

Photochemical production of molecular hydrogen in lake water and coastal seawater

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Abstract

Samples of lake water and coastal seawater from Nova Scotia, Canada, were irradiated with natural or artificial sunlight to investigate the potential for photochemical hydrogen production. Hydrogen photo-production was observed in all natural water samples. Rates of hydrogen formation were highest in coloured lake water (range: 98–163 pmol L⁻¹h⁻¹) and lower in seawater (range: 19–45 pmol L⁻¹ h⁻¹). Dilutions of the most highly coloured lake sample (Kejimikujik Lake) showed a positive linear relationship between H₂ production rates and CDOM concentration. Photo-production rates normalised to UV absorption coefficients at 350 nm indicated that the photochemical efficiency of hydrogen formation varied between samples, perhaps due to differences in the CDOM composition. Photochemical hydrogen formation was also seen in solutions of syringic acid and acetaldehyde: two low-molecular-weight carbonyl compounds found in natural waters. Photochemistry may therefore offer least a partial explanation for the persistently high levels of hydrogen observed in the low-latitude surface ocean.

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1. Introduction

Molecular hydrogen (H₂) is an indirect greenhouse gas that influences the Earth's climate by regulating both the oxidising capacity of the troposphere and stratospheric water vapour (Ehhalt and Prather, 2001). Supersaturation of dissolved hydrogen is commonly observed in the low-latitude surface ocean but remains an unexplained phenomenon (Scranton et al., 1982; Setser et al., 1982; Herr et al., 1984). Vertical profiles of

dissolved H₂ in these warm water regions have shown that concentrations are usually highest near the surface and decline with increasing depth (Scranton et al., 1982; Conrad and Seiler, 1988). Herr et al. (1984) reported a cycle of hydrogen concentration in the surface waters of the South Atlantic that was positively correlated with solar radiance. Assuming that water column microbial H₂ uptake rates are independent of irradiance, these observations are consistent with a photobiological or photochemical hydrogen production mechanism.

It is well known that hydrogen is a product of nitrogen fixation, although studies of the globally important marine nitrogen fixer *Trichodesmium* (*Oscillatoria*) *thiebautii* have indicated that this organism is

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not a major net source of hydrogen to the water column (Scranton et al., 1987). Under certain conditions, photobiological hydrogen production has been observed in laboratory cultures of marine photosynthetic bacteria (Ohta et al., 1981) and unicellular green algae (Melis and Happe, 2001). In contrast, the potential for non-biological, photochemical hydrogen production in aquatic environments is largely unknown. It has been suggested that photolysis of marine aldehydes could be a source of molecular hydrogen (Zika, 1981; Herr et al., 1984). Atmospheric formaldehyde dissociates into H_2 and CO upon exposure to ultra violet (UV) light (Clark et al., 1978) while CO, CH_4 and H_2 are products of acetaldehyde photolysis (Horowitz and Calvert, 1982). Formaldehyde, acetaldehyde and higher aldehydes are also products of the photo-degradation of marine chromophoric dissolved organic matter (CDOM) (Kieber et al., 1990; Mopper et al., 1991; Zhou and Mopper, 1997), but as an aqueous solution of formaldehyde exists almost exclusively in the form of the hydrate $CH_2(OH)_2$ and is relatively transparent to UV, significant H_2 production is more likely to arise from photolysis of higher aldehydes.

The aim of this work was to determine whether photochemical rather than biological processes can produce molecular hydrogen in natural waters. This investigation was prompted by observations of unusually high concentrations of hydrogen in the surface water of a coastal embayment in Nova Scotia, Canada, on sunny days (Punshon et al., 2007). A series of three trial photochemical experiments under natural sunlight with filtered seawater collected from the embayment indicated the potential for hydrogen production in the absence of biology. These experiments were followed with a series of laboratory irradiations of filtered lake water and coastal seawater under artificial sunlight. In addition, solutions of two carbonyl compounds, syringic acid and acetaldehyde, were irradiated in an effort to identify pathways for photochemical H_2 production.

2. Methods

2.1. Study sites

Water samples were collected from freshwater and salt-water sites in Nova Scotia, Canada, from July 2006 to June 2007. Freshwater samples were obtained from Kejimikujik Lake ($44^\circ 23' N 65^\circ 15' W$) and Stillwater Lake ($44^\circ 69' N 63^\circ 82' W$). Kejimikujik Lake is a shallow oligotrophic lake situated in a relatively pristine National Park (Beauchamp, 1983) whereas Stillwater Lake is partially encroached by suburban housing development. Both lakes have catchments consisting mainly of coniferous forest and bog and are char-

acterised by high levels of CDOM. Coastal seawater samples were collected from the Bedford Basin ($44^\circ 41' N 63^\circ 38' W$), the NW Arm ($44^\circ 64' N 63^\circ 61' W$), Sandy Cove ($44^\circ 28' N 63^\circ 33' W$) and Lunenburg Bay ($44^\circ 34' N 64^\circ 23' W$). The Bedford Basin and Northwest Arm are sheltered eutrophic inlets within Halifax Harbour whereas the Sandy Cove and Lunenburg Bay sites are more exposed to the Atlantic Ocean.

2.2. Experimental procedures

For the first three trial experiments, Bedford Basin surface water samples were collected in a glass carboy and filtered sequentially with GF/F glass microfibre filters (Whatman, USA) and 0.2 μm pore size nylon membranes (Millipore, USA). Each sample was then transferred to a 4 L glass bottle without headspace, then subdivided into 4–6 acid-cleaned 300 mL borosilicate glass BOD bottles (Wheaton, USA). Irradiations were carried out on the roof of the Dalhousie oceanography building under full sun where the bottles were held in a shallow water bath to maintain their temperature at about $25^\circ C$, and tilted so that the bottle walls were normal to the incident light. The bottles were analysed sacrificially for dissolved hydrogen at around 1 h intervals. As irradiance was not measured in these initial trial experiments the irradiances outside of the sample bottles were estimated (Clear sky solar irradiances at the Earth's surface normal to the incident beam) using the equations of Bird and Hulstrom (1991) in conjunction with a National Oceanic and Atmospheric Association solar position calculator (Cornwall et al., 2007).

Water samples from the other sites were collected in 2.5 L acid-rinsed glass bottles, filtered at low pressure through Whatman GF/F glass fibre filters and either analysed immediately or stored at $4^\circ C$ in the dark. Prior to irradiation, each 2.5 L sample was purged for 1 h with zero air at a flow rate of $200 mL min^{-1}$ to remove a large fraction of the dissolved hydrogen, then transferred without headspace into 125 ml quartz irradiation tubes of 3 cm diameter which were then sealed with tapered ground quartz stoppers secured with plastic clips. A sub-sample was analysed immediately to provide the time zero measurement and subsequent measurements of irradiated samples were made at 1–2 h intervals. Irradiations were carried out with a Suntest CPS (Atlas, USA) solar simulator equipped with a 1 kW xenon tube, an infrared mirror to reduce sample heating and a glass plate cut-off filter to remove radiation $<290 nm$ wavelength. This instrument was also equipped with a control to vary the light output of the lamp. The first two sets of measurements were made at minimum lamp output with the irradiation tubes cooled by circulating air. With this arrangement, the sample temperatures stabilised at about $26^\circ C$. Later measurements used the maximum lamp output with the irradiation tubes held horizontally in a shallow water bath maintained at $22^\circ C$. For comparison, the sample light fields at the minimum and maximum outputs were measured with a scalar irradiance meter (Biospherical Instruments Inc.) giving mean values of 332 and $570 W m^{-2}$ respectively. As this instrument

measured only visible light (400–700 nm) the total irradiances will clearly be underestimated by the contribution of the UVA and UVB components (290–400 nm); however, it seems reasonable to suppose that the difference in UV irradiance between the minimum and maximum lamp output will be in proportion to that of the visible spectrum.

2.2.1. Hydrogen measurements

Dissolved hydrogen concentrations were determined by the headspace equilibration method detailed by Punshon et al. (2007). In brief, water samples were drawn into a 50 mL glass syringe fitted with a 3-way nylon stopcock and the sample volume adjusted to 35 mL. A 5 mL headspace of zero air, free of H₂ and CO, was then introduced and the sample shaken for 3 min. The equilibrated headspace was then injected into the 1 mL sample loop of a gas chromatograph equipped with a reducing compound photometer (Peak Laboratories, USA) which is based on the principle of mercuric oxide reduction. Hydrogen and carbon monoxide were separated isothermally at 104 °C on a 2 m column packed with molecular sieve 13× giving retention times of 51 s and 126 s respectively. The overall analytical uncertainty was ±2% and the detection limit of dissolved hydrogen was <10 pmol L⁻¹. The method was calibrated with a 0.9 ppm H₂ standard prepared by diluting a measured volume of UHP hydrogen in a gravimetrically determined amount of UHP nitrogen. The detector response was linear up to about 80 pmol H₂, equivalent to an H₂ mixing ratio of around 2 ppm with the 1 mL sample loop used in these experiments. Net hydrogen production rates were obtained from sum of least-squares linear regressions of the changes in H₂ concentration over time. The uncertainties were estimated from the standard error of the regression slopes at the 95% confidence level.

2.2.2. Light absorption

Light absorption was measured in water samples collected in summer 2007 using a Cary 300 dual beam spectrophotometer (Varian Inc.) equipped with matching 10 cm quartz cuvettes. Samples were filtered with GF/F glass fibre filters and either measured immediately or stored in amber glass bottles at 4 °C. Optical density spectra in the range 250–800 nm at 1 nm resolution referenced to Nanopure water were converted to absorption coefficients (m⁻¹) using the expression of Kirk (1994):

$$a(\lambda) = 2.303D(\lambda)/L$$

where $a(\lambda)$ is the absorption coefficient at wavelength λ , $D(\lambda)$ is the corrected optical density at wavelength λ and L is the cuvette path length in metres. The absorption coefficient at a wavelength of 350 nm (a_{350}) is frequently used as a proxy for CDOM concentration. Light absorption by CDOM increases exponentially with decreasing wavelength (Kirk, 1994), and the exponential slope coefficient S of the absorption spectrum can be used to characterise CDOM composition (Kowalczyk et al., 2003; Zhang et al., 2007). Slope coefficients were derived from simple non-linear least-squares regressions of the absorption coefficient spectra in the wavelength range 300–450 nm.

3. Results and discussion

3.1. Hydrogen photo-production in natural water samples

Table 1 shows collated salinity, irradiance and H₂ production rate data from the study. The rates of H₂ increase measured in the three Bedford Basin samples were remarkably similar (35–37 pmol L⁻¹ h⁻¹). The H₂ production rate in the July 4th experiment appeared to increase during the experiment (Fig. 1). This may have been due to varying light intensity during the irradiation period. The second and third series of samples were irradiated under uninterrupted sun and showed linear increases of H₂ concentration with time. Two dark control samples included with the July 19th series showed no increase in dissolved hydrogen. Net H₂ microbial loss rates measured by dark incubations of unfiltered Bedford Basin seawater samples were 75, 62 and 55 pmol L⁻¹ h⁻¹ for the 4th, 11th and 19th July. These losses, together with loss to the atmosphere from supersaturated surface waters, are higher than the measured rates of photo-production. This discrepancy

Table 1
Sample details, irradiance and H₂ photo-production rates collated from this study

Sample	Sampling date	Salinity	Irradiance Wm ⁻²	H ₂ production rate (pmol H ₂ L ⁻¹ h ⁻¹)
<i>Summer 2006</i>				
Bedford Basin	4 Jul 06	23.3	740	37±5
Bedford Basin	11 Jul 06	27.3	717	37±4
Bedford Basin	19 Jul 06	25.6	701	35±2
<i>Winter 2006/2007</i>				
Kejimikujik Lake	5 Dec 06	0	332	98±2
Stillwater Lake	17 Dec 06	0	332	100±3
Kejimikujik Lake	5 Dec 06	0	570	163±5
NW Arm	10 Jan 07	19.2	570	31±3
Sandy Cove	15 Jan 07	29.8	570	19±4
<i>Summer 2007</i>				
Kejimikujik Lake	31 May 07	0	570	122±2
Stillwater Lake	6 Jun 07	0	570	119±4
Lunenburg Bay	7 Jun 07	29.2	570	42±3
NW Arm	12 Jun 07	17.9	570	45±2
Sandy Cove	20 Jun 07	28.9	570	28±2
NW Arm+		17.9	570	256±4
1.0 mM acetaldehyde				
Pure water+		0	570	311±8
1.3 mM acetaldehyde				

Natural sunlight irradiance was estimated using a solar radiance model (Bird and Hulstrom, 1991). Solar simulator irradiance was estimated from visible light measurements with a scalar irradiance meter.

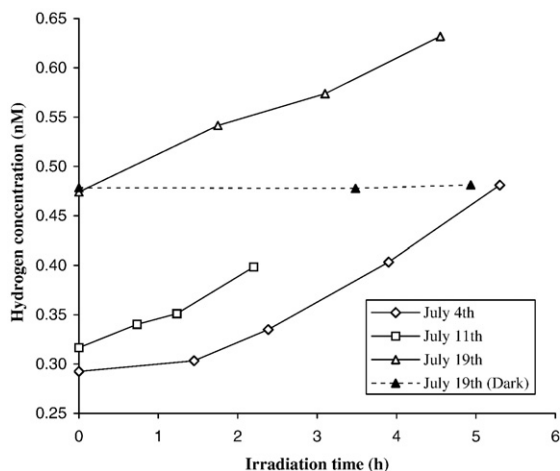


Fig. 1. Increases in dissolved hydrogen concentration in irradiated samples from the Bedford Basin, Nova Scotia, collected on the 4th July (open diamonds), 11th July (open squares), and 19th July 2006 (open triangles). The solid triangles represent 19th July dark control samples.

may be due to attenuation of short wavelength UV light by the borosilicate glass irradiation bottles (Transmittance=3% at 300 nm, 36% at 320 nm, 76% at 350 nm). If photochemical hydrogen production results primarily from the absorption of UVB light (290–320 nm) by CDOM, then the H_2 photo-production rates obtained from the three Bedford Basin experiments would be underestimated by >50%.

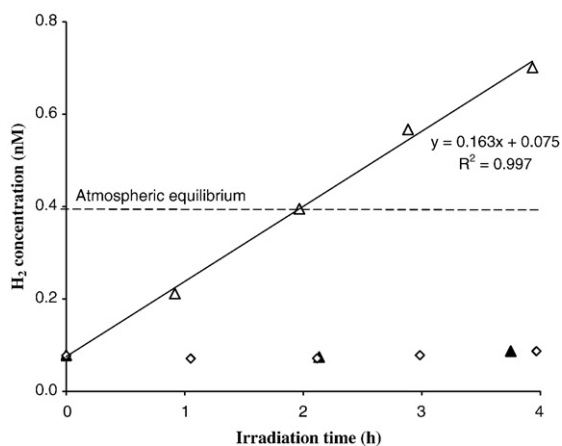


Fig. 2. Measurements of dissolved hydrogen over time in irradiated samples of Kejimikujik Lake water (open triangles), dark control samples (solid triangles) and irradiated Nanopure water (open diamonds). The bulk water samples were purged with zero air to remove dissolved hydrogen prior to being transferred to the irradiation tubes. The horizontal dashed line represents the hydrogen concentration of an equivalent pure water sample at equilibrium with the atmosphere assuming an atmospheric H_2 mixing ratio of 520 ppb.

Table 2

Optical data for the sites sampled during summer 2007 where a_{300} and a_{350} are the absorbance coefficients (m^{-1}) at 300 and 350 nm and $S_{(300-450)}$ is the spectral slope coefficient for the range of wavelengths 300–450 nm

Sampling site	a_{300} (m^{-1})	a_{350} (m^{-1})	$S_{(300-450)}$ (nm^{-1})
Kejimikujik Lake	50.46	25.81	0.0147
Stillwater Lake	33.09	15.90	0.0162
Lunenburg MB1	2.74	1.44	0.0148
NW Arm	5.00	2.35	0.0151
Sandy Cove	1.93	1.28	0.0123

The Kejimikujik and Stillwater lake samples collected in winter gave almost identical linear rates of H_2 production (100 and 98 $pmol L^{-1} h^{-1}$) under the minimum solar simulator light intensity. At maximum light intensity, H_2 production in Kejimikujik Lake water increased in proportion to the estimated 1.7 fold increase in irradiance (Table 1). No increase in hydrogen over time was seen in the dark-incubated samples or in irradiated Nanopure deionised water (Fig. 2). In summer 2007, the H_2 photo-production rates from the lakes were again very similar, although lower for Kejimikujik Lake than in the winter sample. In contrast, hydrogen photo-production rates for the NW Arm and Sandy Cove coastal water samples collected in summer (45 and 28 $pmol L^{-1} h^{-1}$) were rather higher than for those collected in winter (31 and 19 $pmol L^{-1} h^{-1}$). Table 2 shows the optical data for the samples obtained in summer 2007. For comparison, hydrogen production rates from the various freshwater and seawater samples were normalised to a_{350} (Fig. 3). H_2 production rates determined in Kejimikujik Lake water, pure water and dilutions of 20% and 50% Kejimikujik Lake water in pure water, were linearly related to CDOM concentration ($R^2=0.997$). This was unexpected given the range of optical densities involved.

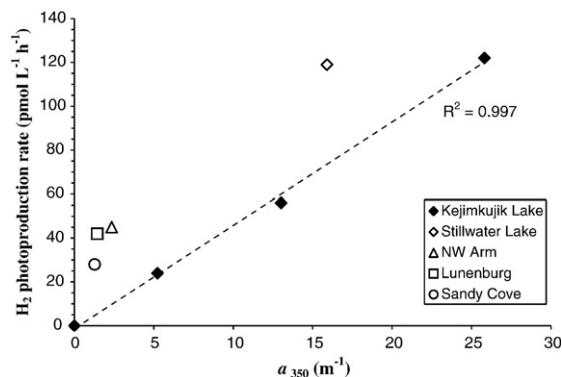


Fig. 3. Hydrogen photo-production rates in natural lake and coastal water samples normalised to absorption coefficients at 350 nm (a_{350}). The four solid diamonds represent a range of CDOM concentrations where the endpoints consist of deionised water and undiluted Kejimikujik Lake water and the two intermediate points are dilutions of 20% and 50% lake water.

With a mean pathlength L of about 2 cm for the irradiation tubes, the absorbance of the undiluted sample, $a_{350} \times L$, was >0.5 , i.e. “optically thick” making it very likely that the H_2 photo-production rate was underestimated due to the inner filter effect (Zepp et al., 2002). The observed linear relationship would be reasonable if the most important wavelength responsible for H_2 was longer than 350 nm, thus rendering all of the samples “optically thin”. Further experiments using cut-off filters would be necessary to determine the wavelength effect. Hydrogen photo-production was more efficient in all the other natural water samples. The coastal waters were around 5 times more reactive than Kejimikujik Lake water, and the Stillwater Lake sample was almost twice as reactive. The cause of this variability is not certain but a comparison with trophic status can be drawn. Kejimikujik Lake is considered to be oligotrophic and was the least photochemically reactive water body whereas the NW Arm and Lunenburg Bay are highly eutrophic due to anthropogenic discharges and also were the most reactive. If the level of photochemical reactivity is linked to the presence of labile compounds exuded during biological activity, e.g. photosynthetic growth or grazing, then it might also explain why H_2 photo-production rates in coastal seawater were higher in summer than in winter, although not why the reverse was seen in Kejimikujik Lake samples.

The spectral slope coefficients S for Kejimikujik Lake, Stillwater Lake, NW Arm and Lunenburg Bay summer samples were very similar (range $0.0147\text{--}0.0162\text{ nm}^{-1}$), suggesting an overriding influence of terrestrial CDOM in these two coastal sites. For Sandy Cove, S was notably lower (0.0123 nm^{-1}) and this may have resulted from the biological or photochemical transformation of terrestrial CDOM. The spectral slope data do not seem to offer any obvious clues to explain the variability in photochemical efficiency.

In the tropical South Atlantic, Herr et al. (1984) reported an average rate of increase in dissolved hydrogen of $90\text{ pmol L}^{-1}\text{ h}^{-1}$ during the period of maximum solar irradiance. Although this would have been a low-end estimate of the true production rate as it included dispersive losses and biological consumption, it is at least double the rate of H_2 formation in the coastal seawater samples measured in this study. Furthermore, published absorption coefficients for oligotrophic seawater are an order of magnitude lower than the least optically dense coastal sample here (Nelson et al., 1998; Kowalczyk et al., 2003), therefore it seems unlikely that photochemistry can entirely explain the findings of Herr et al. (1984).

3.2. Hydrogen photo-production from solutions of two carbonyl compounds

The CDOM in pristine freshwater lakes such as Kejimikujik Lake is characterised by phenolic groups derived from the degradation of terrestrial plant lignin (Malcolm, 1990). Syringic acid is one of the most common mono-phenols to be released into soils as a result of lignin degradation (Thoss et al., 2002), and may be a useful model for more complex, high-molecular-weight humic substances. The irradiation of a 0.5 mM solution of syringic acid in pure water produced an exponential increase

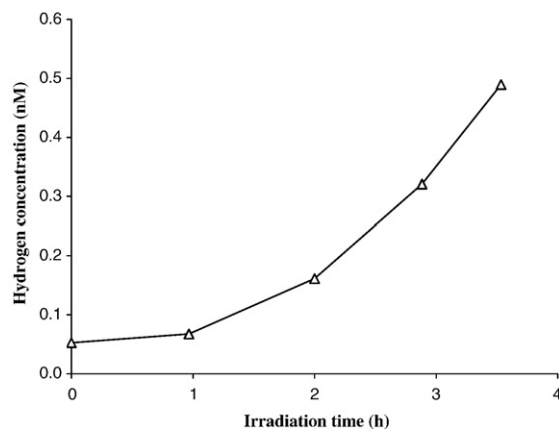
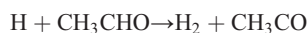
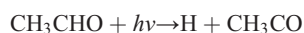


Fig. 4. The change in dissolved hydrogen concentration with time in an irradiated solution of 0.5 mmol L^{-1} syringic acid in deionised water.

in dissolved hydrogen (Fig. 4). This was accompanied by the development of a yellow colouration, barely noticeable after the first hour but then becoming much more pronounced, presumably due to the oxidation of phenoxy radicals to form yellow *o*-quinones (Heitner, 1993 and references therein). The reason for a non-linear increase in H_2 in the irradiated syringic acid solution over time, contrasting with linear increases in natural lake waters, is not clear. One possibility is that the yellow *o*-quinones act as a sensitiser or photochemical catalyst so that the rate of H_2 production accelerates as the colour develops. Alternatively the hydrogen is produced from an intermediate formed by photo-reaction of the syringic acid.

Hydrogen is known to be a minor photochemical product of acetaldehyde photolysis at wavelengths in the range 290–331 nm (Horowitz et al., 1982; Horowitz and Calvert, 1982). The authors proposed a pathway involving free H radicals:



Acetaldehyde, along with a range of other low-molecular-weight carbonyl compounds, is formed in natural waters from UV photo-degradation of humic substances (Moran and Zepp, 1997; Zhou and Mopper, 1997). The addition of mM amounts of acetaldehyde to NW Arm seawater and pure water samples resulted in the highest linear rates of hydrogen photo-production measured in this work (Table 1).

While the concentrations of syringic acid and acetaldehyde in these experiments were probably very high compared to those found in lakes or coastal seawater, these results illustrate the potential for photochemical hydrogen formation from low-molecular-weight molecules associated with CDOM.

4. Conclusions

These experiments demonstrated that molecular hydrogen can be produced non-biologically by the

action of light on natural water samples. It is likely that the photochemical pathways responsible for hydrogen production involve CDOM, as H_2 production rates were positively correlated to a_{350} , a proxy for CDOM concentration. In addition, irradiated solutions of two carbonyl compounds associated with the degradation of humic substances also produced hydrogen. Given that CDOM concentrations in the oligotrophic ocean may be an order of magnitude lower than in the coastal sites studied here, it seems unlikely that photochemistry can fully account for the persistently supersaturated levels of hydrogen in low-latitude surface waters, but may at least offer a partial explanation. Photochemical measurements from open ocean sites will be required to help unravel the enigma of dissolved hydrogen.

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