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Photochemical and microbial degradation of external dissolved organic matter inputs to rivers

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ABSTRACT: Photochemical and microbial degradation of external inputs of dissolved organic matter (DOM) from both natural (forests) and anthropogenic (swine and equine pastures) non-point sources to rivers were examined through field and laboratory microcosm experiments. Little or no photochemical degradation of DOM to inorganic N or P occurred in either the agricultural or forest runoff. The dissolved organic carbon (DOC), dissolved organic nitrogen (DON), NH_4^+, and PO_4^{3-} concentrations did not change during the photochemical experiments for any of the sources examined. A small, but significant increase in the NO_3^-/NO_2^- (+0.7 µM; p = 0.004) concentration was detected in the forest runoff, suggesting that a small fraction (4 to 9%) of the DON may be photochemically degraded to dissolved inorganic nitrogen (DIN). Bacteria readily utilized DOC and DON in the agriculture and forest runoff. The percent of DOC and DON consumed by the bacteria ranged from 6 to 14% and 21 to 25%, respectively. Light exposure did not alter the biological availability of the DOC and DON in either the equine pasture or forest runoff. Our results emphasize the importance of microbial processes in degrading DOM in riverine environments; they appear to degrade DOM more rapidly than photochemical processes and may be more important in affecting the quantity and quality of the DOM exported from rivers to estuaries.

KEY WORDS: Bacteria · Dissolved organic carbon · Dissolved organic nitrogen · Non-point sources · Photochemical processes · Rivers

INTRODUCTION

Photochemical and microbial processes are important pathways for altering and removing dissolved organic matter (DOM) in aquatic systems. These processes act in conjunction with each other to affect the amount and rate at which DOM, both the carbon (DOC) and nitrogen (DON) components, are incorporated into the microbial food web (Wetzel et al. 1995, Bushaw et al. 1996, Miller & Moran 1997, Jørgensen et al. 1998, Bushaw-Newton & Moran 1999). Photochemical processes can alter the DOM pool by releasing inorganic compounds such as ammonia (NH_4^+), nitrite (NO_2^-), phosphate (PO_4^{3-}), dissolved inorganic carbon (DIC: sum of dissolved CO_2, H_2CO_3, HCO_3^-, and CO_3^{2-}), and carbon monoxide (CO) (Francko & Heath 1982, Miller & Zepp 1995, Bushaw et al. 1996, Granéli et al. l996, Gardner et al. 1998, Kieber et al. 1999). Sunlight can also cleave large DOM molecules into smaller and potentially more labile entities (Mopper & Stahovec 1986, Kieber & Mopper 1987, Kieber et al. 1989, Wetzel et al. 1995, Jørgensen et al. 1998). As a result of these processes, the DOM and its photo-products can then be taken up by bacteria and phytoplankton and incorporated into the biological cycle. Bacteria and phytoplankton can directly take up DOM through the secretion of exoenzymes and cell surface oxidation (e.g. Palenik & Morel 1990, Anita et al. 1991, Pantoja & Lee 1994). Microorganisms can also remineralize the DOM, releasing NH_4^+, PO_4^{3-}, and CO_2 back into the surrounding environment (Goldman et al. 1987).

Riverine DOM inputs were historically considered recalcitrant because of their high C:N ratio (~50), the reported conservative mixing in some estuaries, and

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the predominance of high molecular weight (HMW) compounds (Mantoura & Woodward 1983, Amon & Benner 1996a). Recent studies have begun to demonstrate that not all of the HMW DOM pool is refractory. On average, about 17% of the carbon component in DOM from lakes, rivers, and marine environments has been found to be biologically available (Søndergaard & Middelboe 1995). Bioassays and non-conservative mixing curves in river plumes have demonstrated that the nitrogen component in DOM is also labile (Carlsson et al. 1993, 1999, López-Veneroni & Cifuentes 1994, Peierls & Paerl 1997, Seitzinger & Sanders 1997, 1999, Stepanauskas et al. 1999). In the Delaware and Hudson rivers, from 40 to 72% of the DON was found to be biologically available to estuarine microbes (Seitzinger & Sanders 1997).

The relative importance of photochemical and microbial degradation of DOM in the aquatic environment is not yet well understood. Numerous studies have examined either photochemical or microbial degradation of DOM; however, few have directly compared the 2 pathways. These studies have focused primarily on the degradation of DOC; researchers have only begun to examine DON. The goal of this study was to examine photochemical and microbial degradation of DOC and DON from anthropogenic and natural non-point sources. Non-point source runoff was chosen as a DOM source because it may be an important external input of DOM and pollution to rivers (Sharpley et al. 1988, Heathwaite 1993). Photochemical and microbial degradation of DOC and DON were examined through both field and laboratory microcosm experiments. Photochemical degradation experiments investigated the ability of different regions of the electromagnetic spectrum to degrade DOC and DON into inorganic components. Microbial experiments further examined how photochemical processes affect DOM biological availability to the bacteria community.

MATERIALS AND METHODS

Sample collection. Agriculture and forest sites located in New Jersey were selected for non-point source runoff collection. These sites included swine and equine pastures located on Cook College, Rutgers University, New Brunswick (40° 28′ 65″ N, 74° 26′ 20″ W) and a mixed hardwood forest located on Round Mountain, Stanton (40° 34′ 25″ N, 74° 50′ 17″ W). Agriculture runoff was collected down-slope of the animal pastures in a subsurface water collector (Seitzinger et al. unpubl. data) consisting of a PVC pipe with drainage holes wrapped in a GeoSieve (Drainage Products™, Inc. Windsor Locks, CT) sleeve. The collectors were buried 18 to 23 cm below the soil surface and above a layer of red/orange clay. The animal density in the pastures ranged from 2 to 3 ha^{-1}. Forest runoff was sampled from a first-order stream, approximately 30 cm wide, running through a mixed hardwood forest dominated by black oak *Quercus velutina*, white oak *Quercus alba*, American beech *Fagus grandifolia*, yellow poplar *Liriodendron tulipfera*, red maple *Acer rubrum*, and bitternut hickory *Carya cordiformis*.

Runoff was collected from each site during or immediately following a rainstorm event in June or August of 1997. Water was collected during times of increased riverine discharge when soluble organic matter concentrations are known to be high (Richey et al. 1985, Lewis & Saunders 1989). The water was collected in an acid-washed 20 l polyethylene cubitainer and transported on ice to the laboratory. Here, it was sequentially filtered through 1.0 and 0.5 µm string-wound polypropylene canister filters into an acid-washed 20 l cubitainer and immediately frozen at –20°C. The canister filters were flushed with 20 l of deionized water (DIW) before filtering the runoff. Before the photochemical experiment, the runoff was sterile filtered through a 10^6 dalton polysulphone filter (tangential flow ultrafiltration; Filtron Technologies, Northborough, MA) on ice into acid-washed and autoclaved 10 l polypropylene containers, and immediately frozen at –20°C. During this filtering process, water from a single source was collected in 3 separate containers. In order to maintain sterile conditions, water from the 3 containers was not mixed after filtering was complete. Thus, each container and subsequently replicate treatment flasks had a different starting DOC and DON concentration. Sample exposure to light was minimized during all processing steps.

Photochemical degradation experiments. Photochemical degradation experiments were performed at Lacawac Sanctuary, Lake Ariel, Pennsylvania (41° 22′ 57″ N, 75° 17′ 35″ W), during August, September, and October 1997. Sterile filtered runoff (swine, equine, and forest) and control water (autoclaved DIW) were allocated into sterile and pre-combusted 1.5 l quartz (light treatments) and 2 l borosilicate boiling (dark controls) flasks. Duplicate flasks were irradiated under natural sunlight in incubators constructed out of black Plexiglas with tops built from either UF-5 (Q = downwelling irradiance; Q_{PAR}, 400 to 700 nm), UVT and Mylar D, ($Q_{PAR+UVA}$, 320 to 700 nm), and UVT ($Q_{PAR,UVA+UVB}$, 280 to 700 nm), and black Plexiglas (no light: control). Light transmission cutoffs for the Plexiglas tops were 412 nm for UF-5, 317 nm for UVT and Mylar D, and below 280 nm for UVT. The thickness of the UF-5 and UVT Plexiglas was 3.2 mm and that of Mylar D was 0.05 mm. Water in the flasks was continuously mixed with sterile Teflon-coated stir bars during the course of the experiment. Fluctuations in water temperature

were minimized during the experiment by circulating water through the incubators and adding ice. Average water temperatures for the August, September, and October experiments were (20 ± 5°C), (20 ± 3°C), and (19 ± 2°C), respectively.

Initial and time-series nutrient samples for NH_4^+, NO_3^-/NO_2^-, PO_4^{3-}, total dissolved nitrogen (TDN), and DOC were taken over the course of 3 to 4 d. The swine pasture, equine pasture, and forest runoff were exposed to approximately 35, 21.5, and 38 h of sunlight, respectively. Sterile sampling procedures were used throughout the experiments. NH_4^+ was measured using both standard autoanalyzer and manual methods (Lachat, Inc. QuickChem 31-107-06-1-A, Milwaukee, WI; Solórzano 1969). Both NO_3^-/NO_2^- (Lachat QuickChem Method 31-107-04-1-A) and PO_4^{3-} (Lachat QuickChem Method 31-115-01-3-A) were measured using standard autoanalyzer methods. TDN was analyzed by high-temperature combustion followed by chemiluminescent detection of nitric oxide using an Antek Model 7000 Total N Analyzer (Antek, Inc., Houston, TX) equipped with a quartz combustion tube (1000 ± 10°C) and a ceramic insert (Seitzinger & Sanders 1997). TDN samples were preserved in capped autosampler vials with 3N HCl (7.5 µl acid per 1.5 ml sample) and stored in the dark at 4°C. Blanks consisted of DIW. Both inorganic (NH_4^+ and NO_3^-/NO_2^-) and organic (urea) standards for TDN analysis were prepared in DIW. DON was determined by the difference between TDN and DIN. DOC was measured by high temperature combustion (Shimadzu TOC-5000A) following the recommendations of Sharp et al. (1993). All nutrient and DOC samples were immediately frozen at –20°C following sampling. Immediately following each photochemical degradation experiment, water from each treatment flask was frozen at –20°C in an acid-washed 500 ml polyethylene container and stored for up to 2 mo before being used in the microbial degradation experiments.

Light measurements were made with a Biospherical Instruments Inc. (BSI) GUV-521 UV radiometer at Lacawac Sanctuary. The radiometer measured downwelling irradiance simultaneously at 4 wavebands in the UV region (380, 340, 320, and 305 nm; 8 to 10 nm bandwidths) as well as broadband PAR (400 to 700 nm). Irradiance was recorded by a Campbell Scientific, Inc. CR-10 datalogger at 1 s intervals and averaged at 15 min intervals. Estimates of total incident UVB and UVA were obtained from the narrow band data using a model described in Morris & Hargreaves (1997). Spectra generated from the model were integrated to estimate daily incident UVB and UVA irradiance. UVB and UVA exposure for each treatment was calculated by multiplying the daily incident irradiance (J m^{-2} nm^{-1} at 1 nm intervals) from the modeled solar spectrum by the transmittance (at 1 nm intervals) of the Plexiglas filters. The UVB and UVA dose received by each treatment over the course of the experiment was calculated by summing the daily irradiance (280 to 320 nm for UVB and 321 to 400 nm for UVA) (Table 1).

Table 1. Light exposure (J m^{-2}) in photochemical degradation experiments UF-5: Q_{PAR}, 400 to 700 nm; UVT + Mylar D: $Q_{PAR+UVA}$, 320 to 700 nm; UVT: $Q_{PAR,UVA+UVB}$, 280 to 700 nm

Plexiglas filter	UVB	UVA	PAR
Swine pasture runoff (Aug 19–22, 1997)			
UF-5	48.5	3230	2 630 000
UVT+Mylar D	33 300	2 500 000	2 630 000
UVT	115 000	2 590 000	2 630 000
Equine pasture runoff (Sep 17–19, 1997)			
UF-5	45.2	3010	2 660 000
UVT+Mylar D	31 100	2 330 000	2 660 000
UVT	108 000	2 420 000	2 660 000
Forest runoff (Oct 7–10, 1997)			
UF-5	41.2	2750	2 690 000
UVT+Mylar D	28 400	2 130 000	2 690 000
UVT	98 100	2 210 000	2 690 000

Microbial degradation experiments. Lability of DOM before and after light exposure was quantified through a series of microbial degradation experiments (Fig. 1). The biological availability of the DOM was determined by changes in the DOC and DON concentration over the course of the experiments. Our first experiment

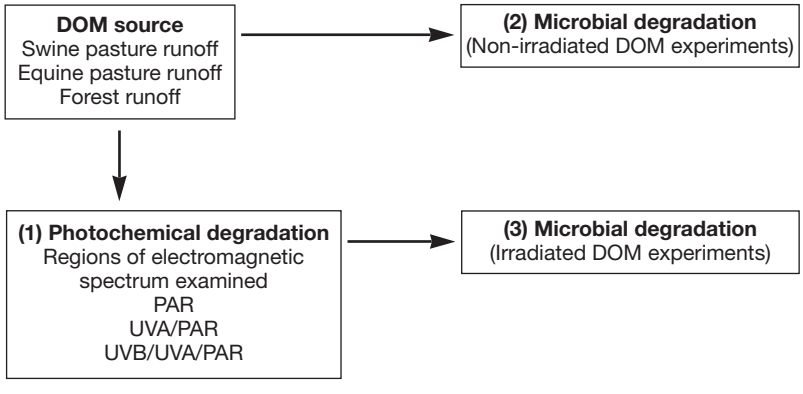

Fig. 1. Experimental design for photochemical and microbial DOM degradation experiments. (1) DOM from non-point source runoff was exposed to different regions of the electromagnetic spectrum using natural sunlight; (2) biological availability of non-irradiated DOM was examined through laboratory microcosm experiments using the same non-point source runoff; (3) further microbial experiments examined how photochemical processes affect DOM biological availability to the microbial community

looked solely at the microbial degradation of DOM (swine and equine pasture and forest runoff; non-irradiated DOM experiment). Our second experiment examined the effect of previous light exposure on the biological availability of DOM (equine pasture and forest runoff; irradiated DOM experiment). In this second experiment, water from the replicate photochemical treatment flasks was combined prior to sterile filtration to ensure that each treatment had the same initial DOC and DON concentrations.

The experimental design for both microbial degradation experiments consisted of adding freshwater bacterial concentrate to sterile filtered runoff (swine, equine, and forest) and control water (DIW) and then monitoring nutrient concentrations and bacterial production in these waters (Seitzinger & Sanders 1997). The runoff and control water were sterile filtered through a DIW-rinsed 0.2 µm Nucleopore filter into a pre-combusted 1 l Erlenmeyer flask. The water was then divided into 2 pre-combusted 500 ml borosilicate Erlenmeyer flasks to which 5 ml of the bacteria concentrate were added to give an initial bacterial abundance of around 10^5 cells ml^{-1} (DAPI staining method: Porter & Feig 1980). Water for the bacteria inoculum was collected from Round Valley Reservoir, New Jersey (40° 36′ 40″ N, 74° 50′ 42″ W), a freshwater source with a bacterial community not endemic to the runoff. The water for the bacteria inoculum was collected and filtered through a DIW-rinsed 0.5 µm string-wound polypropylene canister filter to remove large particles. The inoculum was prepared by concentrating 18 l of the reservoir water to 200 ml using a 10^6 dalton polysulphone filter (tangential flow ultrafiltration; Filtron Technologies) and pulse-sonicating it to remove the remaining protists (Seitzinger & Sanders 1997). The flasks were covered with aluminum foil, gently stirred with Teflon-coated stir bars, and incubated in the dark at 22°C for 10 d. Nutrient samples were analyzed for NH_4^+, NO_3^-/NO_2^-, PO_4^{3-}, DON, and DOC using the procedures described above. Water for nutrient analysis was filtered through pre-combusted, DIW-rinsed GF/F filters and stored frozen at –20°C until analysis. All glassware used for filtering water was acid-washed and muffled at 500°C prior to use.

Bacterial production was measured by ^{3}H-leucine incorporation using a method modified from Smith & Azam (1992). We added 1.7 ml of sample water to sterile 2.0 ml-capacity screw-cap microcentrifuge tubes with o-rings followed by the addition of 5 µl of L-4, 5 ^{3}H-leucine (TRK 510, Amersham, UK; 1 mCi ml^{-1}). The solution of sample water and isotope was mixed well and incubated in the dark at 22°C for 30 min. Blanks for the procedure consisted of 90 µl of 100% trichloroacetic acid (TCA), 1.7 ml sample water, and 5 µl ^{3}H-leucine. Triplicate microcentrifuge tubes were run for each flask and blanks were run for each treatment. The centrifugation, vortex, and wash sequence prescribed in Smith & Azam (1992) was followed with the addition of a final 80% ethanol wash. The microcentrifuge tubes were placed into scintillation vials and radioassayed in a liquid scintillation counter (Beckman LS 6000IC). Measured ^{3}H-leucine incorporation rates were converted to estimates of bacterial biomass production using theoretical conversion factors (Kirchman 1993). The increase in bacterial biomass over the course of the experiment was estimated by plotting the bacterial biomass production rate over the course of the experiment and integrating under the curve. We normalized the integrated bacterial biomass production for each source to its initial DOC concentration in order to compare bacterial biomass production estimates between sources (Meyer et al. 1987, Hopkinson et al. 1998).

Statistical analysis. Changes in the DOC, DON, NH_4^+, NO_3^-/NO_2^-, and PO_4^{3-} concentrations over the course of the photochemical degradation experiments were examined through linear regression analysis (α = 0.05). Differences between light regimes for the photochemical degradation experiments were examined by 1-way analysis of variance (ANOVA; Systat®, 6.0 software; α = 0.10). Power transformations were conducted on data sets in order to satisfy the normality requirement for the ANOVA.

Statistical analyses were performed on the data from the non-irradiated and irradiated DOM microbial experiments where possible. Out of the 110 nutrient time-series measurements made for these experiments, 3 are not included in the data set (Table 2) because of unexplainable variability. Linear regression analysis (α = 0.05) was used to examine the effect of microbial processes on the non-irradiated DOM concentration. ANOVA (Systat®, 6.0 software; α = 0.05) was used to examine differences in the DOM biological availability between runoff sources and photochemical light treatments. Rank-transformations were conducted on data sets in order to satisfy the equality of variance requirement for the ANOVA (Potvin & Roff 1993). Post hoc analyses were performed using the Tukey test (α = 0.05).

RESULTS

Photochemical degradation of DOM

DOC and DON concentrations in the agriculture and forest runoff did not significantly change ($p > 0.05$) over the course of the photochemical experiments in 45 out of the 48 time-series measurements (Fig. 2). The variability seen in both the DOC and DON concentra-

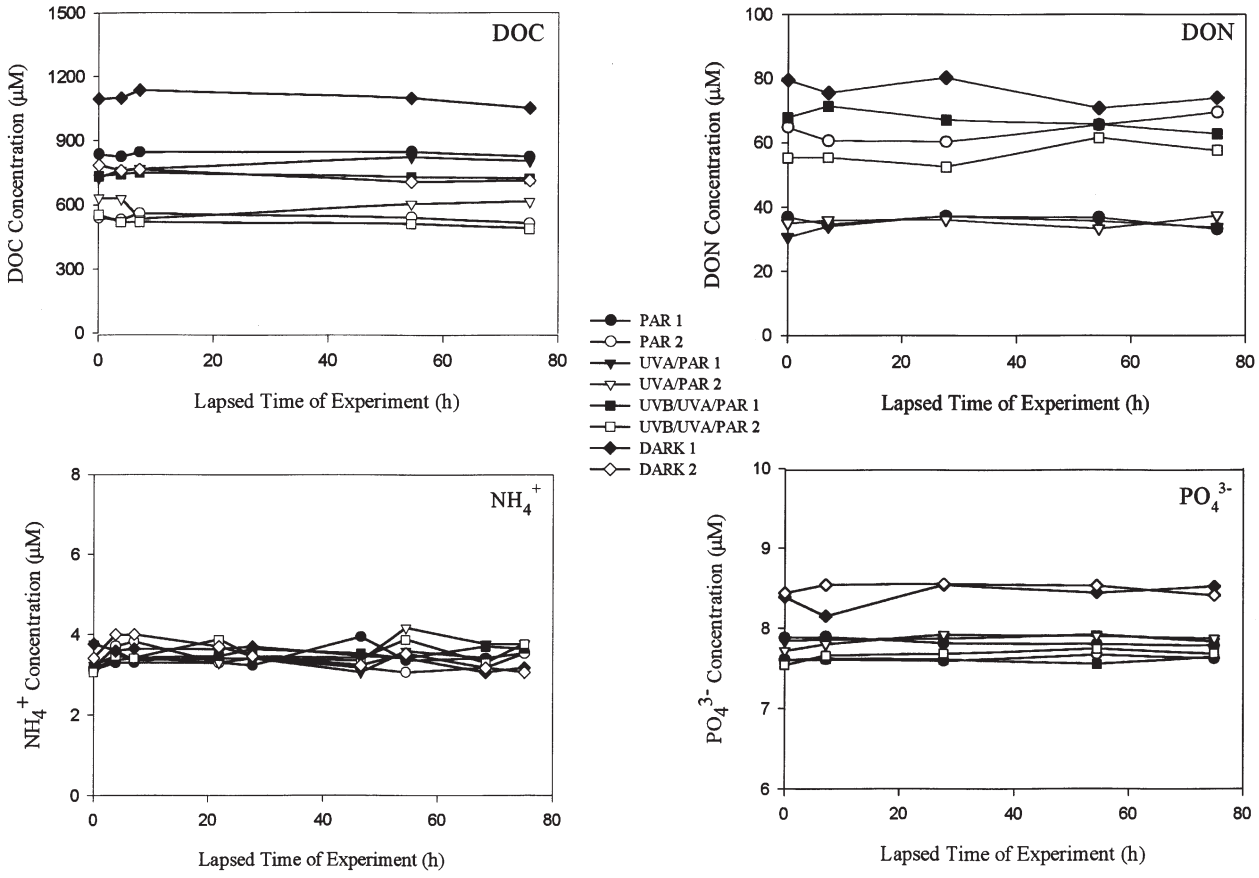

Fig. 2. DOC, DON, NH_4^+, and PO_4^{3-} concentrations in swine pasture runoff from the photochemical degradation experiment. Samples were exposed to 35 h of sunlight over the course of 75 h. Similar patterns for DOC, DON, NH_4^+, and PO_4^{3-} concentrations were seen for the equine pasture and forest runoff

tions during these experiments is similar to the analytical variability associated with the DOC (5%) and DON (10%) methods. The NH_4^+ and PO_4^{3-} concentrations in either the agriculture or forest runoff did not significantly change ($p > 0.05$) during the experiments in 44 out of 48 time-series measurements (Fig. 2). DOC, DON, NH_4^+, and PO_4^{3-} concentrations from the irradiated swine pasture runoff are presented as examples of the patterns observed in the photochemical degradation experiments for all sources (Fig. 2).

In contrast, a small, but significant increase in the NO_3^-/NO_2^- concentration (0.37 to 0.76 µM NO_3^-/NO_2^-) was detected for all light treatments in the irradiated forest runoff (power-transformed, $p = 0.004$) (Fig. 3). No difference was found between light treatments, suggesting that UV did not affect the release of NO_3^-/NO_2^- from the DON. The rate of NO_3^-/NO_2^- production per sunlight hour ranged from 0.016 to 0.021 µM NO_3^-/NO_2^- h^{-1}. The amount of NO_3^-/NO_2^- released over the experiment represents 4 to 9% of the original DON concentration in the forest runoff. This percent change in the DON concentration was not

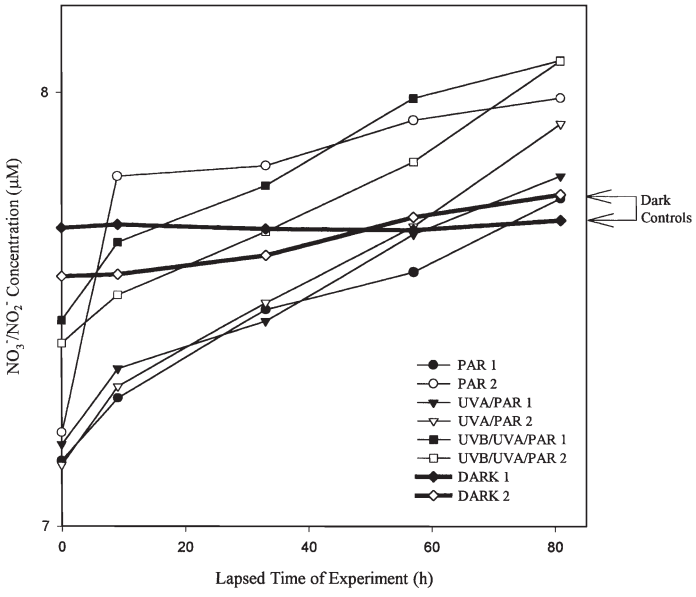

Fig. 3. Photochemical production of NO_3^-/NO_2^- from forest runoff. Samples were exposed to 38 h of sunlight over the course of 75 h

detected, because it was within the range of analytical variability associated with the DON analysis (10%). In the irradiated swine and equine pasture runoff, little or no photochemical release of NO_3^-/NO_2^- occurred.

Microbial degradation of non-irradiated DOM

The microbial community readily utilized the DOM, both the C and N components, from the agriculture and forest runoff (Fig. 4). The bacteria significantly decreased the DOC concentration ($p < 0.05$) in the agriculture and forest runoff; the absolute amount of DOC used by the bacteria ranged from 20 to 70 µM DOC (Table 2). Similar absolute amounts of DOC were consumed in the swine and equine pasture runoff; this amount was at least 2 times greater than the amount used in the forest runoff (Table 2). A similar percent of DOC was consumed in the agriculture and forest runoff; it ranged from 6 to 14% (Table 2). Runoff from the animal pastures and forest supported statistically different amounts of bacterial production per initial µM DOC available ($p = 0.001$; Table 3). Runoff from the equine pasture supported the highest amount of bacterial production per initial µM DOC available, followed by the forest and swine pasture, respectively (Table 3).

In most cases, the microbial community significantly decreased the DON concentration in the agriculture and forest runoff ($p < 0.05$). The absolute amount of DON removed by the bacteria ranged from 2 to 17 µM (Table 2). The percent of DON consumed from the different runoff sources was similar, ranging from 21 to 25% (Table 2).

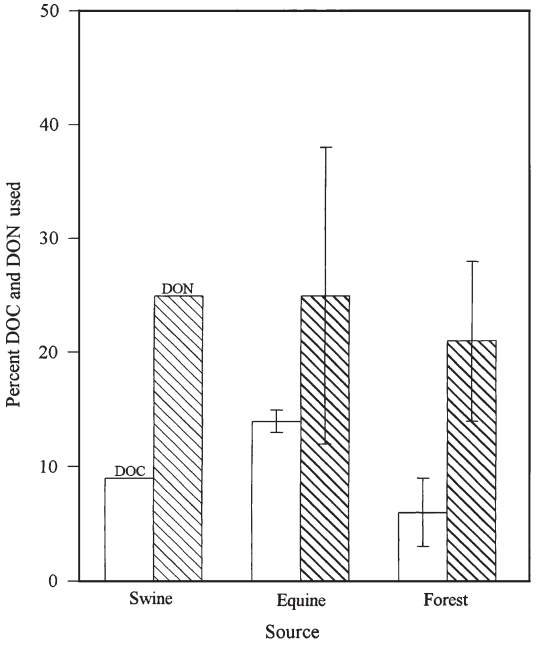

Fig. 4. Microbial degradation of non-irradiated DOC and DON. Degradation is shown as percent of original DOC and DON concentration utilized after 10 d. Data are averages (±SD) for duplicate treatment flasks

Small decreases in the NH_4^+ and PO_4^{3-} concentration were measured over the course of the experiment for the swine pasture, equine pasture, and forest runoff (Table 4). The NO_3^-/NO_2^- increased in the equine pasture runoff and decreased slightly in the swine pasture and forest runoff (Table 4).

Table 2. Microbial utilization (µM) of DOC and DON in non-irradiated and irradiated DOM experiments. Data are averages (±SD) for duplicate treatment flasks. All experiments ran for 10 d

DOM source	Light treatment	DOC			DON			Initial C:N	Final C:N
		Initial conc.	Amount used	% used	Initial conc.	Amount used	% used		
Non-irradiated DOM									
Swine pasture	DARK	642 (±28)	61	9	61 (±12)	17	25	11 (±2)	12
Equine pasture	DARK	487 (±2)	70 (±6)	14 (±1)	47 (±1)	11.5 (±6)	25 (±13)	10 (±0)	19 (±1)
Forest	DARK	346 (±17)	20 (±11)	6 (±3)	15 (±3)	2 (±2)	21 (±7)	24 (±6)	28 (±4)
Irradiated DOM									
Equine pasture	PAR	437 (±23)	24 (±8)	5 (±2)	50 (±9)	4	6	9 (±2)	8
	UVA/PAR	635 (±27)	100 (±36)	16 (±5)	54 (±14)	22 (±8)	44 (±27)	12 (±4)	22 (±15)
	UVB/UVA/PAR	465 (±23)	80 (±29)	17 (±5)	49 (±2)	5 (±5)	11 (±10)	10 (±0)	9 (±1)
	DARK	553 (±3)	89 (±2)	16 (±0)	54 (±8)	13 (±5)	25 (±14)	10 (±2)	12 (±4)
Forest	PAR	293 (±3)	14 (±3)	5 (±1)	7 (±1)	0.9	12	45 (±10)	42
	UVA/PAR	294 (±5)	18 (±3)	6 (±1)	6 (±2)	2.4 (±0.8)	48 (±33)	55 (±20)	144 (±120)
	UVB/UVA/PAR	292 (±1)	27 (±4)	9 (±1)	7 (±0)	1.3 (±0.1)	17 (±1)	41 (±1)	45 (±1)
	DARK	404 (±3)	24 (±3)	6 (±1)	14 (±0)	1.3 (±1.4)	10 (±10)	29 (±1)	31 (±2)

Table 3. Average (±SD) integrated bacterial production (µM bacterial C μM^{-1} DOC) in non-irradiated and irradiated DOM experiments. Bacterial production measurements were normalized to initial concentrations of DOC present in the non-irradiated and irradiated DOM experiments

DOM source	Light treatment	Integrated bacterial production
Non-irradiated DOM		
Swine pasture	DARK	0.09 (±0.003)
Equine pasture	DARK	0.12 (±0.002)
Forest	DARK	0.10 (±0.001)
Irradiated DOM		
Equine pasture	PAR	0.09 (±0.01)
	UVA/PAR	0.10 (±0.01)
	UVB/UVA/PAR	0.15 (±0.06)
	DARK	0.17 (±0.02)
Forest	PAR	0.10 (±0.02)
	UVA/PAR	0.13 (±0.01)
	UVB/UVA/PAR	0.16 (±0.02)
	DARK	0.10 (±0.002)

Microbial degradation of irradiated DOM

Irradiated DOC and DON from the equine pasture and forest runoff were readily used by the microbes (Table 2). In the equine pasture runoff, the absolute amount (rank-transformed; $p = 0.30$) and the percent of DOC consumed (rank-transformed; $p = 0.30$; Table 2) as well as the bacterial production (per initial µM DOC available; rank-transformed; $p = 0.12$; Table 3) were similar for both the light and dark control treatments. On average, the absolute amount of DOC consumed by the bacteria in the equine pasture runoff was 73 (±36) µM; this amount of C constituted 14% (±6) of the initial amount present in the runoff (Table 2). In the forest runoff, the absolute amount ($p = 0.05$) and the percent of DOC consumed (rank-transformed; $p = 0.027$; Table 2) as well as the bacterial production (per initial µM DOC available; $p = 0.05$; Table 3) were significantly different only between the PAR and UVB/UVA/PAR treatments. The absolute amount of DOC consumed in the forest runoff ranged from 14 to 27 µM; this amount comprised between 5 to 9% of the DOC initially present in the runoff (Table 2).

In the irradiated equine pasture runoff, a similar absolute amount and percent of DON was consumed in both the light and dark control treatments (Table 2). A similar pattern was observed for the irradiated forest runoff (Table 2). The variability in the amount and percent of DON consumed in both DOM sources is similar to the variability observed in the non-irradiated DOM experiment (Table 2).

In both the equine pasture and forest runoff, there were generally small decreases in the NH_4^+ and PO_4^{3-} concentration and small increases in the NO_3^-/NO_2^- concentration (Table 4). The NO_3^-/NO_2^- concentration increase in the light treatments in the forest runoff was negligible; the observed change in concentration was below the analytical detection range of the NO_3^-/NO_2^- method. In contrast, similar amounts of NO_3^-/NO_2^- were consumed in the irradiated forest runoff dark control and its counter part in the non-irradiated DOM experiment (Table 4).

DISCUSSION

Role of photochemical degradation

Studies examining photochemical degradation of DOM have primarily concentrated on DOC. Photochemical removal of DOC and production of DIC have

Table 4. Net decreases (–) and increases (µM) in dissolved inorganic nitrogen and dissolved inorganic phosphate in non-irradiated and irradiated DOM experiments. Data are averages (±SD) for duplicate flasks

DOM source	Light treatment	NH_4^+		NO_3^-/NO_2^-		PO_4^{3-}	
		Initial conc.	Net change	Initial conc.	Net change	Initial conc.	Net change
Non-irradiated DOM							
Swine pasture	DARK	3.5 (±0.1)	–1.1 (±0.6)	30.3 (±0.2)	–0.2 (±0.3)	8.3 (±0.0)	–0.3 (±0.1)
Equine pasture	DARK	22.8 (±0.5)	–1.6 (±0.7)	107.9 (±0.5)	2.4 (±2.2)	1.6 (±0.0)	–0.4 (±0.0)
Forest	DARK	1.0 (±0.3)	–0.8 (±0.3)	7.5 (±0.1)	–0.4 (±0.1)	0.9 (±0.0)	–0.2 (±0.0)
Irradiated DOM							
Equine pasture	PAR	25.6 (±0.0)	–1.7 (±0.1)	105.7 (±2.1)	0.5 (±3.7)	1.0 (±0.1)	–0.2 (±0.0)
	UVA/PAR	28.5 (±0.0)	–3.7 (±0.6)	108.7 (±0.5)	2.0 (±1.0)	1.2 (±0.1)	–0.3 (±0.0)
	UVB/UVA/PAR	25.3 (±0.3)	–0.02 (±0.9)	104.4 (±1.8)	5.1 (±1.3)	1.3 (±0.1)	–0.4 (±0.2)
	DARK	25.8 (±1.2)	–1.4 (±1.5)	107.2 (±0.8)	3.1 (±0.9)	1.2 (±0.2)	–0.2 (±0.2)
Forest	PAR	0.2 (±0.0)	–0.04 (±0.1)	8.0 (±0.1)	0.04 (±0.0)	0.7 (±0.0)	–0.1 (±0.0)
	UVA/PAR	0.5 (±0.0)	–0.2 (±0.1)	7.9 (±0.0)	0.2 (±0.1)	0.7 (±0.0)	–0.2 (±0.0)
	UVB/UVA/PAR	0.9 (±0.1)	–0.6 (±0.1)	8.1 (±0.1)	0.02 (±0.1)	0.7 (±0.0)	–0.1 (±0.0)
	DARK	0.4 (±0.0)	0.03 (±0.0)	7.8 (±0.1)	–0.5 (±0.2)	0.9 (±0.0)	–0.2 (±0.0)

Table 5. Photochemical removal of DOC from aquatic environments under natural sunlight

Location	Initial DOC (µM)	Light treatment	Sunlight (h)	% DOC removed	Source
Rivers					
Canadian headwater streams	725–1500	UVB/UVA/PAR	108	24–50	Molot & Dillon (1997)
Rio Negro, Amazon	780–833	UVB/UVA/PAR	4–27	2–15	Amon & Benner (1996b)
Rio Solimóes, Amazon	271	UVB/UVA/PAR	6	2	Amon & Benner (1996b)
Lakes					
Humic pond water, Norway	1000	UVB/UVA/PAR	78	24–31	Hongve (1994)
Clear and humic lakes, Sweden	325–1620	UVB/UVA/PAR	18	1.7–3.7	Granéli et al. (1996)
Lake Lacawac, USA	450	UVB/UVA/PAR	84	20	Morris & Hargreaves (1997)
Lake Wagnewood, USA	475	UVB/UVA/PAR	84	17	Morris & Hargreaves (1997)
Lake Giles, USA	133	UVB/UVA/PAR	84	0	Morris & Hargreaves (1997)
Other					
Nordic fulvic acid	1833	UVB/UVA/PAR	78	22–32	Hongve (1994)
Algal DOC	17	UVB/UVA/PAR	8	0.2	Tranvik & Kokalj (1998)
Swine pasture runoff	552–734	UVB/UVA/PAR	35	0	This study
Equine pasture runoff	560–605	UVB/UVA/PAR	21.5	0	This study
Forest runoff	271–308	UVB/UVA/PAR	38	0	This study

been reported for environments spanning lakes to estuaries (Tables 5 & 6). Photochemical removal of DOC in these environments ranges from 0 to 50% under natural sunlight (Table 5) and up to 60% using artificial light sources (Table 6). The range in photochemical removal of DOC may result from the use of different DOC and light sources (spectral light distribution and intensity), as well as length of light exposure. Photochemical production of DIC has also been reported to occur with little or no change in the DOC concentration in high-carbon waters (Granéli et al. 1996, Jørgensen et al. 1998). This situation can occur when the amount of DOC photochemically degraded to DIC is much smaller than the amount of DOC originally present in the water. In our experiment, DOC may have been photochemically degraded to DIC; however, the amount of DOC degraded may have been too small for our DOC analysis to detect against the high DOC concentration background (271 to 734 µM DOC).

Large DOC molecules can also be photochemically broken down into small organic compounds such as low molecular weight carbonyls, urea, amino acids, and carbohydrates (Kieber et al. 1990, Wetzel et al. 1995, Jørgensen et al. 1998). The DOC in our study may have been photochemically broken down into

Table 6. Photochemical removal of DOC from aquatic environments under artificial sunlight sources. nd: value not reported in this paper

Location	Initial DOC (µM)	Light treatment	Exposure time (h)	% DOC removed	Source
Rivers					
Suwanee River, USA	4100–5150	UVB/UVA/PAR	0.8	0.6–0.8	Miller & Zepp (1995)
Lakes					
Rådasla, Sweden (surface)	833	254 nm	30	20–60	Allard et al. (1994)
Lake Savojärvi, Finland	1417–1767	254 nm	1–4	0–22	Backlund (1992), Corin et al. (1996)
Lake Savojärvi, Finland	1717	UVB/UVA/PAR	168	60	Kulovaara & Backlund (1993)
Lake Bjän, Sweden	1325	UVA	89	4	Dahlén et al. (1996)
Coastal					
Gulf of Mexico	170	UVB/UVA/PAR	2.2–17.6	0.7–4	Miller & Zepp (1995)
Saplo Island Marsh, USA	500	UVB/UVA/PAR	2.2–89.9	2–7	Miller & Zepp (1995)
Other					
Aldrich soil humic acid	667	254 nm	60	57	Allard et al. (1994)
Aged algal DOC	nd	300–400 nm	15	0	Thomas & Lara (1995)
Nordic fulvic acid	5500–25000	254 nm	80	24	Corin et al. (1996), Kulovaara et al. (1996)
Nordic humic acid	10417	254 nm	80	35	Corin et al. (1996), Kulovaara et al. (1996)

smaller organic compounds, but our measurements of DOC did not distinguish between small and large DOC molecules. However, the biological availability of the DOC in our equine pasture and forest runoff did not change after being exposed to light.

Less is known about what happens to the N component when DOM is exposed to light. Studies to date have reported the photochemical release of NH_4^+, NO_2^-, and small organic nitrogen compounds (Bushaw et al. 1996, Gardner et al. 1998, Jørgensen et al. 1998, Bushaw-Newton & Moran 1999, Kieber et al. 1999). During our photochemical experiments, there was little or no change in either the DON or NH_4^+ concentration for any of the sources (Fig. 2). Other studies have also reported no significant changes in the DON or NH_4^+ pool after sunlight exposure (Jørgensen et al. 1998, Bertilsson et al. 1999), but in some cases they have detected an increase in the urea and free amino acids concentration (Jørgensen et al. 1998). DON from our sources may have been broken down into smaller organic nitrogen compounds; however, its lability was not altered by light exposure (Table 2).

Photochemical reactions involving NO_3^- and NO_2^- are well established. In these reactions, NO_3^- can be photochemically reduced to NO_2^- and nitric oxide (NO) by ultra-violet radiation, resulting in either no net change or a decrease in the NO_3^-/NO_2^- pool (Zafiriou & True 1979a,b). Increases in the combined NO_3^-/NO_2^- pool in the irradiated (all light treatments) forest runoff suggest that this process was not responsible for the observed pattern. Recent work has demonstrated that NO_2^- may be photochemically released from the nitroalkenes in the humic substances through oxidation by singlet oxygen under natural sunlight (Kieber et al. 1999). This process may provide a mechanism for the increased concentration of NO_3^-/NO_2^- seen in the forest runoff experiment (Fig. 3). The rate of NO_3^-/NO_2^- increase in our photochemical experiment ranged from 0.016 to 0.021 µM NO_3^-/NO_2^- h^{-1}, which was on average 4 to 5 times higher than the reported rate for nitrite production from humic substances (0.0014 to 0.0067 µM NO_2^- h^{-1}: Kieber et al. 1999). The difference in NO_3^-/NO_2^- production rates from these 2 studies may result from the use of different organic matter sources, light distributions, and light intensities.

Phosphate can also be photochemically released from DOM. UV radiation reduces iron complexes that bind PO_4^{3-} to humic substances, releasing PO_4^{3-} into the surrounding environment (Francko & Heath 1982). In our experiment, there was no measurable change in the PO_4^{3-} concentration, suggesting that any PO_4^{3-} bound to humic substances in our water was not photochemically released (Fig. 2).

Role of microbial degradation of DOM

The extent to which bacteria are degrading and incorporating allochthonous DOC into the biological cycle is becoming more readily recognized. DOC lability has been measured for a variety of DOM sources including point and non-point sources, rivers, lakes, estuaries, and the open ocean (Table 7). From 0 to 75% of the DOC in these environments has been shown to be labile to bacteria (Table 7); the percent of DOC consumed in our experiments ranged from 6 to 14% (Table 2).

From an ecosystem perspective, it is not only important to quantify how much DOC is removed by microbial processes, but also how much is incorporated into the microbial food web and higher trophic levels. One factor that has been demonstrated to affect the amount of DOC incorporated into bacterial biomass is DOM chemical composition (Sun et al. 1997, Hopkinson et al. 1998). In our study, the bacterial production supported by the DOC in the agriculture and forest runoff (Table 3) was not solely a function of the initial amount of DOC available or the absolute amount consumed (Table 2). These results suggest that there were qualitative differences between the DOC in the swine, equine, and forest runoff. Future research will help to more clearly define these patterns and provide data to develop a model to predict bioavailable DOC in a river based on its watershed's land-use distribution.

The biological availability of the nitrogen component in DOM has been measured in a few types of water: rain (Timperley et al. 1985, Peierls & Paerl 1997, Seitzinger & Sanders 1999), river (Carlsson et al. 1993, 1999, Seitzinger & Sanders 1997), estuarine (Glibert et al. 1991, Bronk & Glibert 1993), and wetland (Stepanauskas et al. 1999). The percent of DON degraded in these waters ranges from 0 to 75%, which parallels or supersedes that of DOC (Table 8). In our study, a similar percent of DON was degraded for all DOM sources (Table 2). This result suggests that DON from all 3 sources was equally labile.

There appeared to be a trend of higher percent DON utilization by the bacteria relative to the DOC in the agriculture and forest runoff (Fig. 4). Several biological processes may result in higher utilization of DON relative to DOC; these include enzymatic cleavage of N-containing functional groups in the DOM molecule, selective decomposition of whole N-rich molecules within the DOM mixture, and/or selective cleaving of the DOM molecule at the N component of the ring structure and preferential digestion of this component first. Our results suggest that N and C in DOM may be cycling at different rates in the aquatic environment. The preferential utilization of N relative to C may result in the export of N-deplete allochthonous DOM from rivers to estuaries.

Table 7. Microbial degradation of DOC in aquatic environments. nd: value not reported in this paper

Location	Initial DOC (µM)	Length of experiment (d)	% DOC utilized	Source
Point and non-point sources				
Brussels' main sewage collector, Belgium	1050	15	43	Servais et al. (1987)
Windermere Basin (Lake Ontario), Canada	1683	12	75	Markosova (1991)
STELCO Plant (Lake Ontario), Canada	1392	12	57	Markosova (1991)
Rivers				
Tamagawa River, Japan	750	30	67	Ogura (1975)
Vistula River, Poland	600–783	90	23–36	Pempkowiak (1985)
Forest River, Belgium	150	15	11	Servais et al. (1987)
Meuse River, Belgium	291–412	15–28	19–34	Servais et al. (1987, 1989)
Scheldt River, Belgium	738–1108	15–28	17–59	Servais et al. (1987, 1989)
Rupel River, Belgium	625–942	28	26–54	Servais et al. (1989)
Coweeta Hydrological Laboratory, USA	500	134	25.8	Qualls & Haines (1992)
Seine River, France	nd	30	50–61	Servais & Garnier (1993)
Savannah River, USA	267–358	35–58	6.5–17.7	Moran et al. (1999)
Ogeechee River, USA	317	35	7	Moran et al. (1999)
Altamaha River, USA	258–267	35–58	6–7.3	Moran et al. (1999)
Satilla River, USA	275–2117	35–98	1.7–8.8	Moran et al. (1999)
St. Marys River, USA	350	35	8.3	Moran et al. (1999)
Lakes				
Danish lakes	100–1250	10–21	8–53	Søndergaard (1984), Søndergaard & Borch (1992)
Bog lakes, Japan	916	90	16–41	Satoh & Abe (1987)
Humic lakes, Sweden	1558–2567	7	7–11	Tranvik (1988)
Clear water lakes, Sweden	408–1400	7	5.9–13.7	Tranvik (1988)
Lake Ontario, Canada	1000	12	66	Markosova (1991)
Estuarine/coastal				
Woods Hole Harbor, USA	350	30	48–50	Barber (1968)
Sagami Bay, Japan	167	40	55	Ogura (1975)
Tokyo Bay, Japan	133–256	40–41	22–60	Ogura (1975)
Baltic Sea, Poland	417–475	90	30–43	Pempkowiak (1985)
Schelds Estuary, Belgium	494	15	25	Servais et al. (1987)
Belgian coastal zone	223	15	30	Servais et al. (1987)
Elorn Estuary, France	62.5–333	240	22–34	Aminot et al. (1990)
Roskilde Fjord, Denmark	567–683	28	15	Middelboe et al. (1992)
North Zealand coast	383–442	28	11–18	Middelboe et al. (1992)
Northern Bothnian Sea	320	5	7	Zweifel et al. (1993)
Open ocean				
North Atlantic (36° 54′ N, 68° 11′ W)	300	60	0	Barber (1968)
North Equatorial Pacific	80	50	23	Ogura (1972)

Table 8. Microbial degradation of DON in aquatic environments

Location	Initial DON (µM)	Length of experiment (d)	% DON utilized	Source
Rivers				
Delaware River, USA	12.9–46.5	8–15	40–72	Seitzinger & Sanders (1997)
Hudson River, USA	33.5	10	40	Seitzinger & Sanders (1997)
Rain				
Philadelphia, USA	17	8–9	46–75	Seitzinger & Sanders (1999)
Wetlands				
Amboke, Sweden	16–32	6–14	0–6.1	Stepanauskas et al. (1999)
Vomb, Sweden	13–109	6–14	0–1.5	Stepanauskas et al. (1999)
Isgrannatorp, Sweden	176–180	6–14	0.7–1.4	Stepanauskas et al. (1999)

Effects of light exposure on DOM lability

Light exposure did not consistently alter DOC lability in the equine pasture and forest runoff. Light exposure did not affect the biological availability of the DOC in the equine pasture runoff (Table 2). Research to date has shown that exposure of DOC to light has contrasting effects on its biological availability to bacteria (Benner & Biddanda 1998, Obernosterer et al. 1999). Exposure of DOC to sunlight has been shown to enhance, inhibit, and not change the bacterial consumption of the DOC (Lindell et al. 1995, Wetzel et al. 1995, Naganuma et al. 1996, Miller & Moran 1997, Tranvik & Kokalj 1998). These contrasting effects of sunlight exposure may result from differences in the DOC and bacterial community composition, as well as in the type of light (intensity and spectral distribution) used in these experiments.

In the forest runoff, the DOC exposed to PAR had a lower lability than the DOC exposed to UVB/UVA/PAR (Table 2). It is not clear why the DOC exposed to PAR had a lower biological availability compared to the UVB/UVA/PAR treatment, but not the other light treatments and the dark control. Radical production (i.e. hydrogen peroxide) from DOM may have altered its structure and lability by forming side chains and ring products (Mill et al. 1980); however, the likelihood that this mechanism altered the DOC lability in the PAR treatment is small. Previous studies have found that UV wavelengths are primarily responsible for radical production (Mopper & Zhou 1990, Scully et al. 1996). The fact that PAR was also present in the other light treatments where the DOC lability did not differ from the dark control suggests that PAR may have not directly affected the DOC lability (Table 2). The low DOC lability observed in the PAR treatment is also not likely to have been an artifact of not mixing the runoff after ultrafiltration, since the initial DOC concentration in the PAR and UVB/UVA/PAR treatments were similar, suggesting that they were collected at comparable times during ultrafiltration.

The biological availability of DON in the equine pasture and forest runoff also was not affected by light (Table 2). The amount and the percent of DON consumed in the light and dark treatments were comparable for both sources (Table 2). Other studies have suggested that light exposure enhances DON lability; however, such studies did not directly measure the consumption of irradiated DON (Bushaw et al. 1996, Jørgensen et al. 1998, Bushaw-Newton & Moran 1999). Their increased DON lability has been inferred from the fact that measured photochemical N products (amino acids and NH_4^+) could not support the measured increase in bacterial production and abundance (Bushaw et al. 1996, Jørgensen et al. 1998, Bushaw-Newton & Moran 1999). The contrasting effects of sunlight on DON bioavailability are not surprising, given the contrasting effects seen with DOC.

DOM in rivers

Both photochemical and microbial processes have been shown to affect the amount and the rate at which DOC and DON are incorporated into the aquatic biological cycle (Wetzel et al. 1995, Bushaw et al. 1996, Miller & Moran 1997, Jørgensen et al. 1998, Bushaw-Newton & Moran 1999). In our study, we found that microbial processes are more effective at degrading DOC and DON from agricultural and forest runoff than photochemical ones. Our DOC results from photochemical and microbial experiments are consistent with the previous findings in the literature (Miller & Moran 1997). On average, photochemical (natural sunlight) and microbial degradation remove 11 ± 10% (Table 5) and 27 ± 17% (Table 7) of the DOC from different source waters, respectively. In our study, microbial processes removed 6 to 14% of the DOC from the agriculture and forest runoff (Table 2). Photochemical processes removed little to no DOC in either the agriculture or forest runoff (Fig. 2). As for DON, the microbes removed 21 to 25% of the DON from the runoff (Table 2); photochemical processes, at most, removed 4 to 9% of the DON through the release of NO_3^-/NO_2^- (Fig. 3). Exposing the DOC and DON in the equine pasture and forest runoff to light did not change their biological availability.

In the river environment, UV-driven photochemical processes are primarily limited to the near-surface waters, whereas microbial processes take place almost everywhere. Even under ideal conditions for photochemical processes like those found in riverine surface waters, photochemical processes had little to no effect on the concentration and bioavailability of the DOM from our sources. On the same time scale, microbial processes removed up to 14 and 25% of the DOC and DON from our source waters, respectively. In the context of the river, our results suggest that microbial processes may be more efficient at removing DOM than photochemical ones, and more important in affecting the quantity and quality of DOM exported from rivers to estuaries.

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