Carbon monoxide apparent quantum yields and photoproduction in the estuary Tyne

A. Stubbins\textsuperscript{1,*}, C. S. Law\textsuperscript{2,**}, G. Uher\textsuperscript{1}, and R. C. Upstill-Goddard\textsuperscript{1}

\textsuperscript{1}School of Marine Science and Technology, Newcastle University, UK
\textsuperscript{2}Plymouth Marine Laboratory, Plymouth, UK
\*now at: Skidaway Institute of Oceanography, Savannah, Georgia, USA
\**now at: NIWA, Wellington, New Zealand

Received: 13 September 2010 – Accepted: 30 September 2010 – Published: 13 October 2010
Correspondence to: A. Stubbins (aron.stubbins@skio.usg.edu)

Published by Copernicus Publications on behalf of the European Geosciences Union.
Abstract

Carbon monoxide (CO) apparent quantum yields (AQYs) are reported for a suite of riverine, estuarine and sea water samples, spanning a range of coloured dissolved organic matter (CDOM) sources, diagenetic histories, and concentrations (absorption coefficients). CO AQYs were highest for high CDOM riverine samples and almost an order of magnitude lower for low CDOM coastal seawater samples. A conservative mixing model predicted only 4% decreases in CO AQYs between the head and mouth of the estuary, whereas measured reductions in CO AQYs were between 47 and 80%, indicating that a highly photoreactive pool of terrestrial CDOM is lost during estuarine transit. The CDOM absorption coefficient ($a$) at 412 nm was identified as a good proxy for CO AQYs (linear regression $r^2 > 0.8; n = 12$) at all CO AQY wavelengths studied (285, 295, 305, 325, 345, 365, and 423 nm) and across environments (high CDOM river, low CDOM river, estuary and coastal sea). These regressions are presented as empirical proxies suitable for the remote sensing of CO AQYs in natural waters, including open ocean water and were used to estimate CO AQY spectra and CO photoproduction in the Tyne estuary based upon annually averaged estuarine CDOM absorption data. Annual CO photoproduction in the Tyne was estimated to be between 1.38 and 3.57 metric tons of carbon per year, or 0.005 to 0.014% of riverine dissolved organic carbon (DOC) inputs to the estuary. Extrapolation of CO photoproduction rates to estimate total DOC photomineralisation indicate that less than 1% of DOC inputs are removed via photochemical processes during transit through the Tyne estuary.

1 Introduction

Photochemistry, initiated when sunlight is absorbed by coloured dissolved organic matter (CDOM), represents an important pathway in the aquatic carbon-cycle. The net effects of dissolved organic matter (DOM) photodegradation include: the alteration of DOM bioavailability (Moran and Zepp, 1997; Mopper and Keiber, 2000; Miller et al.,
the bleaching of CDOM colour (Del Vecchio and Blough, 2002; Helms et al., 2008); and the production of a suite of photoproducts, including CO$_2$ and CO (Valentine and Zepp, 1993; Miller and Zepp, 1995; Stubbins et al., 2006a). Photoproduction is the dominant source of CO in natural waters and results in surface water CO supersaturation and emission to the atmosphere (Conrad et al., 1982; Bates et al., 1995; Stubbins et al., 2006b).

Precise and accurate quantification of CO photoproduction is facilitated by sensitive analytical techniques and low background CO. Consequently, CO has been suggested as a useful proxy from which other, less easily quantified, photoreaction rates can be extrapolated. For instance, the ratio of dissolved inorganic carbon:CO photoproduction is approximately 15:1 (Miller and Zepp, 1995; Gao and Zepp, 1998). CO has also emerged as a key tracer for use in testing and tuning models of mixed layer processes (Kettle, 2005; Doney et al., 1995; Najjar et al., 1995) and for the exploration of photochemical mechanisms (Stubbins et al., 2008). As quantitatively the second largest product of CDOM photomineralization (Miller and Zepp, 1995; Mopper and Kieber, 2001), CO photoproduction is also a significant term in the global carbon-cycle.

Calculating the rate of a photoreaction in the natural environment requires knowledge of its spectral efficiency or quantum yield (QY). The QY is defined as the number of moles of product formed or reactant lost per mole of photons (einstins; $E$) absorbed at a given wavelength ($\lambda$). If the molar absorption coefficient and concentration of a reactant are known, true reaction QYs can be calculated. However, as CDOM chromophores are not well characterized, QYs are usually normalized to the total absorbance of dissolved constituents, providing an apparent quantum yield (AQY). AQYs for photoreactions involving CDOM display near-monotonic decreases with increasing wavelength between 270 and 600 nm (Valentine and Zepp, 1993), necessitating the determination of AQY spectra to account for this wavelength dependence.

CO AQY spectra have been reported for a variety of waters. Most studies report CO AQY spectra either exclusively for fresh water (Valentine and Zepp, 1993; Gao and Zepp, 1998) or exclusively for seawater (Kettle, 1994; Ziołkowski, 2000; Zafiriou et al.,...
2003), finding relatively minor, unexplained variations between samples. However, if data from different environments are compared, clear variations can be seen between marine and freshwater CO AQY spectra (Stubbins, 2001; Zhang et al., 2006). The most noticeable of these is that values for seawater are around 5–10 times lower than those for freshwaters. These variations have been ascribed to a combination of qualitative relationships, including a reduction in the concentration of aromatic chromophores, as indicated by lower CDOM light absorption at higher salinities, differences in the chemistry of terrestrial versus marine derived DOM, and a reduction in CO AQY with increasing irradiance dose (Stubbins, 2001; Zhang et al., 2006).

In the open ocean CO AQYs and CDOM levels are relatively constant allowing CO photoproduction to be reasonably well constrained (30–90 Tg CO-C yr$^{-1}$; Zafiriou et al., 2003; Stubbins et al., 2006a). However, variability in CDOM concentration and reactivity complicates predicting photoreaction rates in terrestrially influenced waters. Here we report variations in CO AQYs across strong gradients in CDOM concentration, source and reaction history in the Tyne estuary, England, and in four other British rivers (North Tyne, South Tyne, Tay and Tamar). A resulting relationship between CDOM light absorption and CO AQYs is recommended for use in predicting the photoreactivity of natural waters using in situ or remotely sensed measurements of CDOM absorption coefficients. This approach to predicting CO AQYs is used to estimate annual CO photoproduction within the Tyne estuary.

2 Methods

2.1 Field site

The River Tyne (Fig. 1), North East England, has two main tributaries, the North and South Tyne. Inputs of organic carbon from thick ($\leq 10$ m) blanket peats give the North Tyne high DOC concentrations (mean: 1099 µM; Spencer et al., 2007), whereas, the South Tyne drains predominantly moorland covered limestone and has lower DOC
concentrations (mean: 456 µM; Spencer et al., 2007). The catchment is mainly pastoral below the confluence of the two tributaries, with some arable and industrial land. DOC concentrations at the head of the estuary range from ∼600–2300 µM (mean ∼1200 µM; Spencer et al., 2007). These high inputs of terrestrial DOC dominate over anthropogenic point sources, the latter being confined to the seaward end of the estuary (Spencer et al., 2007). The estuary is 35 km long, macrotidal and partially mixed, with an average annual residence time of ∼12 days (Watts-Rodrigues, 2003) and a mean spring tidal range of 5.0–0.7 m (www.PortofTyne.co.uk). The estuary and lower river were canalized in the latter half of the 19th century, with islands removed and meanders straightened. In 1850, the Tyne Improvement Commission began dredging the estuary, stretching 16 km inland. Today the river is navigable 24 km inland, which includes all estuarine sampling sites in the current study (Stations 1–14). Dredging maintains depths of 9.1 m below Chart Datum throughout most of the estuary (Stations 4–12; Table 1) and 12.1 m below Chart Datum below the Riverside Quay (Station 13 and 14; Table 1) (www.PortofTyne.co.uk). The canalized nature of the lower river and estuary, along with other factors including the absence of substantial areas of tidal flooding and drainage, make the Tyne a near-ideal system for determining the impacts of estuarine mixing upon CDOM photoreactivity. In addition, the predominance of peat derived DOC in the Tyne makes it representative of most UK catchments (Hope et al., 1997) and northern peatlands generally.

Samples from the River Tamar (South West England) and the River Tay (South East Scotland) are also included. The Tamar’s catchment is dominated by moorland, deciduous woodland, and hill farms. DOC concentrations in the River Tamar are lower than for the peat dominated Tyne, reaching a maximum of about 480 µM (Miller, 1999). The Tay is one of the least contaminated rivers in Europe (Sholkovitz, 1979) and the largest river in the UK based upon mean annual discharge (Maitland and Smith, 1987). To our knowledge, no DOC data exists for the Tay. The catchment is dominated by moorland and rough grazing, with minimal arable (8%), forestry (5%) and urban (1%) land (Bryant and Gilvear, 1999). Soils are thin and underlain by metamorphic rocks
(Bremner, 1939). These samples, together with those from the moorland/limestone dominated South Tyne and the coastal North Sea, give the data set relevance beyond peat dominated systems.

Tyne estuary and North Sea samples were collected onboard RV Bernicia (April 2001) and the Tamar sample from RV Tamaris (April 2001). The Tay, North Tyne and South Tyne samples were collected from riverbanks (May 2001). All samples were collected using a pre-cleaned (10% hydrochloric acid, ultrapure laboratory water from a Millipore Q185 system hereafter referred to as Milli-Q) and sample rinsed polyethylene bucket and placed in similarly cleaned high density polyethylene carboys. Samples were transported in the dark and then 0.1 µm filtered through a Millipore POLYCAP 150 TC filter capsule which had been flushed with acetonitrile, Milli-Q, and sample. Filtration was carried out in a darkroom (lit using a red photographic “safe” light) within 24 h of collection. Samples were stored refrigerated in complete darkness for <2 weeks before use.

2.2 Irradiations and apparent quantum yields

Further sample processing and irradiations took place in the temperature controlled darkroom. Samples were allowed to reach room temperature and then re-filtered immediately prior to irradiation (0.1 µm); the latter in order to remove potential bacterial re-growth that could have led to microbial CO oxidation and an underestimation of CO AQYs. No DOM precipitation was noticed in between filterings and CDOM absorption coefficients remained constant (less than 0.5% variations at 300 nm), indicating negligible losses of CDOM due to repeated filtering or microbial activity. Samples were then bubbled with zero-grade, CO scrubbed air (Hopcalite scrubber) for ≥1 h to reduce background CO and ensure consistent pre-irradiation levels of other dissolved gases. The same bottle of zero-grade air was used throughout. Volatile DOM, pH and $pCO_2$, which may have had an influence on sample CO photoproduction, were not measured pre- and post-purging. Purged sample was introduced through clean Tygon tubing into a quartz cell (diameter = 17.3 mm, length = 200 mm, volume = 84 mL) which had been...
pre-rinsed with hydrochloric acid (0.1 M), Milli-Q and sample. The cell was flushed and allowed to overflow before it was capped with gas-tight nylon SwageLok fittings and placed in the light beam exiting the monochromator beam. The monochromator (25 cm grating monochromator, Model 77200; Oriel Instruments) was used with a 1 kW Hg-Xe light source and 5 nm bandpass. Irradiations were run at 25°C and at the following wavelengths: 285, 295, 305, 325, 345, 365 and 423 nm. Photon flux into the irradiation cell was determined using potassium ferrioxalate liquid-phase chemical actinometry (Calvert and Pitts, 1967). Thirty minute irradiations were routinely used for determining CO AQYs. Due to low production rates the North Sea water sample was irradiated for 60 min at 365 and 423 nm. For each irradiated sample an aliquot of filtered water was placed in a 60 mL gas tight crimp top vial. Vials were prepared and filled as described above for the irradiation cell and were then incubated at 25°C in the dark to provide dark controls for each irradiation. All CO AQY spectra were calculated following Zafiriou et al. (2003).

2.3 Ultraviolet-visible absorption spectra

CDOM absorption coefficient spectra (250 to 800 nm) were determined in the same 1 cm quartz cuvette using a scanning UV-visible, double-beam, spectrophotometer (Kontron, Uvicon 923) with Milli-Q water as a reference beam blank. CDOM spectra were corrected for offsets due to scattering and instrument drift by subtraction of the average absorbance between 700 and 800 nm. Data output from the spectrophotometer was in the form of dimensionless absorbance or optical density (OD) and was converted to the Napierian absorption coefficient, \( a \) (m\(^{-1}\); Hu et al., 2002).

2.4 Carbon monoxide

Dark and light CO samples were collected and processed immediately after irradiation. Differences between darks and lights were used to determine the amount of CO produced during irradiation. In the darkroom, crimp top vials (60 mL) were flushed
with sample before sealing with Teflon faced butyl septa. CO scrubbed carrier gas was introduced through the vial septa via a needle to create a 25 mL headspace. Following 30 min dark equilibration using a wrist action shaker, CO scrubbed water was introduced to the vial through a syringe. A second syringe was used to collect 15 to 20 mL of the displaced headspace gas. The CO mixing ratio within the headspace was measured using a reduction gas detector with UV-photometer (RGD2, Trace Analytical, Menlo Park, USA) following separation by gas chromatography (Stubbins et al., 2006b). The RGD2 sensitivity is quoted at ±1 ppbv CO with greater than 98% reproducibility (Trace Analytical) and has been shown to be linear over a wide range of CO concentrations (0 to 900 ppbv, Sjöberg, 1999). Precision of this method when measuring standards was better than ±1%. Mean percentage standard errors for sample replicates were ≤2%. A method blank was determined by irradiating CO purged MilliQ water. CO photoproduction was undetectable in this blank.

3 Results and discussion

3.1 Measured apparent quantum yields

Measured freshwater and seawater CO AQY spectra (Fig. 2) exhibited near log-linear decreases with increasing wavelength. AQYs at the head of the Tyne estuary were 2 to 6 times higher than high salinity AQYs, CO AQYs at a given wavelength fell rapidly with increasing salinity, indicating that CDOM photoreactivity varied markedly across the river-sea transition (see Fig. 3 for AQYs at 325 nm and Table 2 for all wavelengths). These results are consistent with previously published CO AQY spectra from fresh (Valentine and Zepp, 1993; Kettle, 1994; Gao and Zepp, 1998) and marine (Ziolkowski, 2000; Zafiriou et al., 2003) waters, and similar salinity dependence of CO AQYs observed in the St Lawrence estuarine system, Canada (Zhang et al., 2006).
3.2 Endmember mixing

A simple 2 component mixing model was employed to investigate the quantitative and qualitative variations in CO AQYs in the Tyne estuary. This model predicted CO AQYs based on the conservative mixing of two endmembers – Tyne water from Scotswood Bridge at the head of the estuary (salinity: 0.1) and coastal North Sea water (salinity: 32.4; Table 2). These two endmembers were those from the 9 April 2001 transect during which samples for all estuarine CO AQYs were collected. At a specific estuarine station and wavelength the proportion of aCDOM derived from river water assuming conservative mixing, \( (R-a\text{CDOM}_\lambda @ St_n) \) was calculated as:

\[
R-a\text{CDOM}_\lambda @ St_n = \frac{(St_n-a\text{CDOM}_\lambda - NS-a\text{CDOM}_\lambda \ast St_n-SAL/NS-SAL)}{St_n-a\text{CDOM}_\lambda}
\]

where \( St_n-a\text{CDOM}_\lambda \) is aCDOM at wavelength, \( \lambda \), measured at station n; NS-aCDOM\( _\lambda \) is aCDOM\( _\lambda \) of North Sea water; St\( _n \)-Sal is measured salinity at station n; and NS-Sal is North Sea salinity (in this transect 32.4). CO AQY at a specific station and wavelength (St\( _n \)-CO AQY\( _\lambda \)) was then calculated as:

\[
St_n-CO\text{ AQY}_\lambda = St_n-R-C\text{DOM}_\lambda \ast R-CO\text{ AQY}_\lambda + (1 - St_n-R-C\text{DOM}_\lambda) \ast NS-CO\text{ AQY}_\lambda
\]

where R-CO AQY\( _\lambda \) and NS-CO AQY\( _\lambda \) are wavelength specific CO AQYs determined for Tyne River and North Sea water, respectively.

The above conservative mixing model indicates only a 4% decrease in CO AQYs at 325 nm between the head of the estuary and salinity 28.3 (station “Tyne plume”, Fig. 3, Table 2). However, actual reductions in spectrally averaged CO AQYs were 70% at 325 nm (Fig. 3; results at 325 nm are broadly consistent with other wavelengths), indicating non-conservative decreases in CDOM photoreactivity in the estuary. This observation is consistent with the addition of low photoreactivity CDOM, removal of high photoreactivity CDOM, or some combination of the two, during estuarine mixing. The estuary is DOC rich due to riverine inputs with minimal estuarine carbon inputs from mudflats, tributaries or primary production (Ahad et al., 2008). It is therefore unlikely that AQYs fell due to additional inputs of CDOM. Instead, we consider the removal of
highly photoreactive CDOM to be the most likely for reductions in CO AQYs with increasing salinity. In support of this we previously reported an average 35% removal of Tyne CDOM \( a \) at 350 nm, during estuarine mixing, presumably due to a combination of CDOM adsorptive removal and flocculation at low salinity (Uher et al., 2001) or its progressive photochemical and microbial degradation throughout the estuary. Of these possible removal processes, only photo-degradation has been shown to reduce CO AQYs for CDOM (Stubbins, 2001; Zhang et al., 2006). Further work is thus required to determine whether microbial degradation, flocculation or adsorption onto suspended matter alter CDOM photoreactivity and to quantify their effects, along with that of photo-degradation, upon the photoreactivity of riverine CDOM exported to the oceans.

### 3.3 Absorption coefficient versus apparent quantum yields

Considering the above results, a simple conservative mixing model cannot be used to predict variations in CO AQY in the Tyne estuary and a more robust approach is therefore necessary. Our data analysis revealed correlations between CO AQYs and sample CDOM absorption coefficients at various wavelengths. We subsequently selected the CDOM absorbance coefficient at 412 nm (CDOM \( a_{412} \)) as a suitable proxy for three reasons: (1) CDOM \( a_{412} \) is readily measurable in situ; (2) there is a large historical CDOM data set for the Tyne and other aquatic systems; and (3) robust estimates of CDOM \( a_{412} \) can be retrieved from SeaWiFS (http://oceancolor.gsfc.nasa.gov/SeaWiFS) and MODIS (http://modis.gsfc.nasa.gov) datasets.

Considering only samples from the Tyne, linear regressions of CO AQYs at all wavelengths versus CDOM \( a_{412} \) had \( r^2 \) values greater than 0.8, indicating that CDOM \( a_{412} \) is a useful proxy for CO AQY in the North Tyne, lower River Tyne and Tyne estuary (Fig. 4), which show high levels of peat derived DOC. With samples from four other, non-peat dominated systems (the South Tyne, River Tamar, River Tay, and coastal North Sea) included in the analysis \( r^2 \) remained >0.8 for all wavelengths excepting 285 nm, for which \( r^2 \) was 0.77 (Fig. 4 and additional details in caption), indicating that
CDOM $a_{412}$ is a suitable proxy for CO AQYs in marine waters and in peat and non-peat carbon dominated rivers. Zhang et al. (2006) and Stubbins (2001) presented similarly robust relationships between CO AQY and CDOM absorbance properties but they used shorter CDOM absorbance wavelengths, which are unsuitable for remote sensing. The equations presented here represent the first means of predicting environmental CO AQY spectra from remotely sensed optical properties of natural water bodies.

The equations provided in Stubbins (2001) relate CO AQYs to CDOM light absorption at the CO AQY irradiation wavelength and were used to derive a CO AQY spectrum based upon open ocean CDOM light absorption (Stubbins et al., 2006a). This spectrum was representative of other CO AQY spectra measured directly by irradiation of seawater samples (Ziolkowski, 2000; Zafiriou et al., 2003). As part of the current study, we recalculated the open ocean CO AQY spectrum using the open ocean CDOM absorbance data at 412 nm from Stubbins et al. (2006a) along with the equations in the caption to Fig. 4. The derived AQY spectrum is again representative of measured open ocean CO AQY spectra (Fig. 5), demonstrating the robustness of using CDOM light absorption coefficients at 412 nm to predict riverine, estuarine and open ocean CO AQYs.

### 3.4 Modelled carbon monoxide photoproduction in the Tyne estuary

Although the causality underlying the empirical correlation between CO AQY and CDOM $a_{412}$ remains unclear, the relationship between these two parameters offers a robust and simple proxy for the prediction of CO AQYs in natural waters. Therefore, this proxy was used to model CO AQY spectra and CO photoproduction in the Tyne estuary.

The equation and parameters described in the caption to Figure 4 were used to calculate CO AQY spectra using annual average CDOM $a_{412}$ for sites in the Tyne estuary (Table 1). Best fit parameterisations were obtained by dividing the CO AQY spectra into two sections (285–345 nm and 345–423 nm) each fitted using a power regression.
(Stubbins et al., 2006a). These CO AQY spectra were then used to calculate CO photoproduction via Equation 3 (Stubbins et al., 2006a):

$$\sum_{\text{Station Area}} \int_{280}^{800} \left( \text{irradiation} \times \text{attenuation}_{1+2} \times A_{\text{CDOM}}/A_{\text{Total}} \times \left[ 1 - 10^{A_{\text{CDOM}}} \right] \times \text{CO AQY} \right)_\lambda$$  \hspace{1cm} (3)

where irradiance is annual global spectral solar irradiance at 55° north (latitude of Tyne estuary), attenuation factors 1 and 2 are corrections for the reflection of light by cloud (0.8; Nelson et al., 1998; Zafiriou et al., 2003) and water surface albedo (non-spectral, 0.93; Zepp and Cline, 1977), and $A_{\text{CDOM}}$ and $A_{\text{Total}}$ are the CDOM and total light absorption (optical density) in the water column.

Annual solar irradiance was calculated following the rationale presented in Stubbins et al. (2006a). Firstly, the average daily spectral global irradiance at 55° north for the winter and summer solstices, spring and winter equinoxes, and mid points between each was generated using SMARTS2, giving a total of 8 equidistant dates. Following Stubbins et al. (2006a), seasonal variations in irradiance were graphed over the spectral range 280–800 nm (resolution 1 nm) and the areas under the curves calculated by integration (SPSS SigmaPlot) to determine annual irradiance at each wavelength. Annual photon fluxes ($E \, yr^{-1}$) were then determined for each Tyne estuary section, using section surface areas in Table 1, and CO photoproduction calculated following Eq. (5).

CDOM $a_{412}$, particulate matter $a_{412}$ and rates of CO photoproduction versus salinity are shown in Fig. 6. The $a_{412}$ data (Fig. 6, top panel) show CDOM absorbance to dominate at the head of the estuary. Downstream the proportion of light absorbed by particulate matter increases so that from a salinity of $\sim 10$ to the mouth of the estuary light absorption at 412 nm by CDOM and particulates are roughly equal (Fig. 6).

Modeled CO photoproduction falls steeply as particulate absorbance increases between salinities of 0 and 2 at the head of the estuary. Modelled CO photoproduction continues to fall until salinity $\sim 12$ and then remains constant throughout the rest of the estuary as CO AQYs decline. Fluctuations in CDOM, particulate absorbance and CO photoproduction between salinities 10 and 16 reflect inputs of low CDOM, high
particulate load waters from a nearby wastewater outfall (Howdon). Whole estuary CO photoproduction from CDOM was estimated to be 1.38 Tonnes-C yr$^{-1}$.

Recent work has shown that CO photoproduction from coloured particulate matter (CPM) is approximately as efficient as CO photoproduction from CDOM (Xie and Zafiriou, 2009). Therefore, CO photoproduction was further calculated assuming all light entering the water column to be absorbed by photoreactive chromophores, whether particulate or dissolved (i.e. the terms $A_{\text{CDOM}}$ and $A_{\text{Total}}$ were removed from Eq. 5). This provides an upper limit to CO production in the Tyne (3.57 Tones-C yr$^{-1}$), which is more than twice as high as when estimated assuming only CDOM to be photoreactive.

3.5 Photomineralization of dissolved organic carbon

A first order estimate of total dissolved organic carbon (DOC) photomineralization in the Tyne estuary was made by extrapolating from CO photoproduction using a ratio of dissolved inorganic carbon:biolabile DOC:CO photoproduction of 20:13:1 (Miller and Zepp, 1995; Gao and Zepp, 1998; Miller et al., 2002). Estimated production of dissolved inorganic carbon, mineralization through photoproduction of biolabile carbon and total DOC mineralization were thus 19–50, 18–46 and 39–100 Tonnes-C yr$^{-1}$, respectively. Riverine DOC inputs to the Tyne estuary were estimated at $\sim$25 600 Tonnes-C yr$^{-1}$ based upon an annually averaged freshwater flow rate of 55 m$^3$ s$^{-1}$ for the period 1998–2001 (Environment Agency, UK; http://www.environment-agency.gov.uk) and an annually averaged freshwater DOC concentration of 1230 µM (Spencer et al., 2007). Using these values, estimated DOC removal through CO photoproduction amounts to a modest 0.005–0.014% of total DOC inputs and total photochemical losses of DOC within the estuary are similarly small: 0.15–0.39% of the DOC input.
4 Conclusions

A conservative mixing model involving freshwater and marine CDOM is unable to account for the large decrease in CO AQYs observed between the head and mouth of the Tyne estuary. Instead, the absorption coefficient of CDOM at 412 nm was found to be a useful proxy of CO AQYs for the suite of riverine, estuarine and coastal waters studied here. Percentage root mean square errors calculated from differences between measured estuarine CO AQYs and those predicted with the endmember mixing model show that an empirical proxy deriving from the linear relationship between CDOM $a_{412}$ and CO AQYs gives robust estimates of AQY spectra for the Tyne estuary. This relationship is also a robust predictor of open ocean AQYs and allows assessing CDOM photoreactivity in a water body from wavelength specific satellite ocean colour data (e.g. SeaWiFS, bandwidth 402–422 nm; MODIS, bandwidth 405–420 nm). Further work is required to determine the veracity of this approach in other systems with varying sources of CDOM.

Extrapolating modelled CO photoproduction in the Tyne to rates of total DOC photomineralization implies a minor role for photochemistry in the C-cycle of the Tyne estuary; <1% of the riverine DOC input is removed during estuarine transport. This is perhaps not surprising because the Tyne estuary (~55° N) is subject to moderate light levels and receives inputs of high DOC river water (average: 1200 µM; Spencer et al., 2007), which is rapidly exported to the coastal North Sea (average residence time: ~12 days; Watts-Rodrigues, 2003).

In contrast, measured CO AQYs fell by between 47% at 285 nm to 80% at 345 nm during transit from the head to the mouth of the estuary, with only ~4% of this decrease ascribable to the mixing of high AQY freshwaters with low photoreactivity sea water. This rapid drop in photoreactivity indicates that a highly photoreactive fraction of the CDOM pool is rapidly and preferentially lost during estuarine transit. Therefore, in estuary processes appear to have a major impact upon the photoreactivity (i.e., CO AQYs) of CDOM exported to the coastal North Sea. Previous work has shown CO AQYs to fall
rapidly with irradiation time (photons absorbed; Zhang et al., 2006), indicating that the reduction in CDOM photoreactivity may be driven by in estuary CDOM photobleaching. Further quantitative modelling studies are required to determine whether photobleaching can indeed drive the drop in photochemistry observed as CDOM is exported from river-to-sea.

Acknowledgements. We would like to thank Vassilis Kitidis and Gordon Henry for their help running the irradiation system; Ali and Kate, the crew of RV *Bernicia*; and Kenneth Mopper for editorial reviews. Laboratory work was funded by the National Environmental Research Council (grant number GR3 11665), Newcastle University and Plymouth Marine Laboratory, data handling, modelling and writing were funded by the National Science Foundation (OCE-0728634). Any opinions, findings, and conclusions or recommendations expressed in this paper are those of the authors and do not necessarily reflect the views of the funding bodies.

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Stubbins, A.: Aspects of aquatic CO photoproduction from CDOM, Ph.D. Thesis, University of
Table 1. Tyne estuary station numbers, geographical coordinates, surface areas, residence times, mean annual salinity and mean annual coloured dissolved organic matter absorption coefficient at 412 nm. Standard errors are reported for salinity and CDOM $a_{412}$ data, together with sampling number, $n$, reported in parenthesis.

<table>
<thead>
<tr>
<th>Station</th>
<th>Lat (N) : Long (W)</th>
<th>Surface Area (km$^2$)</th>
<th>Residence Time (d$^{-1}$)</th>
<th>Volume (10×6 m$^3$)</th>
<th>Salinity (−)</th>
<th>CDOM $a_{412}$ (m$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>54°57.9:01°41.0</td>
<td>0.85</td>
<td>0.22</td>
<td>1.263</td>
<td>0.4±0.3 (5)</td>
<td>18.1±0.8 (5)</td>
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<tr>
<td>2</td>
<td>54°57.8:01°39.7</td>
<td>0.40</td>
<td>0.20</td>
<td>1.149</td>
<td>0.6±0.6 (4)</td>
<td>17.2±1.0 (4)</td>
</tr>
<tr>
<td>3</td>
<td>54°57.5:01°38.1</td>
<td>0.38</td>
<td>0.21</td>
<td>1.206</td>
<td>1.2±0.9 (5)</td>
<td>17.0±1.1 (5)</td>
</tr>
<tr>
<td>4</td>
<td>54°58.0:01°36.7</td>
<td>0.31</td>
<td>0.18</td>
<td>1.085</td>
<td>2.0±1.4 (5)</td>
<td>15.8±0.7 (5)</td>
</tr>
<tr>
<td>5</td>
<td>54°58.0:01°35.3</td>
<td>0.13</td>
<td>0.06</td>
<td>0.437</td>
<td>6.0±1.3 (14)</td>
<td>14.5±1.0 (14)</td>
</tr>
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<td>54°57.9:01°34.4</td>
<td>0.22</td>
<td>0.16</td>
<td>1.097</td>
<td>7.0±1.8 (10)</td>
<td>13.4±1.2 (10)</td>
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<td>7</td>
<td>54°57.7:01°32.4</td>
<td>0.53</td>
<td>0.41</td>
<td>2.915</td>
<td>7.4±2.0 (10)</td>
<td>12.5±1.1 (10)</td>
</tr>
<tr>
<td>8</td>
<td>54°59.0:01°31.7</td>
<td>0.70</td>
<td>0.61</td>
<td>4.882</td>
<td>10.4±2.1 (4)</td>
<td>11.0±1.6 (4)</td>
</tr>
<tr>
<td>9</td>
<td>54°59.2:01°29.1</td>
<td>0.44</td>
<td>0.34</td>
<td>2.851</td>
<td>11.4±5.0 (10)</td>
<td>7.1±2.9 (10)</td>
</tr>
<tr>
<td>10</td>
<td>54°59.3:01°28.4</td>
<td>0.31</td>
<td>0.23</td>
<td>2.075</td>
<td>13.5±2.2 (5)</td>
<td>7.7±1.3 (5)</td>
</tr>
<tr>
<td>11</td>
<td>54°59.2:01°27.6</td>
<td>0.62</td>
<td>0.52</td>
<td>4.982</td>
<td>14.4±3.9 (5)</td>
<td>7.7±1.8 (5)</td>
</tr>
<tr>
<td>12</td>
<td>55°00.0:01°26.5</td>
<td>0.44</td>
<td>0.35</td>
<td>3.814</td>
<td>17.0±4.3 (10)</td>
<td>6.7±1.9 (10)</td>
</tr>
<tr>
<td>13</td>
<td>55°00.5:01°25.8</td>
<td>0.99</td>
<td>0.78</td>
<td>8.734</td>
<td>17.6±2.7 (10)</td>
<td>7.1±1.2 (10)</td>
</tr>
<tr>
<td>14</td>
<td>55°00.8:01°24.0</td>
<td>0.85</td>
<td>0.56</td>
<td>8.303</td>
<td>21.7±2.4 (11)</td>
<td>5.2±1.0 (11)</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>7.16</td>
<td>4.84</td>
<td>44.800</td>
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</tbody>
</table>
Table 2. carbon monoxide apparent quantum yields (CO AQYs; moles CO E\(^{-1}\)) for Tyne estuary samples of varying salinity (all samples from 9 April 2001).

<table>
<thead>
<tr>
<th>Station Name</th>
<th>Salinity</th>
<th>Wavelength (nm)</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Scotswood Bridge (1)</td>
<td>0.08</td>
<td>285</td>
<td>295</td>
<td>305</td>
<td>295</td>
<td>325</td>
<td>345</td>
<td>365</td>
</tr>
<tr>
<td>Near Howdon (9)</td>
<td>10.2</td>
<td>1.60\times10^{-04}</td>
<td>1.36\times10^{-04}</td>
<td>9.87\times10^{-05}</td>
<td>6.25\times10^{-05}</td>
<td>3.48\times10^{-05}</td>
<td>2.22\times10^{-05}</td>
<td>no data</td>
</tr>
<tr>
<td>Tynemouth Piers (12)</td>
<td>21.8</td>
<td>1.37\times10^{-04}</td>
<td>1.16\times10^{-04}</td>
<td>8.78\times10^{-05}</td>
<td>4.96\times10^{-05}</td>
<td>3.09\times10^{-05}</td>
<td>1.68\times10^{-05}</td>
<td>7.19\times10^{-06}</td>
</tr>
<tr>
<td>Tyne Plume (13)</td>
<td>28.3</td>
<td>1.08\times10^{-04}</td>
<td>8.25\times10^{-05}</td>
<td>5.35\times10^{-05}</td>
<td>2.50\times10^{-05}</td>
<td>1.00\times10^{-05}</td>
<td>8.62\times10^{-06}</td>
<td>5.35\times10^{-06}</td>
</tr>
<tr>
<td>North Sea (14)</td>
<td>32.4</td>
<td>8.04\times10^{-04}</td>
<td>7.26\times10^{-05}</td>
<td>4.30\times10^{-05}</td>
<td>2.27\times10^{-05}</td>
<td>8.57\times10^{-06}</td>
<td>6.01\times10^{-06}</td>
<td>4.28\times10^{-06}</td>
</tr>
</tbody>
</table>
Table 3. Percentage root mean squared errors for the two modelling approaches (conservative mixing and coloured dissolved organic matter absorbance coefficient at 412 nm (CDOM $a_{412}$)) for the prediction of carbon monoxide apparent quantum yields (CO AQYs) in the Tyne estuary when compared to measured CO AQYs at the studied wavelengths.

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Mixing</th>
<th>CDOM $a_{412}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>285</td>
<td>37</td>
<td>11</td>
</tr>
<tr>
<td>295</td>
<td>45</td>
<td>7</td>
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<tr>
<td>305</td>
<td>40</td>
<td>17</td>
</tr>
<tr>
<td>325</td>
<td>58</td>
<td>13</td>
</tr>
<tr>
<td>345</td>
<td>69</td>
<td>28</td>
</tr>
<tr>
<td>364</td>
<td>72</td>
<td>18</td>
</tr>
<tr>
<td>423</td>
<td>62</td>
<td>5</td>
</tr>
<tr>
<td>Spectral Mean</td>
<td>55</td>
<td>14</td>
</tr>
</tbody>
</table>
Table 4. Parameters describing the slopes in Fig. 4.

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>$y_0 \times 10^{-6}$</th>
<th>$m \times 10^{-6}$</th>
<th>$r^2$</th>
<th>$p$</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>285</td>
<td>110.3</td>
<td>5.796</td>
<td>0.77</td>
<td>0.0009</td>
<td>10</td>
</tr>
<tr>
<td>295</td>
<td>83.05</td>
<td>5.740</td>
<td>0.87</td>
<td>&lt;0.0001</td>
<td>10</td>
</tr>
<tr>
<td>305</td>
<td>61.98</td>
<td>4.341</td>
<td>0.81</td>
<td>0.0004</td>
<td>10</td>
</tr>
<tr>
<td>325</td>
<td>26.77</td>
<td>3.706</td>
<td>0.86</td>
<td>0.0003</td>
<td>9</td>
</tr>
<tr>
<td>345</td>
<td>14.26</td>
<td>2.137</td>
<td>0.83</td>
<td>0.0003</td>
<td>10</td>
</tr>
<tr>
<td>365</td>
<td>9.49</td>
<td>1.435</td>
<td>0.83</td>
<td>0.0002</td>
<td>10</td>
</tr>
<tr>
<td>423</td>
<td>4.14</td>
<td>0.472</td>
<td>0.88</td>
<td>0.0002</td>
<td>9</td>
</tr>
</tbody>
</table>
**Fig. 1.** Tyne catchment with North Tyne, South Tyne and Tyne estuary marked. Inset: map of UK showing location of the Tyne catchment.
Fig. 2. Carbon monoxide apparent quantum yield spectra for the Tyne estuary.
Fig. 3. Measured and modelled carbon monoxide apparent quantum yields (CO AQYs) versus salinity in the Tyne estuary. Grey fill squares are measured values. No fill triangles are values predicted based upon a conservative mixing model of the river water and marine endmembers of the Tyne estuary. Black fill triangles are values predicted using in situ CDOM $a_{412}$ as a proxy for CO AQYs.
Fig. 4. Measured riverine, estuarine and coastal seawater carbon monoxide apparent quantum yields (CO AQYs) versus sample absorption coefficient at 412 nm (CDOM $a_{412}$). Black fill squares are from the North Tyne, River Tyne, Tyne estuary and coastal North Sea (North East England); grey fill diamond is from the South Tyne (North East England); grey fill square is from the Tamar River (South West England); and no fill diamond is from the River Tay (South East Scotland). Straight lines are linear regressions of all data: where $\text{CO AQY}_\lambda = y_0 + m \times a_{412}$, $y_0$ is the y-intercept (CO AQY) and $m$ the slope of linear regressions of CO AQY at wavelength, $\lambda$, against sample CDOM absorption coefficient at 412 nm ($a_{412}$). Curve parametrisations can be found in Table 4.
Fig. 5. Open ocean carbon monoxide apparent quantum yields (CO AQYs). Solid filled squares represent data calculated using parameters listed in the Fig. 5 legend inset together with the open ocean CDOM absorbance coefficient at 412 nm (absorbance data from Stubbins et al., 2006a). Other CO AQY spectra are for the Pacific Ocean (Zafiriou et al., 2003; long grey dash) and the Atlantic Ocean (Ziolkowski, 2000; solid grey line).
Fig. 6. Top panel: seasonally averaged coloured dissolved organic matter (CDOM; black fill) and particulate (grey fill) absorption coefficient at 412 nm versus salinity in the Tyne estuary. Bottom panel: seasonally averaged carbon monoxide versus salinity in the Tyne estuary. Black fill, assuming only photons absorbed by CDOM are involved in carbon monoxide (CO) photoproduction; grey fill, assuming all photons absorbed by chromophores (i.e., CDOM plus particulates) are involved in CO photoproduction.