

**Apparent quantum
yields and
photoproduction in
the river Tyne**

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Carbon monoxide apparent quantum yields and photoproduction in the estuary Tyne

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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.,

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2002); the bleaching of CDOM colour (Del Vecchio and Blough, 2002; Helms et al., 2008); and the production of a suite of photoproducts, including CO₂ 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 super-saturation 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 (einsteins; E) absorbed at a given wavelength (λ). 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; Ziolkowski, 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 (≤ 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

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(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 $p\text{CO}_2$, 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

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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

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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 $\pm 1\%$. Mean percentage standard errors for sample replicates were $\leq 2\%$. 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).

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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 *a*CDOM derived from river water assuming conservative mixing, ($R\text{-}a\text{CDOM}_\lambda @ \text{St}_n$) was calculated as:

$$R\text{-}a\text{CDOM}_\lambda @ \text{St}_n = (\text{St}_n\text{-}a\text{CDOM}_\lambda - \text{NS}\text{-}a\text{CDOM}_\lambda * \text{St}_n\text{-}\text{SAL} / \text{NS}\text{-}\text{SAL}) / \text{St}_n\text{-}a\text{CDOM}_\lambda \quad (1)$$

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

$$\text{St}_n\text{-}\text{CO AQY}_\lambda = \text{St}_n\text{-}\text{R}\text{-}\text{CDOM}_\lambda * \text{R}\text{-}\text{CO AQY}_\lambda + (1 - \text{St}_n\text{-}\text{R}\text{-}\text{CDOM}_\lambda) * \text{NS}\text{-}\text{CO AQY}_\lambda \quad (2)$$

where $\text{R}\text{-}\text{CO AQY}_\lambda$ and $\text{NS}\text{-}\text{CO AQY}_\lambda$ 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

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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

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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):

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

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_{CDOM} and A_{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 ~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 ~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

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particulate load waters from a nearby wastewater outfall (Howdon). Whole estuary CO photoproduction from CDOM was estimated to be $1.38 \text{ Tonnes-C yr}^{-1}$.

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_{CDOM} and A_{Total} were removed from Eq. 5). This provides an upper limit to CO production in the Tyne ($3.57 \text{ Tones-C yr}^{-1}$), 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 $\sim 25\,600 \text{ Tonnes-C yr}^{-1}$ based upon an annually averaged freshwater flow rate of $55 \text{ m}^3 \text{ s}^{-1}$ for the period 1998–2001 (Environment Agency, UK; <http://www.environment-agency.gov.uk>) and an annually averaged freshwater DOC concentration of $1230 \mu\text{M}$ (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.

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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 ($\sim 55^\circ$ N) is subject to moderate light levels and receives inputs of high DOC river water (average: 1200 μ M; 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 $\sim 4\%$ 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

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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.

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References

- Ahad, J. M. E., Barth, J. A. C., Ganeshram, R. S., Spencer, R. G. M., and Uher, G.: Controls on carbon cycling in two contrasting temperate zone estuaries: The Tyne and Tweed, UK, *Estuar. Coast. Shelf Sci.*, 78, 685–693, 2008.
- Andrews, S. S., Caron, S., and Zafiriou, O. C.: Photochemical oxygen consumption in marine waters: A major sink for colored dissolved organic matter?, *Limnol. Oceanogr.*, 45, 267–277, 2000.
- Bates, T. S., Kelly, K. C., Johnson, J. E., and Gammon, R. H.: Regional and seasonal variations in the flux of carbon monoxide to the atmosphere, *J. Geophys. Res.*, 100(D11), 23093–23101, 1995.
- Bremner, A.: The late glacial geology of the Tay Basin from pass of Birnam to Grandtully and Pitlochry, *Trans. Edinburgh Geol. Soc.*, 13, 473–483, 1939.
- Bryant, R. G. and Gilvear, D. J.: Quantifying geomorphic and riparian land cover changes either side of a large flood event using airborne remote sensing: River Tay, Scotland, *Geomorphology*, 29, 307–321, 1999.
- Calvert, J. G. and Pitts Jr., J. N.: *Photochemistry*, John Wiley and Sons, New York, 1966.
- Conrad, R., Seiler, W., Bunse, G., and Giehl, H.: Carbon monoxide in seawater (Atlantic Ocean), *J. Geophys. Res.*, 87(C11), 8839–8852, 1982.

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- Del Vecchio, R. and Blough, N. V.: Photobleaching of chromophoric dissolved organic matter in natural waters: Kinetics and modeling, *Mar. Chem.*, 78, 231–253, 2002.
- Del Vecchio, R. and Blough, N. V.: On the origin of the optical properties of humic substances, *Environ. Sci. Technol.*, 38, 3885–3891, 2004.
- 5 Doney, S. C., Najjar, R. G., and Stewart, S.: Photochemistry, mixing and diurnal cycles in the upper ocean, *J. Mar. Res.*, 53, 341–369, 1995.
- Gao, H. Z. and Zepp, R. G.: Factors influencing photoreactions of dissolved organic matter in a coastal river of the southeastern United States, *Environ. Sci. Technol.*, 32, 2940–2946, 1998.
- 10 Gnanadesikan, A.: Modeling the diurnal cycle of carbon monoxide: Sensitivity to physics, chemistry, biology, and optics, *J. Geophys. Res.*, 101(C5), 12177–12191, 1996.
- Graedel, T. E. and Crutzen, P. J.: *Atmospheric Change, An Earth System Perspective*, W. H. Freeman and Company, 1993.
- Gueymard, C.: SMARTS2: A Simple Model of the Atmospheric Radiative Transfer of Sunshine: Algorithms and performance assessment, Florida Solar Energy Center, Report No.: FSEC-PF-270-95, 1995.
- 15 Helms, J. R., Stubbins, A., Ritchie, J. D., Minor, E. C., Kieber, D. J., and Mopper, K.: Absorption spectral slopes and slope ratios as indicators of molecular weight, source, and photobleaching of chromophoric dissolved organic matter, *Limnol. Oceanogr.*, 53, 955–969, 2008.
- 20 Hope, D., Billett, M. F., Milne, R., and Brown, T. A. W.: Exports of organic carbon in British rivers, *Hydrol. Process.*, 11(3), 325–344, 1997.
- Hu, C. M., Muller-Karger, F. E., and Zepp, R. G.: Absorbance, absorption coefficient, and apparent quantum yield: A comment on common ambiguity in the use of these optical concepts, *Limnol. Oceanogr.*, 47, 1261–1267, 2002.
- 25 Johnson, J. E. and Bates, T. S.: Sources and sinks of carbon monoxide in the mixed layer of the tropical South Pacific Ocean, *Global Biogeochem. Cy.*, 10(2), 347–359, 1996.
- Kettle, A. J.: A model of the temporal and spatial distribution of carbon monoxide in the mixed layer, M.Sc. Thesis. Woods Hole Oceanogr. Inst.-Mass. Inst. of Technol. Joint Program in Oceanogr., Woods Hole, MA, 1994.
- 30 Kettle, A. J.: Diurnal cycling of carbon monoxide (CO) in the upper ocean near Bermuda, *Ocean Model.*, 8, 337–367, 2005.
- Maitland, P. S. and Smith, I. R.: *The River Tyne: ecological changes from source to estuary*, *Philos. Roy. Soc. Edinb.*, 92B, 373–392, 1987.

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- Miller, W. L. and Zepp, R. G.: Photochemical production of dissolved inorganic carbon from terrestrial organic-matter: Significance to the oceanic organic-carbon cycle, *Geophys. Res. Lett.*, 22(4), 417–420, 1995.
- 5 Miller, W. L., Moran, M. A., Sheldon, W. M., Zepp R. G., and Opsahl, S.: Determination of apparent quantum yield spectra for the formation of biologically labile products, *Limnol. Oceanogr.*, 47(2), 343–352, 2002.
- Miller, A. E. J.: Seasonal investigations of dissolved organic carbon dynamics in the Tamar Estuary, UK, *Estuar. Coast. Shelf S.*, 49(6), 891–908, 1999.
- 10 Mopper, K. and Kieber, D. J.: Marine photochemistry and its impact on carbon cycling, in: *The Effects of UV Radiation in the Marine Environment*, edited by: de Mora, S., Demers, S., and Vernet, M., Cambridge Environ. Chem. Ser., vol. 10, Cambridge Univ. Press, New York, 101–129, 2000.
- Mopper, K. and Kieber, D. J.: Impact of DOM Photochemistry on the Biogeochemical Cycling of Carbon, Nitrogen, Sulfur and Phosphorus in the Sea, in: *Biogeochemistry of Marine Dissolved Organic Matter*, edited by: Carlson, C. and Hansell, D., Academic Press, 456–503, 2001.
- 15 Moran, M. A. and Zepp, R. G.: Role of photoreactions in the formation of biologically labile compounds from dissolved organic matter, *Limnol. Oceanogr.*, 42, 1307–1316, 1997.
- Najjar, R. G., Erickson III, D. J., and Madronich, S.: Modeling the air-sea fluxes of gases formed from the decomposition of dissolved organic matter: Carbonyl sulfide and carbon monoxide, in: *The Role of Nonliving Organic Matter in the Earth's Carbon Cycle: Report of the Dahlem Workshop on the Role of Nonliving Organic Matter in the Earth's Carbon Cycle*, edited by: Zepp, R. G. and Sonntag, C., Berlin 1993, 12–17 September, John Wiley, New York, 107–132, 1995.
- 20 Nelson, N. B., Siegel, D. A., and Michaels, A. F.: Seasonal dynamics of colored dissolved organic material in the Sargasso Sea, *Deep-Sea Res. Pt. I*, 45(6), 931–957, 1998.
- Sjöberg, T. N.: The distribution and cycling of dissolved carbon monoxide in estuarine, coastal and shelf break environments, Ph.D. thesis, Univ. of East Anglia, UK, 1999.
- Spencer, R. G. M., Ahad, J. M. E., Baker, A., Cowie, G. L., Ganeshram, R., Upstill-Goddard, R. C., and Uher, G.: The estuarine mixing behaviour of peatland derived dissolved organic carbon and its relationship to chromophoric dissolved organic matter in two North Sea estuaries (UK), *Estuar. Coast. Shelf S.*, 74, 131–144, 2007.
- 30 Stubbins, A.: Aspects of aquatic CO photoproduction from CDOM, Ph.D. Thesis, University of

Apparent quantum yields and photoproduction in the river Tyne

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Newcastle-upon-Tyne, UK, 2001.

Stubbins, A., Uher, G., Kitidis, V., Law, C. S., Upstill-Goddard, R., and Woodward, E. M. S.: The open ocean source of atmospheric carbon monoxide, *Deep-Sea Res. Pt. II*, 53, 1685–1694, 2006.

5 Stubbins, A., Uher, G., Law, C. S., Mopper, K., Robinson, C., and Upstill-Goddard, R. C.: Open ocean carbon monoxide photoproduction, *Deep-Sea Res. Pt. II*, 53, 1695–1705, 2006.

Stubbins, A., Hubbard, V., Uher, G., Aiken, G., Law, C. S., Upstill-Goddard, R. C., and Mopper, K.: Relating carbon monoxide photoproduction to dissolved organic matter functionality, *Environ. Sci. Technol.*, 42, 3271–3276, 2008.

10 Thompson, A. M. and Cicerone, R. J.: Atmospheric CH₄, CO and OH from 1860 to 1985, *Nature*, 321, 6066, 148–150, 1986.

Valentine, R. L. and Zepp, R. G.: Formation of Carbon-Monoxide from the Photodegradation of Terrestrial Dissolved Organic-Carbon in Natural-Waters, *Environ. Sci. Technol.*, 27, 409–412, 1993.

15 Watts-Rodrigues, P.: Modelling nitrous oxide production in two contrasting British estuaries: The Forth and the Tyne, Ph.D. Thesis, University of Newcastle-upon-Tyne, UK, 2003.

Whitehead, R. F. and de Mora, S.: Marine photochemistry and UV radiation, in: Hester, R.E., Harrison, R.M. (Eds.), *Causes and environmental implications of increased UV-B radiation*, The Royal Society of Chemistry, 37–60, 2000.

20 Xie, H. and Zafiriou, O. C.: Evidence for significant photochemical production of carbon monoxide by particles in coastal and oligotrophic marine waters, *Geophys. Res. Lett.*, 36, L23606, doi:10.1029/2009GL041158, 2009.

Zafiriou, M. C., Andrews, S. S., and Wang, W.: Concordant estimates of oceanic carbon monoxide source and sink processes in the Pacific yield a balanced global “blue-water” CO budget, *Global Biogeochem. Cy.*, 17(15), 15–13, 2003.

25 Zepp, R. G. and Cline, D. M.: Rates of direct photolysis in aquatic environments, *Environ. Sci. Technol.*, 11, 359–366, 1977.

Zhang, Y., Xie, H., and Chen, G.: Factors affecting the efficiency of carbon monoxide photoproduction in the St. Lawrence estuarine system (Canada), *Environ. Sci. Technol.*, 40, 7771–7777, 2006.

30 Ziolkowski, L.: Marine photochemical production of carbon monoxide, M.Sc. thesis, Dalhousie Univ., CA, 2000.

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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.

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

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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.

Wavelength (nm)	Mixing	CDOM a_{412}
285	37	11
295	45	7
305	40	17
325	58	13
345	69	28
364	72	18
423	62	5
Spectral Mean	55	14

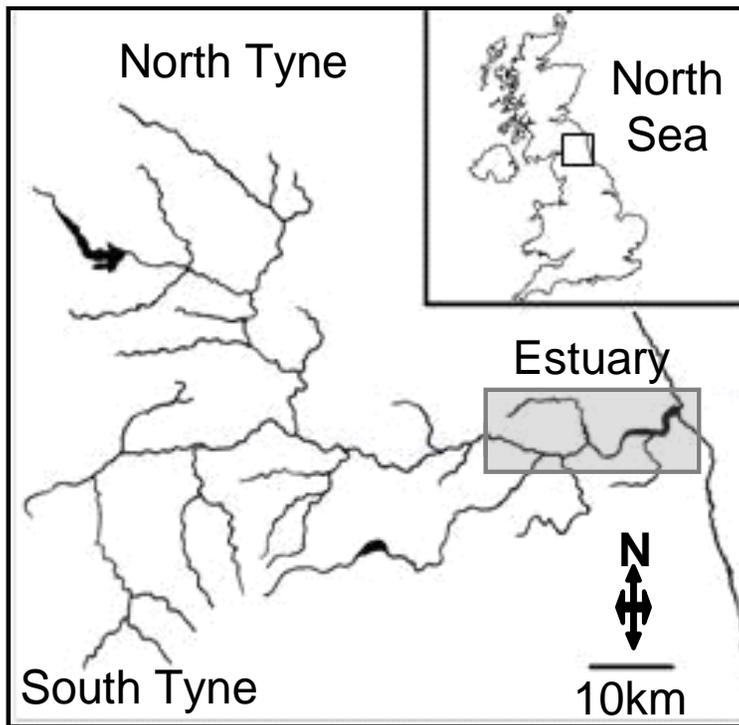


Fig. 1. Tyne catchment with North Tyne, South Tyne and Tyne estuary marked. Inset: map of UK showing location of the Tyne catchment.

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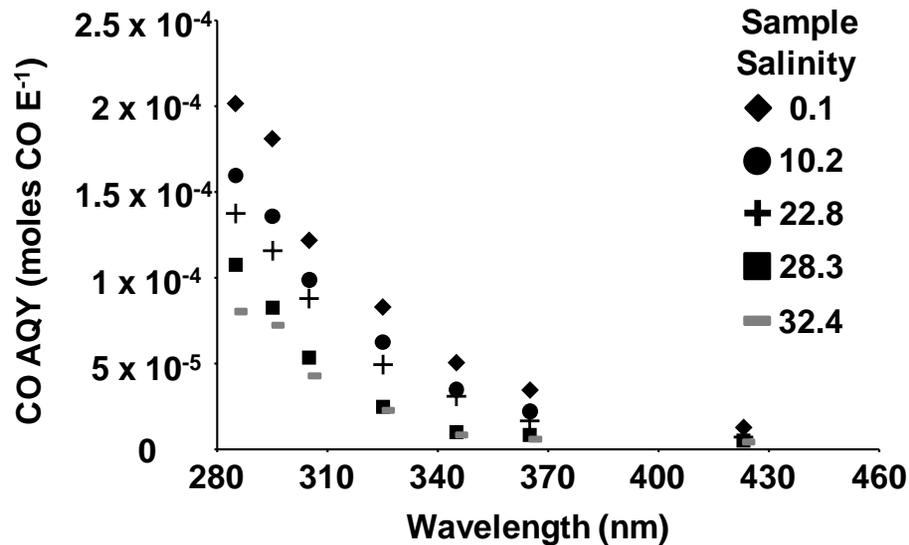


Fig. 2. Carbon monoxide apparent quantum yield spectra for the Tyne estuary.

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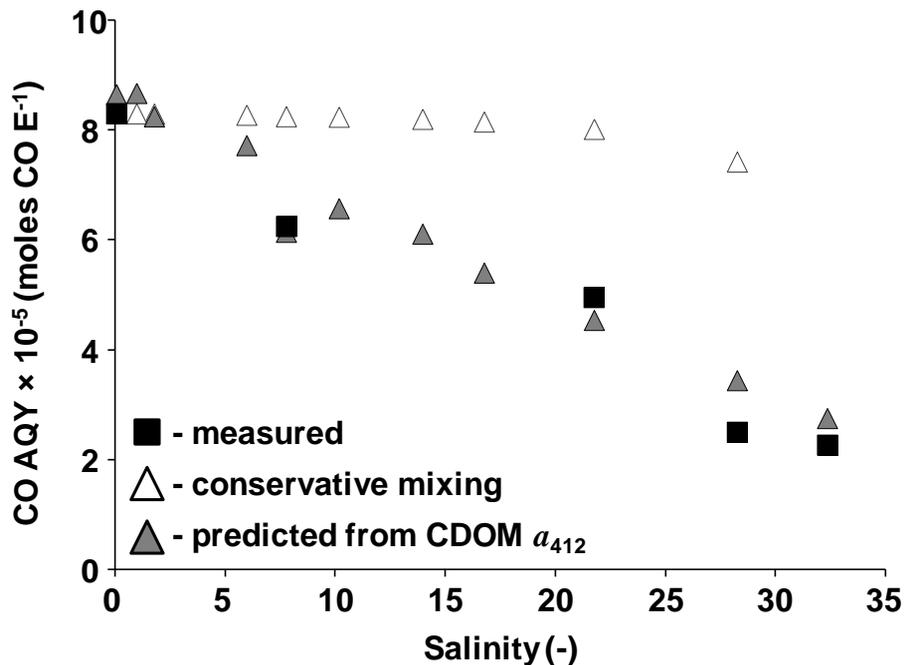


Fig. 3. Measured and modelled carbon monoxide apparent quantum yields (CO AQYs) versus salinity in the Tyne estuary. Grey fill squares are measured values. No fill triangles are values predicted based upon a conservative mixing model of the river water and marine endmembers of the Tyne estuary. Black fill triangles are values predicted using in situ CDOM a_{412} as a proxy for CO AQYs.

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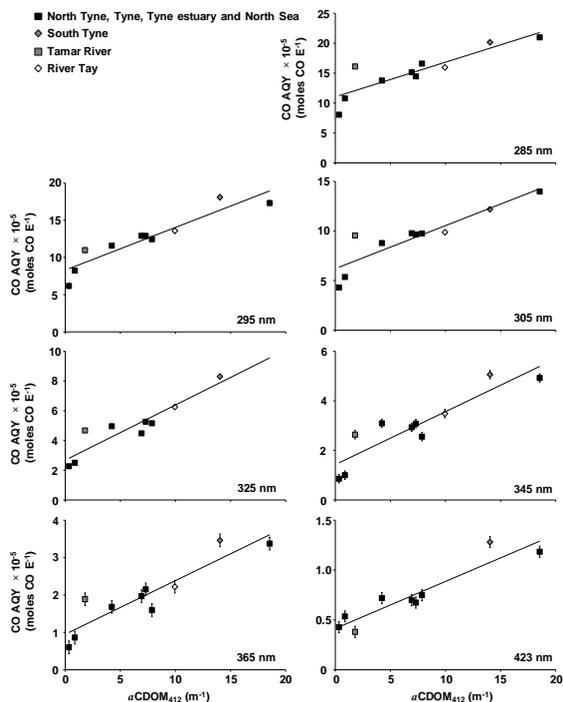


Fig. 4. Measured riverine, estuarine and coastal seawater carbon monoxide apparent quantum yields (CO AQYs) versus sample absorption coefficient at 412 nm ($CDOM_{412}$). Black fill squares are from the North Tyne, River Tyne, Tyne estuary and coastal North Sea (North East England); grey fill diamond 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 $CO\ AQY_{\lambda} = y_0 + m \times a_{412}$, y_0 is the y-intercept (CO AQY) and m the slope of linear regressions of CO AQY at wavelength, λ , against sample CDOM absorption coefficient at 412 nm (a_{412}). Curve parametrisations can be found in Table 4.

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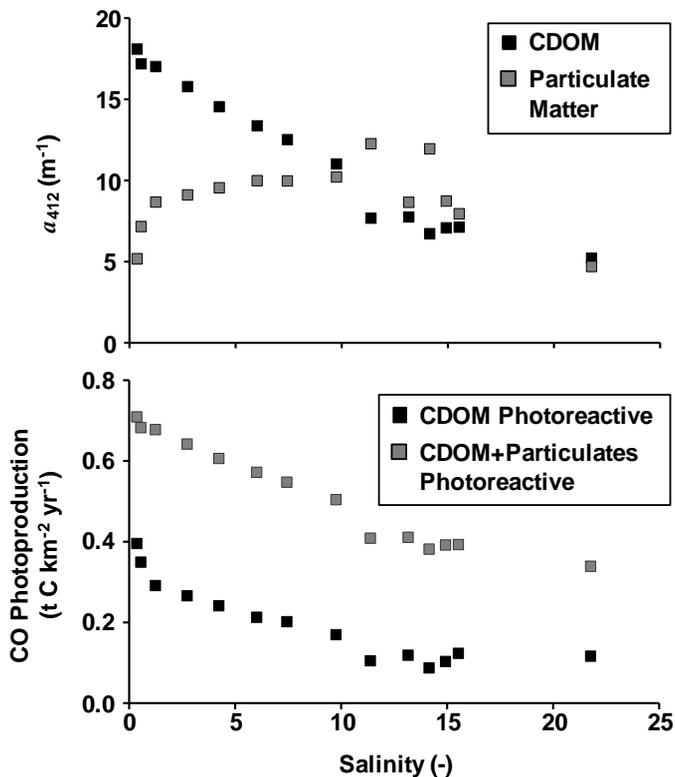


Fig. 6. Top panel: seasonally averaged coloured dissolved organic matter (CDOM; black fill) and particulate (grey fill) absorption coefficient at 412 nm versus salinity in the Tyne estuary. Bottom panel: seasonally averaged carbon monoxide versus salinity in the Tyne estuary. Black fill, assuming only 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.

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