 Supplement to the 17th Edition. American Public Health Association, Washington, DC, p. 1449.

Hayase, K., Zepp, R.G., 1991. Photolysis of copper(II)-amino acid complexes in water. Environmental Science and Technology 25 (7), 1273–1279.

Jones, B.N., Paabo, S., Stein, S., 1981. Amino acid analysis and enzymatic sequence determination of peptides by an improved o-phthaldialdehyde precolumn labeling procedure. Journal of Liquid Chromatography 4 (4), 565–586.

Leck, C., Bigg, E.K., 1999. Aerosol production over remote marine areas—a new route. Geophysical Research Letters 26 (23), 3577–3580.

Lide, D.R., 1992. CRC Handbook of Chemistry and Physics. CRC Press, Boca Raton, FL., p C-724.

Martell, A.E., Smith, R.M., 1974. Critical stability constants. Volume 1: Amino acids. Plenum Press, New York.

McGregor, K.G., Anastasio, C., 2001. Chemistry of fog waters in California's Central Valley: 2. Photochemical transformations of amino acids and alkyl amines. Atmospheric Environment 35 (6), 1091–1104.

Milne, P.J., Zika, R.G., 1993. Amino acid nitrogen in atmospheric aerosols—occurrence, sources and photochemical modification. Journal of Atmospheric Chemistry 16 (4), 361–398.

Mopper, K., Zika, R.G., 1987. Free amino acids in marine rains: evidence for oxidation and potential role in nitrogen cycling. Nature 325, 246–249.

Neste, A.V., Duce, R.A., Lee, C., 1987. Methylamines in the marine atmosphere. Geophysical Research Letters 14 (7), 711–714.

Rice, M.A., 1999. Uptake of dissolved free amino acids by northern quahogs, mercenaria and its relative importance to organic nitrogen deposition in Narragansett Bay, Rhode Island. Journal of Shellfish Research 18 (2), 547–553.

Rosenstock, B., Simon, M., 1993. Use of dissolved combined and free amino acids by planktonic bacteria in Lake Constance. Limnology and Oceanography 38 (7), 1521–1531.

Sattler, B., Puxbaum, H., Psenner, R., 2001. Bacterial growth in supercooled cloud droplets. Geophysical Research Letters 28 (2), 239–242.

Saxena, V.K., 1983. Evidence of the biogenic nuclei involvement in Antarctic coastal clouds. Journal of Physical Chemistry 87, 4130–4134.

Saxena, P., Hildemann, L.M., 1996. Water-soluble organics in atmospheric particles—a critical review of the literature and application of thermodynamics to identify candidate compounds. Journal of Atmospheric Chemistry 24 (1), 57–109.

Scheller, E., 2001. Amino acids in dew—origin and seasonal variation. Atmospheric Environment 35 (12), 2179–2192.

Spitzy, A., 1990. Aminos acids in marine aerosol and rain. In: Ittekkot, V., Kempe, S., Michaelis, W., Spitzy, A. (Eds.), Facets of Modern Biogeochemistry. Springer, Berlin, pp. 313–317.

Suzuki, J., Ueki, T., Shimizu, S., Uesugi, K., Suzuki, S., 1985. Formation of mutagens by photolysis of amino acids in neutral aqueous solution containing nitrite or nitrate ion. Chemosphere 14 (5), 493–500.

Szyrmer, W., Zawadzki, I., 1997. Biogenic and anthropogenic sources of ice-forming nuclei: a review. Bulletin of the American Meteorological Society 78 (2), 209–228.

Tarr, M.A., Wang, W.W., Bianchi, T.S., Engelhaupt, E., 2001. Mechanisms of ammonia and amino acid photoproduction from aquatic humic and colloidal matter. Water Research 35 (15), 3688–3696.

Thorn, K.A., Pettigrew, P.J., Goldenberg, W.S., 1996. Covalent binding of aniline to humic substances 0.2. N-15 NMR studies of nucleophilic addition reactions. Environmental Science and Technology 30 (9), 2764–2775.

Tong, Y.Y., Lighthart, B., 2000. The annual bacterial particle concentration and size distribution in the ambient atmosphere in a rural area of the Willamette valley, Oregon. Aerosol Science and Technology 32 (5), 393–403.

Tsugita, A., Uchida, T., Mewes, H.W., Ataka, T., 1987. A rapid vapor-phase acid (hydrochloric acid and trifluoroacetic acid) hydrolysis of peptide and protein. Journal of Biochemistry 102 (6), 1593–1597.

Walrant, P., Santus, R., 1974. *N*-formyl-kynurenine, a tryptophan photooxidation product, as a photodynamic sensitizer. Photochemistry and Photobiology 19, 411–417.

Weathers, K.C., Lovett, G.M., Likens, G.E., Caraco, N.F.M., 2000. Cloudwater inputs of nitrogen to forest ecosystems in

southern Chile: forms, fluxes, and sources. Ecosystems 3 (6), 590–595.

Yu, Z., Zhang, Q., Kraus, T.E.C., Dahlgren, R.A., Anastasio, C., Zasoski, R.J., 2002. Contribution of amino compounds to dissolved organic nitrogen in forest soils. Biogeochemistry 61 (2), 173–198.

Zhang, Q., Anastasio, C., 2001. Chemistry of fog waters in California's Central Valley—Part 3: concentrations and speciation of organic and inorganic nitrogen. Atmospheric Environment 35 (32), 5629–5643.

Zhang, Q., Anastasio, C., Jimenez-Cruz, M., 2002a. Water-soluble organic nitrogen in atmospheric fine particles ($PM_{2.5}$) from Northern California. Journal of Geophysical Research-Atmospheres 107(D11), 10.1029/2001JD000870.

Zhang, Q., Carroll, J.J., Dixon, A.J., Anastasio, C., 2002bb. Aircraft measurements of nitrogen and phosphorus in and around the Lake Tahoe Basin: implications for possible sources of atmospheric pollutants to Lake Tahoe. Environmental Science and Technology 36, 4981–4989.