The estuarine mixing behaviour of peatland derived dissolved organic carbon and its relationship to chromophoric dissolved organic matter in two North Sea estuaries (U.K.)

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Abstract

The mixing behaviour of dissolved organic carbon (DOC) was investigated in two U.K. estuaries with peatland derived river inputs (Tyne and Tweed), under varying discharge regimes and in different seasons. DOC removal (i.e. non-conservative) was common to both estuaries at low salinities, but DOC addition also occurred in the Tyne at higher salinities due to inputs from a large sewage treatment works and polluted urban rivers. DOC in freshwater endmembers was in the range 608.1–2326.5 μM (mean 1229.6 μM, $n = 7$) for the Tyne and was 226.1 and 668.2 μM on two occasions in the Tweed; the high DOC concentrations reflecting the peatland nature of the catchments and high river discharge. DOC removal in the Tyne estuary was in the range 0–58% ($n = 7$) (one transect exhibits 0% removal as pollution sources of DOC dominate medium to high salinity samples so it was not possible to extrapolate a conservative mixing line back to low salinities). Highest percent removals were at highest river flows and correspondingly high turbidity and DOC concentrations in the Tyne estuary. In contrast, DOC removal in the Tweed estuary was consistently 6% ($n = 2$), and appeared independent of river flow, turbidity and DOC concentration on the two transects conducted. Both estuaries exhibited a strong correlation between the chromophoric dissolved organic matter (CDOM) absorption coefficient at 350 nm (a_{350}) and DOC which was seasonally robust; Tweed ($r^2 = 0.98$, $p < 0.001$, $n = 20$), Tyne ($r^2 = 0.85$, $p < 0.001$, $n = 87$) and Tyne without potentially anthropogenic or sedimentary derived DOM source samples ($r^2 = 0.93$, $p < 0.001$, $n = 74$). The robust nature of these relationships implies that remotely sensed CDOM characteristics have the potential to improve the spatio-temporal resolution of estuarine DOC. This study highlights the variation in estuarine removal of peatland derived DOC between the two estuaries and in the Tyne estuary it shows how differences in river regime can result in significant changes in DOC removal at low salinities. Our findings demonstrate the need to conduct DOM sampling under varying seasons and hydrological regimes to accurately quantify the removal of terrigenous DOM in estuaries and its subsequent flux to the oceans.

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1. Introduction

The annual global river discharge of terrigenous dissolved organic carbon (DOC) is ~ 0.25 Pg. Understanding the subsequent fate of this DOC in the ocean is key to interpreting the global carbon cycle (Hedges et al., 1997). DOC is a bulk characteristic of the dissolved organic matter (DOM) pool, which undergoes a variety of biogeochemical reactions in estuaries that ultimately influence both the concentration and the composition of DOM (and DOC) reaching the ocean. Perhaps unsurprisingly, the behaviour of terrigenous DOM (and DOC) during estuarine mixing is variable. Conservative behaviour of DOC in many estuaries (e.g. Mantoura and Woodward, 1983; Alvarez-Salgado and Miller, 1998; Abril et al., 2002) has been interpreted to reflect comparatively small estuarine modification of the terrigenous DOM input. In other estuaries non-conservative mixing behaviour at low salinities has been attributed to removal of specific DOM components (Benner and Opsahl, 2001; Hernes and Benner, 2003) and flocculation or adsorption of the humic-rich high molecular weight (HMW) fraction of DOM (Sholkovitz et al., 1978; Fox, 1983; Uher et al., 2001). However, it is important to be aware of the distinct estuarine behaviour of different DOM fractions or bulk characteristics such as DOC and its molecular size fractions. Sholkovitz et al. (1978) for example observed 60–80% removal of humic acids by flocculation at low salinities in the Amazon, but the corresponding removal of DOC was only 3–6%. Estuaries draining peatland catchments were previously found to show only minor DOM removal (<5%), largely attributed to flocculation (Amon and Meon, 2004 and references therein). In addition to flocculation, DOM adsorption onto suspended sediments has also been documented (Uher et al., 2001; Shank et al., 2005) presumably due to high suspended particle loads in combination with the increase in ionic strength at the land-ocean interface (Fig. 1).

In addition to flocculation and adsorptive DOM removal, both microbial degradation (Amon and Benner, 1996a; Hernes and Benner, 2003) and photochemical degradation (Kieber et al., 1990) may also be important removal processes for terrigenous DOM (Fig. 1). Lignin-derived phenols are terrigenous biomarkers that have been shown to undergo both net removal and compositional changes (including a decrease in the percentage of lignin in the HMW fraction) during terrigenous DOM photooxidation (Opsahl and Benner, 1998; Hernes and Benner, 2003). Furthermore, a number of studies have shown the photochemical degradation of DOM to result in a range of bioavailable products (Bushaw et al., 1996; Miller and Moran, 1997; Moran and Zepp, 1997). This is particularly true in the case of terrigenous DOM which has been found to be generally more susceptible to photochemical degradation than marine DOM and combined photochemical followed by microbial degradation has been shown to be a significant process for its removal in the marine system (Kieber et al., 1990; Amon and Benner, 1996b; Miller and Moran, 1997; Hernes and Benner, 2003). Finally, apparent non-conservative behaviour of DOM within estuaries is often a result of inputs from sources such as anthropogenic activity (e.g. the Scheldt), phytoplankton (e.g. Chesapeake Bay and the Mississippi), intertidal areas (e.g. the Sado and the Ems), tributaries (e.g. the Pearl) and desorption from sediments and mixing of porewaters (e.g. the Tamar and the Gironde) (Abril et al., 1999; Miller, 1999; Benner and Opsahl, 2001; Abril et al., 2002; Rochelle-Newall and Fisher, 2002; Chen et al., 2004) (Fig. 1).

A number of recent studies have highlighted increasing DOC concentrations in U.K. rivers and catchments draining uplands dominated by peatland areas and attributed these findings to global climate change (Freeman et al., 2001; Worrall et al., 2003, 2004) with potentially important consequences for the flux of terrigenous DOC to the ocean. In this study we report DOC distributions in two U.K. estuaries (Tyne and Tweed) which are fed by rivers draining predominantly peatland catchments. The aim of this part of the study was to determine the estuarine mixing behaviour of DOC under varying riverine discharge and to ascertain the controlling factors on any deviation away from conservative mixing behaviour (e.g. DOM concentration and composition, suspended particulate loads). We further report relationships between DOC and the CDOM absorption coefficient measured at 350 nm (a_{350}) in these estuaries to examine the potential for rapid and inexpensive monitoring of DOC export in estuaries and coastal regions by utilising CDOM as a proxy. Numerous recent studies have utilised CDOM absorbance as a tracer of terrigenous inputs (Blough et al., 1993; Vodacek et al., 1997; Hernes and Benner, 2003; Stedmon et al., 2006). In this study a_{350} was chosen to investigate terrigenous DOM behaviour in the two estuaries as previous studies have shown correlations between the absorption of light at ~ 350 nm and terrigenous DOM (see Hernes and Benner, 2003 and references therein) and as such it has potential for remote sensing applications.

2. Materials and methods

2.1. Study sites

The Tyne estuary (Fig. 2a) is ~ 33 km in length. It is a partially mixed mesotidal estuary which undergoes significant stratification during neap tides which gives way to well-mixed conditions during spring tide regimes. Mean freshwater residence is in the range 6.3–23.4 days (annual mean ~ 11.7 days) (Watts-Rodrigues, 2002). The River Tyne draining a predominantly rural catchment of 2935 km^2 and with a mean freshwater discharge of ~ 45 m^3 s^{-1} accounts for $\sim 90\%$ of all freshwater in the estuary. The remaining $\sim 10\%$ of the freshwater discharge into the Tyne estuary is provided by three polluted urban rivers; the Derwent, the Team and the Ouseburn (Fig. 2a). The catchment of the R. Tyne is dominated by large areas of open and afforested peatland that are potentially large sources of DOC to the river and estuary. Within the Tyne catchment soils are thin and slow draining, the underlying bedrocks having low permeability; thus resulting in a strong dominance of surface runoff over baseflow. Consequently precipitation even in remote areas of the catchment, typically reaches the R. Tyne within 24 h. In comparison to the Tweed catchment the Tyne catchment has little arable agricultural land ($\sim 5\%$) as a result of the
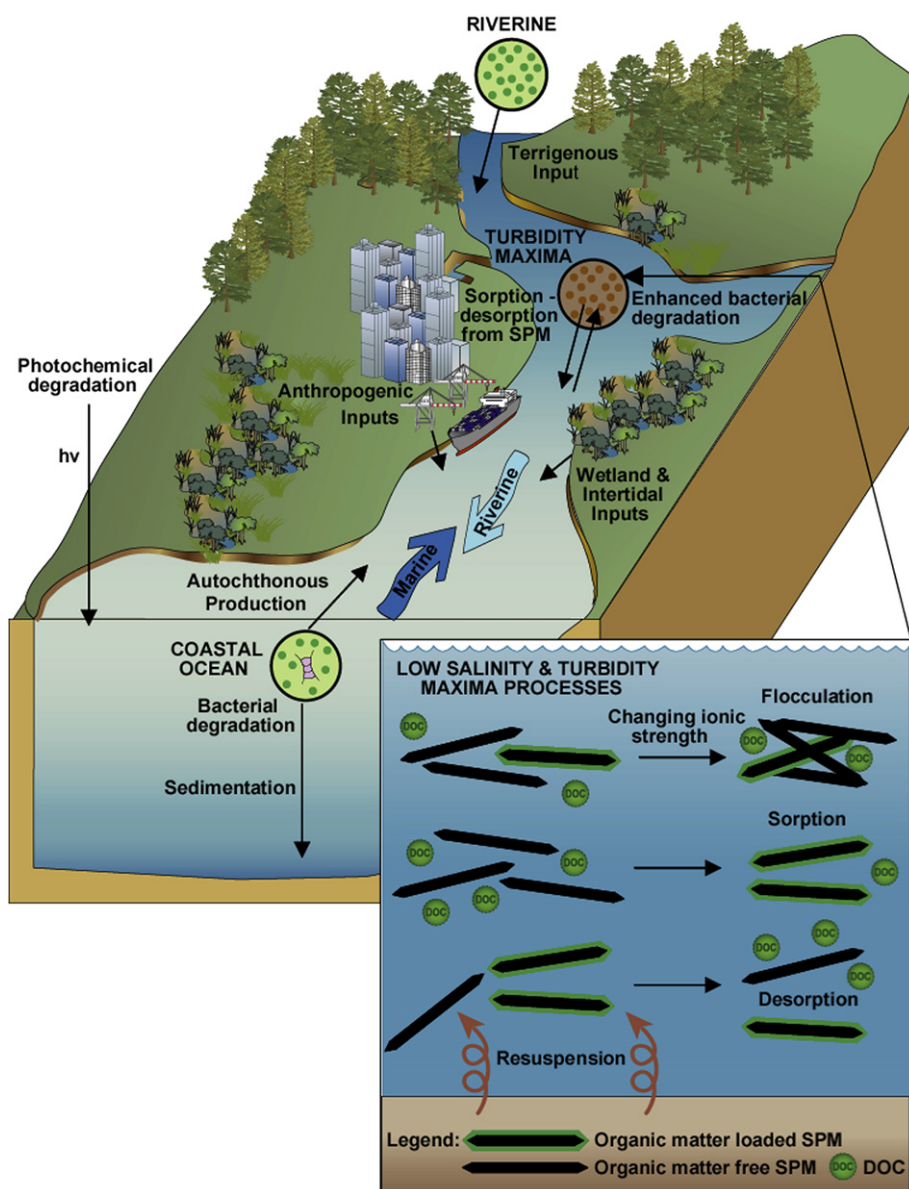
Fig. 1. Dissolved organic matter sources and removal processes in the estuarine environment highlighting low salinity and turbidity maxima zone processes (insert).

dominance of blanket peat bog and moorland in the catchment. Although the R. Tyne catchment maybe considered relatively pristine, estuarine water quality is modified by inputs associated with a population of ∼900,000 people centered on the city of Newcastle-upon-Tyne (Fig. 2a). These inputs include 214 consented discharges from sewage treatment works (STW), 126 consented industrial discharges and 492 storm sewage discharges. The most important STW is Howdon (secondary treatment) (Fig. 2a) which is the third largest estuarial discharge in the U.K. with potentially important contributions of dissolved nutrients and organic matter in the lower estuary.

The Tweed estuary (Fig. 2b) is ∼13 km in length, is microtidal, ranges from partially mixed to stratified, and has a freshwater residence time ∼1 day (Uncles and Stephens, 1996). The River Tweed with a mean freshwater discharge of 84 m^3 s^{-1} (Fox, 1997) accounts for ∼90% of all freshwater in the estuary, the remainder deriving from the River Whiteadder (Fig. 2b). The combined catchment of the Rivers Tweed and Whiteadder covers 4900 km^2. The upper Tweed catchment drains an area of predominantly Ordovician and Silurian greywackes and shales and the upper catchment is characterised by low intensity land uses such as sheep grazing, significant coniferous forestry and large areas of heather moorland. In the lower reaches of the catchment the dominant geology shifts to sandstones and volcanic rocks and moorland gives way to extensive areas of arable agricultural land. In contrast to the Tyne the Tweed estuary experiences only very mild anthropogenic impact (from agriculture) and has been described as showing high water quality (Uncles and Stephens, 1996).

2.2. Estuarine sampling

Estuarine axial transects were conducted from a rigid inflatable boat (RIB) and RV *Bernicia*; nine in the Tyne and two in
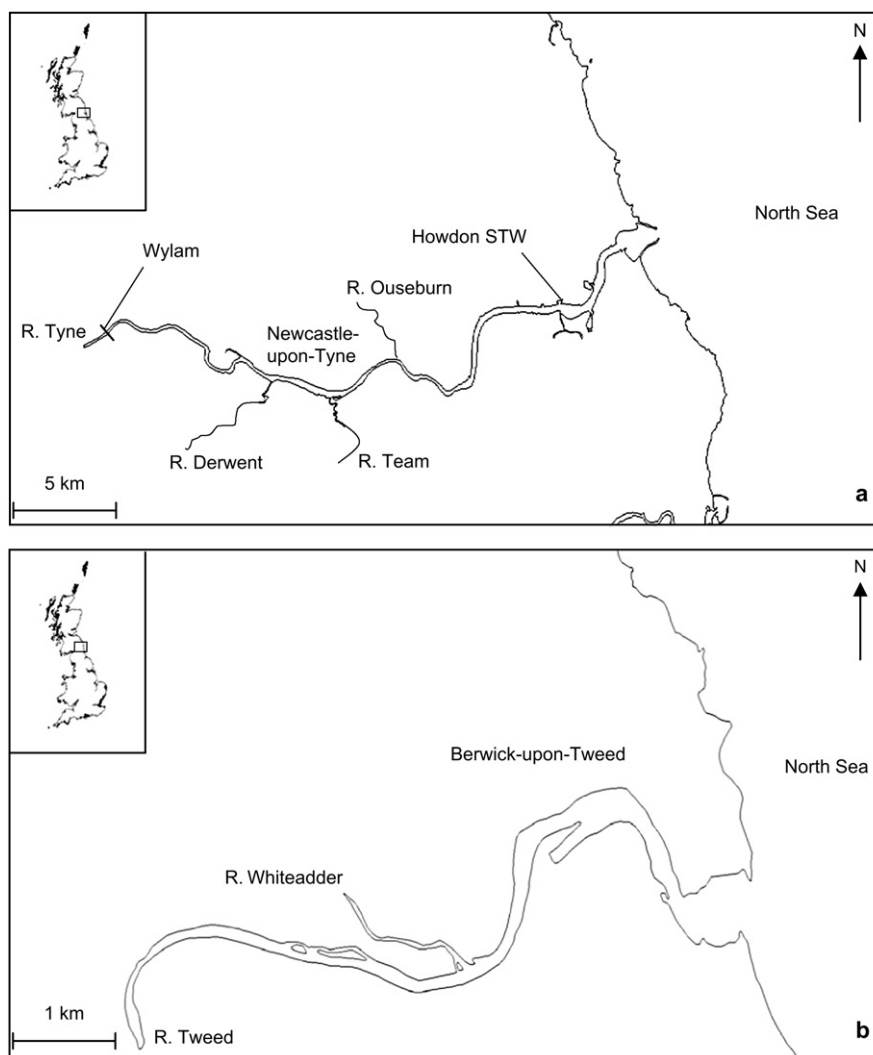
Fig. 2. (a) Map of the Tyne estuary. (b) Map of the Tweed estuary.

the Tweed. The sampling of both estuaries was always timed to span high tide and was carried out in ≤2 h. Near-surface water samples (1–2 m depth) were collected by submersible pump, at selected salinities measured in situ using a portable multiparameter probe (Horiba model U-10) or a conductivity meter (Hanna Instruments, model HI 8633). On two occasions in the Tyne (04-10-2002 & 23-07-2003) no low salinity samples (below salinity 11.0 and 13.9 respectively) could be collected due to the risk of grounding associated with low river discharge, and in another Tyne transect (01-08-2002) a representative seawater endmember could not be collected due to high river flow (low salinity waters extending far offshore) coupled with severe adverse weather.

Water samples for DOC and CDOM analysis were immediately filtered (Whatman GF/F, 0.7 μm, precombusted at 450 °C for 4 h) into acid cleaned, precombusted (550 °C for 8 h) 20 ml glass vials with Teflon-lined caps which were triple rinsed with filtrate before final collection. Samples for DOC analysis were also acidified upon collection to pH ∼ 2 (Baker Analysed, HCl) and then both DOC and CDOM samples were stored in the dark at 4 °C until return to the laboratory. On

return to the laboratory samples for DOC analysis to be stored in excess of 2 weeks were frozen (−20 °C). Turbidity in nephelometric turbidity units (NTU) was measured in situ (Horiba U-10 probe) or gravimetrically as suspended particulate matter (SPM) on preweighed quartz fibre filters (Whatman GF/F, 0.7 μm, precombusted at 450 °C for 4 h).

2.3. Dissolved organic carbon/total dissolved nitrogen analysis

DOC and total dissolved nitrogen (TDN) analyses were by high temperature catalytic oxidation (HTCO) using a coupled Shimadzu TOC 5000A to either a Sievers NCD 255 or an Antek 705E nitrogen chemiluminesence detector (NCD). The acidified samples were sparged with ultra pure oxygen (i.e. carbon free: BOC 99.999% O_2 also used as system carrier gas) at 75 ml min^{-1} for 8 min and 100 μl of sample was injected onto the analytical column/catalyst (0.5% Pt/Al_2O_3) at 680 °C. The combusted gases were subsequently dried using a dehumidifier, purified in a halogen scrubber and analysed for CO_2 concentration with a non-dispersive infra-red detector

(NDIRD). The signal (voltage) from the NDIRD was recorded using a data collection and integration system and the peak area was used to quantify the DOC concentration. The combustion gases on exiting the NDIRD were routed directly into the NCD by means of a vacuum pump. The NO in the combustion gases was then reacted with O_3 produced within the NCD to form electronically excited NO_2* which chemiluminesces upon decay to its ground state. The light emitted (hυ) was detected by a photomultiplier tube (PMT) and the signal (voltage) was recorded using a data collection and integration system, with peak area used to quantify the TDN concentration. DON concentration was calculated from TDN concentration minus dissolved inorganic nitrogen (DIN) species concentrations. DIN analyses were carried out following established protocols with a Skalar San^{plus} analyser (for a detailed description of DIN methodology see Spencer et al., 2007).

All DOC and DON data reported in this paper are the mean of three to five replicate injections, for which the coefficient of variance (c.v.) was always <2%. Daily instrument calibration used a mixture of potassium hydrogen phthalate and glycine solutions (C:N, 6:1) prepared in analytical grade water (Millipore Milli-Q plus 185). The c.v. for DOC analysis was typically <1% at 100 μM C ($n = 3–5$) and for TDN typically <1.5% at 25 μM N ($n = 3–5$). As no individual compound can fully represent naturally occurring DOM, certified reference materials (CRM's) obtained from the Biogeochemical Group at the Division of Marine and Atmospheric Chemistry, University of Miami, USA were used. Deep Sargasso Seawater (44–45 μM DOC and 21 μM TDN) was run routinely at the start of every batch of analysis and also between samples and the values obtained (40–48 μM DOC and 19–22 μM TDN) are in good agreement with the certified values. In addition an inhouse standard (R. Tyne water: 733.0 μM DOC and 80 μM TDN; collected 11/07/2002) was also run with every DOC/TDN batch analysis and the values obtained over the course of the analyses (731.6–735.9 μM DOC and 77.5–82.2 μM TDN) are also in good agreement with the initial analysis.

As some samples for DOC and DON measurement were stored frozen and some samples analysed after refrigeration a storage experiment was undertaken for 12 months to investigate any changes in DOC and DON concentrations. On comparison of samples stored refrigerated vs. frozen there was no observable change in DOC and DON concentrations with time (SD 0.5%). Previous studies have also found insignificant differences between these two storage methods with respect to measurement of DOC concentration (Tupas et al., 1994).

2.4. CDOM absorbance analysis

CDOM absorbance was determined over the 250–800 nm wavelength range, on a double beam UV-visible spectrophotometer (Kontron Instruments, Uvicon 923). All samples were measured in quartz cuvettes sequentially pre-rinsed with 0.1 M HCl, copious amounts of Milli-Q and three volumes of sample. All samples were analysed at least in duplicate within 24 h of collection at a constant laboratory temperature of 20 °C. Short pathlength (10 mm) cuvettes were typically used for river and low salinity estuarine samples (absorbance ≥0.02 at 350 nm). If absorbance values were <0.02 at 350 nm measured in a 10 mm cuvette, a long pathlength cuvette (100 mm) was used (typically high salinity estuarine and North Sea samples). All spectra were referenced to a blank Milli-Q spectrum and corrected for a small offset due either to long-term baseline drift or potentially derived from glass fibre particles during filtration (Blough et al., 1993) by subtracting the average absorbance between 700 and 800 nm. CDOM absorption coefficients, $a(\lambda)$, were calculated from:

$$a(\lambda) = 2.303A(\lambda)/l \tag{1}$$

where $A(\lambda)$ is the absorbance and l is the cell pathlength in metres (Green and Blough, 1994). All absorbance data presented in this manuscript are expressed as $a(\lambda)$ in units of m^{-1} (Hu et al., 2002).

3. Results and discussion

3.1. Riverine dissolved organic carbon variability

Riverine discharge data are an important aid to evaluating mixing behaviour in estuaries. Riverine discharge data (Fig. 3) are shown for the time period covering estuarine sampling and the discharge data described are typical of rivers in the region. High river discharge is observed in winter and typically low river discharge is observed in summer with occasional high flow storm events.

DOC concentration in the Tyne riverine end member ranged from 608.1 to 2326.5 μM (mean 1229.6 μM, $n = 7$) (Fig. 4a–i). The concentration of DOC measured in the R. Tyne is high compared to concentrations in other rivers, both in the U.K. and worldwide (Mantoura and Woodward, 1983; Miller, 1999; Abril et al., 2002; Benner, 2002) and, notably, exceeds levels observed even in other peatland rivers (Lobbes et al., 2000; Amon and Meon, 2004). The DOC concentrations in the Tweed riverine endmember ranged from 226.1 to 668.2 μM (mean 447.2 μM, $n = 2$) (Fig. 4j,k). DOC concentrations in the R. Tweed are comparable to other U.K. rivers (Mantoura and Woodward, 1983; Alvarez-Salgado and Miller, 1998; Miller, 1999) and are ∼3 fold below those in the R. Tyne.

High flow in the R. Tyne (Fig. 3a) corresponded to elevated riverine DOC concentrations (e.g. Fig. 4b,c) and low flow to lower riverine DOC concentrations. For example, the highest measured R. Tyne DOC concentrations (2243.5 and 2326.5 μM) occurred at the highest measured river flows (Fig. 3a; 31-07-2002 and 01-08-2002) during a summer storm event. The R. Tweed exhibited a pattern between river flow (Fig. 3b) and DOC concentration similar to that in the R. Tyne showing increased DOC concentrations at high river flow and decreased DOC concentrations at low river flow (Fig. 4j,k). For both rivers there was a greater than 3 fold increase in DOC concentration from
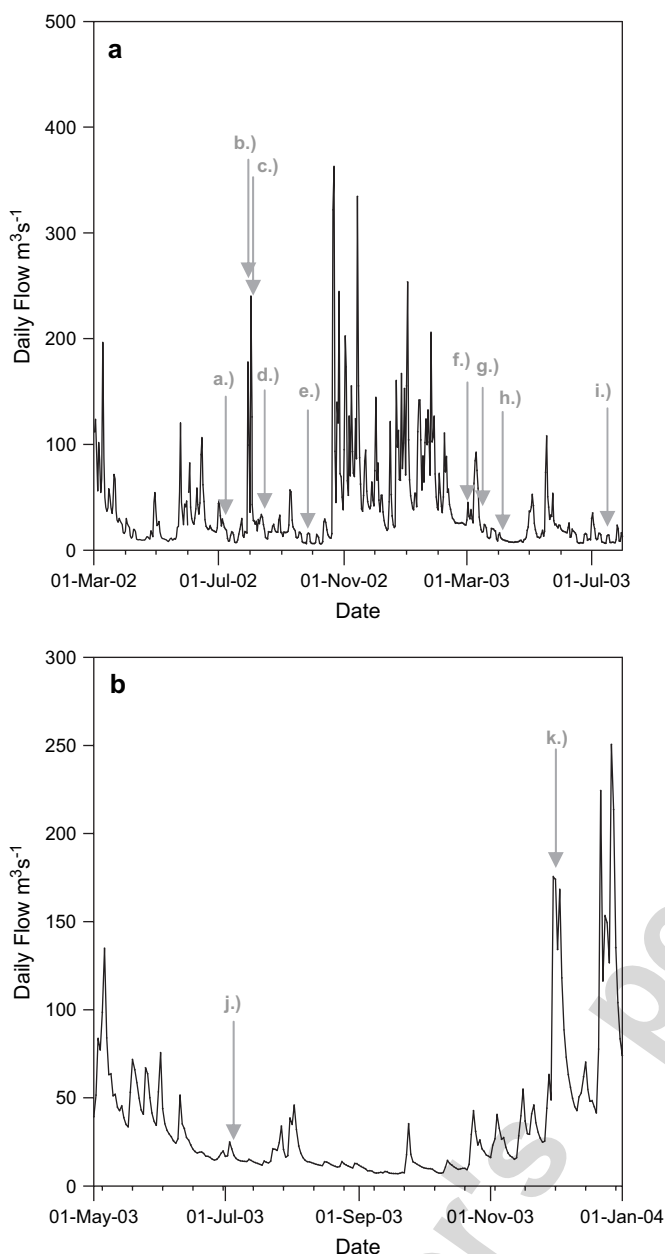
Fig. 3. Daily river discharge data: (a) River Tyne; and (b) River Tweed. Sampling dates are indicated by arrows; letters in grey correspond to respective graphs shown in Fig. 4.

Additionally, high DOC concentrations and fluxes have been reported in peatlands associated with disturbances, particularly afforestation (Cannell et al., 1999; Worrall et al., 2003) and so the high DOC concentrations in the R. Tyne may to some extent be as a result of the large afforestation on peatland (Kielder Forest) on the N. Tyne catchment.

3.2. Estuarine point sources of dissolved organic carbon

Howdon STW and the polluted urban rivers represented variable sources of DOC to the Tyne estuary in all transects; these were visible as mid-estuarine DOC maxima of varying magnitudes that certainly reflected changes in DOC input concentrations, water discharge rates and tidal state (Fig. 4a–i). Small sources of DOC could be observed across the mid-estuary (Fig. 4a,d–f; grey arrows) related to anthropogenic inputs (e.g. polluted urban rivers) and in one instance the mid-estuarine maximum even exceeded the concentration of DOC in the river water endmember (Fig. 4h; grey arrow). Hence, such inputs could affect DOC distributions both in the mid-estuary and potentially impact on adjacent coastal seawater under certain conditions. Howdon STW (Fig. 4; black arrows) could be seen to have variable impacts on DOC in the estuary from a small effect such as at salinities 30.9 in Fig. 4a, salinity 25.1 in Fig. 4b and salinity 27.1 in Fig. 4i and undoubtedly represented a significant source of DOC to the lower estuary at low river flow and potentially high STW discharge (Fig. 4g,h).

The highest measured DOC concentration (2479.5 μM) in all estuarine transects was recorded in the Tyne estuary correspondent with the highest river flow (Fig. 3a) and at a site in the estuary with a distinct spike showing the highest recorded turbidity in this study (Fig. 4c). This high DOC concentration may reflect mixing with DOC rich porewaters during sediment resuspension, as has been hypothesised for the high dissolved CH_4 observed in this region of the Tyne (Upstill-Goddard et al., 2000), or particle desorption due to changes in surface mineral structures under changing redox conditions during resuspension (Abril et al., 1999; Miller, 1999). In other words the estuary may be acting as a "fluidisied bed reactor" at this location, as observed in other estuaries such as the Humber (Alvarez-Salgado and Miller, 1998), the Tamar (Miller, 1999) and the Gironde (Abril et al., 1999).

3.3. Estuarine mixing and quantification of removal

Percent DOC removal at low salinities was estimated by initially deriving linear correlations between DOC and salinity for the most saline samples from each transect. Lower salinity samples were then progressively added, and the correlation was re-evaluated at each step, until the correlation coefficient began to decay (i.e. $r^2 \geq 0.99$; $n \geq 3$) due to the progressive decrease in linearity. With this procedure we obtained regression lines based on apparent conservative mixing behaviour of DOC in the lower estuary which could be extrapolated to zero salinity in order to obtain a riverine DOC concentration value for each transect. This extrapolated, riverine DOC

low flow to high flow river regimes. Chapman et al. (2001) found that the DOC concentration of a number of upland streams in Scotland was related to peat cover. DOC concentration of aquatic systems draining peatlands has been shown to be dependent on soil organic carbon content and therefore on the degree of peat degradation (Kalbitz and Geyer, 2002). Thus, the higher DOC concentrations observed in the R. Tyne likely result from the larger area of intact peatland in its catchment compared to the Tweed. The catchment of the R. Tyne also encompasses a large region of peatland on intermediate upland catchments and it has been hypothesised that this is expected to be the site of thickest organic horizons (Clark et al., 2004).
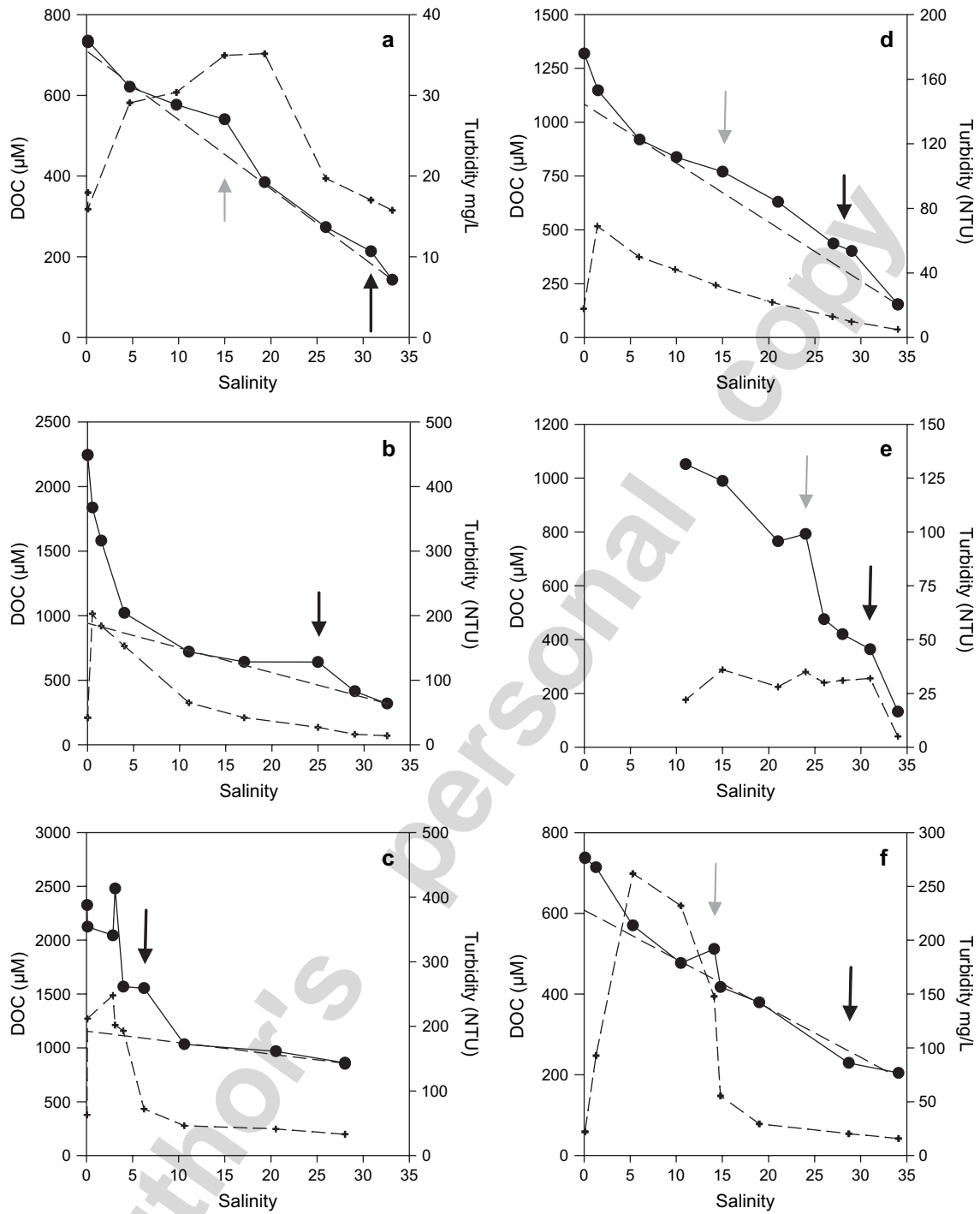
Fig. 4. The distribution of DOC and turbidity in the Tyne estuary, (a–i) and the Tweed estuary, (j, k). DOC (black circles, black lines); Turbidity (black crosshairs, dashed grey lines); Arrows represent anthropogenic sources (grey – polluted urban rivers, black – Howdon STW); Extrapolated linear conservative mixing line from higher salinities to the point where it crosses the y axis (DOC μM) (dashed black lines). (a) 11-07-2002; (b) 31-07-2002; (c) 01-08-2002; (d) 13-08-2002; (e) 04-10-2002; (f) 03-03-2003; (g) 19-03-2003; (h) 04-04-2003; (i) 23-07-2003; (j) 08-07-2003; and (k) 03-12-2003.

concentration was assumed to represent the effective input DOC concentration as modified by estuarine removal (extrapolation lines are shown in Fig. 4, dashed black lines; extrapolated DOC values are shown in Table 1). Removal of DOC at low salinities is exhibited in all the estuarine profiles with one exception (Tyne: 04-04-2003) (Fig. 4h). Because of the complicating effects of lower and mid-estuarine features of DOC

plots arising from secondary inputs (polluted urban rivers and Howdon STW), data associated with these features were excluded from the stepwise regression procedure, contributing some additional uncertainty to the removal estimates. Identifying these features was aided by estuarine NH_4^+ distributions (Spencer et al., 2007) that indicated these point sources (Fig. 4; black arrows represent Howdon STW, grey arrows
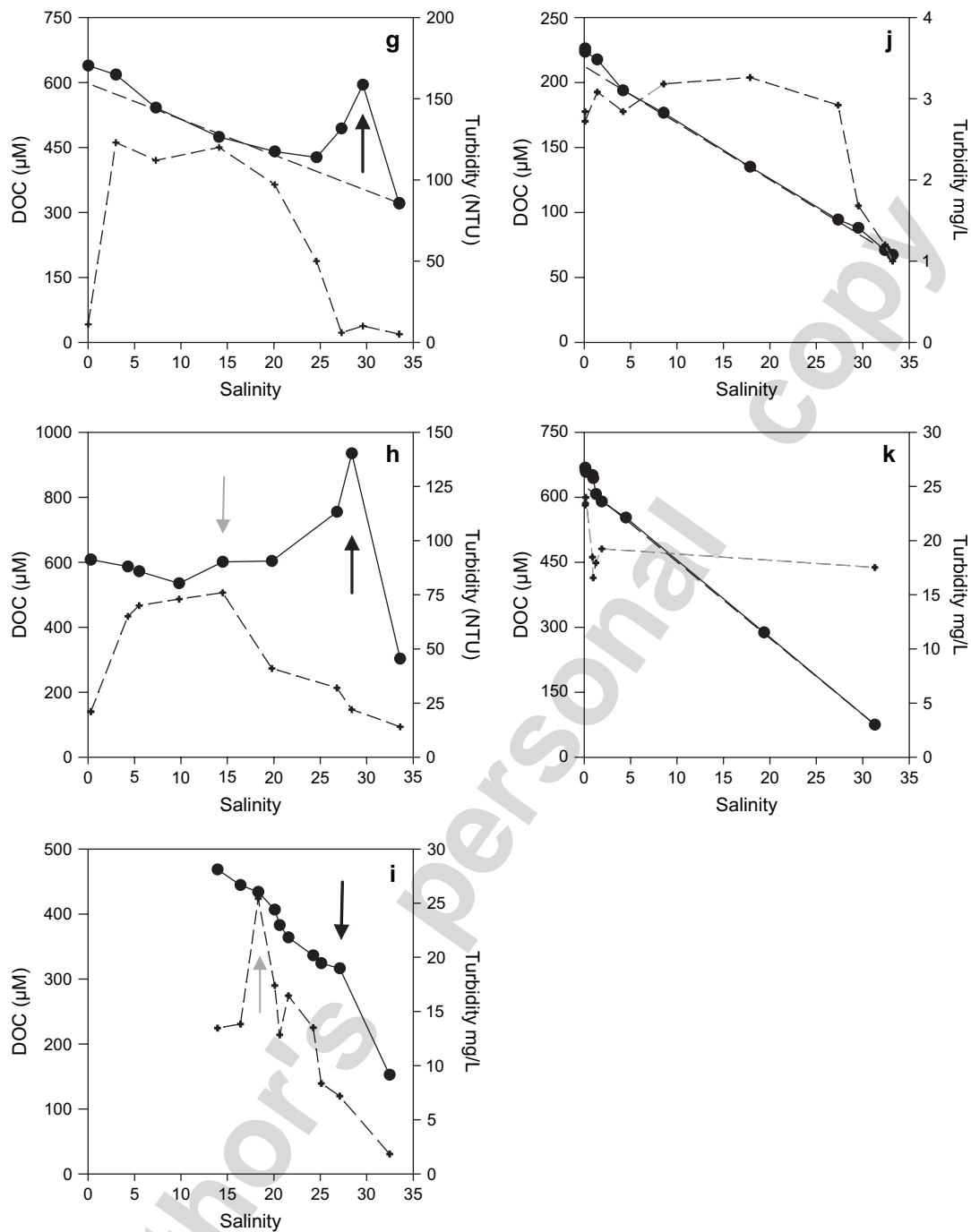
Fig. 4 (*continued*).

represent polluted urban rivers). The concentration of NH_4^+ in the R. Tyne ranged from 1.9 to 13.9 μM (mean 7.4 μM, $n = 7$), however, NH_4^+ concentrations in the Howdon STW plume ranged from 30.7 to 123.5 μM (mean 69.2 μM, $n = 9$) (Spencer et al., 2007) and therefore STW impacted plume samples were easily identifiable from other estuarine samples. As well as the source of NH_4^+ from Howdon STW the polluted urban rivers which drain into the Tyne estuary were seen to be a point source of NH_4^+ on a number of transects at medium to low river flow. Tyne estuarine sites impacted by these rivers ranged in NH_4^+ concentration from 7.3 to 159.2 μM

(mean $= 54.8$ μM, $n = 6$) (Spencer et al., 2007) and so were also readily identifiable in comparison to other estuarine samples with respect to NH_4^+. As there were no intertidal areas in this region of the estuary concurrent inputs of mudflat derived DOC and NH_4^+ that were reported from some other estuaries (Abril et al., 2002) could be excluded.

The results of the DOC removal calculations are summarised in Table 1. DOC removal in the Tyne estuary ranged from 0 to 58% and in both transects of the Tweed estuary was 6%. In the Tyne transect Fig. 4h (04-04-2003) we found no DOC removal. However, removal of DOC at low salinities

Table 1

The percentage removal of DOC at low salinities in the Tyne and Tweed estuaries; calculated by extrapolation of linear conservative mixing at higher salinities. For the Tyne transect exhibiting 0% removal it was not possible to construct an apparent conservative mixing line suited to extrapolation of riverine DOC for that transect due to DOC inputs (Howdon STW and urban rivers) which on this occasion were dispersed over a wide range of salinities (9.8—28.4) aided by the prevailing low river flow. For two other Tyne transects (04-10-02 and 23-07-03) no estimates of low salinity DOC removal could be calculated due to no riverine endmember DOC data being collected for these two transects

Date	Location	Riverine DOC (μM)	Extrapolated DOC (μM)	% Removal
11-07-2002	Tyne	735.3	710.2	3.4
31-07-2002	Tyne	2243.5	941.0	58.1
01-08-2002	Tyne	2326.5	1155.1	50.4
13-08-2002	Tyne	1318.5	1083.1	17.9
04-10-2002	Tyne	—	—	—
03-03-2003	Tyne	738.0	608.0	17.6
19-03-2003	Tyne	638.5	597.2	6.5
04-04-2003	Tyne	608.3	608.3	0
23-07-2003	Tyne	—	—	—
08-07-2003	Tweed	226.1	212.4	6.1
03-12-2003	Tweed	668.2	627.2	6.1

Table 2

River Tyne dissolved organic nitrogen (DON) concentration (μM) and DOM C:N data

Date	Riverine DON (μM)	Riverine DOM C:N
11-07-2002	35.9	20.5
31-07-2002	21.8	103.1
01-08-2002	22.9	101.8
13-08-2002	25.6	51.6
04-10-2002	—	—
03-03-2003	26.8	27.6
19-03-2003	10.1	63.4
04-04-2003	16.5	36.8
23-07-2003	—	—

could have been masked by DOC inputs from Howdon STW and the urban rivers which on this occasion were dispersed over a wide range of salinities (9.8—28.4) aided by the prevailing low river flow. Therefore it was not possible to construct an apparent conservative mixing line suited to extrapolation of riverine DOC for that transect. For two other Tyne transects (04-10-02 and 23-07-03) no estimates of low salinity DOC removal could be calculated due to no riverine endmember DOC data being collected for these two transects.

In the Tyne axial transects, differences in estuarine mixing behaviour of DOC appeared to be related to variations in river inputs. At medium-low river flow (Fig. 3a) the Tyne estuary showed apparent conservative or slight non-conservative (<7% removal) mixing of DOC (Fig. 4a,g,h), if point sources from Howdon STW and the urban rivers were excluded. However during high river flow events (Fig. 4b,c) and in periods immediately after high river flow events (Fig. 4d,f) increased estuarine DOC removal was observed. Estuarine DOC removal was ∼18% in transects conducted after high riverine input and 50—58% in transects conducted during periods of high river flow (Table 1). The Tweed exhibited non-conservative mixing behaviour in both transects and showed removal of 6% DOC at low salinities (<5), with apparent conservative mixing in mid-high salinities. In comparison to the Tyne estuary, the Tweed estuary showed no variation in terms of DOC removal rates with respect to riverine input.

The DOM C:N ratio in the R. Tyne ranged from 20.8 to 103.1 (mean = 57.9, $n = 7$; Table 2). During high flow in the Tyne estuary the riverine derived DOM was observed to have a very high C:N ratio (∼103; Table 2) in comparison to other global rivers including peatland derived rivers (13.2—69.1; Lobbes et al., 2000; Bronk, 2002 and references therein). Humic material (which typically has high DOC:DON ratios; Thurman, 1985), has been shown to undergo extensive removal in estuaries with preferential removal of the humic acid fraction during estuarine mixing (Sholkovitz et al., 1978; Fox, 1983). Such large changes in the DOM C:N ratio in the Tyne freshwater endmember between different riverine regimes are indicative of differences in DOM composition. The linear regression analysis between DOM C:N ratio and percent DOC removal at low salinity ($r^2 = 0.77$, $p < 0.05$, $n = 7$; Fig. 5a) highlights the susceptibility of DOM proportionally plentiful in DOC to estuarine low salinity removal processes.

In the Tyne estuary the region of low salinity DOC removal coincides with elevated turbidity or the site of the turbidity maximum zone (TMZ), which is controlled by the hydrodynamics of the estuary. At high river flow increased bed sheer stress leads to enhanced sediment resuspension and hence increased turbidity. In this study the highest river flows produced maximum turbidities of 203—248 NTU (Fig. 4b,c), values typically three-fold higher than during medium to low river flow (∼75 NTU, $n = 3$). The linear regression analysis for turbidity at the TMZ and percent DOC removal at low salinity ($r^2 = 0.79$, $p < 0.05$, $n = 5$; Fig. 5b) in the Tyne estuary shows that turbidity is related to DOC removal. Both field and laboratory studies have shown previously that elevated turbidity may result in adsorptive DOM removal (Uher et al., 2001; Abril et al., 2002; Shank et al., 2005). With respect to the Tyne estuary the data indicate that DOC removal is potentially a function of both DOM characteristics and the degree of turbidity. As turbidity in the Tyne estuary is primarily controlled by the hydrodynamics of the estuary an increase in energy in the system at high river flow leads to an increase in the size of the TMZ, but river flow also exhibits a control on the DOM characteristics as clearly seen in the highest DOC:DON ratios at the highest river flow.

In the region of the upper Tweed estuary where DOC removal was observed in the winter transect (Fig. 4k), we also found a TMZ associated with the freshwater-seawater interface (FSI) whereas in the summer transect turbidity was relatively low across the estuary (Fig. 4j). The turbidity in the Tweed winter transect (03-12-03) was an order of magnitude higher than observed in the summer transect (08-07-03) and overall turbidity in the Tweed was lower in comparison to the Tyne estuary. Likewise, Uncles and Stephens (1997) found that turbidity was high in the freshwater Tweed at high river inflow. Furthermore, Uncles and Stephens (1997) described
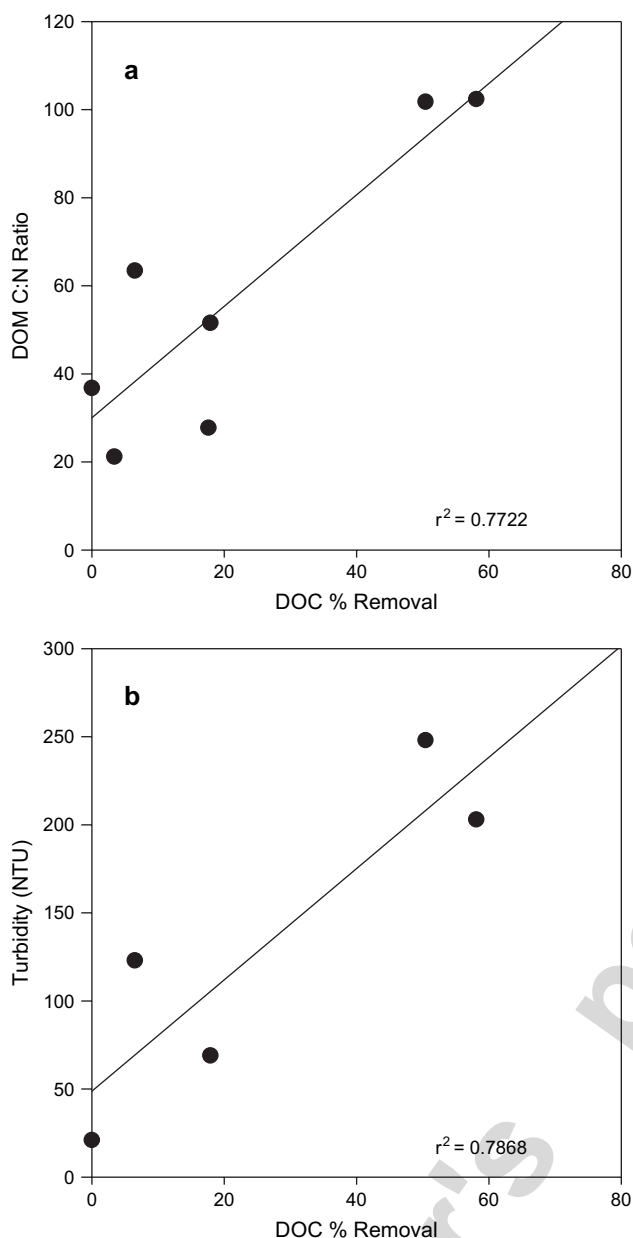
Fig. 5. (a) The relationship between *R*. Tyne DOM C:N ratio and percent DOC removal at low salinity in the Tyne estuary. (b) The relationship between turbidity at the turbidity maxima zone and percent DOC removal at low salinity in the Tyne estuary.

that very fine-grained particles were responsible for turbidity in the central and upper reaches of the Tweed estuary while wave activity was shown to maintain turbidity in the lower estuary which was primarily derived from resuspended sandy material. Therefore it appears likely that the turbidity found at low salinities was due to SPM of the finest silt and clay whereas turbidity at higher salinities was associated with wave action resuspended sandy material and so turbidity could be maintained at relatively constant levels across the estuary (Fig. 4j). We therefore attributed the DOC removal in both Tweed estuary transects to flocculation and adsorption processes at low salinities (Sholkovitz et al., 1978; Fox, 1983; Uher et al., 2001) involving the fine-grained particles in the

upper reaches of the Tweed which appear to be almost continuously suspended (Uncles and Stephens, 1997).

Estuarine DOC removal can also result from the processes of photochemical and microbial degradation or a combination of these processes (Kieber et al., 1990; Amon and Benner, 1996b; Moran and Zepp, 1997; Hernes and Benner, 2003). However, photochemical degradation of DOM in the Tyne and Tweed estuaries is less likely to occur at the low salinity areas identified with DOC removal in this study, chiefly due to high turbidity (particularly in the Tyne estuary), shading from CDOM and short residence times. However microbial degradation remains a possibility as the SPM associated with the TMZ offers sites for bacterial attachment and heterotrophic activity has been shown to be enhanced at the TMZ in estuaries (Morris et al., 1978). Bacterial utilisation of DOM during estuarine transport however has typically been shown to be small especially in organic rich waters (Amon and Benner, 1996b). In fact DOM from Arctic rivers with a similar peatland source has been shown to be highly degraded (Dittmar et al., 2001; Amon and Meon, 2004) and relatively resistant to microbial degradation (Meon and Amon, 2004).

The DOC concentration of the marine endmembers ranged from 132.3 to 861.0 μM and from 67.2 to 74.9 μM in the Tyne and Tweed estuaries respectively. In comparison to the Tyne the Tweed marine DOC values are lower due to the lack of an anthropogenic input (Howdon STW in the Tyne) near the mouth and also the lower terrigenous input of DOC. The lower DOC concentration for the Tweed marine endmember was recorded in summer at a higher salinity than the higher winter value (33.2 and 31.3 respectively) and so was presumably less influenced by terrigenous inputs. The highest value of 861.0 μM at the mouth of the Tyne estuary was collected on 01-08-2002 at a salinity of 28.0. We therefore attributed this high DOC concentration to the effects of both the high riverine input on this transect and also the Howdon STW plume being restricted to the surface layers in the stratified conditions at high riverine input. On all other Tyne axial transects marine samples with salinities ≥ 32.5 were obtained and the DOC concentration for these samples ranged from 132.3 to 321.4 μM (mean 216.1 μM, $n = 8$). This DOC concentration range is comparable to that recorded at the mouths of other estuaries (Miller, 1999; Rochelle-Newall and Fisher, 2002).

3.4. The relationship between DOC and CDOM

The relationships between DOC and a_{350} for the Tyne and Tweed estuaries are shown in Fig. 6a,b respectively. The relationship between DOC and a_{350} in the Tyne estuary shows a number of samples which appear to have higher DOC than a_{350} in relation to the total data set. In Fig. 6a these data points are highlighted by the two grey ellipses or are shown with grey triangles. The four data points highlighted by the grey ellipse with DOC ranging from 493 to 935 μM and absorbance values for a_{350} of <5 m^{-1} correspond to sites impacted by the Howdon STW plume (as indicated by elevated NH_4^+ concentrations; Spencer et al., 2007) on 19-03-2003 and 04-04-2003 at low river flow. These Howdon STW plume waters exhibited
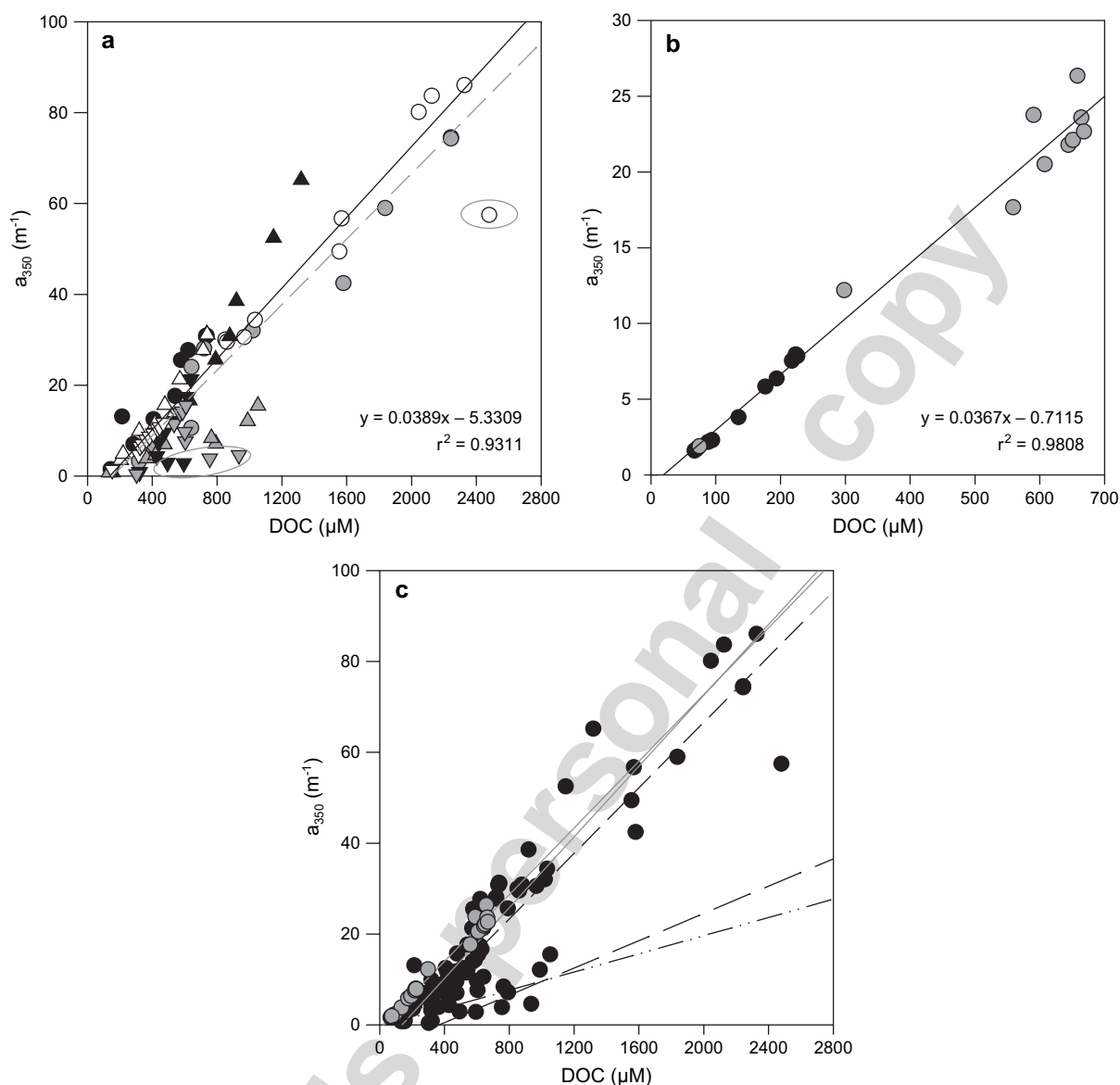
Fig. 6. (a) Tyne estuary relationship between a_{350} (m^{-1}) and DOC for all data (dashed grey line; $y = 0.0361x - 5.5321$; $r^2 = 0.8461$), and excluding heavily anthropogenically impacted and potentially sedimentary derived samples (solid black line; $y = 0.0389x - 5.3309$; $r^2 = 0.9311$). The data points excluded are those encompassed by the grey ellipses and the grey triangles (04-10-2002) (see Section 3.2). Black circles (11-07-2002), grey circles (31-07-2002), white circles (01-08-2002), black triangles (13-08-2002), grey triangles (04-10-2002), white triangles (03-03-2003), inverted black triangles (19-03-2003), inverted grey triangles (04-04-2003), inverted white triangles (23-07-2003). (b) Tweed estuary relationship between a_{350} (m^{-1}) and DOC. Black circles (08-07-2003), grey circles (03-12-03). (c) Comparison of the relationship between a_{350} (m^{-1}) and DOC in the Tyne estuary (black circles) (all samples, short dash black line; excluding anthropogenic and potentially sedimentary derived samples, black line), the Tweed estuary (grey circles) (grey line), the Southern Baltic Sea (long dash grey line) (Ferrari et al., 1996; Ferrari, 2000) and Chesapeake Bay (dash-dot-dot grey line) (Rochelle-Newall and Fisher, 2002).

strongly elevated DOC (Fig. 4g,h) but low a_{350} due to the nature of the sewage derived DOM. In addition, the Tyne estuarine transect from 04-10-2002 (grey triangles in Fig. 6a) also showed higher DOC than a_{350} in relation to the total data set. This data was collected at the lowest river flow of all Tyne transects and showed the highest NH_4^+ concentrations of all transects indicative of water heavily impacted by anthropogenic sources (Spencer et al., 2007), presumably due to the lack of comparatively clean river water to dilute anthropogenic sources at low flow.

Therefore, due to these data points being the manifestation of anthropogenic DOM sources they were removed from the

linear regression plot. One further data point was also removed, highlighted by the grey ellipse (Fig. 6a) (DOC: 2479.5 μM; a_{350}: 57.5 m^{-1}). This data point was potentially attributed to the mixing of DOC rich porewaters or due to desorption processes at high turbidity during high river flow and therefore potentially derives from a sedimentary source of DOM (see Section 3.2). The linear regression correlation coefficient (solid black line, Fig. 6a) was observed to increase on removal of the thirteen data points described above from potentially anthropogenic or sedimentary sources ($r^2 = 0.93$, $n = 74$; $p < 0.001$) due to the subsequent increased prevalence of terrestrially derived DOM in comparison to that inclusive

of these thirteen data points (dashed black line, Fig. 6a) ($r^2 = 0.85$, $n = 87$, $p < 0.001$). In addition the linear regression line became steeper (i.e. increased a_{350} per unit DOC) on removal of the thirteen samples which were from potentially anthropogenic or sedimentary sources. In both the Tyne and the Tweed (Fig. 6b) ($r^2 = 0.98$, $n = 20$; $p < 0.001$) a significant correlation was observed between DOC and a_{350} indicating a dominance of DOC of predominantly terrigenous origin in these estuaries. Overall the DOC:CDOM relationship was statistically highly significant, with probability levels similar to or stronger than those observed in previous studies (Ferrari et al., 1996; Ferrari, 2000; Rochelle-Newall and Fisher, 2002). Although this study focuses on a_{350}, other commonly used wavelengths (e.g. a_{254} and a_{440}) (Weishaar et al., 2003; Bowers et al., 2004) were also compared to DOC and showed identical highly significant correlations for both the Tyne and Tweed estuaries. The absorption coefficient at 350 nm was found to correlate to a_{254} and a_{440} in both estuaries with highly significant relationships ($r^2 > 0.99$; $p < 0.001$) indicating one dominant CDOM source in these estuaries of terrigenous origin.

All of the relationships between DOC and a_{350} (Fig. 6c) exhibit a positive intercept on the x axis and therefore indicate a portion of DOC which is not light absorbing. The non-chromophoric fraction of DOC was found to be equivalent to 19.4 μM in the Tweed estuary and 137.0 μM in the Tyne estuary. This equates to 4.3% of the DOC in the Tweed estuary and 11.1% in the Tyne estuary being non-chromophoric. The higher percentage of non-chromophoric DOC in the Tyne estuary may be attributed to the numerous anthropogenic sources of DOC to the Tyne estuary.

The DOC vs. a_{350} relationships from a number of previous studies (Ferrari et al., 1996; Ferrari, 2000; Rochelle-Newall and Fisher, 2002) are compared with those for the Tyne and Tweed estuaries in Fig. 6c. Notably, the Tyne and Tweed estuarine relationship plots have much steeper slopes than those from either the southern Baltic Sea (long dash grey line) (Ferrari et al., 1996; Ferrari, 2000) or Chesapeake Bay (dash-dot-dot grey line) (Rochelle-Newall and Fisher, 2002). Previous work showed terrigenous DOM to have a much greater absorbance per unit carbon than marine autochthonous DOM, or either microbially or photochemically degraded DOM (Chin et al., 1994; Stubbins, 2001). Given that HMW aromatic compounds are the dominant light absorbing components of DOM (Hernes and Benner, 2003) Fig. 6c indicates that the terrestrially derived DOM in the Tyne and Tweed estuaries contains proportionally more HMW and aromatic DOM than either the southern Baltic Sea or Chesapeake Bay DOM, consistent with their peatland DOM source. Furthermore, it indicates the Tyne estuary to be of slightly higher aromaticity and HMW DOM than the Tweed estuary.

Previous studies of the relationship between CDOM and DOC in estuarine and marine waters have often found large variability both at the temporal and spatial scale (Ferrari et al., 1996; Vodacek et al., 1997; Ferrari, 2000; Rochelle-Newall and Fisher, 2002). By contrast the relationship between DOC and a_{350} in the Tyne and Tweed estuaries is relatively constant between seasons. Furthermore, there is even good correlation between the two sites in comparison to Chesapeake Bay for example (Rochelle-Newall and Fisher, 2002), presumably reflecting their similar HMW aromatic nature in comparison to autochthonous DOM, or DOM which has undergone photochemical or microbial degradation or both of these processes.

Finally, few studies have examined the relationship between CDOM and DON and CDOM and DOM C:N. No significant relationship was observed between a_{350} and DON in either the Tyne ($r^2 = 0.06$; $n = 87$) or the Tweed ($r^2 = 0.01$; $n = 20$) estuaries presumably due to low or non-chromophoric sources of organic nitrogen in these estuaries (e.g. pollution sources in the Tyne and autochthonous sources in the Tweed). However, a_{350} did show a significant relationship with DOM C:N in the Tyne ($r^2 = 0.79$; $n = 87$, $p < 0.001$) and Tweed ($r^2 = 0.93$; $n = 20$, $p < 0.001$) estuaries. As already described for the Tyne estuary, DOM C:N was observed to increase with increasing riverine input and also so was a_{350}. Increasing aromaticity of DOM would be expected to result in increasing absorbance and thus it seems a_{350} may have potential as a proxy for DOM C:N, however, the robustness of this relationship will be highly dependent on source.

4. Conclusions

This study clearly highlights the variation in estuarine removal of peatland derived DOC in the Tyne and Tweed estuaries, and in the Tyne estuary also illustrates how differences in river regime can result in significant changes in DOC removal at low salinities. It seems apparent that with differences in riverine input in certain estuaries a range of behaviour with respect to DOM removal at low salinities will be observed due to changes in DOM concentration and composition entering the estuary and impacts on the SPM and TMZ within the estuary. Conversely, the Tweed estuary shows relatively constant removal rates of DOC independent of riverine input while other estuaries were reported to exhibit quasi-conservative mixing (e.g. Mantoura and Woodward, 1983; Alvarez-Salgado and Miller, 1998). Therefore to further understand estuarine dynamics of DOM and to improve quantification of the terrigenous flux of DOM to the oceans, sampling under varying seasons and hydrological regimes is of key importance.

CDOM measurements clearly show potential for rapid and inexpensive monitoring of DOC export in estuaries and coastal regions once relationships are established. The absorption coefficient at 350 nm (and also a_{254} and a_{440}) as a proxy for terrigenous DOC was found to correlate strongly in both estuaries and this may prove a very useful tool in areas subjected to significant terrigenous inputs of DOM, which are often especially susceptible to global environmental change such as other peatland derived estuaries. The deployment of relatively cheap robust in situ sensors utilising optical proxies to monitor terrigenous inputs to the ocean may allow for the seasonal monitoring of river-estuary systems even in remote and less accessible areas (e.g. the Yenisei, Ob, Lena, Mackenzie and Yukon which drain the vast areas of Arctic peatland).

The prospect of acquiring continuous real-time data via in situ and remote sensing techniques for monitoring terrigenous DOM fluxes to the oceans is of direct relevance for improving spatio-temoral quantification of DOM export and the refining of carbon budgets at the land-ocean interface.

References

Abril, G., Etcheber, H., Le Hir, P., Bassoullet, P., Boutier, B., Frankignoulle, M., 1999. Oxic/anoxic oscillations and organic carbon mineralisation in an estuarine turbidity maximum turbidity zone (The Gironde, France). Limnology and Oceanography 44, 1304−1315.

Abril, G., Nogueira, M., Etcheber, H., Cabecadas, G., Lemaire, E., Brogueira, M.J., 2002. Behaviour of organic carbon in nine contrasting European estuaries. Estuarine, Coastal and Shelf Science 54 (2), 241−262.

Alvarez-Salgado, X.A., Miller, A.E.J., 1998. Dissolved organic carbon in a large macrotidal estuary (the Humber, U.K.): behaviour during estuarine mixing. Marine Pollution Bulletin 37 (3−7), 216−224.

Amon, R.M.W., Benner, R., 1996a. Bacterial utilization of different size classes of dissolved organic matter. Limnology and Oceanography 41 (1), 41−51.

Amon, R.M.W., Benner, R., 1996b. Photochemical and microbial consumption of dissolved organic carbon and dissolved oxygen in the Amazon River system. Geochimica et Cosmochimica Acta 60 (10), 1783−1792.

Amon, R.M.W., Meon, B., 2004. The biogeochemistry of dissolved organic matter and nutrients in two large Arctic estuaries and potential implications for our understanding of the Arctic Ocean system. Marine Chemistry 92, 311−330.

Benner, R., 2002. Chemical composition and reactivity. In: Hansell, D.A., Carlson, C.A. (Eds.), Biogeochemistry of Marine Dissolved Organic Matter. Academic Press, Elsevier Science, San Diego, pp. 59−90.

Benner, R., Opsahl, S., 2001. Molecular indicators of the sources and transformations of dissolved organic matter in the Mississippi river plume. Organic Geochemistry 32, 597−611.

Blough, N.V., Zafiriou, O.C., Bonilla, J., 1993. Optical absorption spectra of water from the Orinoco River outflow: terrestrial input of colored organic matter to the Caribbean. Journal of Geophysical Research 98, 2271−2278.

Bowers, D.G., Evans, D., Thomas, D.N., Ellis, K., Williams, P.J., le, B., 2004. Interpreting the colour of an estuary. Estuarine, Coastal and Shelf Science 59, 13−20.

Bronk, D.A., 2002. Dynamics of DON. In: Hansell, D.A., Carlson, C.A. (Eds.), Biogeochemistry of Marine Dissolved Organic Matter. Academic Press, Elsevier Science, San Diego, pp. 153−247.

Bushaw, K.L., Zepp, R.G., Tarr, M.A., Shulz-Jander, D., Bourbonniere, R.A., Hodson, R.E., Miller, W.L., Bronk, D.A., Moran, M.A., 1996. Photochemical release of biologically available nitrogen from aquatic dissolved organic matter. Nature 381, 404−407.

Cannell, M.G.R., Milne, R., Hargreaves, K.J., Brown, T.A.W., Cruickshank, M.M., Bradley, R.I., Spencer, T., Hope, D., Billett, M.F., Adger, W.N., Subak, S., 1999. National inventories of terrestrial carbon sources and sinks: the U.K. experience. Climatic Change 42 (3), 505−530.

Chapman, P.J., Edwards, A.C., Cresser, M.S., 2001. The nitrogen composition of streams in upland Scotland: some regional and seasonal differences. Science of the Total Environment 265, 65−83.

Chen, Z.Q., Li, Y., Pan, J.M., 2004. Distributions of colored dissolved organic matter and dissolved organic carbon in the Pearl River Estuary, China. Continental Shelf Research 24 (16), 1845−1856.

Chin, Y.P., Aiken, G., O'Loughlin, E., 1994. Molecular-weight, polydispersity and spectroscopic properties of aquatic humic substances. Environmental Science and Technology 28 (11), 1853−1858.

Clark, M.J., Cresser, M.S., Smart, R., Chapman, P.J., Edwards, A.C., 2004. The influence of catchment characteristics on the seasonality of carbon and nitrogen species concentrations in upland rivers of Northern Scotland. Biogeochemistry 68, 1−19.

Dittmar, T., Fitznar, H.P., Kattner, G., 2001. Origin and biogeochemical cycling of organic nitrogen in the eastern Arctic Ocean as evident from D- and L-amino acids. Geochimica et Cosmochimica Acta 65 (22), 4103−4114.

Ferrari, G.M., 2000. The relationship between chromophoric dissolved organic matter and dissolved organic carbon in the European Atlantic coastal area and in the west Mediterranean Sea (Gulf of Lions). Marine Chemistry 70, 339−357.

Ferrari, G.M., Dowell, M.D., Grossi, S., Targa, C., 1996. Relationship between the optical properties of chromophoric dissolved organic matter and total concentration of dissolved organic carbon in the southern Baltic Sea region. Marine Chemistry 55, 299−316.

Freeman, C., Evans, C.D., Monteith, D.T., Reynolds, B., Fenner, N., 2001. Export of organic carbon from peat soils. Nature 412, 785.

Fox, L.E., 1983. The removal of dissolved humic acid during estuarine mixing. Estuarine, Coastal and Shelf Science 16 (4), 431−440.

Green, S.A., Blough, N.V., 1994. Optical absorption and fluorescence properties of chromophoric dissolved organic matter in natural waters. Limnology and Oceanography 39 (8), 1903−1916.

Hedges, J.I., Keil, R.G., Benner, R., 1997. What happens to terrestrial organic matter in the ocean? Organic Geochemistry 27, 195−212.

Hernes, P.J., Benner, R., 2003. Photochemical and microbial degradation of dissolved lignin phenols: implications for the fate of terrigenous dissolved organic matter in marine environments. Journal of Geophysical Research 108, C9.

Hu, C., Muller-Karger, F.E., Zepp, R.G., 2002. Absorbance, absorption coefficient, and apparent quantum yield: a comment on common ambiguity in use of these optical concepts. Limnology and Oceanography 47 (4), 1261−1267.

Kalbitz, K., Geyer, S., 2002. Different effects of peat degradation on dissolved organic carbon and nitrogen. Organic Geochemistry 33, 319−326.

Kieber, R.J., Zhou, X., Mopper, K., 1990. Formation of carbonyl compounds from UV-induced photodegradation of humic substances in natural waters: fate of riverine carbon in the sea. Limnology and Oceanography 35, 1503−1515.

Lobbes, J.M., Fitznar, H.P., Kattner, G., 2000. Biogeochemical characteristics of dissolved and particulate organic matter in Russian rivers entering the Arctic Ocean. Geochimica et Cosmochimica Acta 64 (17), 2973−2983.

Mantoura, R.F.C., Woodward, E.M.S., 1983. Conservative behaviour of riverine dissolved organic carbon in the Severn estuary: chemical and geochemical implications. Geochimica et Cosmochimica Acta 47, 1293−1309.

Meon, B., Amon, R.M.W., 2004. Heterotrophic bacterial activity and fluxes of dissolved free amino acids and glucose in the Arctic rivers Ob, Yenisei and the adjacent Kara Sea. Aquatic Microbial Ecology 37 (2), 121−135.

Miller, A.E.J., 1999. Seasonal investigations of dissolved organic carbon dynamics in the Tamar Estuary, U.K. Estuarine, Coastal and Shelf Science 49 (6), 891−908.

Miller, W.L., Moran, M.A., 1997. Interaction of photochemical and microbial processes in the degradation of refractory dissolved organic matter from a coastal marine environment. Limnology and Oceanography 42, 1317–1324.

Moran, M.A., Zepp, R.G., 1997. Role of photoreactions in the formation of biologically labile compounds from dissolved organic matter. Limnology and Oceanography 42, 1307–1316.

Morris, A.W., Mantoura, R.F.C., Bale, A.J., Howland, R.J.M., 1978. Very low salinity regions of estuaries: important sites for chemical and biological reactions. Nature 274, 678–680.

Opsahl, S., Benner, R., 1998. Photochemical reactivity of dissolved lignin in river and ocean waters. Limnology and Oceanography 43 (6), 1297–1304.

Rochelle-Newall, E.J., Fisher, T.R., 2002. Chromophoric dissolved organic matter and dissolved organic carbon in Chesapeake Bay. Marine Chemistry 77, 23–41.

Shank, C.G., Zepp, R.G., Whitehead, R.F., Moran, M.A., 2005. Variations in the spectral properties of freshwater and estuarine CDOM caused by partitioning onto river and estuarine sediments. Estuarine, Coastal and Shelf Science 65, 289–301.

Sholkovitz, E.R., Boyle, E.A., Price, N.B., 1978. The removal of dissolved humic acids and iron during estuarine mixing. Earth Planetary Science Letters 40, 130–136.

Spencer, R.G.M., Baker, A., Ahad, J.M.E., Cowie, G.L., Ganeshram, R., Upstill-Goddard, R.C., 2007. Discriminatory classification of natural and anthropogenic waters in two U.K. estuaries. Science of the Total Environment 373 (1), 305–323.

Stedmon, C.A., Markager, S., Sondergaard, M., Vang, T., Laubel, A., Borch, N.H., Windelin, A., 2006. Dissolved organic matter (DOM) export to a temperate estuary: Seasonal variations and implications of land use. Estuaries and Coasts 29 (3), 388–400.

Stubbins, A.P., 2001. Aspects of aquatic CO photoproduction from CDOM. PhD Thesis, University of Newcastle-upon-Tyne, 201 pp.

Thurman, E.M., 1985. Organic Geochemistry of Natural Waters. Martinus Nijhoff/Dr W. Junk Publishers.

Tupas, L.M., Popp, B.N., Karl, D.M., 1994. Dissolved organic carbon in oligotrophic waters: experiments on sample preservation, storage and analysis. Marine Chemistry 45, 207–216.

Uher, G., Hughes, C., Henry, G., Upstill-Goddard, R.C., 2001. Non-conservative mixing behaviour of colored dissolved organic matter in a humic-rich turbid estuary. Geophysical Research Letters 28 (17), 3309–3312.

Uncles, R.J., Stephens, J.A., 1996. Salt intrusion in the Tweed Estuary. Estuarine, Coastal and Shelf Science 43 (3), 271–293.

Uncles, R.J., Stephens, J.A., 1997. Dynamics of turbidity in the Tweed estuary. Estuarine, Coastal and Shelf Science 45 (6), 745–758.

Upstill-Goddard, R.C., Barnes, J., Frost, T., Punshon, S., Owens, N.J.P., 2000. Methane in the southern North Sea: low-salinity inputs, estuarine removal and atmospheric flux. Global Biogeochemical Cycles 14 (4), 1205–1217.

Vodacek, A., Blough, N.V., DeGrandpre, M.D., Peltzer, E.T., Nelson, R.K., 1997. Seasonal variation of CDOM and DOC in the Middle Atlantic Bight: terrestrial inputs and photooxidation. Limnology and Oceanography 42, 674–686.

Watts-Rodrigues, P.P.G., 2002. Modelling nitrous oxide production in tow contrasting British estuaries: the Forth and the Tyne. PhD Thesis, University of Newcastle-upon-Tyne, 154 pp.

Weishaar, J.L., Aiken, G.R., Bergamaschi, B.A., Fram, M.S., Fuji, R., Mopper, K., 2003. Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. Environmental Science and Technology 37 (20), 4702–4708.

Worrall, F., Burt, T., Shedden, R., 2003. Long term records of riverine dissolved organic matter. Biogeochemistry 64, 165–178.

Worrall, F., Harriman, R., Evans, C.D., Watts, C.D., Adamson, J., Neal, C., Tipping, E., Burt, T., Grieve, I., Monteith, D., Naden, P.S., Nisbet, T., Reynolds, B., Stevens, P., 2004. Trends in dissolved organic carbon in U.K. rivers and lakes. Biogeochemistry 70, 369–402.