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Effect of ultraviolet light on dissolved nitrogen transformations in coastal lagoon water

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Abstract

The effect of ultraviolet radiation on the production of inorganic nitrogen, urea, and amino acids from aquatic dissolved organic matter (DOM) was investigated for waters from Hog Island Bay, a coastal lagoon in Virginia. Waters representing distinct sources of DOM to the lagoon were subjected to UV light mimicking the natural solar spectrum. Dissolved organic nitrogen concentrations did not change measurably during the 36-h incubation, while calculated dissolved organic carbon concentrations dropped by up to 17%, resulting in decreases in estimated C/N for some samples. Nitrate and urea levels were not consistently altered in the light, while ammonium photoproduction rates of up to 0.032 μmol N L^{-1} h^{-1} were observed. Changes in dissolved free amino acids were measured in a groundwater sample obtained from a shoreline seep, and this sample exhibited photoproduction of glycine and alanine at rates of 0.8–1.1 nmol N L^{-1} h^{-1}. The rates of ammonium and amino acid formation, when scaled up to estimate photoproduction in the lagoon system, appeared to be minor relative to other sources to and fluxes within the system.

The concentration and type of dissolved organic matter (DOM) and dissolved inorganic nutrients are important factors affecting microbial metabolism in aquatic ecosystems (e.g., Vallino et al. 1996). Natural photochemical processes can cause sunlight-induced cleavage of the chemical bonds in DOM, which frequently results in reduced DOM concentrations, altered DOM character, and the release of smaller inorganic or organic molecules (Miller 1998). Studies of natural DOM photodegradation have demonstrated consistently and convincingly the production of small, quantifiable carbon byproducts such as carboxylic acids and aldehydes (Kieber et al. 1990; Bertilsson et al. 1999), CO_2 (Miller and Moran 1997), and CO (Mopper et al. 1991; Valentine and Zepp 1993), but studies of photochemical nitrogen transformations have shown varied results.

Direct measurements of dissolved organic nitrogen (DON) from natural waters in photodegradation studies are scarce, and those that do exist have not shown consistent measurable changes in DON concentration following light treatment (Bushaw et al. 1996; Jørgensen et al. 1998). However, production of dissolved inorganic nitrogen (DIN) byproducts from photodegradation of concentrated solutions of amides and amines including amino acids was observed as early as 65 years ago (Rao and Dhar 1934). More recently, photoproducts such as nitrite (NO_2^-) (Kieber et al. 1999) and ammonium (NH_4^+) (Bushaw et al. 1996; Gao and Zepp 1998; Wang et al. 2000) have been documented in studies of highly humic natural DOM and isolated humic materials. It is unclear whether NH_4^+ photoproduction occurs ubiquitously or at high enough rates to be of ecological significance across broad regions. Bushaw et al. (1996) suggested that increased bacterial growth on humic DOM photoproducts from the southeastern U.S. was due to a release from N limitation resulting from the photoproduction of NH_4^+. Using rates calculated from humic-rich freshwaters, they estimated that photochemical conversion of DON to NH_4^+ on the U.S. southeastern continental shelf would increase estimates of available terrestrially derived N by 20% (Bushaw et al. 1996). Other studies including water from lakes, groundwater, and agriculture and forest runoff found no evidence of consistent NH_4^+ photoproduction (Jørgensen et al. 1998; Wiegner and Seitzinger 2001; Koopmans and Bronk 2002)

Photoinduced alterations of DOM are likely to affect secondary production by changing the quantity and bacterial bioavailability of the DOM (e.g., Moran and Zepp 1997). In addition, the photoproduction of DIN or other small forms of usable N such as dissolved free amino acids (DFAAs) may have ramifications for both primary and secondary productivity. Variations in DIN concentration influence the composition of plant/algae communities and the magnitude of primary production (Howarth 1988; Valiela et al. 1992). Certain types of DON can be taken up directly by phytoplankton (Seitzinger and Sanders 1999) and macroalgae (Tyler et al. 2001) as well as by bacteria (Coffin 1989). In particular, DFAAs can supply in excess of 100% of the N requirements of bacteria in coastal and marine waters (Keil and Kirchman 1991; Jørgensen et al. 1993) and have been shown to contribute to phytoplankton nutrition as well (Jørgensen 1987).

The production of bioavailable N is likely to be of particular ecological significance in nitrogen-limited coastal zones (e.g., Boynton et al. 1996). Research on photoreactions involving coastal/estuarine N compounds is very limited, but recent studies of humic materials isolated from estuarine waters in the southeastern U.S. demonstrated photoproduction of DFAAs (Tarr et al. 2001), NH_4^+, and dissolved primary amines (Bushaw-Newton and Moran 1999). A study of unconcentrated natural waters from the coastal Baltic Sea

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yielded results varying from production to consumption of DFAAs upon subjection to sunlight (Jørgensen et al. 1999).

Here we report direct measurements of UV light-induced N transformations using unconcentrated natural saline water samples from Hog Island Bay, a coastal lagoon in Virginia. This approach represents a departure from previous DON photodegradation studies that used either highly humic freshwaters (e.g., Bushaw et al. 1996) or concentrated humic material (e.g., Bushaw-Newton and Moran 1999) to generate estimates of coastal NH_4^+ photoproduction. The central questions posed in our study are (1) Does photodegradation of DON supply DIN or DFAAs to the lagoon at ecologically relevant rates? and (2) Are DON photodegradation rates increased by enhanced levels of UV-B radiation such as those that might occur following extensive stratospheric ozone depletion (e.g., Kerr and McElroy 1993)?

Methods

Site description—Hog Island Bay is part of the Virginia Coast Reserve long-term ecological research (LTER) site. The Virginia Coast Reserve is comprised of a small section of the eastern shore of the Delmarva Peninsula near its southern end plus 13 barrier islands and numerous shallow shoals, deep channels, mudflats, marsh islands, fringing *Spartina alterniflora* marshes, and tidal creeks. With the exception of the Great Machipongo Channel, which empties into the Atlantic Ocean, average water depth within the lagoon is <1–2 m at mean low water. The mean tidal range within the lagoon varies from 1.2 to 1.5 m, and salinity varies from 30 to 33 psu. Mean annual water column light extinction coefficients for several sites in Hog Island Bay range from 1.7 to 2.2 m^{-1} for photosynthetically available radiation (PAR) as measured by a Li-Cor light meter with spherical 4π sensor (McGlathery et al. 2001). Mean water column UV extinction coefficients (calculated using the total irradiance from wavelengths <400 nm) range from 2.4 to 3.5 m^{-1} for sites in Hog Island Bay based on May 2002 measurements using an Ocean Optics USB 2000 spectral radiometer.

Total dissolved nitrogen (TDN) concentrations in the lagoon typically range from 15 to 25 μmol L^{-1} and are dominated by organic nitrogen (Tyler et al. 2001). There is a gradient of organic matter and nutrient inputs across Hog Island Bay from the mainland to the islands, with the highest concentrations of dissolved N and sediment organic matter found closest to the mainland (McGlathery et al. 2001). There are no riverine inputs to the lagoon, and the primary sources of allochthonous N to Hog Island Bay are seepage of nutrient-enriched groundwater (Reay et al. 1992) and atmospheric deposition (Paerl et al. 1990). Leaching of organic N from *S. alterniflora* biomass may be a source of N to the lagoon at times. Within Hog Island Bay, nitrogen is mobilized by sediment/water exchange and transformed by algal and bacterial uptake, remineralization, nitrification, and denitrification (McGlathery et al. 2001; Tyler et al. 2001; Anderson et al. in press).

Sample collection, incubation, and analysis—Water samples for incubation were collected from a variety of source areas in the Hog Island Bay system in April 2000. Samples were obtained from the Machipongo Inlet at the mouth of the lagoon (lagoon sample), from a mainland groundwater seep just before it entered the lagoon (groundwater sample), and from a small creek draining a *S. alterniflora* marsh on Hog Island (creek sample). All water samples were filtered immediately in the field through a prerinsed 0.2-μm Gelman minicapsule cartridge into acid-washed, deionized water rinsed high density polyethylene (HDPE) carboys and were sheltered from sunlight. Water temperatures at the time of sampling varied from 12°C to 18°C. The leachate sample (representing lagoon water contacting the adjacent marshes and leaching out DOM from the *S. alterniflora* over time) was prepared by stirring 250 g wet weight of standing dead *S. alterniflora* stalks in 5 liters of filter-sterilized lagoon water at 5°C in the dark. Before the incubation, the *S. alterniflora* was cleaned of epiphytes, invertebrates, and sediment. The water was bubbled periodically with medical air passed through a Hepa-vent filter to maintain oxic conditions. After 24 h, the leachate was filtered through a prerinsed 0.2-μm Gelman minicapsule cartridge.

Water samples were stored at 4°C in the dark for not more than 4 d between collection and beginning incubation. Groundwater and creek samples were diluted 1 : 2 with lagoon water in order to more closely simulate the salinity and water chemistry of Hog Island Bay, resulting in salinity in the range of 22–33 for all samples. This reduced variability in inorganic water chemistry between samples and more accurately mimicked the natural system, in which we expect the DOM inputs to be diluted by lagoon water by the time they receive considerable exposure to sunlight. In addition to these four water samples, a deionized water (DIW) sample (Barnstead Nanopure, 18.3 Mohm) was incubated under identical conditions as a control to monitor any contamination that might occur. All samples were filter-sterilized with a prerinsed 0.2-μm Gelman Supor filter immediately prior to incubation. Samples were incubated in horizontally positioned 600-ml quartz tubes capped with silicone stoppers in a climate-controlled chamber at 6–8°C for 36 h. Temperature does not typically have a significant effect on photochemical reaction rates (Zepp et al. 1998), and the samples were kept cool to discourage bacterial growth.

Triplicate tubes containing 500 ml of each sample were subjected to each of three light treatments. Irradiance spectra (Fig. 1) were measured with an Ocean Optics USB 2000 radiometer, calibrated to a National Institute of Standards and Technology (NIST)-traceable standard light source. The two UV light treatments combined white incandescent and fluorescent bulbs with two different types of UV bulbs for a total irradiance of approximately 65 W m^{-2}. The A treatment used UV-A 340 fluorescent bulbs (Q-Panel) resulting in an irradiance spectrum including 1.8 W m^{-2} UV-B (280–320 nm), 24 W m^{-2} UV-A (320–400 nm), and 31 W m^{-2} PAR (400–700 nm). The B treatment used UV-B 314 bulbs (Q-Panel), resulting in an irradiance spectrum including 10 W m^{-2} UV-B, 11 W m^{-2} UV-A, and 29 W m^{-2} PAR. The third treatment was a dark control in which the quartz tubes were covered in heavy-duty aluminum foil during incubation. The A treatment gave a comparable amount of UV-A and UV-B radiation relative to midday sunlight on a clear

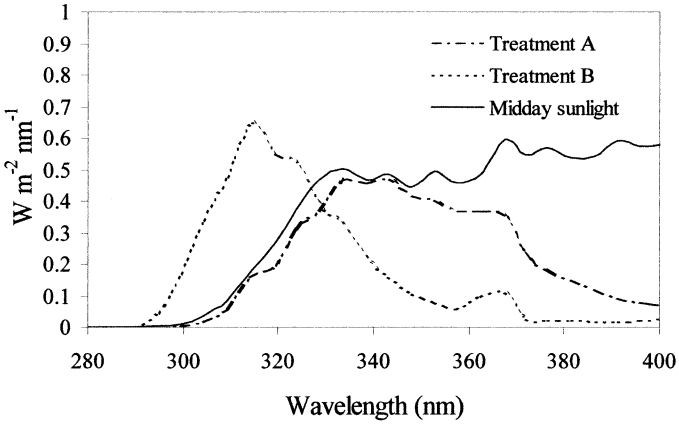

Fig. 1. Mean irradiance levels for the two UV light treatments and for midday sunlight on a clear mid-June day in Charlottesville, Virginia (38°N).

summer day at 38°N latitude (Fig. 1). UV-A 340 bulbs have been used by other researchers to simulate the UV region of sunlight for experiments in immunology (Beasley et al. 1996) and natural DOM photochemistry (Bertilsson and Tranvik 2000). The B treatment simulated harsher, more high-energy UV-B light levels that might occur following significant stratospheric ozone depletion.

For the creek and groundwater samples, additional tubes were subjected to natural sunlight in Charlottesville, Virginia (38°N latitude) concurrent with the 36-h photodegradation experiment. Changes in absorbance (bleaching) were measured for these samples in order to compare bleaching by natural sunlight to bleaching in our incubation experiment using an artificial UV light source. Weather conditions were mostly cloudy for the 100-h natural incubation, and the overall mean irradiance during the daylight (57 h) was approximately 360 W m^{-2} based on continuous measurements made at the Hog Island LTER weather station. This included 70 W m^{-2} PAR (Hog Island weather station) and approximately 13 W m^{-2} UV-A radiation and 0.7 W m^{-2} UV-B radiation (relative proportions of UV radiation calculated for 40°N latitude) (Zepp 1982).

Subsamples were taken from each tube for chemical analyses immediately prior to beginning the incubation and after 36 h of incubation. Samples for absorbance spectra were measured immediately with an HP UV-Vis 8453 scanning spectrophotometer. Absorbance was corrected for turbidity/blank drift by subtracting A_{700} from the entire wavelength range for each sample and converted to extinction coefficients (absorptivity) using $a_\lambda = 2.303 \times A_\lambda \times l^{-1}$, where a_λ = absorptivity (units of m^{-1}) at wavelength λ, A_λ = absorbance (unitless) at wavelength λ, and l = cell pathlength (0.01 m). Spectral slope coefficients were calculated using $a_\lambda = a_{\lambda_0} e^{-S(\lambda-\lambda_0)}$, where λ_0 = a reference wavelength and S is the spectral slope coefficient, a parameter characterizing the rapidity with which the absorption decreases with increasing wavelength (Blough and Green 1995). Samples for nitrate + nitrite (NO_3^- + NO_2^-), NH_4^+, TDN, urea, and amino acid analyses were stored frozen at −20°C in separate sterile whirlpak bags until analysis. Samples for dissolved organic carbon (DOC) analysis were acidified to pH 2 with concentrated H_3PO_4 and stored at 4°C in precombusted, prerinsed 20-ml glass Environmental Protection Agency (EPA) vials with Teflon septum liners until analysis. Bacterial samples were preserved in 20-ml glass scintillation vials with 2% v/v 0.2-μm filtered formalin and stored at 4°C until analysis.

Ammonium was measured using the phenol hypochlorite method (Solorzano 1969). Nitrate + nitrate was measured using an Perstorp flow solution autoanalyzer (Perstorp 1992) equipped with a cadmium reduction coil. Urea was measured using a modification of the methods described by Mulvenna and Savidge (1992) and Goeyens et al. (1998). Total dissolved nitrogen was measured as NO_3^- by Perstorp autoanalyzer following alkaline persulfate digestion in precombusted sealed glass ampoules (modified from Koroleff 1983, detailed method described in Tyler et al. 2001). DON was calculated as the difference between TDN and DIN (DIN = NO_3^- + NO_2^- + NH_4^+). C/N was calculated for each sample as the molar ratio of DOC to DON.

Free amino acids were measured for selected samples by fluorimetric detection following precolumn derivatization with o-phthaldialdehyde and separation by HPLC using a Dionex 4000 gradient pump, Alltech guard column, and Adsorbosphere OPA HR separator column (detailed method described in Tyler 2002). Following sparging with ultrapure O_2 to remove dissolved inorganic carbon, DOC was determined with a Shimadzu TOC-5000A carbon analyzer using high temperature combustion. Potassium hydrogen phthalate (KHP) standards were used, and the DOC concentration in the deionized water blank was accounted for when calculating sample concentrations. Bacterial abundance was determined by epifluorescence spectroscopy using acridine orange (Hobbie et al. 1977). For each slide, 5–10 fields of 20–200 cells were counted, ensuring that at least 200 bacteria were enumerated per sample.

With the raw incubation data, each site was examined separately for significant changes in any analytes due to light treatment using a one-way multivariate ANOVA (SPSS 8.0 statistical package, Treatment = fixed factor with four levels including initial, dark treatment, A treatment, B treatment). Analytes with significant differences were examined further, with Tukey's honestly significant difference (HSD) used to correct for multiple comparisons. In order for an individual sample treatment ($n = 3$) to be considered significant, it had to be different from the initial value ($n = 3$) for that site with $p < 0.05$.

DOC-absorbance correlation experiment—A systematic leaching of carbon from the silicone stoppers during the experiment resulted in increases in DOC for all treatments, masking photoinduced DOC changes. There was no evidence of N contamination, since TDN remained stable over time, as did individual N species in the dark controls. The contaminant did not absorb UV or PAR significantly since dark samples had stable absorbance spectra throughout the incubation. A separate photodegradation experiment was run in October 2000 with water samples from the same sites in order to establish a relationship between DOC concentration and absorbance in the absence of contamination. This experiment was identical to the first with the following exceptions: the water samples were collected in October instead

Table 1. Initial values for all sites. Samples were collected and incubated in April 2000. Numbers in parentheses are standard deviations of nine tubes, except in the case of DOC and C/N, which are the standard deviation of three tubes. Creek–source and groundwater–source were single samples as collected in the field, prior to dilution with lagoon water. Analytical detection limit was defined as twice the standard deviation of blanks, while analytical uncertainty was equal to the mean standard deviation of identical samples analyzed on different runs. BD, below detection limit; NA, not analyzed.

Sample	Salinity	DOC (μmol C L^{-1})	DON (μmol N L^{-1})	Urea (μmol N L^{-1})	NO_3^- (μmol N L^{-1})	NH_4^+ (μmol N L^{-1})	DOC/DOC (molar ratio)	a_{280} (m^{-1})	a_{350} (m^{-1})	Spectral slope coeffficient (unitless)
DIW	0	35 (6)	BD	BD	BD	BD	NA	BD	BD	BD
Lagoon	33	141 (8)	8.2 (0.6)	BD	0.4 (0.5)	BD	17.2 (1.5)	3.5 (0.3)	1.1 (0.2)	0.0141
Creek	30	461 (27)	22.0 (1.0)	BD	0.5 (0.7)	3.5 (0.7)	20.5 (1.5)	21.1 (0.2)	6.0 (0.1)	0.0180
Groundwater	22	612 (11)	37.0 (1.2)	0.7 (0.2)	4.3 (0.4)	0.8 (0.2)	16.2 (0.5)	52.1 (0.9)	19.7 (0.4)	0.0159
Leachate	33	893 (43)	28.4 (0.6)	0.8 (0.2)	0.5 (0.4)	0.9 (0.3)	31.4 (1.5)	47.9 (0.3)	17.3 (0.1)	0.0148
Creek–source	25	1063	52.8	BD	BD	8.4	20.1	59.7	17.3	0.0153
Groundwater–source	0	1504	88.2	2.1	11.7	2.1	17	156.4	59.6	0.0177
Detection limit (analytical uncert.)	NA	10 (15)	1.0 (1.2)	0.2 (0.1)	0.3 (0.4)	0.2 (0.3)	NA (1.5)	1.2 (0.5)	NA	NA

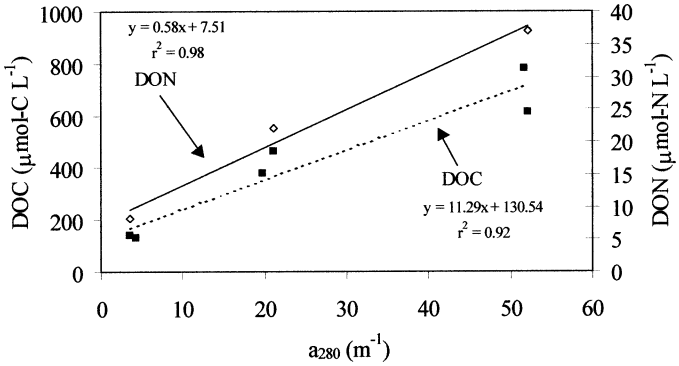

Fig. 2. DOC and DON concentrations of the natural water samples (lagoon, creek, and groundwater) as a function of sample absorptivity at 280 nm. Lagoon samples have the lowest absorptivity, creek intermediate, and groundwater highest. DON concentrations are from the main experiment (April 2000), while DOC concentrations are from both April 2000 and the October 2000 DOC-absorbance correlation experiment. Initial DOC concentration and a_{280} was not consistent for the leachate sample (not shown), which varied from 893 μmol L^{-1} DOC (April 2000) to 5,041 μmol L^{-1} DOC (October 2000) with approximately the same a_{280} (*see Table 1 and Fig. 3*).

of April, the containers used were smaller (15-ml volume, 1.5-cm diameter) quartz tubes had ground-glass stoppers instead of silicone stoppers, samples were taken in duplicate at each of three time points (0 h, 22 h, 80 h), and the only analyses performed were absorbance spectra and DOC concentration. The resulting linear relationships between DOC concentration and absorbance at 280 nm for each site were used to estimate the loss of DOC due to photodegradation in the original experiment.

Results

Initial characteristics of DOM—The initial absorbance spectra showed a pattern of an exponential curve diminishing with increasing wavelength, typical of natural organic matter samples (Miller 1998). The spectral slope coefficient of the exponential varied from 0.014 to 0.018 for the four samples (Table 1), similar to marine aquatic humus, which averages 0.015 (Zepp and Schlotzhauer 1981), and recent values reported for Swedish lakes varying from 0.014 to 0.021 (Bertilsson and Tranvik 2000). Absorptivity in the UV range was linearly correlated to DOC ($r^2 = 0.92$) and DON ($r^2 = 0.98$) for the natural water samples lagoon, creek, and groundwater (Fig. 2). Compared to the natural water samples, the leachate sample had higher DOC and lower DON relative to its absorbance at 280 nm (Table 1). Initial DOC, DON, and C/N varied considerably between the four samples, with the lagoon sample having the lowest concentrations for all solutes measured. The groundwater sample was highest in DON, and leachate highest in DOC and C/N. Initial DIN and urea concentrations were low for all samples (Table 1).

Light-induced changes—Bacterial abundance measurements at the end of the experiment confirmed that with the

exception of the creek–dark treatment, all samples had remained effectively sterile, with bacterial abundance $<0.02 \times 10^6$ cells ml^{-1}, equivalent to the concentration measured in a filtered DIW blank. Bacterial abundance in the creek–dark sample was 0.6×10^6 cells ml^{-1} at the end of the 36-h incubation, but no significant changes were observed between the initial creek sample and the final creek–dark sample for any of the chemical parameters measured. It appears that the amount of bacteria present did not have a measurable effect on the analytes of interest during the incubation period.

All water samples showed little or no absorbance change in the dark but were bleached considerably in the UV range by treatments A and B, with the B treatment resulting in more rapid bleaching. Absorbance loss at 280 nm was 21.2–34.2% for samples subjected to treatment A and 35.9–58.1% for samples subjected to treatment B. At 350 nm, absorbance loss was 27.5–53.0% for treatment A and 28.9–61.6% for treatment B. The natural sunlight treatment for creek and groundwater samples (57 h of daylight with mostly cloudy conditions at 38°N) resulted in bleaching in the UV range intermediate between the A and B incubation treatments at 280 nm and slightly greater than the A and B treatments at 350 nm. This suggests that the incubation conditions reasonably mimic natural sunlight conditions with respect to UV degradation of DOM.

DOC loss was related to bleaching at 280 nm for each of the sites in a separate experiment in October 2000. DOC concentration was linearly correlated to a_{280} for leachate, groundwater, and creek (Fig. 3), but there was no apparent relationship for lagoon water or the DIW control, since the DOC did not change significantly for those samples. The *y* intercepts of the lines, which indicate the amount of DOC projected to remain after the respective samples are completely bleached at 280 nm, were 80–90% of the initial DOC concentration. This suggests that only 10–20% of the original DOC was photolabile, since once a sample is completely bleached it will not absorb more light and thus is not photoreactive. It should be noted, however, that DOC and absorbance relationships are not always constant as bleaching continues (e.g., Moran et al. 2000); thus there is some uncertainty associated with this estimate of the size of the photolabile DOC pool. The slope of the relationship between DOC and a_{280} in this bleaching experiment was used to estimate changes in DOC for the creek, groundwater, and leachate samples in the main incubation experiment. In order to apply this calculation, we made the assumption that the size of the photolabile DOC pool is correlated with the absorbance. The size of the total DOC pool was also correlated with absorbance for our natural waters, even across sites and at different times of year (Fig. 2). However, this relationship did not hold true for the leachate sample, which had a much higher total DOC concentration relative to a_{280} in the autumn sampling than in the spring sampling.

In the main incubation experiment, calculated DOC dropped significantly in the creek, groundwater, and leachate light treatments, with the B treatment resulting in a larger DOC decrease than the A treatment. The amount of NH_4^+ generated from these samples after 36 h would suggest the breakdown of 1–4% of the DON (Table 2), and measured

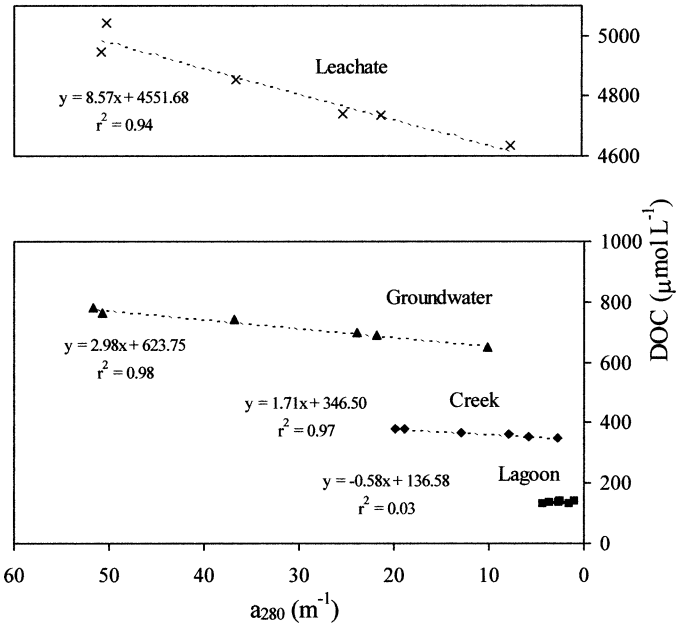

Fig. 3. DOC concentration versus absorptivity at 280 nm for each of the samples. Measurements were taken in a separate incubation experiment with samples collected in October 2000. For each site, the points shown represent the following treatments: Initial; dark treatment (80 h); A treatment (22 h); A treatment (80 h); B treatment (22 h); B treatment (80 h). All samples were bleached at 280 nm by the light treatments, and the leachate, groundwater, and creek samples lost DOC proportionally to the decrease in a_{280}, with the best-fit lines shown on the figure.

DON changes for groundwater and leachate samples were not significant and never greater than 6%. DOC, on the other hand, was estimated to decrease by 7–17% for groundwater and leachate in the light, resulting in a decrease in estimated C/N. The estimated C/N for groundwater decreased from 16.6 (initial) to 15.6 (A treatment) and 14.5 (B treatment). For leachate, estimated C/N decreased from 31.4 (initial) to 28.0 (A treatment) and 27.8 (B treatment).

The DIW sample functioned effectively as a control sample with respect to N species concentrations, and the dark treatment functioned as a control treatment. There were no significant changes in the concentrations of any measured N species for DIW (i.e., no measurable contamination) or in the dark (ANOVA, $p > 0.05$). There was no consistent effect of light on concentrations of NO_3^-, urea, or DON (Fig. 4), but for isolated samples, some of these parameters changed. For instance, urea increased in the groundwater-B treatment, and DON dropped in the leachate-B treatment. However, due to the statistical correction for multiple comparisons made, none of these resulted in significant changes. For NH_4^+, however, the light treatments consistently resulted in increased concentrations, with the B treatment typically resulting in larger increases than the A treatment (Fig. 4D). The groundwater sample gave significant increases in NH_4^+ for both A and B treatments of 1.2 ± 0.1 μmol L^{-1} and 1.6 ± 0.3 μmol L^{-1}, respectively (ANOVA, $p < 0.05$). The rate of production of NH_4^+ for the A treatment for the different samples ranged up to 32 nmol L^{-1} h^{-1} (groundwater) (Table 2). As-

Table 2. Synthesis of results (photoproduction rates of NH_4^+ and DFAA) from this and other DOM photodegradation studies that emphasize nitrogen dynamics.

Sample water used	Light regime	NH_4^+ production rate (μmol N L^{-1} h^{-1})	Normalized NH_4^+ production rate* (μmol N L^{-1} m h^{-1})	NH_4^+ production as fraction of initial DON (% h^{-1})	Rate of production of other measured amine groups (μmol N L^{-1} h^{-1})	Reference
Humic pond, swamp, river waters, and isolated fulvics	Natural sunlight or solar simulator, 18 h Total = 860 W m^{-2}	0.05–0.34	0.0032–0.0042	0.25–0.92	Not measured	(Bushaw et al. 1996)
Humic Satilla River water	Solar simulator, 4 h = mid-June sun at 34°N	0.1	0.011	0.25	Not measured	(Gao and Zepp 1998)
Swedish clear-water lake, epilimnion and hypolimnion	Natural sunlight, 7 h Total = 345 W m^{-2}	No change	No change	No change	0.010–0.017† (DFAA) 0.057† (DCAA, epilimnion only)	(Jørgensen et al. 1998)
Concentrated humic acids from river and estuary	Natural sunlight, 7 h UV = 9.4 W m^{-2}	0.058–0.060	0.0010–0.0015	0.11–0.17	0.009–0.041 (DPA)	(Bushaw-Newton and Moran 1999)
Humic lakes, streams, rivers in Sweden	UVA-340 lamps, 12 h 2.1 W m^{-2} UV-B 20 W m^{-2} UV-A 5 W m^{-2} PAR	No change	No change	No change	Not measured	(Bertilsson et al. 1999)
Coastal waters from the Gulf of Riga	UVA-340 lamps, 12 h 0.3 W m^{-2} UV-B 20 W m^{-2} UV-A 6.1 W m^{-2} PAR	−0.03–0.0	Not reported	−0.16–0.0	−0.014–0.006 (DFAA) 0.0–0.17 (DCAA)	(Jørgensen et al. 1999)
Humic bayou and river water and isolated riverine humics and fulvics	Solar simulator, 10 h Total = 600 or 765 W m^{-2}	0.11–1.9	0.002–0.056	0.8–2.6	Up to 0.011 (various individual amino acids)	(Wang et al. 2000) (Tarr et al. 2001)
Groundwater and DOM concentrated from estuarine water	Natural sunlight or solar simulator, 5–10 h	−0.31–0.13	−0.002–0.0015	−0.81–0.91	No change for most samples	(Koopmans and Bronk 2002)
S. alterniflora leachate and samples from high-salinity lagoon system	UVA-340 lamps, 36 h 4 W m^{-2} UV-B 42 W m^{-2} UV-A 57 W m^{-2} PAR	0.006–0.032	0.0005–0.007	0.028–0.087	Up to 0.00094‡ (various individual amino acids)	This study
S. alterniflora leachate and samples from high-salinity lagoon system	UVB-314 lamps, 36 h 27 W m^{-2} UV-B 25 W m^{-2} UV-A 47 W m^{-2} PAR	0.001–0.046	0.0009–0.010	0.013–0.208	Up to 0.0011‡ (various individual amino acids)	This study

* Production rate normalized to absorptivity of water at 350 nm.
† Production rate estimated from graphical representation of data.
‡ DFAA measured in groundwater sample only.

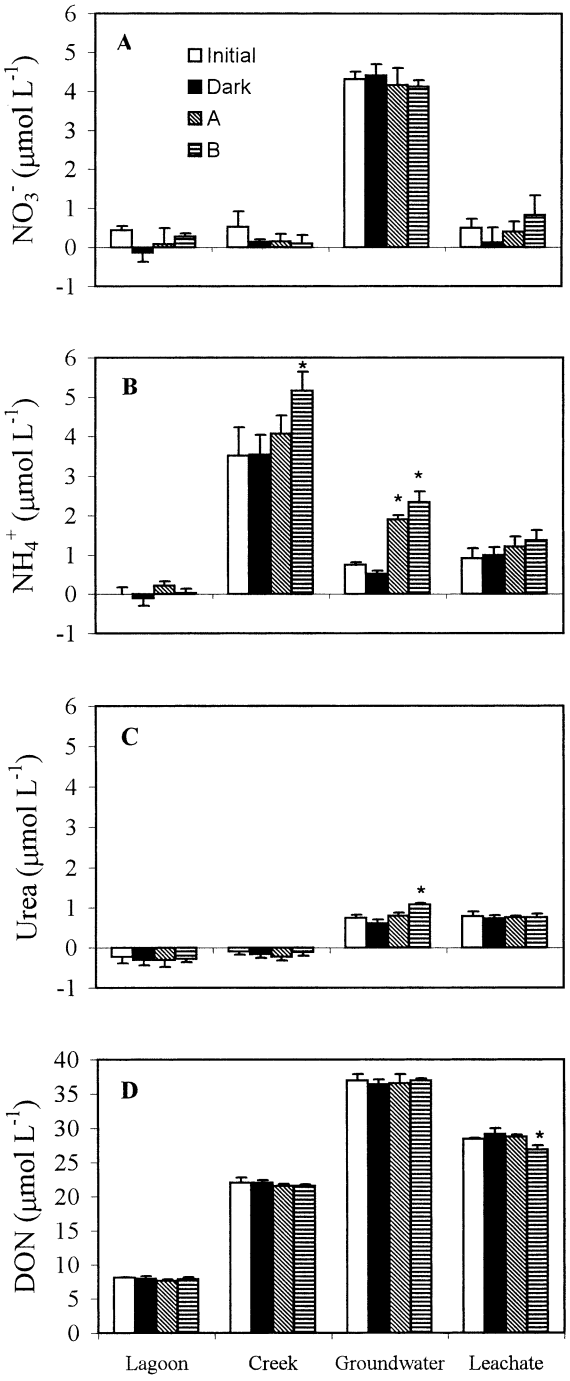

Fig. 4. Initial values for nitrogen species measured in the four environmental sample waters incubated, and values after 36 h of incubation for the control (dark) treatment and the two UV light treatments for (A) NO_3^-, (B) NH_4^+, (C) urea, and (D) DON concentrations. Error bars represent standard deviations from triplicate incubation tubes. Asterisks denote a significant difference between the treatment and initial samples (ANOVA, $\alpha = 0.05$). DIW control samples did not show significant changes in any measured parameters.

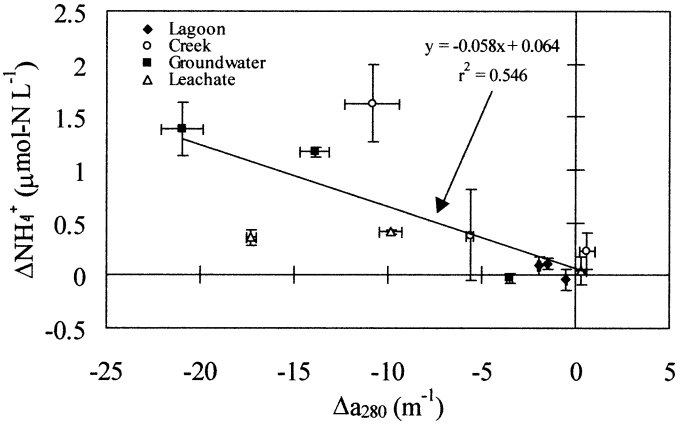

Fig. 5. Change in NH_4^+ concentration versus changes in a_{280} (absorptivity at 280 nm) for all samples and treatments (A, B, and dark control). For each sample, the dark treatment resulted in little or no change in a_{280}, the A treatment resulted in an intermediate decrease in a_{280} (bleaching), and the B treatment resulted in a larger decrease in a_{280}. Increases in NH_4^+ concentration are proportional to bleaching at 280 nm, which suggests that photodegradation of DOM is linked to NH_4^+ production.

suming NH_4^+ production occurs as a direct result of the breakdown of the DON pool, this corresponds to DON loss rates ranging from 0.03% h^{-1} (leachate) to 0.09% h^{-1} (groundwater) (Table 2). The production of NH_4^+ was linearly related to the degree of bleaching in the UV region (Fig. 5), with the leachate sample releasing less NH_4^+ relative to the natural water samples.

Individual DFAAs were analyzed for the groundwater samples in addition to the DIW control. The groundwater samples were chosen for this additional analysis because groundwater demonstrated the highest and most reproducible rate of NH_4^+ photoproduction. No amino acids were detected in the DIW control, either initially or as a result of any of the three treatments. The amino acids glutamic acid, aspartic acid, serine, glycine, and alanine were detected in the initial groundwater sample (detection limit = 5 nmol L^{-1}) (Fig. 6). DFAA standard addition experiments confirmed the identity

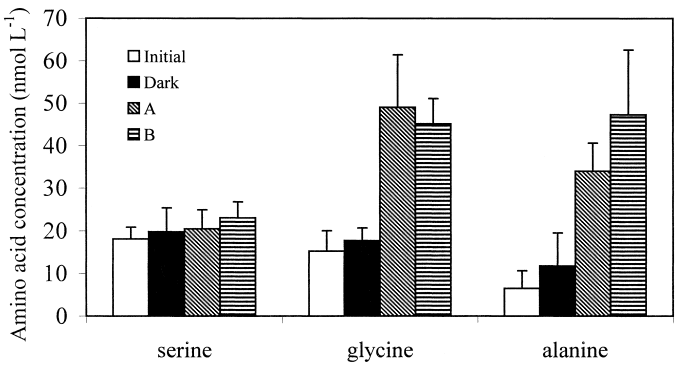

Fig. 6. Summary of groundwater DFAA initial concentrations and concentrations after 36-h incubation. The DFAA peaks detected in measurable concentrations using OPA-derivatization HPLC analysis were serine, glycine, and alanine. Error bars represent the standard deviation of triplicate incubation tubes.

of all peaks as known DFAAs, with the exception of an unidentified peak eluting immediately following the valine standard. The concentrations of glutamic acid and aspartic acid could not be determined reliably due to the presence of a large DOM peak fluorescing in the same region, but the concentrations of serine, alanine, and glycine were corroborated with DFAA standard additions. Initial concentrations of these three amino acids ranged from 7 nmol L^{-1} (alanine) to 18 nmol L^{-1} (serine) (Fig. 6). All amino acids measured for the groundwater site were unchanged in the dark, but glycine and alanine increased significantly in the light (one-way ANOVA, $p < 0.05$) (Fig. 6). The two light treatments did not differ significantly from one another. Rates of production varied from 0.8 nmol N L^{-1} h^{-1} to 1.1 nmol N L^{-1} h^{-1} for glycine and alanine in the light.

Estimated rates of photoproduction in Hog Island Bay—To our knowledge there is no published action spectrum for the photoproduction of NH_4^+ from natural DOM. However, NH_4^+ photoproduction appears to be primarily due to UV radiation (Bushaw et al. 1996), and for the purposes of our calculations we assumed that the amount of incident UV radiation (defined as wavelengths below 400 nm) could be used as a proxy for the amount of photoactive radiation with respect to NH_4^+ production. Photoproduction in Hog Island Bay was estimated from photoproduction in the incubation by normalizing both to incident photoactive (UV) radiation and to the concentration of photoabsorbing material (DOM). With this approach, the mean annual NH_4^+ photoproduction rate for Hog Island Bay was estimated using

$$P_{\mathrm{HIB}} = \left[\frac{P}{I_{\mathrm{UV}} a_{350}}\right]_{\mathrm{INC}} [I_{\mathrm{UV}} a_{350}]_{\mathrm{HIB}}$$

where P_{HIB} is the mean annual water column photoproduction rate of NH_4^+ in Hog Island Bay, P_{INC} is the photoproduction rate of NH_4^+ in the incubation experiment, I_{UV} is the average incident UV irradiance reaching the water in a given sample, and a_{350} is the absorptivity at 350 nm of a filtered water sample, a proxy for the concentration of photoabsorbing DOM. For the incubation experiment, production normalized to UV irradiance and a_{350} gave a mean value of 7.8×10^{-5} μmol N L^{-1} h^{-1} W^{-1} m^3 for samples with significant NH_4^+ production from the A treatment. Using mean annual solar UV irradiance values (I_0) for our region of 12.0 W m^{-2} (Zepp 1982) and measured water column UV extinction coefficients (k) of 2.4–3.5 m^{-1} for Hog Island Bay, we calculated a depth-integrated mean UV irradiance range (I_{UV}) of 2.3–3.2 W m^{-2} for the Hog Island Bay water column using

$$I_{\mathrm{UV}} = I_0 \left(\int_{d=0}^{d=D} e^{-kd} \right) D^{-1}$$

where D is the mean depth of the water column (1.5 m). With this range for I_{UV} in Hog Island Bay and the mean a_{350} for filtered lagoon water (1.0 m^{-1}), we calculated a mean annual NH_4^+ photoproduction rate for Hog Island Bay of 6–9 μmol N m^{-2} d^{-1}.

Discussion

Changing character of DOM—The absorbance patterns we observed during the incubation generally agree with patterns previously noted by others for light-induced degradation of natural organic matter (e.g., Moran et al. 2000), with absorbance losses considerably greater than DOC losses (e.g., Fig. 4). Estimated DOC losses coupled with insignificant changes in DON concentrations resulted in a light-induced decrease in estimated C/N for the groundwater and leachate samples. Although DOC photodegradation has been well documented in a number of aquatic systems (e.g., Mopper et al. 1991), measurements of light effects on DON or C/N are scarce (Jørgensen et al. 1998). In one notable study, with a concentrated solution of humic material isolated from a loamy soil, Schmitt-Kopplin et al. (1998) observed that organic carbon was lost at a significantly more rapid rate than organic nitrogen, oxygen, or hydrogen when exposed to UV radiation under an O_2 atmosphere. Structural differences in DOM molecules resulted in different rates of photodegradation, with lignins and lipids degrading rapidly as compared to carbohydrates, alkylbenzenes, and N-containing structures (Schmitt-Kopplin et al. 1998). Direct photolysis of carboxyl groups (e.g., Zafiriou et al. 1984) may account for the bulk of the photolabile DOC pool, while cleavage of inorganic N functionalities from DOM is likely to occur by a less direct process.

The light-induced decrease in estimated C/N for the groundwater and leachate samples suggests the potential for increased DOM bioavailability. Microbial production and growth efficiencies are frequently correlated with C/N and other elemental ratios of their DOM source (e.g., Vallino et al. 1996), typically with lower C/N correlated with higher growth (e.g., Sun et al. 1997). A variety of molecular factors is responsible for determining DOM bioavailability, and changes in C/N may not always be causally linked to changes in bioavailability. However, we suggest that a decrease in C/N may be typical of natural DOM photodegradation processes and is an indication of the changing molecular character of photodegraded DOM, which may alter its availability to bacteria.

Ammonium photoproduction—Rates of NH_4^+ photoproduction have been measured infrequently in other recent photochemical studies, with varied results (Table 2). Highly humic surface waters from the southeastern U.S., and in some cases humic acids isolated from those waters, have been shown repeatedly to release NH_4^+ at rates of up to 0.3 μmol N L^{-1} h^{-1} when exposed to natural or artificial sunlight (e.g., Bushaw et al. 1996; Gao and Zepp 1998). In a detailed kinetic study, even higher rates of NH_4^+ production were observed for highly humic bayou and river water in Louisiana, and a duckweed decomposition product resulted in NH_4^+ photoproduction of nearly 5 μmol N L^{-1} h^{-1} (Wang et al. 2000). However, other studies of DOM photodegradation in natural waters from a variety of sources in Sweden gave no evidence of NH_4^+ production (Jørgensen et al. 1998; Bertilsson et al. 1999), and surficial groundwater from the southeastern U.S. subjected to sunlight resulted in consumption of NH_4^+ more frequently than production (Koopmans and

Table 3. Summary of nitrogen species pools, fluxes, sources, and cycling rates that have been measured within the HIB system. Photoproduction rates of NH_4^+ and DFAA estimated from this study are included. NA, not analyzed.

Nitrogen pool/flux	Units (annual mean values)	Reference
1. Standing stock in Hog Island Bay water column	μmol N m^{-2}	
Macroalgal biomass	Up to 130,000–570,000*	(McGlathery et al. 2001)
DIN	3,000	(Tyler et al. 2001)
DON	12,000	(Tyler et al. 2001)
DFAA	120–140	(Tyler 2002)
2. Sources to Hog Island Bay system	μmol N m^{-2} d^{-1}	
Atmospheric deposition—DIN	150†	(Meyers et al. 2000)
Groundwater—DIN	?	NA
Atmospheric deposition—DON	33†	(Meyers et al. 2000)
N fixation—DON	?	NA
Marine input—DON/DIN	?	NA
Atmospheric deposition—DFAA	0.05–8.0‡	(Milne and Zika 1993; Gorzelska et al. 1997)
3. Cycling within Hog Island Bay	μmol N m^{-2} d^{-1}	
Benthic microalgal uptake	7,680	(Anderson et al. in press)
Benthic macroalgal uptake	Up to 9,500*	(McGlathery et al. 2001)
Phytoplankton uptake	Up to 26,400*	(McGlathery et al. 2001)
Water column microbial mineralization	100–300§	(T. Lunsford & I.C. Anderson, unpubl. data)
Sediment microbial mineralization	3,710§	(Anderson et al. in press)
Photoproduction—DIN (NH_4^+)	6–9	This study
Sediment/algae release—DON	100–300	(Tyler et al. 2001)
Benthic algal uptake—DFAA	Up to 22*	(Tyler 2002)
Photoproduction—DFAA	0.4–0.6	This study

* Maximum values observed, for certain sites and certain times of year. All other values reported are temporal and spatial means.
† Based on annual means for Chesapeake Bay water body, including wet and dry deposition.
‡ Based on range for marine samples.
§ Gross mineralization rate.

Bronk 2002). Our rates of NH_4^+ photoproduction (up to 0.032 μmol N L^{-1} h^{-1}) are approximately an order of magnitude lower than those observed by Bushaw et al. (1996) and up to two orders of magnitude lower than those determined by Wang et al. (2000). Normalization to initial DON concentration does not remove this disparity, but when normalized to absorbance, the rates from all three studies are similar (Table 2). Valentine and Zepp (1993) observed a similar pattern for carbon monoxide photoproduction from a variety of freshwater sites, with normalization to a_{350} accounting for almost all of the variability. Similarly, Bushaw et al. (1996) suggested that NH_4^+ photoproduction potential could be more readily predicted by UV absorbance than by DON concentration alone. In our study we found no correlation between changes in DON and changes in NH_4^+ during the incubation, while bleaching at 280 nm and NH_4^+ production were correlated.

There are a number of possible additional explanations for the variation in NH_4^+ photoproduction rates. Ammonium production or lack thereof does not appear to be closely linked to the type of light used, since both results have been obtained using natural and artificial light (Table 2). There may be basic differences between DOM in surface waters resulting from source or prior radiation exposure that cause them to be differently disposed to NH_4^+ photoproduction. Photolability is influenced by the chemical bond types and structure of the DOM, which dictate the radiation energy (wavelength) required to break bonds and alter the chemical structure (Miller 1998). The DOM found in humic rivers, swamps, and lakes is derived largely from terrestrial sources. These tend to contain a large fraction of aromatic, humic-rich molecules that have a high capacity to absorb UV radiation and thus are photoreactive (Miller 1998). Marine and coastal waters tend to contain more autochthonous organic matter, which may be relatively photorefractory. Algal DOM was found to be highly resistant to light degradation (Thomas and Lara 1995), and in a Swedish study, DOM from lakes with higher levels of in situ primary production was less rapidly photodegraded (Bertilsson and Tranvik 2000). There are also water chemistry characteristics that affect rates of photooxidation, such as iron concentration, pH, and conductivity (Gao and Zepp 1998; Bertilsson et al. 1999). Wang et al. (2000) demonstrated a strong effect of pH on NH_4^+ photoproduction, with approximately fourfold higher rates upon decreasing pH from 6.0 to 2.1. This may be due to rapid irreversible reattachment of NH_3 to humic molecules after photochemical cleavage at high pH (Thorn and Mikita 1992; Wang et al. 2000), and/or acid-catalyzed hydrolysis of photolysed peptide/amide linkages as suggested by Wang et al. (2000). The high pH of marine waters may thus inhibit free NH_4^+ production. If so, studies of NH_4^+ photoproduction using low-pH freshwaters or humic extracts cannot be reliably scaled up to estimate production in coastal areas without taking into account the effect of water chemistry regime.

In comparison with other known sources of DIN to Hog Island Bay (Table 3), NH_4^+ photoproduction would appear to be a measurable but minor contributor, much less than atmospheric deposition, and only representing a reduction of about 0.1% d^{-1} of the water column DON pool. Within the lagoon system, sediment–water column exchange and mi-

crobial processing rates are considerably higher than the calculated NH_4^+ photoproduction rate. However, although the rate of NH_4^+ photoproduction could not support the rapid algal growth observed during blooms (Table 3), it could be responsible for helping to maintain a constant low-level background supply of DIN in the water column.

The calculation of the maximum potential rate of NH_4^+ photoproduction in the shallow coastal zone is in part dependent upon the estimate of the rate of production/introduction versus consumption of the photolabile pool of DON. To our knowledge rates of production of photolabile (UV absorbing) DON have not been measured for these systems in the context of photochemical studies, although several studies have estimated the size of the photolabile pool at a given point in time. In one notable kinetic study, Bushaw et al. (1996) observed maximum NH_4^+ photoproduction rates for humic boreal pond and swamp water after 22 h of incubation, with rates considerably slowed by 72 h (at which point 7–16% of DON had been converted to NH_4^+), which suggests depletion of the most labile portion of the DON pool by that point. The lack of measurable DON degradation in our incubation experiment, even with considerable bleaching after 36 h (Table 2), suggests that the photolabile DON pool in our coastal waters was effectively a small fraction of the total DON pool. A continuation of our incubation to 108 h demonstrated that NH_4^+ photodegradation rates were significantly lower following 36 h, further suggesting a depletion of the photolabile DON pool (data not shown).

Other researchers have noted the photorefractory nature of DON relative to DOC. Schmitt-Kopplin et al. (1998) found that N functionalities were among the most robust molecular portions of humics. It was discovered recently that a large fraction of marine humic material was represented by amide functional groups (McCarthy et al. 1997), consistent with the idea of a persistent N-containing functionality resistant to both photochemical and microbial degradation. Nevertheless, even if the photolabile DON pool is a small fraction of total DON, NH_4^+ photoproduction could be sustained in natural systems with short residence time (rapid water exchange) and/or a constant source of new DON inputs. It is unclear whether this is the case for Hog Island Bay, but the system does have inputs of DON from groundwater, internal production by algae, and exchange with sediments and marine waters, as well as periodic atmospheric deposition of DON (Table 3).

Amino acid photoproduction—Glycine and alanine were each produced at rates of close to 1 nmol N L^{-1} h^{-1} in the light treatments for the groundwater sample, similar to rates of production of DFAAs in other recent photodegradation studies (Table 2). DFAAs were produced in a photodegradation study of lake water at a rate of 10–17 nmol N L^{-1} h^{-1} total (Jørgensen et al. 1998), and in a recent study of dissolved fulvic acid and colloidal fractions of bayou water, photoproduction of at least 20 amines was observed (Tarr et al. 2001). Concentrations of the amino acids alanine, asparagine, citrulline, glutamic acid, histidine, norvaline, and serine increased in the range of 0.03–9.5 nmol N L^{-1} h^{-1} total (Tarr et al. 2001).

If the absorbance-normalized rates of DFAA production that we measured for the groundwater sample were similar for the other sites, as appeared to be the case for NH_4^+ photoproduction, then DFAA production could be scaled up to estimate the rates occurring in Hog Island Bay. Applying the same method used for scaling up NH_4^+ production, mean annual photoproduction rates for the DFAAs (alanine and glycine) were estimated to be 0.4–0.6 μmol N m^{-2} d^{-1}, with rates up to 2.0–2.9 μmol N m^{-2} d^{-1} estimated for times of peak insolation (a sunny summer midday). This is small relative to the water column standing stock and considerably lower than measured algal uptake rates in Hog Island Bay and potential uptake rates by bacteria (Table 3). Bacterial DFAA assimilation rates measured in other coastal systems typically fall in the range of 0.005–0.05 μmol N L^{-1} h^{-1} (Coffin 1989; Jørgensen et al. 1993), which translates into 180–1,800 μmol N m^{-2} d^{-1} if the Hog Island Bay water column has similar rates.

Other sources of amino acids to Hog Island Bay include atmospheric deposition and groundwater influx. The DFAAs in the groundwater sample (diluted 1 : 2 with lagoon water) used in this study were at least 0.05 μmol N L^{-1}, approximately 0.14% of the DON. Nearly all amino acids occur in appreciable concentrations in sea salt aerosols (Milne and Zika 1993), and measured concentrations of total dissolved amino acids (free and combined) in marine rain are highly variable and range from a few nmol N L^{-1} to several μmol N L^{-1} (e.g., Gorzelska et al. 1997). Our calculated DFAA photoproduction rate for Hog Island Bay was comparable to or slightly lower than estimated precipitation inputs (Table 3) and considerably lower than assimilation rates for macroalgae measured in Hog Island Bay (Tyler 2002) and bacteria in other coastal systems (Jørgensen et al. 1999). This suggests that photochemical DFAA production within Hog Island Bay is probably of minor ecological consequence.

It is likely that DFAA gross photoproduction is actually higher than the observed net production if the amino acids are rapidly further broken down by sunlight to release NH_4^+ and small carboxylic acids or CO_2. Rao and Dhar (1934) observed rates of DFAA breakdown of up to 200 μmol N L^{-1} h^{-1} for concentrated solutions of glycine and alanine upon exposure to sunlight in the presence of an oxidizing catalyst. More recently, a mechanistic study by Tarr et al. (2001) demonstrated that many amino acids are photodegraded to NH_4^+ and other products in the presence of DOM, although DFAA degradation did not appear to be a major source of NH_4^+ formation relative to other pathways. If the gross rate of DFAA photoproduction is higher than measured production, and if biological uptake outpaces photodegradation of the amino acids, the ecological impact in Hog Island Bay could be greater than we have predicted (Table 3).

Effect of increasing UV-B radiation—Atmospheric ozone depletion has resulted in enhanced UV-B irradiation at the Earth's surface, and continued ozone depletion is predicted to further augment UV-B (Zepp et al. 1998). Enhanced levels of UV-B radiation have been shown to impact aquatic biota and biogeochemical cycles (Zepp et al. 1998). In our experiments, NH_4^+ photoproduction showed an increasing trend with increased bleaching at 280 nm due to UV-B (Figs. 4B,

5), while glycine and alanine photoproduction rates were not significantly different between the two light treatments (Fig. 6). In the DOC-absorbance correlation experiment, the B treatment resulted in a greater rate of DOC loss than the A treatment, proportional with the increased bleaching rate (Fig. 3). Bushaw et al. (1996) also saw increasing NH_4^+ production with increased UV-B, and the enhancing effect of UV-B on DOC degradation is well documented (Zepp et al. 1998). When normalized to the degree of bleaching at 280 nm, the changes that we measured for NH_4^+ and selected amino acids and estimated for DOC and C/N were not significantly different between the two light treatments in our incubation. Increases in environmental levels of UV-B resulting from ozone depletion are expected to cause an increase in the rate of DOC depletion and NH_4^+ production from natural DOM in our system.

Importance of photochemical N transformations in the coastal zone—The rates of NH_4^+ and amino acid formation, when scaled up to estimate photoproduction in Hog Island Bay, appeared to be small relative to other sources to and fluxes within the system and thus of minor ecological significance (Table 3). Photoproduction of bioavailable N compounds such as NH_4^+ and DFAAs may be of greater ecological importance in other systems, for instance on the coastal shelf, which has relatively long residence times, clear waters, and greater water column : sediment surface ratio and is frequently N limited (Bushaw et al. 1996). Recent studies using concentrated DOM from humic freshwaters have begun to describe the effects of pH and have proposed basic mechanisms for photoproduction (Wang et al. 2000; Tarr et al. 2001). However, further research is required to determine whether the same patterns apply for more dilute waters and DOM from less humic-rich sources and coastal zones.

Changes in the N pool due to photochemistry have been demonstrated in this study and several others (Bushaw et al. 1996; Gao and Zepp 1998), but the connection between photochemical N transformations and changes in microbial activity has been inconsistent between different studies (Bushaw et al. 1996; Bertilsson et al. 1999). There is a need for continued research addressing the specific causes of increased microbial growth following photodegradation, to distinguish between the effects of increased availability of various compounds including labile DOC, labile DON, DFAAs, and NH_4^+.

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