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Photodestruction of Dissolved Organic Nitrogen Species in Fog Waters

Cort Anastasio* and Keith G. McGregor
DEPARTMENT OF LAND, AIR & WATER RESOURCES, UNIVERSITY OF CALIFORNIA, ONE SHIELDS AVENUE, DAVIS, CA 95616-8627

ABSTRACT. Despite the fact that significant quantities of organic nitrogen (ON) have been measured in rain drops and aerosol particles, relatively little is known about the chemical and photochemical reactivity of ON species in tropospheric condensed phases. The preliminary work presented here reports on the photodestruction of a number of dissolved organic nitrogen (DON) species in illuminated fog waters collected in Davis, CA. Results from these experiments show that a number of DON compounds, including pyrrole, methionine, and tryptophan, are rapidly destroyed in illuminated fog waters. Calculated half-lives for these compounds in fog waters illuminated with midday, winter-solstice sunlight range from 0.6–2.3 h. The other DON compounds studied were destroyed more slowly; half-lives in winter-solstice sunlight ranged from ~10 to over 48 h. Indirect photooxidation as a result of photoformed reactive species was the dominant mechanism for destruction of the DON species examined. Hydroxyl radical was a minor sink for the DON compounds that were most rapidly photodestroyed but was a significant sink for the amino acids which had longer lifetimes. The destruction of ON in these experiments indicates that tropospheric photoreactions might play a significant role in the biogeochemical cycling of nitrogen and likely increase the bioavailability of nitrogen in atmospheric deposition.

INTRODUCTION
Historically, studies of reactive nitrogen species in the troposphere have primarily focused on inorganic forms such as NO\textsubscript{x} (NO, NO\textsubscript{2}), NO\textsubscript{2} (such as HNO\textsubscript{3}, N\textsubscript{2}O\textsubscript{5}, and peroxyacetylnitrate), and NH\textsubscript{3}/NH\textsubscript{4} (e.g., Stedman and Shetter 1983; Seinfeld and Pandis 1998). The amount known about these inorganic nitrogen species is in stark contrast to the little known about organic nitrogen (ON) species. Yet ON is also likely to play significant roles in the troposphere: i) since ON species can be major components of aerosols (Novakov et al. 1972) they might influence the radiative behavior and toxicity of aerosol particles; ii) there is preliminary evidence that ON species are oxidized or transformed heterogeneously in the troposphere (e.g., Mopper and Zika 1987; Milne and Zika 1993), and thus they might be a previously unknown source of

*Corresponding author.
nitrate and/or ammonium, and iii) because tropospheric ON can be a utilisable source of nitrogen for phytoplankton (Timperley et al. 1985; Antia et al. 1991), the deposition of ON will likely increase phytoplankton growth in surface waters (Prospero et al. 1996; Peierls and Paerl 1997), as does the deposition of inorganic nitrogen (Paerl 1985; Owens et al. 1992).

Measurements of dissolved organic nitrogen (DON) in rain and snow were first made in the 1950s (Fonselius 1954; Wilson 1959). Since then there has been increasing interest in characterizing the concentrations and identities of tropospheric ON (Timperley et al. 1985 and references therein; Mopper and Zika 1987; Gorzelska et al. 1992; Scudlark et al. 1998; Russell et al. 1998; Cornell et al. 1998). These and other studies have shown that there are significant concentrations of DON in tropospheric condensed phases: concentrations of DON in rain and snow over the U.S., for example, are typically 5–35 μmole-nitrogen L⁻¹ (based on compilations of Prospero et al. 1996 and Scudlark et al. 1998). Furthermore, the concentrations of ON are often comparable to (and sometimes greater than) the concentrations of inorganic nitrogen species (NO⁻, NO₂⁻, and NH₄⁺) in dry and wet deposition. As shown in Table 1, ON often represents 20–80% of the total nitrogen present in rain, snow, and dry deposition samples collected in the U.S. ON is similarly important in deposition samples collected in other countries, and in rainwater collected from over the oceans, typically representing 20–90% of the total nitrogen in these samples (Nichols and Cox 1978; Timperley et al. 1985; Mopper and Zika 1987; Cornell et al. 1995, 1998). To date there have apparently been no reported measurements of DON in fog or cloud drops but, based on the above results, concentrations in these hydrometeors are expected to also be significant.

Relatively little is known about the speciation of ON in tropospheric drops and particles. Compounds that have been identified, or that are known to be emitted into

<table>
<thead>
<tr>
<th>Sample Location</th>
<th>Sample Type</th>
<th>Mean Concentration (μmole-N/L)</th>
<th>[ON]/[TN]</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>ON</td>
<td>IN</td>
<td>TN</td>
</tr>
<tr>
<td>California D</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>California W</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Delaware R</td>
<td></td>
<td>9.1</td>
<td>35</td>
<td>44</td>
</tr>
<tr>
<td>Florida R</td>
<td></td>
<td>29</td>
<td>21</td>
<td>50</td>
</tr>
<tr>
<td>Florida R,D</td>
<td></td>
<td>33</td>
<td>25</td>
<td>58</td>
</tr>
<tr>
<td>Maryland W,D</td>
<td></td>
<td>21</td>
<td>54</td>
<td>75</td>
</tr>
<tr>
<td>North Carolina R</td>
<td></td>
<td>9</td>
<td>34</td>
<td>43</td>
</tr>
<tr>
<td>North Carolina R</td>
<td></td>
<td>5.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(D = \text{dry deposition}; W = \text{wet deposition (rain, snow, ice)}; R = \text{rain.}\)

\(\text{Mean concentrations of individual or composite samples. ON = organic nitrogen (note that the papers cited used several different techniques to determine ON); IN = inorganic nitrogen (generally } NO_3^- + NH_4^+ \text{, sometimes including } NO_2^-; \text{ note that typically } [NO_2^-] \ll [NO_3^-]; \text{ TN = total nitrogen. Units are } \mu\text{mole-nitrogen per liter of solution. Values from references B, C, and D are volume-weighted means. Samples from references E and F were filtered prior to analysis; other samples were not (or were not specified).}\)

\(\text{Fraction of total nitrogen that was organic.}\)

\(\text{References: A: Jassby et al. 1994; B: Scudlark et al. 1998; C: Hendry and Brezonik 1980; D: Jordan et al. 1995; E: Cornell et al. 1995; F: Peierls and Paerl 1997.}\)
the troposphere, include amino acids, alkyl amines, amides (Chang and Novakov 1975; Gundel et al. 1979; Mopper and Zika 1987; Van Neste and Duce 1987; Gorzelska and Galloway 1990; Gorzelska et al. 1992), urea (Timperley et al. 1985; Cornell et al. 1998), organic nitrates (Roberts 1990), pyridino-compounds (Novakov et al. 1972), and a number of other heterocyclic nitrogen compounds (Graede et al. 1986). There are also likely to be significant concentrations of high molecular weight (>1000 daltons) organic nitrogen (Likens et al. 1983) such as proteins (Bank and Castillo 1987) and humic/fulvic matter (Parsons and Tinsley 1975; Anastasio et al. 1997). The ON in humic and fulvic materials is present in a variety of functional groups including aniline, pyridine, and pyrrole structures (Schulten and Schnitzer 1998). Despite all of these known ON species, their relative and absolute importance in tropospheric drops and particles remains largely unknown.

Furthermore, in contrast to our knowledge of the chemistry of inorganic nitrogen in the troposphere, extremely little is known about the chemistry and photochemistry of ON species. Based on measurements in marine rains, Mopper and Zika (1987) suggested that methionine is heterogeneously oxidized to methionine sulfoxide in the troposphere. Milne and Zika (1993) subsequently reviewed the possible photochemical transformations of free and combined amino acids in tropospheric aerosol particles and concluded that photochemically formed oxidants such as hydroxyl radical might be a significant sink for these amino compounds in marine aerosols. In addition, the authors suggested that this oxidation of amino nitrogen might be a source of NH₃, amides, and possibly NO₃⁻.

Photodestruction of compounds in the troposphere can occur either through direct photolysis (where the compound absorbs light and is subsequently transformed) or indirect photooxidation (where the compound is destroyed by an intermediate reactive species). Many compounds in the troposphere do not absorb solar radiation and are therefore photodestroyed only indirectly via reaction with species such as hydroxyl radical (·OH). The sources of oxidants such as ·OH to tropospheric condensed phases include in situ photoformation within the drop or particle (e.g., Faust 1994; Arakaki and Faust 1998) and transport from the gas phase (e.g., Chameides and Davis 1982; Lelieveld and Crutzen 1991).

The goal of the preliminary research presented here is to examine the photochemical destruction of DON species in illuminated fog waters. These photochemical reactions will determine the lifetimes of ON in tropospheric condensed phases and will affect the bioavailability of ON in atmospheric deposition. Studies of the photodestruction of 2 broad groups of DON are presented here: i) aromatic ON compounds (aniline, pyridine, and pyrrole) and ii) amino acids. The former group is of interest in part because these compounds are representative of nitrogen functional groups present in humic/fulvic materials (Schulten and Schnitzer 1998). Humic and fulvic materials can be entrained in the troposphere through wind blown soil dust (e.g., Delany and Zenchelsky 1976) and appear to be present in atmospheric condensed phases in significant amounts (e.g., Anastasio et al. 1997). Aniline, pyridine, and pyrrole are also of interest because they are emitted directly from anthropogenic sources (Graedel et al. 1986) and are toxic (Sittig 1991; Keith and Walker 1995). The latter group of compounds studied here—amino acids—is one of the most extensively measured groups of ON in the atmosphere and is nearly ubiquitous in precipitation and aerosol particles (Fonselius
EXPERIMENTAL

All chemicals used were reagent grade or better. Aniline (99.5%; Aldrich), pyridine (98%; Aldrich), and pyrrole (99 +%; TCI) were used as received. Individual L-amino acids (≥98%; Sigma or Aldrich) were used to make an aqueous stock solution that was diluted as needed for experiments. This stock solution was frozen when not in use and was remade periodically. All stock solutions were prepared in Milli-Q water (≥18.2 MΩ-cm) from a Millipore Milli-Q Plus system.

Fog waters were collected at the CIMIS-Turf plot of the University of California at Davis, approximately 2 miles west-southwest of the center of the city of Davis (38° 33' N, 121° 38' W), using a compact Caltech Active Strand Cloudwater Collector (CASCCL2; Demoz et al. 1996). Prior to the 2 fog events studied here the collection surfaces (Teflon strands and sample drain) were removed from the collector, thoroughly washed in the laboratory (Alconox wash, Milli-Q rinse, ethanol wash, copious rinses with Milli-Q, air dried), and then replaced in the collector. Other parts of the collector were rinsed copiously with Milli-Q in the field. Prior to collecting the 1997 sample the collection surfaces were rinsed with Milli-Q water, and this rinse water was collected. Once the fog event started the sampler was run for 15–30 min to rinse the collection surfaces with ~2–5 ml of (discarded) fog water. The sample was then collected into a precleaned high density polyethylene bottle that was mounted directly onto the sample drain. The 1998 sample was collected in the same way except that a rinse water was not collected so that none of the initial fog event had to be discarded. The fog waters discussed in this paper were collected from 3:55–7:51 a.m. on January 30, 1997 (DA97-A01) and 1:15–4:30 a.m. on January 23, 1998 (DA98-06F). After collection samples (and rinse waters) were filtered through 0.45 μm un-laminated Teflon membranes (MSI) using a precleaned glass filtration apparatus. Samples were kept frozen (−22°C) until use.

The aerosol sample was collected onto a Teflon Zefluor filter (Pall Gelman) using an IMPROVE sampler (particle diameter ≤2.5 μm; Malm et al. 1994) run for 48 h (6:00 p.m. on February 27, 1998 to 6:00 p.m. on March 1, 1998) at ~21 L min⁻¹. After collection the filter was extracted by sonicating (Fisher FS30) for 60 min in a cleaned, capped glass tube containing 8.0 mL of Milli-Q water and then filtered (0.22 μm Teflon; Cameo 13F syringe filter).

Aniline, pyridine, and pyrrole were analyzed using an isocratic HPLC system consisting of a C-18, 5 μm, 3.0 × 250 mm analytical column (Keystone BetaBasic-18) with accompanying guard column; Shimadzu LC-10AT pump; and a Shimadzu SPD-10AV UV-visible absorption detector set to 281, 256, and 230 nm, respectively. A mixture of 60% acetonitrile (Fisher Optimax) and 40% Milli-Q water, adjusted to pH ~8 with ~1 mM borate, was used for eluent. Amino acids were analyzed using the pre-column derivatization method of Mopper and Lindroth (1982), as modified by Gorzelska et al. (1992), using the same HPLC columns described above, 2 Shimadzu pumps (LC-10AT and LC-10ATVP), and a Shimadzu RF-551 fluorescence detector (with detection and emission wavelengths of 330 and 420 nm, respectively). UV-visible absorption spectra were taken with a Shimadzu UV-2501 PC (2 nm slit width; slow scan speed) using Milli-Q water as reference. Measurements of pH were made with a MI-414 electrode (Microelectrodes, Inc.) and Orion 420A pH meter.
using at least 4 buffers (Fisher) between pH 4.00 and 10.00.

Immediately prior to use samples were spiked with low concentrations of either 5.0 \( \mu \)M of aniline, pyridine, or pyrrole or a mixture of 12 amino acids (see Table 2 in the results section for identities) containing individual compounds at concentrations of 0.50 or 1.0 \( \mu \)M and a total concentration of 7.5 \( \mu \)M. In the original (unspiked) samples concentrations of aniline, pyridine, and pyrrole were all \( \leq 0.2 \) \( \mu \)M, while concentrations of individual amino acids ranged from below detection limits; 50 nM to a few micromolar. Because rate constants for the loss of organic N species were determined from plots of \( \ln([i]/[i]_0) \) versus illumination time (see below), these rate constants are independent of the initial concentration of ON species. Furthermore, because Central Valley fog waters typically contain 1–2 millimole-C L\(^{-1}\) of organic carbon (Anastasio 1994; Collett et al. 1999), addition of the ON compounds at micromolar levels should not affect the fog water chemistry. Addition of DON species caused <2% dilution in the sample.

DON-spiked samples were illuminated in stirred 2 cm quartz cells (Spectrocell) at 20°C using either 313 nm light from a monochromatic illumination system (Arakaki et al. 1995) or simulated sunlight obtained by modifying the output from a 1000 W Xe lamp (Osram Sylvania XBO 1000 W/HS OFR) using an IR filter and a series of optical filters (Faust 1993). Prior to illumination, and periodically during illumination, aliquots were removed from the sample cell and analyzed for the DON species of interest. An identical spiked sample kept in the dark was monitored simultaneously as a check for dark reactions.

First-order rate constants for the photodestruction of compound \( i \) (\( j_{i,\text{SOLSIM}} \) for compounds studied using simulated sunlight; \( j_{i,313} \) for those studied with 313 nm light) were determined from the slope of plots of \( \ln([i]/[i]_0) \) versus illumination time, where \([i]\) and \([i]_0\) are the concentrations of \( i \) at any time and time 0, respectively. These rate constants were corrected for any thermal loss of compound by subtracting the corresponding rate constant observed in the dark. For samples studied with 313 nm light the quantum efficiency proportionality constant for the destruction of \( i \), \( Q_{i,313} \) (L einstein\(^{-1}\)), was calculated as

\[
Q_{i,313} = \frac{j_{i,313}}{I_{313}(1 - 10^{-\alpha_{313}})},
\]

where \( I_{313} \) is the actinic flux of the lamp (einstein L\(^{-1}\) s\(^{-1}\)) determined from 2-nitrobenzaldehyde actinometry (Anastasio et al. 1994), \( \alpha_{313} \) is the absorbance per cm of the fog water at 313 nm (cm\(^{-1}\)), \( I \) is the path length of the quartz cell used during the experiment (cm). (Note that \( Q_{i,313} \) is related to \( \Phi_{i,313} \), the apparent quantum efficiency for destruction of \( i \), by \( \Phi_{i,313} = Q_{i,313} [i] \).) Based on these results, the rate constant of destruction of \( i \) in winter solstice sunlight was estimated from

\[
j_{i,\text{SUN}} = 2300 Q_{i,313} \sum \left( I'_\lambda \alpha_\lambda \right),
\]

where \( I'_\lambda \) is solar actinic flux (einstein cm\(^{-2}\) s\(^{-1}\)) at wavelength \( \lambda \) for solar noon in Davis on the winter solstice (solar zenith angle = 62°; values extrapolated from data of Peterson 1976) and \( \alpha_\lambda \) (cm\(^{-1}\)) is the fog water absorbance per cm at \( \lambda \). Note that this calculation assumes that \( Q_i \) is constant for all wavelengths and therefore might lead to an overestimation of \( j_{i,\text{SUN}} \).

For samples studied with simulated sunlight the expected rate constant for disappearance of \( i \) in midday, winter solstice sunlight at Davis (\( j_{i,\text{SUN}} \)) was calculated from

\[
j_{i,\text{SUN}} = j_{i,\text{SOLSIM}} \left( \frac{j_{A,\text{SUN}}}{j_{A,\text{SOLSIM}}} \right)
\]
where $j_{A,\text{SUN}}$ (0.0070 s$^{-1}$) is the rate constant for disappearance of 2-nitrobenzaldehyde actinometer measured in Davis at solar noon on December 18th (i.e., near the winter solstice) and $j_{A,\text{SOLSIM}}$ is the rate constant for disappearance of actinometer measured in the solar simulator on the same day as the fog water illumination. Rate constants were not adjusted to account for any attenuation of light by the sample during experiments; these adjustments would increase rates of DON destruction by approximately 10–40% (Anastasio 1994). Half-lives were calculated as $(\ln 2/j_{i,313})$ or $(\ln 2/j_{i,\text{SUN}})$ for samples illuminated with 313 nm light or simulated sunlight, respectively.

Steady-state concentrations of hydroxyl radical were determined using previously described methods (Zhou and Mopper 1990; Arakaki and Faust 1998). In these methods several different concentrations of probe (benzene or benzoic acid) are added to separate aliquots of the same sample and the rate of formation of product (phenol or m-hydroxybenzoic acid, respectively) is measured in each aliquot. The steady-state concentration of $^\cdot\text{OH}$ in the unaltered sample is then determined from a plot of the inverse of product formation rate versus the inverse of added probe concentration.

RESULTS
As shown in Figure 1, the fog waters studied absorbed significantly between 290 nm (approximately the shortest wavelength of solar radiation in the troposphere) and 500 nm. While the compounds responsible for this absorbance are not known, it is clear

![Figure 1. UV-visible absorption spectra of 2 fog waters (DA97-A01 and DA98-06F), an aqueous extract of aerosol particles (ADA98-09), and a rinse water control (DA97R02F; note that the spectrum is nearly indistinguishable from the baseline). Sample ADA98-09 was prepared by extracting 0.30 mg of particulate matter (≤2.5 μm diameter) into 8.0 mL of Milli-Q water (see text). All samples were filtered (0.2 μm Teflon). Note that the spectra of DA97R02F and ADA98-09 are noisier than the fog water spectra because the former were acquired using a low-volume microcuvette.](image-url)
from the spectra that there is significant potential for photochemical reactions in the samples. The aqueous extract of an aerosol sample collected a few weeks after fog water collection exhibited similar absorbance (Figure 1). The figure also shows that there was no significant absorption ($\alpha < 0.003$ cm$^{-1}$) in the rinse water (DA97R02F) collected prior to the 1997 sample; all other rinse waters collected in 1997 and 1998 also exhibited negligible absorbance (e.g., $\alpha_{313} < 0.002$; data not shown). While concentrations of specific compounds (e.g., metals, organic carbon) were not measured in the rinse waters, the rinse water absorption spectra, especially when compared with the absorbance of the fog waters (Figure 1), suggest that the collection and filtration processes did not introduce significant levels of contaminants into the samples.

**Aniline, Pyridine, and Pyrrole**

Initial experiments were run with sample DA97-A01 spiked separately with either aniline, pyridine, or pyrrole and illuminated with 313 nm light. While all 3 compounds were destroyed during illumination, the rates of destruction were very different (Figure 2). For aniline and pyrrole, the 2 compounds that were destroyed most rapidly, there is evidence of a "biphasic" behavior where rates of destruction during the first 5–10 min of illumination were approximately 2–3 times faster than the rates for the rest of the experiment. This biphasic loss may indicate that there are 2 pools of chromophores in the sample: a longer-lived set that produces a steady state of oxidants throughout the entire photolysis time and a shorter-lived group that is initially very reactive but that is quickly destroyed. The fact that photobleaching occurred in DA97-A01 during 313 nm illumination (the absorbance per cm at 313 nm, $\alpha_{313}$, had an apparent half-life of 5 h) indicates that chromophores were destroyed during illumination. Although insufficient data were obtained in this experiment to determine if the loss of absorbance was
biphasic photobleaching has been observed previously in a cloud water sample illuminated with 313 nm light (Anastasio 1994).

The $pK_a$ values for protonated forms of aniline, pyridine, and pyrrole are 4.6, 5.3, and $\ll 5.3$, respectively (Weast 1981; Kemp and Vellaccio 1980). Thus for each compound the neutral (unprotonated) form will be the dominant species in sample DA97-A01 ($pH = 6.6$). Because neither the neutral or protonated forms of pyridine and pyrrole absorb significantly at 313 nm (molar absorptivities at 313 nm, $\varepsilon_{313}$, are $<1$ and 4 M$^{-1}$ cm$^{-1}$, respectively) their destruction in this sample occurs predominantly through indirect photooxidation. The neutral form of aniline, on the other hand, does absorb significantly at 313 nm ($\varepsilon_{313} = 31$ M$^{-1}$ cm$^{-1}$) and initial data indicate that the quantum efficiency for its destruction at this wavelength is 0.055 (C. Anastasio and K. G. McGregor, manuscript in preparation). Based on this quantum efficiency, approximately 80% of the aniline destruction observed during 313 nm illumination (Figure 2) is due to direct photolysis while the remainder is due to indirect photooxidation.

Measured values for the quantum proportionality constant for indirect photooxidation in 313 nm light, $Q_{i,313}$, were 5.7, 4.5, and 110 L einstein$^{-1}$ for aniline, pyridine, and pyrrole, respectively, in sample DA97-A01. (Note that this value for aniline does not include the contribution due to direct photolysis.) Estimated values of $j_{i,\text{SUN}}$ in midday winter solstice sunlight (Equation 2) for pyridine and pyrrole in DA97-A01 are 0.050 and 1.2 h$^{-1}$, respectively, which correspond to half-lives of 14 and 0.56 h. Note that destruction of these compounds is due solely to indirect photooxidation. For aniline, which undergoes both direct photolysis and indirect photooxidation, the estimated value of $j_{i,\text{SUN}}$ is 0.067 h$^{-1}$, which corresponds to a half-life of 10 h. (As noted in the experimental section, values of $j_{i,\text{SUN}}$ determined using Equation (2) are likely somewhat overestimated because they are calculated assuming that values of $Q_i$ are constant over all wavelengths.) Approximately 9% of the destruction of aniline in winter solstice sunlight is calculated to be due to direct photolysis. Direct photolysis is much less important as a sink for aniline during sunlight illumination (compared with 313 nm illumination) primarily because the molar absorptivity of aniline drops quickly at wavelengths longer than 313 nm.

Because indirect photooxidation was responsible for nearly all of the loss of these 3 compounds (the small direct photolysis of aniline being the only exception), we have started to measure steady-state concentrations of various oxidants in the illuminated sample so that the mechanisms for oxidation can be determined. The first oxidant we have determined is hydroxyl radical ($OH$); the measured concentration of $OH$ in DA97-A01 with 313 nm light was $4.9 \times 10^{-16}$ M. Based on this measured concentration and on published rate constants (Ross et al. 1994), it appears that $OH$ was only a minor sink, responsible for approximately 9% (aniline), 8% (pyridine), and 2% (pyrrole) of the destruction of these 3 compounds during 313 nm illumination.

**Amino Acids**

The photochemistry of 12 amino acids was studied in 2 fog water samples illuminated with simulated sunlight. As shown in Figure 3 and Table 2, the amino acids exhibited a wide range of reactivities in the illuminated fog waters. The most rapidly destroyed compounds, methionine and tryptophan, had half-lives in midday winter solstice sunlight of approximately 1–2 h (Table 2). While histidine and tyrosine were also significantly destroyed during illumination.
TABLE 2. Photochemical destruction of amino acids in 2 fog waters illuminated with simulated sunlight.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Sample DA97-A01 (^a)</th>
<th>Sample DA98-06F (^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Half-life (hr) (^c)</td>
<td>( t_{0\text{OH}} ) (^d)</td>
</tr>
<tr>
<td>Histidine</td>
<td>13</td>
<td>0.24</td>
</tr>
<tr>
<td>Methionine</td>
<td>0.96</td>
<td>0.03</td>
</tr>
<tr>
<td>Tryptophan</td>
<td>1.3</td>
<td>0.05</td>
</tr>
<tr>
<td>Tyrosine</td>
<td>19</td>
<td>0.84</td>
</tr>
<tr>
<td>Others</td>
<td>&gt;48</td>
<td>—</td>
</tr>
</tbody>
</table>

\(^a\) DA97-A01: pH = 6.6;  \( \alpha_{313} = 0.078 \)
\(^b\) DA98-06F: pH = 6.3;  \( \alpha_{313} = 0.128 \)
\(^c\) Half-life at solar noon near the winter solstice in Davis, CA (solar zenith angle = 62°). Relative standard errors are approximately 10% of stated values.
\(^d\) Fraction of destruction of amino acid that was due to reaction with hydroxyl radical. Measured concentrations of \( \cdot \text{OH} \) in each sample (adjusted to conditions of midday, winter solstice sunlight in Davis) were \( 6.7 \times 10^{-16} \) and \( 5.7 \times 10^{-16} \) M for DA97-A01 and DA98-06F, respectively. Relative standard errors are approximately 15% of stated values.

At the pH values of the 2 fog waters studied the amino acids used here will exist predominantly as zwitterions (i.e., with protonated amine groups and deprotonated carboxylic acid groups; Weast 1981). In this form none of the amino acids, except for tryptophan, had any appreciable absorbance (\( \varepsilon < 5 \text{ M}^{-1} \text{ cm}^{-1} \)) at wavelengths \( \geq 300 \text{ nm} \). Thus the destruction of these species was due solely to indirect photooxidation. While tryptophan did absorb light at wavelengths \( \geq 300 \text{ nm} \) (e.g., \( \varepsilon_{300} = 480 \text{ M}^{-1} \text{ cm}^{-1} \) in unbuffered Milli-Q), based on simulated sunlight illumination of a 5.0 \( \mu \text{M} \) solution of tryptophan in Milli-Q (half-lives in midday winter solstice sunlight of 13–28 h; Table 2) the remaining 8 amino acids tested exhibited no appreciable destruction during illumination (half-lives > 48 h; Table 2). Since glycine, the simplest amino acid, is not significantly destroyed during illumination (Figure 3 and Table 2), it appears that destruction of the reactive amino acids depends upon the chemistry of their side chains.

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water (pH 6.9), the rate constant for direct photolytic loss of tryptophan in winter solstice sunlight is $< 1.4 \times 10^{-3}$ h$^{-1}$ (data not shown). Thus $< 1\%$ of the calculated loss of this compound in winter solstice sunlight (Table 2) is expected to be due to direct photolysis.

As discussed previously, initial work at identifying the species responsible for the loss of DON in illuminated fog waters has focused on hydroxyl radical. Concentrations of •OH were $6.4 \times 10^{-16}$ M and $5.7 \times 10^{-16}$ M in DA97-A01 and DA98-06F, respectively, under midday, winter solstice sunlight illumination conditions. Based on these concentrations, and on known rate constants (Ross et al. 1994), •OH can account for all, or nearly all, of the destruction of tyrosine and a significant amount (24–30\%) of the loss of histidine (Table 2). However, for the most reactive compounds (tryptophan and methionine) •OH is an insignificant sink, accounting for $< 1\%$ of the destruction of these compounds (Table 2).

**DISCUSSION AND CONCLUSIONS**

These preliminary results clearly indicate that a number of DON compounds in fog waters are rapidly destroyed during sunlight illumination. Based on the similarity between the absorbance spectra of fog waters and the aqueous extract of aerosol particles (Figure 1) it is likely that DON is also photodegraded in illuminated aqueous aerosol particles. Such reactions probably also occur in other tropospheric hydrometeors such as cloud and rain waters. Rates of destruction of ON in tropospheric drops and particles undoubtedly vary with chromophore composition and, therefore, probably vary significantly as a function of hydrometeor type and source, transport history, and time of year. As an example, half-lives for histidine, tryptophan, and tyrosine were approximately 40–80\% longer in sample DA98-06F compared with DA97-A01, although the half-life for methionine in the 2 samples was nearly the same (Table 2). These differences are likely due to differences in sample composition (as seen in the absorption spectra of Figure 1) which in turn yield different steady-state concentrations of oxidants and other reactive intermediates. Hydrometeor pH could also have a significant effect upon the rate of ON destruction, especially for compounds with pK$_a$ values which are in the range of environmental hydrometeor pH values (e.g., typically pH 3–7 for cloud and fog drops). Destruction rates will likely decrease with decreasing pH for these compounds (e.g., aniline and pyridine) since the protonated form generally reacts more slowly with oxidants than does the neutral (unprotonated) form (Ross et al. 1994).

It should be noted that the rates of ON destruction reported here are only for in situ aqueous phase processes in the drops and that rates of ON destruction in the environment will likely be faster because of the partitioning of gas-phase oxidants to the drops. The rapid destruction of several of the compounds studied here (e.g., pyrrole, methionine, and tryptophan) suggests that these species might be found less commonly, or found at lower concentrations, in atmospheric hydrometeors. This will depend in large part, however, upon the (currently unknown) sources and associated emission rates of ON compounds to the troposphere and the residence time (and history) of the hydrometeors.

Rates of photochemical reactions in fog drops will depend upon irradiance conditions and, therefore, upon factors which affect the solar zenith angle (e.g., time of day, day of year). While fogs in the Central Valley sometimes last for an entire day (or days), they often evaporate before noon and thus will not experience midday sun-
light. The “reference” irradiance condition used here (midday near the winter solstice in Davis, CA; see the Experimental section) corresponds to a solar zenith angle of 62°. In comparison, the solar zenith angles in Davis on February 1 (approximately the collection date for samples described in this paper) at 8 a.m., 10 a.m., and noon are 78°, 60°, and 53°, respectively (Peterson 1976). At these times the rates of sunlight absorption by DA97-A01 are approximately 60% lower, 7% higher, and 20% higher, respectively, than the rate under the “reference” condition (calculated using irradiance values from Peterson (1976) and absorption data from Figure 1). The relative rates of destruction of DON compounds (or other drop constituents) should be similarly altered under these various irradiance conditions. The rate of sunlight absorption (and reaction rate) in a drop will also be affected by factors such as fog thickness and the position of the drop relative to the top of the fog. Cloud modeling by Jacob et al. (1989) suggests that, relative to clear-sky conditions, the irradiance near the top of a fog can be greater by ~15% while the irradiance near the base of the fog can be lower by ~25%.

Nearly all of the photodestruction of the DON compounds studied here was due to indirect photooxidation. As discussed above, for the most reactive DON species hydroxyl radical was a relatively insignificant sink. Previous work has shown that, in addition to \( \cdot \)OH (Faust and Allen 1993; Arakaki and Faust 1998), illumination of cloud and fog drops forms a variety of oxidants including singlet molecular oxygen and peroxyl radicals (Faust and Allen 1992), hydrogen peroxide (Anastasio et al. 1994), and excited triplet states (Anastasio et al. 1997). We are currently working to identify the photooxidants that were most important for DON loss in the fog waters studied here. We are also working to identify the products—including inorganic nitrogen—formed during the destruction of DON. Because ON is an important component of the total nitrogen in tropospheric drops and particles (Table 1), results from this and future studies could significantly alter our understanding of nitrogen in the troposphere and the biogeochemical cycling of this important element.

Atmospheric deposition is a significant, and often dominant, source of exogenous nitrogen to coastal waters, oligotrophic lakes, and remote oceanic regions (e.g. Paerl 1997; Jassby et al. 1994; Prospero et al. 1996) and therefore plays an important role in nitrogen loading, phytoplankton growth, and eutrophication in these waters. Although organic compounds are a major component of the nitrogen in atmospheric deposition (Table 1), the importance of ON as a source of nutrient nitrogen is unclear. Available data indicate that smaller ON compounds (e.g., urea and amino acids) are more readily utilisable as sources of N for phytoplankton and bacteria compared to higher molecular weight ON compounds (Antia et al. 1991). Peierls and Pearl (1997) have shown that while a significant fraction (~20–30%) of DON in rain is bioavailable to phytoplankton over short time scales (<48 h), much of it is not available. The destruction of aniline, pyridine, and pyrrole in our experiments suggests that humic/fulvic material (and similar ON) that is entrained in the troposphere can be photochemically degraded during transport. If these reactions cause the humic material to be broken into smaller pieces, or lead to mineralization of the ON, the bioavailability of this nitrogen could be greater than the original humic/fulvic ON, which is believed to be largely biologically unavailable (Antia et al. 1991).

Similarly, the photodestruction of individual amino acid moieties in proteins or
peptides may lead to cleavage of the parent molecules into smaller peptides and, eventually, free amino acids. Since amino acids tend to be more utilizable sources of N for phytoplankton than proteins or peptides (Antia et al. 1991), these peptide/protein photoreactions may also increase the N bioavailability of atmospheric ON. Recent reports have shown that aqueous photoreactions of aquatic fulvic materials and other high molecular weight organic matter in surface waters lead to the production of ammonia and an increase in the bioavailability of high molecular weight DON (Bushaw et al. 1996; Wang et al. 1997). Results from our experiments suggest that similar photochemical reactions in tropospheric drops and particles may also increase the bioavailability of N in atmospheric deposition and thereby increase the biological impacts of this deposition.

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