

The significance of dissolved organic matter photodegradation as a source of ammonium in natural waters

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Abstract

Samples of sea, river and pond water of different absorbance were exposed to artificial radiation resembling sunlight in the UV range. A statistically significant increase in ammonium concentration was detected in pond water of the highest absorbance after 5 h of irradiation. In sea and river water a corresponding increase ($< 0.5 \mu\text{M}$) was recorded after an exposure time of 25 hours. The bulk characteristics of the analysed samples were insufficient to explain the observed differences.

1. Introduction

Sunlight-induced degradation of dissolved organic matter (DOM) results in the formation of organic and inorganic products. These include CO, CO₂ and other forms of dissolved inorganic carbon (Graneli et al. 1996, Bertilsson et al. 1999). Investigations into photodegradation as a source of inorganic nitrogen in aquatic environments were initiated by Bushaw et al. (1996), who reported ammonium release following natural and artificial irradiation of organic matter from different environments. Several papers containing the results of experiments with photoammonification were subsequently published. However, the information accumulated so far is in some cases contradictory.

The results published hitherto were obtained in experiments with samples of extraordinarily high absorbance collected from ponds and swamps (Bushaw et al. 1996), forest runoff (Weigner & Seitzinger 2001)

and 'black water' rivers (Gao & Zepp 1998, Wang et al. 2000). The present study contains the first results of photodegradation experiments with coastal, riverine and pond waters, the absorbance of which is lower and more representative of natural waters. The aim was to see whether photoinduced ammonium release was detectable in water of more 'typical' spectral characteristics and if so, to assess the environmental significance of this phenomenon. The irradiations were done using a solar simulator with a spectral output comparable to that of sunlight in the UV range.

2. Material and methods

The natural water samples used in the irradiation experiments were collected in October and November 2000. Sea water was sampled in the inner part of the Gulf of Gdańsk, approximately 10 km NE of Gdynia at 10–15 m depth from on board r/v 'Oceanograf' using a 5 dm³ PVC Niskin bottle. The river water samples were collected from the Vistula some 4 km upstream of the mouth, and the pond water from a pool situated in coniferous woodland. The freshwater was collected early in the morning by submerging an open polyethylene container. The unfiltered samples were left for a few days in glass carboys in daylight at room temperature ($\sim 20^{\circ}\text{C}$). After that they were filtered gravitationally through Whatman GF/F filters ($\sim 0.7 \mu\text{m}$ pore size). The next filtration, for bacteria removal, was performed twice using a vacuum pump and Millipore filters ($0.2 \mu\text{m}$ pore size).

Prior to the experiments, all glassware and Whatman filters were muffled overnight at 450°C and rinsed with distilled water. The Millipore filters were thoroughly rinsed with distilled water.

Absorbance measurements were done on a Perkin-Elmer Lambda 3B dual-beam spectrophotometer with Milli-Q water as reference. The measurements were made in 100 mm matched quartz cells.

The dissolved organic carbon (DOC) concentration was determined in Whatman GF/F filtered samples. Prior to analysis the samples were acidified to $\text{pH} = 2\text{--}3$ (HCl – Merck, Suprapure) and purged with high-purity nitrogen for 5 min. DOC was analysed in a Shimadzu Total Organic Carbon Analyser (model 5000) with the quartz furnace tube filled with a highly sensitive platinum catalyst. The volume injected was 0.100–0.250 ml, 3 to 4 injections being made for each sample. The standards used in the measurements were prepared in Milli-Q water using reagent grade potassium hydrogen phthalate. The calibration curve was determined before each series of measurements by a four-point calibration. The results were calculated from the peak areas.

The following analytical methods were used for the nutrient concentrations: nitrites and nitrates by the Bendschneider and Robinson method (nitrates were reduced to nitrites on copperised cadmium prior to analysis), dissolved organic nitrogen by subtracting the sum of inorganic nitrogen compounds from the nitrate concentration measured in the persulphate-oxidised, filtered sample, and the ammonium concentration using Koroleff's blue indophenol method (Grasshoff et al. 1983). The calibration curves were prepared in Milli-Q water. Apart from the natural water samples, a blank and one standard were also analysed. The final results were the average of at least three measurements. The detection limit of ammonium (defined according to IUPAC as the triple standard deviation of the blank) ranged from 0.03 to 0.08 μM .

Filtered samples were exposed to simulated sunlight in quartz tubes closed with ground-glass stoppers without any headspace. The closed tubes were cooled before opening to prevent any loss of gaseous ammonia. The inner diameter of the tubes was 9 mm, the sample volume was 50 ml. The tubes were immersed horizontally in a shallow water bath. The blank sample was additionally covered with aluminium foil. The radiation source was a set of eight parallel fluorescent tubes. The spectral composition of the light resembled solar radiation within the photochemically significant UV range. The radiation intensity was adjusted by altering the distance between the lamp and samples so as to reproduce the solar UV radiation on a sunny day in northern Poland. The intensity in the 280–320 nm bandwidth was determined with an Eijkelpamp SKU 430 sensor and was constant throughout the experiments.

3. Results

The samples used in the irradiation experiments were described by bulk characteristics, including DOC, DON and the absorption coefficient calculated as $a = 2.303 A l^{-1}$, where A is the spectrophotometer absorbance readout and l is the cuvette length in metres. The absorption coefficient at 350 nm wavelength was chosen because this value is used in most of the published studies on photoammonification.

The DOC concentrations in pond water samples were five times greater than the lowest concentrations detected in seawater. The DON content in freshwater samples was comparable, and again, the lowest values were measured in seawater. The range of absorbance values in the samples exceeded one order of magnitude (Table 1). The coloration of organic matter dissolved in the water analysed (expressed as the absorbance per unit of DOC) differed less; the DOC-normalised absorbance of sea water was approximately half that of freshwater.

Table 1. Bulk characteristics of natural water samples used in irradiation experiments

Sample Code	Dissolved organic carbon DOC [mM]	Dissolved organic nitrogen DON [mM]	Absorption coefficient at 350 nm- A_{350} [m ⁻¹]	A_{350}/DOC [nM m ⁻¹]
sea water A	0.52 ± 0.02	0.02 ± 0.01	1.8	3.46
sea water B	0.48 ± 0.03	0.02 ± 0.01	2.1	4.37
sea water C	0.51 ± 0.02	0.03 ± 0.01	1.6	3.13
river water A	1.16 ± 0.04	0.06 ± 0.01	7.8	7.93
river water B	1.05 ± 0.02	0.05 ± 0.01	8.2	7.80
river water C	1.02 ± 0.04	0.04 ± 0.01	8.1	7.94
river water D	0.98 ± 0.02	0.04 ± 0.01	7.1	7.24
pond water A	–	0.04 ± 0.01	21.2	–
pond water B	2.82 ± 0.04	0.05 ± 0.01	23.6	8.36
pond water C	2.60 ± 0.04	0.05 ± 0.01	22.6	8.69

Table 2 contains the results of experiments in which different natural water samples were irradiated. The values are the mean ammonium concentrations measured in 3 or 4 quartz tubes; there were as many irradiated samples as blanks. The significance of the differences between irradiated and blank samples was determined for mean values measured at the end of the irradiation period. Since the intensity of radiation was constant, the irradiation time reflects the radiation dose absorbed by the sample.

The precision of ammonium concentration measurement within the sets of sub-samples (both blank and irradiated) decreased with time. The higher standard deviation observed in the exposed set suggests that one of the reasons for this could have been a difference in the received radiation dose.

During irradiation, a measurable increase in ammonium concentration was detected after 25 h in the sea and river water samples: this did not exceed $\sim 0.5 \mu\text{M}$ and was higher in the river water. The concentration remained practically unchanged after the next 25 h. In contrast to sea and river water samples, the irradiation of pond water resulted in observable photoammonification already after 5 h. The overall increase was up to 5 times higher than that observed in river and sea water samples. In this case the doubled radiation dose (exposure time) resulted in a higher ammonium concentration.

The photo-produced ammonium represented less than 1% of DON in sea and river water but was as high as 2.5% in pond water.

Table 2. Mean concentrations (\pm SD) of NH_4^+ in samples of natural waters irradiated and unexposed to light (blank); the statistically significant differences ($p < 0.05$) are given in bold

Sample code and number of replicates	Initial concentration [μM]	Irradiation time [h]				
		5		10		
		Blank	Irradiated	Blank	Irradiated	
		[μM]				
s. w. A	n = 4	0.09 \pm 0.06	0.11 \pm 0.05	0.08 \pm 0.10	0.11 \pm 0.08	0.14 \pm 0.11
s. w. B	n = 4	0.04 \pm 0.05	0.08 \pm 0.04	0.11 \pm 0.05	0.13 \pm 0.06	0.16 \pm 0.11
s. w. C	n = 3	0.16 \pm 0.03	0.21 \pm 0.08	0.29 \pm 0.11	0.14 \pm 0.11	0.23 \pm 0.18
r. w. A	n = 4	0.07 \pm 0.06	0.11 \pm 0.07	0.04 \pm 0.09	0.14 \pm 0.06	0.08 \pm 0.05
r. w. B	n = 3	0.15 \pm 0.09	0.06 \pm 0.05	0.12 \pm 0.06	–	–
r. w. C	n = 3	0.30 \pm 0.07	0.28 \pm 0.06	0.26 \pm 0.12	0.22 \pm 0.10	0.34 \pm 0.14
r. w. D	n = 4	0.08 \pm 0.06	–	–	0.16 \pm 0.08	0.09 \pm 0.08
p. w. A	n = 4	0.26 \pm 0.06	0.32 \pm 0.04	1.20 \pm 0.15	0.35 \pm 0.14	1.10 \pm 0.24
p. w. B	n = 3	0.41 \pm 0.04	0.64 \pm 0.11	0.88 \pm 0.04	0.54 \pm 0.15	0.90 \pm 0.18
p. w. C	n = 3	0.25 \pm 0.04	0.41 \pm 0.08	0.60 \pm 0.08	0.22 \pm 0.11	0.73 \pm 0.20
			25		50	
			Blank	Irradiated	Blank	Irradiated
			[μM]			
s. w. A	n = 4	0.09 \pm 0.06	0.13 \pm 0.10	0.32 \pm 0.04	0.08 \pm 0.09	0.29 \pm 0.12
s. w. B	n = 4	0.04 \pm 0.05	0.08 \pm 0.09	0.26 \pm 0.05	0.13 \pm 0.11	0.29 \pm 0.11
s. w. C	n = 3	0.16 \pm 0.03	0.16 \pm 0.14	0.37 \pm 0.15	0.22 \pm 0.09	0.44 \pm 0.18
r. w. A	n = 4	0.07 \pm 0.06	0.11 \pm 0.08	0.38 \pm 0.19	0.14 \pm 0.11	0.62 \pm 0.22
r. w. B	n = 3	0.15 \pm 0.09	0.15 \pm 0.14	0.62 \pm 0.11	0.09 \pm 0.08	0.76 \pm 0.11
r. w. C	n = 3	0.30 \pm 0.07	0.22 \pm 0.13	0.54 \pm 0.14	0.26 \pm 0.12	0.54 \pm 0.15
r. w. D	n = 4	0.08 \pm 0.06	0.14 \pm 0.11	0.35 \pm 0.15	0.18 \pm 0.10	0.42 \pm 0.17
p. w. A	n = 4	0.26 \pm 0.06	0.16 \pm 0.11	1.24 \pm 0.24	0.29 \pm 0.12	1.53 \pm 0.19
p. w. B	n = 3	0.41 \pm 0.04	0.32 \pm 0.18	1.12 \pm 0.24	0.62 \pm 0.14	1.62 \pm 0.15
p. w. C	n = 3	0.25 \pm 0.04	0.08 \pm 0.16	0.97 \pm 0.25	0.11 \pm 0.11	1.42 \pm 0.23

s. w. – sea water, r. w. – river water, p. w. – pond water.

4. Discussion

The number of irradiation experiments in this study was insufficient to obtain a statistically significant correlation between their bulk characteristics and ammonium photo-production. Thus, only tentative conclusions can be drawn, principally because the content of the dissolved organic nitrogen in the sample does not appear to influence photo-induced ammonium release. This is evident in sea and pond water of comparable DON concentration. Moreover, photoammonification in seawater is about

5 times lower than that in pond water, while the respective DON ratio is approximately 1:2. DOC coloration, expressed as the absorbance per unit of DOC, was comparable in all freshwater samples, which may suggest a qualitative affinity.

The increases in ammonium concentration presented in Table 2 were caused by a very high radiation intensity, typical of the thin, surface layer of the water column. Such a situation may occur in the river-sea contact zone, where the freshwater layer spreads over the surface of the denser seawater. However, it can't happen that a particular 'parcel' of water will remain at the surface for a long time. As far as the environmental relevance of the experiment is concerned, the effects of long-term irradiation appear to be of limited significance. Thus, the compilation of photo-production rates available in the literature and presented in Table 3 was limited to rates calculated for an exposure time of no longer than 10 hours.

The samples analysed in this study had the lowest absorbance among those values published so far. This may be the reason for no measurable photoammonification in the initial stage of the irradiation of lake and coastal water and the comparatively low production rate measured in pond water. However, analysis of the published results suggests that the relationship between absorbance and photo-production is far from definite. First of all, the range of reported production rates is surprisingly high, considering the limited variability of absorbance values. For example, a water sample of 2-fold greater absorbance shows a ~ 20 fold higher production rate (Bushaw et al. 1996 vs Koopmans & Bronk 2002). Moreover, there are cases when irradiation of a sample of lower absorbance (and DON content) results in a higher production rate (Wang et al. 2000 vs Gao & Zepp 1998, Koopmans & Bronk 2002). The interpretation of the published results is further complicated by reports where no ammonium photo-production was observed in samples of high absorbance and DON content (Bertilsson et al. 1999, Weigner & Seitzinger 2001). To some extent, these discrepancies are likely to be due to differences in the experimental set-ups, so any comparison of the results in this study with those available in the literature should be treated with caution.

There was no measurable increase in ammonium in coastal and river samples for exposure times of up to one day. These results stand in contrast to those obtained by Bushaw et al. (1996), Gao & Zepp (1998) and Wang et al. (2000). Moreover, there was no relationship between photo-production and absorbance as observed by Bushaw et al. (1996). As emerges from Table 2, irradiation of river water with an absorbance ~ 3 -fold lower than that of pond water did not result in a correspondingly lower photo-production detectable within the available limits of precision.

Table 3. Photo-induced ammonium release from natural dissolved organic matter, observed during irradiation times up to 10 h (* rates calculated using data contained in the respective paper, + rates reported for the overall exposure time)

Ammonium photoproduction rate [$\mu\text{M h}^{-1}$]	Irradiation conditions	Absorption coefficient at 350 nm [m^{-1}]	Dissolved organic nitrogen DON [μM]	Dissolved organic carbon DOC [μM]	Sample source	Reference
0.36 ⁺	artificial, >320 nm UVB (overall exposure time 36 h)	–	74	–	Suwannee River	Bushaw et al. 1996
0.34 ⁺	artificial (overall exposure time 18 h)	106*	86	3840	Okefenokee swamp ph = 3.9	Bushaw et al. 1996
0.058	natural (overall exposure time 7 h)	86	34	2200	concentrate of Satilla River Estuary humic substances (2.8 \times)	Bushaw-Newton & Moran 1999
0.1	artificial (overall exposure time 4 h)	94	40	2100	Satilla River	Gao & Zepp 1998
0.018*	artificial (overall exposure time 8 h)	43.8	37	1443*	Satilla River	Koopmans & Bronk 2002

Table 3. (continued)

Ammonium photoproduction rate [$\mu\text{M h}^{-1}$]	Irradiation conditions	Absorption coefficient at 350 nm [m^{-1}]	Dissolved organic nitrogen DON [μM]	Dissolved organic carbon DOC [μM]	Sample source	Reference
0.33	artificial (overall exposure time 10 h)	33*	24.3	3588	West Pearl River ph = 6	Wang et al. 2000
0.22	natural (overall exposure time 4 h)	–	–	–	Lake Maracaibo ph = 7.72	Gardner et al. 1998
0.15 ⁺	artificial (overall exposure time 18 h)	43	55	3000	Boreal pond ph = 7.6	Bushaw et al. 1996
not detected	natural (overall exposure time 35 h)	visible colour (T. Wiegner pers. comm.)	~80*	~1100*	sub-surface ground water	Wiegner & Seitzinger 2001
not detected	artificial (overall exposure time 12 h)	~42* ($a_{350} = 35$)	40	1971	Boreal River	Bertilsson et al. 1999
not detected	natural (overall exposure time 7 h)	–	~6*	~1000	lake water	Jorgensen et al. 1997

Table 3. (continued)

Ammonium photoproduction rate [$\mu\text{M h}^{-1}$]	Irradiation conditions	Absorption coefficient at 350 nm [m^{-1}]	Dissolved organic nitrogen DON [μM]	Dissolved organic carbon DOC [μM]	Sample source	Reference
not detected	artificial (overall exposure time 50 h)	1.6–2.1	20–30	480–510	sea water	This paper
not detected	artificial (overall exposure time 50 h)	7.8–8.1	40–60	1000–1160	river water	This paper
~0.04–0.07	artificial UVB 0.8 W m^{-2} (overall exposure time 50 h)	21.2–23.6	40–50	~2800	pond water	This paper

The lack of such a relationship suggests that photodegradation of DOM in our samples was not a primary photochemical process, i.e. release of ammonium from the organic nitrogen pool was not an immediate result of photons interacting with a light-absorbing molecule. Possibly, the direct relationship observed by Bushaw et al. (1996) in pond and swamp water is observable only in highly absorbent samples where the primary processes dominate the secondary ones. This assumption, however, does not explain the discrepancies in Table 3. It seems that the bulk characteristics generally used to describe DOM are inadequate for explaining and/or predicting the nature of its photodegradation.

To summarise, the samples irradiated in the present experiment were more 'typical' in terms of optical properties than those analysed in the previously published studies. Ammonium photoproduction in river and seawater was detected only after a very long irradiation time, one which is environmentally unrealistic. The rate of photoammonification in pond water was one order of magnitude lower than that reported in experiments with highly absorbent waters. In all cases, the overall ammonium concentration increases were negligible in comparison with ambient ammonium concentrations (Pastuszak 1995). Hence, at least in this particular case, DOM photodegradation should not be regarded as significant source of ammonium.

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