Photochemical Transformation of Dissolved Organic Matter to Carbon Dioxide in Southern England, UK.

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ABSTRACT

Dissolved inorganic carbon (DIC) is photochemically produced from coloured dissolved organic matter (CDOM). This is important since dissolved organic carbon (DOC), which in part is CDOM, has increased in UK rivers since scientists started measuring it, at least half a century ago. Therefore, a DIC increase is a possible effect of the DOC increase. This work has found significant correlation between CDOM and the DIC photoproduction rate (p-value = $4x10^{-5}$), showing that changes in DOC will conclusively affect DIC. This work has also found that changes in DIC photoproduction rate due to CDOM are 3.1 times higher in riverine water than in oceanic water. This change in the DIC photoproduction rate could be due to different elements and compounds limited in riverine water, but in higher concentrations in oceanic water, or differences in CDOM origin and composition.

INTRODUCTION

Over the last half century, scientists have observed an increase in dissolved organic carbon (DOC) concentrations in UK rivers; in some cases, an increase of up to 65% in 12 years [1, 2]. Coloured dissolved organic matter (CDOM) is the fraction of DOC that absorbs light [3], consequently, an increase in DOC will generate an increase in CDOM. Although the causes of the increase are debated [2], the increase in DOC is accepted. The fate of DOC is uncertain. Potentially, this DOC can be remineralised photochemically or biologically.

It is important to understand the effect an increase in DOC will have in dissolved inorganic carbon (DIC). DIC is photochemically produced from CDOM [4, 5], being CDOM a limiting factor for DIC photoproduction.

Models predict the annual global rate of photochemical production of DIC of around 10^{14}-10^{15} moles DIC y^{-1}, is in the orders of magnitude as the sequestration of DIC by new production [6]. This equilibrium is produced by the photochemical oxidation production of DIC, and the consequent phytoplankton sequestration, especially during blooms [6] and by outgassing of CO_2. An increase in DIC creates an imbalance in the equilibrium, therefore, an increase in sequestration or outgassing is possible.

As a result, further analysis is needed to understand this difficult equilibrium, this work has tried to study how the increase in CDOM affects the photoproduction rate of DIC, using samples from Southern England. We have set up a series of experiments to test the hypothesis that DIC photoproduction in dependant of CDOM.

MATERIALS & METHODS

Samples were taken from four different rivers (Dart, Erme, Plym and Tamar rivers) from June to July 2015 and January to April 2016. These rivers were chosen due to a) their proximity to peat marshes, b) their proximity to the marine studied region. The location depended on the accessibility to the site, although samples were taken after the area with peat marshes, and sampled in the middle of the river. Ocean samples were taken from two ocean time series stations. An open-shelf station named E1 (50.03°N, 4.37°W), and a coastal station, L4 (50.25°N, 4.22°W) [7].

Water was sampled in a 20L carboy, which was then gravity filtered through a 0.7µm filter and a 0.2µm Akropak 1000 filter into an acid-washed, distilled water-rinsed, glass Erlenmeyer flask.

Since low concentrations of DIC are produced photochemically, all carbonate species in the initial sample were stripped prior to irradiation. The sample in the Erlenmeyer was acidified to a pH between 3 and 4 using HCl, and bubbled with CO_2 free air for four hours eliminating over 99.6% of the initial DIC. The sample was then re-buffered to approximately their original pH [4, 5]. The sample was then divided into 3 borosilicate bottles for initial DIC, 3 borosilicate bottles for visible irradiance (VIS) irradiation photoproduction DIC, 4 quartz bottles for UV+VIS photoproduction of DIC and 4 quartz bottles for dark/control DIC. The samples were then irradiated in a custom solar simulator for 48h, whilst the initial DIC was measured [7]. DIC was measured using a Dissolved Inorganic Carbon Analyser (Model AS-C3; Apollo SciTech, Bogart, GA, USA), using Certified Reference Materials (A. Dickson, SIO, Batch 140 and 152).

CDOM was also measured for all the samples. This was done in 5cm cuvettes, using a spectrophotometer (Perkin Elmer Lambda 35), obtaining the absorption coefficient using distilled water as the reference.

RESULTS & DISCUSSION

The first aspect we studied was the DIC photoproduction rate variation with CDOM. Multiple measurements where done for the different subsamples, with a small standard deviation inside each subsample. Dark control samples did not change significantly from the initial DIC values. The dark DIC results were subtracted from the DIC values from the UV+VIS samples obtaining the photoproduced DIC. The values where divided by the time they were inside the solar simulator obtaining the DIC photoproduction rate. These values were plotted against the absorption coefficient at 300nm ($CDOM_{300}$) (Fig. 1).

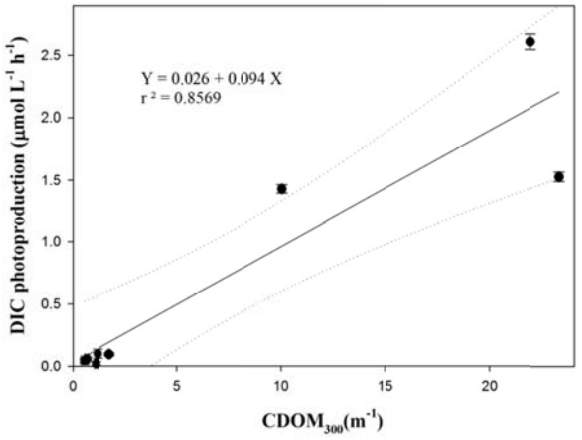

Fig. 1. DIC photoproduction rate variation with $CDOM_{300}$, for oceanic and riverine water. The black line represents the regression line, whilst the dotted line shows the 95% confidence interval.

DIC photoproduction rate for rivers and the ocean stations showed a good positive correlation (p-value = 0.0000429) with $CDOM_{300}$. Confirming that a higher CDOM will produce a higher DIC photoproduction rate.

The second aspect we studied was the DIC photoproduction rate variations in seawater. For this work we analysed weekly samples from L4 for two months (Fig. 2). We observed a correlation between the studied parameters (p-Value = 0.0486). Although the rate at which DIC photoproduction varies with respect to $CDOM_{300}$ in only ocean water, decreased over three folds (Fig. 1 and 2). This means that a small change in CDOM in oceanic water is significantly less important than in riverine water, consequently, the observed increases in DOC in riverine water have had a less important impact in the oceanic water. Therefore, more importance should be given to these changes and further experiments should be done to understand the factors which make the effect differ in the different water types.

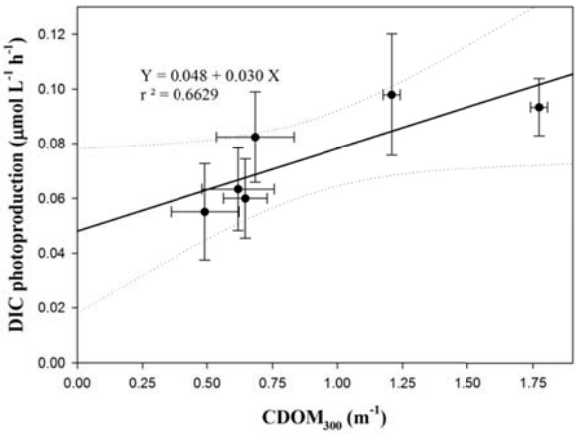

Fig. 2. DIC photoproduction rate variation with $CDOM_{300}$ at L4 during a period of seven weeks (no data for one week).

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