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Coloured dissolved organic matter (CDOM) in Southern North Sea waters: Optical characterization and possible origin

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ABSTRACT

The variability and origin of the Coloured Dissolved Organic Matter (CDOM) were studied in the Belgian coastal and adjacent areas including offshore waters and the Scheldt estuary, through the parameters: absorption at 375 nm, $a_{CDOM}(375)$, and the slope of the absorption curve, S. $a_{CDOM}(375)$ varied between 0.20 and 1.31 m^{-1} and between 0.97 and 4.30 m^{-1} in the marine area and Scheldt estuary, respectively. S fluctuated between 0.0101 and 0.0203 nm^{-1} in the marine area and between 0.0167 and 0.0191 nm^{-1} in the Scheldt estuary. The comparative analysis of $a_{CDOM}(375)$ and S variations evidenced different origins of CDOM in the BCZ. The Scheldt estuarine waters showed decreasing $a_{CDOM}(375)$ values with increasing salinity but constant S value of $\sim$0.018 nm^{-1} suggesting a dominant terrestrial origin of CDOM. On the contrary, samples collected in the marine domain showed a narrow range of $a_{CDOM}(375)$ but highly variable S suggesting the additional presence of autochthonous sources of CDOM. This source was evidenced based on the sorting of the marine offshore data according to the stage of the phytoplankton bloom when they were collected. A clear distinction was made between CDOM released during the growth stage characterized by high S ($\sim$0.017 nm^{-1}) and low $a_{CDOM}(375)$ and the decay phase characterized by low S ($\sim$0.013 nm^{-1}) and high $a_{CDOM}(375)$. This observation was supported by CDOM measurements performed on pure phytoplankton cultures which showed increased CDOM release along the wax and wane of the bloom but decreasing S. We concluded that the high variability of the CDOM signature in offshore waters is explained by the local biological production and processing of CDOM.

1. Introduction

One of the water components that contributes to the ocean colour by absorption of light in aquatic ecosystems is Coloured Dissolved Organic Matter (CDOM), also called 'gelbstoff' or yellow substance because of its colour when present in high concentrations in the water (Kirk, 1994). Due to its strong absorption in the UV and blue region (350–500 nm) of the light spectrum, CDOM has a strong impact on the availability and spectral quality of light in marine regions (Kirk, 1994; Blough and Del Vecchio, 2002) thus affecting processes like primary production. CDOM also affects remote sensing of surface waters (Bricaud et al., 1981; Carder et al., 1989) because its maximum absorption at blue wavelengths interferes with the retrieval of some variables such as chlorophyll *a* (chl *a*) which is usually performed using algorithms based on blue:green wavelength ratios of reflectance (O'Reilly et al., 2000).

CDOM in marine nearshore waters is composed by a mixture of humic and fulvic acids of terrestrial origin brought by rivers (Carder et al., 1989) that adds to locally-produced CDOM as a byproduct of primary and secondary marine production (Bricaud et al., 1981; Nelson et al., 1998; Warnock et al., 1999). This autochthonous CDOM production has been assigned to several processes, such as zooplankton and bacteria excretion (Nelson et al., 1998; Steinberg et al., 2004) and phytoplankton degradation (Rochelle-Newall and Fisher, 2002; Hu et al., 2006). The link between phytoplankton and CDOM production is indirect. Indeed, CDOM production has been associated to bacterial degradation of phytoplankton-derived detritus in cultures (Rochelle-Newall and Fisher, 2002). In agreement, a phase-shift has been observed between temporal patterns of CDOM and phytoplankton pigments in the open ocean suggesting that CDOM in this marine environment is derived from phytoplankton lysis and degradation (Hu et al., 2006). Nevertheless, recent findings show an increase in CDOM absorption along a phytoplankton bloom (Zhao et al., 2009).

The absorption a_{CDOM} at a blue wavelength in the range 375–443 nm is commonly used to quantify the concentration of CDOM (Bricaud et al., 1981; Babin et al., 2003) while the slope of the

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absorption curve, hereafter *S*, can be used to trace the CDOM origin (Carder et al., 1989; Stedmon and Markager, 2001). In particular, it has been shown that marine waters have distinct *S* when compared to freshwater (Markager and Vincent, 2000). Also *S* has been used to study the chemical composition of CDOM which can give information on its origin, including the use of *S* as an indicator of the proportion of humic and fulvic acids (Carder et al., 1989) and the use of *S* ratios in the UV as an indicator of molecular weight distribution (Helms et al., 2008).

The Belgian Coastal Zone (BCZ) in the Southern North Sea is characterized by a high spatial heterogeneity and variability of the inherent optical properties (Astoreca et al., 2006). This is due to water masses resulting from the mixing between inflowing English Channel waters from Atlantic origin and freshwater mainly from the Scheldt and the Rhine rivers (Fig. 1; Lacroix et al., 2004). As a consequence salinity shows large temporal and spatial variations, between 28 and 31 at the Scheldt river mouth and 35 offshore. These nutrient-enriched coastal waters are also characterized by significant blooms of *Phaeocystis globosa* colonies and diatoms (Rousseau, 2000; Breton et al., 2006).

Due to particular hydrodynamic conditions and phytoplankton blooms, it is hypothesised that the CDOM pool may have different origins: terrestrial and autochthonous. In this paper we combine optical measurements (*S*, a_{CDOM}) of CDOM in estuarine, nearshore and offshore waters of the BCZ at different seasons with different stages (exponential growth and decay) of pure phytoplankton cultures to characterize the different CDOM sources in Southern North Sea waters.

2. Material and methods

2.1. Field measurements

Field sampling was conducted in Belgian and Dutch waters and in the Scheldt estuary, crossing a full freshwater-marine water gradient (Fig. 1). Thirteen cruises were conducted between 2004 and 2008 on board of the RV Belgica in marine waters, at different seasons (winter, spring, summer and late summer, Table 1) resulting in 210 measurements. Two Scheldt estuary transects were performed, one during winter 2005 on board of the RV Belgica and the other during summer on board of the RV Luctor. The winter transect was extended offshore. At each station, surface water was sampled for the measurement of CDOM light absorption using a Niskin bottle or a bucket when *P. globosa* were present to avoid colony disruption. Salinity was measured with a Thermosalinometer Seabird 21.

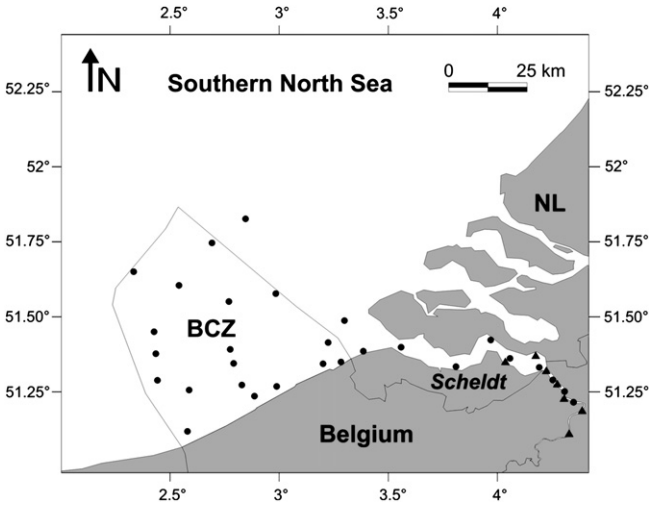

Fig. 1. Location of the sampled stations in the Scheldt estuary, Belgian and Dutch coastal waters. Borders of the Belgian coastal zone (BCZ) are indicated. Winter and summer transects in the Scheldt estuary are indicated with dots and triangles respectively. NL corresponds to The Netherlands.

Table 1
Optical data ranges collected during the surveys performed in the Scheldt estuary and BCZ: $a_{CDOM}(375)$ is the CDOM absorption at 375 nm and *S* is the slope of the absorption curve calculated from 350 to 500 nm.

Stations	Year	Date	Salinity	$a_{CDOM}(375)$ (m^{-1})	*S* (nm^{-1})
Scheldt estuary					
7	2005	03/02	0.7–29.6	0.97–4.22	0.0167–0.0191
7	2006	18/07	2.7–19.9	2.34–4.29	0.0177–0.0185
BCZ					
16	2004	26/04–11/05	28.4–34.8	0.24–1.31	0.0112–0.0168
16		12/07–15/07	31.4–34.8	0.37–1.04	0.0117–0.0166
8	2005	01/02–03/02	29.8–33.6	0.57–0.93	0.0110–0.0203
13		25/04–29/04	28.0–35.0	0.20–0.93	0.0146–0.0197
11		27/06–01/07	28.4–35.0	0.44–1.06	0.0129–0.0203
11		12/09–15/09	31.0–34.8	0.28–0.96	0.0130–0.0228
13	2006	18/04–21/04	27.9–35.1	0.22–1.12	0.0123–0.0190
14		18/09–20/09	30.7–35.0	0.20–0.82	0.0101–0.0168
19	2007	23/04–27/04	27.0–35.0	0.21–1.42	0.0119–0.0184
6		02/07–06/07	28.5–33.5	0.83–2.18	0.0128–0.0157
14		17/09–19/09	27.9–34.8	0.36–1.21	0.0130–0.0198
23	2008	21/04–25/04	28.0–35.1	0.33–1.41	0.0161–0.0232
18		07/07–10/07	28.2–35.1	0.20–1.30	0.0113–0.0191
22		08/09–12/09	31.2–35.0	0.33–1.07	0.0106–0.0200

2.2. Laboratory experiments

Batch cultures of two phytoplankton species representative of the Southern North Sea, the diatom *Skeletonema costatum* and the haptophyte *P. globosa*, were grown in F20 medium (Veldhuis and Admiraal, 1987) at 100 μmol quanta m^{-2} s^{-1} under a 12 h:12 h light:dark cycle in Nalgene bottles placed over a stirring plate in a culture room at 8–10 °C. Cultures were grown for ~30 days in order to mimic the wax and wane of a phytoplankton bloom. Measurements of CDOM light absorption and phytoplankton abundance were performed every day during the exponential phase and every 2 days during the decaying phase of each culture.

2.3. CDOM sampling and absorption measurements

2.3.1. Sample collection and preservation

Seawater (~100 ml) was filtered through a 0.2 μm polycarbonate membrane (Nuclepore) previously rinsed with Milli-Q water. An amber bottle was rinsed with this filtrate, which was then discarded. A second volume was filtered and kept in the bottle at 4 °C until analysis. All glassware was previously combusted at 450 °C for 4 h. CDOM samples were analysed between 1 and 4 days after sampling. For longer cruises, samples were preserved with sodium azide 50 mg L^{-1} as bacteriostatic agent as recommended by Ferrari et al. (1996). The two preservation methods were compared for a few samples, showing no significant difference (not shown).

2.3.2. CDOM spectra analysis

Samples were allowed to reach room temperature before determination of the CDOM absorbance, between 300 and 700 nm, in a 10 cm quartz cuvette. An UVIKON 930 dual beam spectrophotometer was used for analysing the 2004–2006 samples and a PERKIN ELMER Lambda 650 spectrophotometer for the 2007–2008 ones. To check the instrument's baseline, an air versus air baseline was recorded and inspected to be within ±0.0005 absorbance units (Tilstone et al., 2002). The absorbance spectrum

of Milli-Q water was used as reference and was subtracted from the sample absorbance to obtain the CDOM absorbance, $OD_{CDOM}(\lambda)$. A baseline correction was applied to the data by subtracting the average between 683 and 687 nm to the entire spectrum (Babin et al., 2003). The absorbance values at each wavelength were transformed into absorption coefficients using:

$$a_{CDOM}(\lambda) = 2.303 * \frac{OD_{CDOM}(\lambda)}{l}$$

where l is the length of the cuvette (m).

Absorption data were fitted with an exponential function using nonlinear regression between 350 and 500 nm (Bricaud et al., 1981; Babin et al., 2003) to retrieve $a_{CDOM}(\lambda_r)$, the CDOM absorption estimate at a reference wavelength (375 nm) and S, the slope of the absorption curve:

$$a_{CDOM}(\lambda) = a_{CDOM}(\lambda_r) * \exp(-S(\lambda - \lambda_r))$$

The absorption value at 375 nm, $a_{CDOM}(375)$, was chosen to quantify CDOM because this wavelength has been commonly used previously (e.g. Bricaud et al., 1981; Stedmon and Markager, 2001). We also considered $a_{CDOM}(443)$ to allow comparison with other studies when discussing our results.

Fig. 2 shows two examples of CDOM absorption spectra, one nearshore (st.130) and one offshore (st.MH2) and their respective fitted exponential curve. The exponential function fitted very well the absorption spectra between 350 and 500 nm, which is used to calculate S.

2.4. Phytoplankton counts

Phytoplankton culture sub-samples of 10–50 mL, preserved with 1% lugol-glutaraldehyde solution and stored at 4 °C in the dark, were analysed under inverted microscopy (Leitz Fluovert, Germany) according to the Utermöhl (1931) method at a magnification of 40x or 100x for *P. globosa* colonies, and 100x or 200x for *S. costatum*.

3. Results

3.1. Variability of $a_{CDOM}(375)$ and S in the Scheldt estuary and BCZ

The ranges of optical data measured in estuarine and marine waters between 2004 and 2008 are reported on Table 1. As expected, estuarine $a_{CDOM}(375)$ show much higher values compared to marine waters, i.e. 0.97–4.29 m^{-1} and 0.20–2.18 m^{-1} respectively (Table 1). A quite different trend is obtained for S, being almost constant (0.0167–0.0191 nm^{-1}) in estuarine waters while showing a two-fold variability (0.0101–0.0232 nm^{-1}) in marine waters. This observation suggests differences in CDOM quality between estuarine and marine waters on the one hand and nearshore-offshore seasonal gradients within marine waters on the other hand. In the next sections estuarine and marine optical data are discussed separately.

3.1.1. Estuarine waters

Fig. 3 shows the variation of $a_{CDOM}(375)$ and S as a function of salinity obtained along two Scheldt estuary transects (Fig. 1) performed in winter (February 2005) and summer (July 2006). Some marine stations sampled in winter 2005 are also reported allowing the reconstruction of a nearshore-offshore gradient (Fig. 3a). A significant inverse linear relationship is obtained between $a_{CDOM}(375)$ and salinity in the range 0.7–29 for both February ($r^2 = 0.99$; $p < 0.0001$) and July ($r^2 = 0.91$; $p < 0.001$; Table 2). This relationship suggests a conservative behaviour of CDOM along the Scheldt estuary. On the contrary $a_{CDOM}(375)$ data collected in marine waters (salinity 30–35) show some scattering (Fig. 3a). The range of S values measured in the Scheldt estuary (0.0167 and 0.0191 nm^{-1}; Fig. 3b) shows little variation within the salinity gradient 0.7–29 as well as between winter and summer. On this basis we consider that $S \sim 0.018\ nm^{-1}$ is typical for the estuary. Offshore the Scheldt mouth (salinity ~ 29) marine S values show large scattered variation between 0.011 and 0.020 nm^{-1} which suggests that these waters are submitted to different sources of CDOM, although in low quantity as indicated by low $a_{CDOM}(375)$ values (Fig. 3). Interestingly, no seasonal variation is visible between the Scheldt $a_{CDOM}(375)$ and S data collected in winter and summer (Fig. 3).

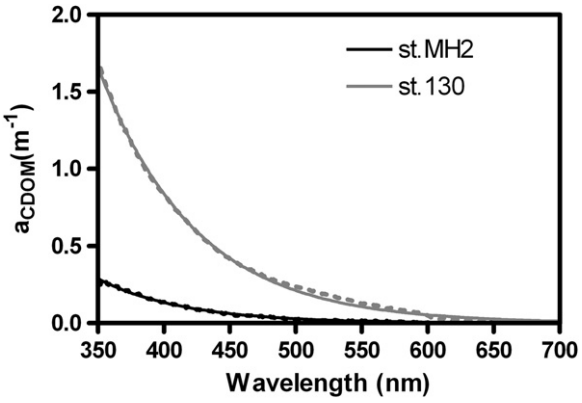

Fig. 2. Examples of measured CDOM absorption spectra (dotted line) and fitted exponential curve (full line) for a coastal sample (st.130 April 2004) and an offshore sample (st.MH2 September 2006).

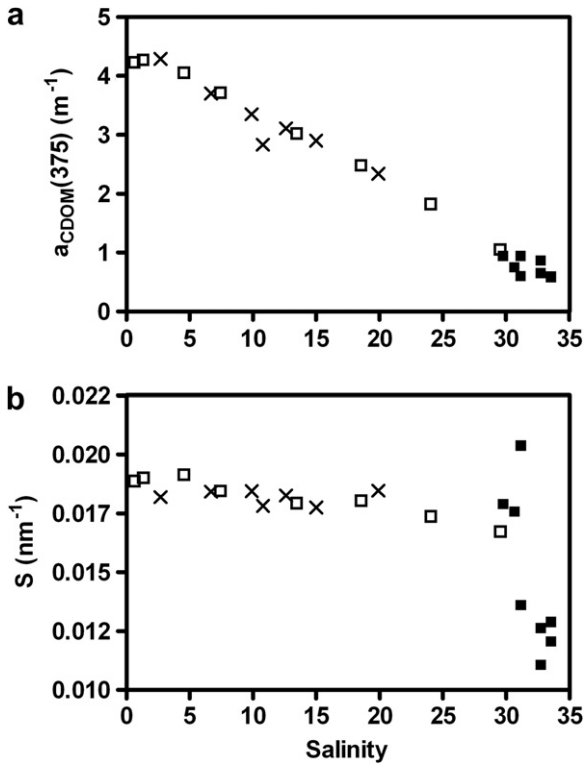

Fig. 3. Variation in $a_{CDOM}(375)$ (a) and S (b) as a function of salinity for winter (February 2005, open squares) and summer (July 2006, crosses) in the Scheldt estuary. Also shown marine BCZ data recorded in February 2005 (filled squares).

Table 2
Parameters of the linear regression between $a_{CDOM}(375)$ and salinity for estuarine waters (Scheldt river) and for marine waters of the BCZ below and above salinity 34. The regression equation is $a_{CDOM}(375) = A * \text{salinity} + B$, with A corresponding to the slope of the regression line and B is the origin ordinate. The standard error for A and B is given between brackets.

Year	Cruises	n	A	B	r^2	p	n	A	B	r^2	p
Estuarine waters		Salinity < 29									
2005	February	8	−0.11 (0.004)	4.47 (0.07)	0.99	0.0001					
2006	July	7	−0.11 (0.016)	4.43 (0.19)	0.91	0.001					
2005–2006		15	−0.11 (0.005)	4.46 (0.07)	0.98	0.0001					
Marine waters		Salinity < 34					Salinity > 34				
2004–2008	Spring	50	−0.11 (0.013)	4.44 (0.42)	0.60	0.0001	32	−0.19 (0.04)	6.96 (1.46)	0.41	0.0001
2004–2008	Summer	24	−0.11 (0.035)	4.49 (1.09)	0.32	0.004	38	−0.19 (0.17)	7.13 (5.78)	0.04	0.26
2004–2008	Late summer	33	−0.10 (0.012)	3.97 (0.38)	0.70	0.0001	29	−0.13 (0.08)	4.99 (2.80)	0.09	0.11
2004–2008	All data	107	−0.11 (0.011)	4.43 (0.35)	0.50	0.0001	99	−0.18 (0.07)	6.65 (2.52)	0.06	0.02

3.1.2. Marine waters

As a first attempt to decode the influence of seasonal biological activity on the CDOM pool, Fig. 4 explores relationships between $a_{CDOM}(375)$ and salinity on the one hand and S and salinity on the other hand, for data obtained in spring (Fig. 4a,d), summer (Fig. 4b,e) and late summer (Fig. 4c,f) in marine waters. For each season, $a_{CDOM}(375)$ decreases with increasing salinity with higher values close to the Scheldt mouth (salinity ~ 29) and lower values offshore (salinity 34–35). Remarkably, whatever the season considered, a relationship exists between $a_{CDOM}(375)$ and salinity up to salinity 34. Table 2 reports values of statistical parameters characterizing the linear relationship between $a_{CDOM}(375)$ and salinity obtained when grouping data below and above salinity 34 and compares them to similar calculation performed for the estuary (salinity 0–29). No significant difference is observed between the slopes of the regressions (A; the dilution rate) and origin ordinates (B; the terrestrial end-member of CDOM) obtained in the BCZ for salinity < 34 and those obtained in the Scheldt estuary ($A = -0.11$, S.E. = 0.005, $B = 4.46$, S.E. = 0.07). This suggests that dilution of terrestrial CDOM into the nearshore waters is the major process determining the concentration of CDOM in the BCZ. Despite an inverse relationship between a_{CDOM} and salinity, some scattering is visible at salinity > 34. No significant correlation is obtained between $a_{CDOM}(375)$ and salinity > 34 ($r^2 = 0.06$, $n = 99$, Table 2), suggesting that autochthonous production rather than terrestrial inputs is determining the CDOM concentration in offshore waters of the BCZ.

This is confirmed by the S-salinity relationships where S shows a high range of variation at salinity > 34 (Fig. 4d–f). No significant correlation was found between S and salinity neither for all cruises together (Pearson $r = -0.44$; Fig. 4d–f) nor separately. A slight inverse trend can be detected in April–May 2004, July 2004 and 2007, September 2006 and 2008, at salinities < 34 with high S values near the Scheldt mouth (salinity ~ 29) and decreasing values at higher salinities.

The origin and variability of CDOM in the BCZ was better explored by relating S to $a_{CDOM}(375)$ for different salinity ranges used as descriptors of water masses (Fig. 5). Within the marine nearshore and offshore waters a large range of S is visible, which contrast the rather constant S found for the Scheldt estuary (Fig. 3). For marine nearshore waters (salinity 30–34), the range of S and $a_{CDOM}(375)$ is respectively between 0.011 and 0.021 nm^{-1} and 0.53 and 1.51 m^{-1}. In marine offshore waters (salinity 34–35), S varies from 0.009 to 0.023 nm^{-1} and $a_{CDOM}(375)$ varies from 0.18 to 1.61 m^{-1}.

These results suggest the existence of another CDOM source in the marine offshore waters other than the terrestrial one. As an important source of organic matter, phytoplankton could well be a potential source of CDOM in these coastal waters. In the next section, this hypothesis has been tested both experimentally by measuring CDOM kinetics during the wax and wane of cultured phytoplankton, and by analysing field data in relationship to phytoplankton bloom stages.

3.2. Optical characterization of phytoplankton-derived CDOM

3.2.1. CDOM accumulation in phytoplankton cultures

An experiment was performed to characterize the release of CDOM during the wax and wane of pure cultures of *S. costatum* and *P. globosa* (Fig. 6). Measurements of cell densities, $a_{CDOM}(375)$ and S were performed every day during the exponential phase of the cultures and every 2 days during the decaying phase. After an exponential growth phase, *S. costatum* reached maximum cell densities (572×10^6 cells L^{-1}; Fig. 6a) on day 10 and *P. globosa* (1000×10^6 cells L^{-1}; Fig. 6d) on day 9. Cell densities were afterwards decaying up to 135×10^6 cells L^{-1} on day 26 for *S. costatum* (Fig. 6a) and up to 10×10^6 cells L^{-1} on day 36 for *P. globosa* (Fig. 6d). The CDOM accumulation, denoted by an increase in $a_{CDOM}(375)$, for both cultures was visible at the end of the exponential phase and increased throughout the decaying phase of the culture for *S. costatum* (Fig. 6b) but remained stable for *P. globosa* (Fig. 6e). For both cultures the slope S increased until the end of the growth phase where it reached maximum values of 0.0195 nm^{-1} for *S. costatum* and 0.0549 nm^{-1} for *P. globosa* and then decrease until the end of the experiment (Fig. 6b and e). Fig. 6c suggests an inverse relationship between S and CDOM accumulation for *S. costatum* suggesting some change in the CDOM molecular signature along the accumulation process. Fig. 6f suggests some difference in the CDOM molecular signature between the growing and the decaying phase of the *P. globosa* culture. During the exponential growth the values of $a_{CDOM}(375)$ and S are positively correlated showing an increasing trend. In contrast during the decay, the value of S is significantly decreasing while $a_{CDOM}(375)$ showed little variation (Fig. 6f).

3.2.2. CDOM characterization during offshore marine phytoplankton blooms

The relationship between CDOM accumulation and phytoplankton blooms was tested in the BCZ marine offshore waters, i.e. in absence or little influence of terrestrial CDOM. In these offshore waters, the CDOM optical data (Fig. 5) were related to phytoplankton bloom stage, i.e. growth or decay. This was primarily done by comparison between the cruise date and a MERIS chl *a* time series of the BCZ (Fig. 7). In addition, a combination of extra parameters including physiological state, species composition, biomass level, nutrient concentrations and presence of grazers was used to sort data into either growing or decaying stages of the bloom.

The relationship between S and $a_{CDOM}(375)$ is an asymptote with high S at low $a_{CDOM}(375)$ during the growth stage of the bloom and high $a_{CDOM}(375)$ but low S during the decay phase (Fig. 8). The S and $a_{CDOM}(375)$ values obtained during phytoplankton growth

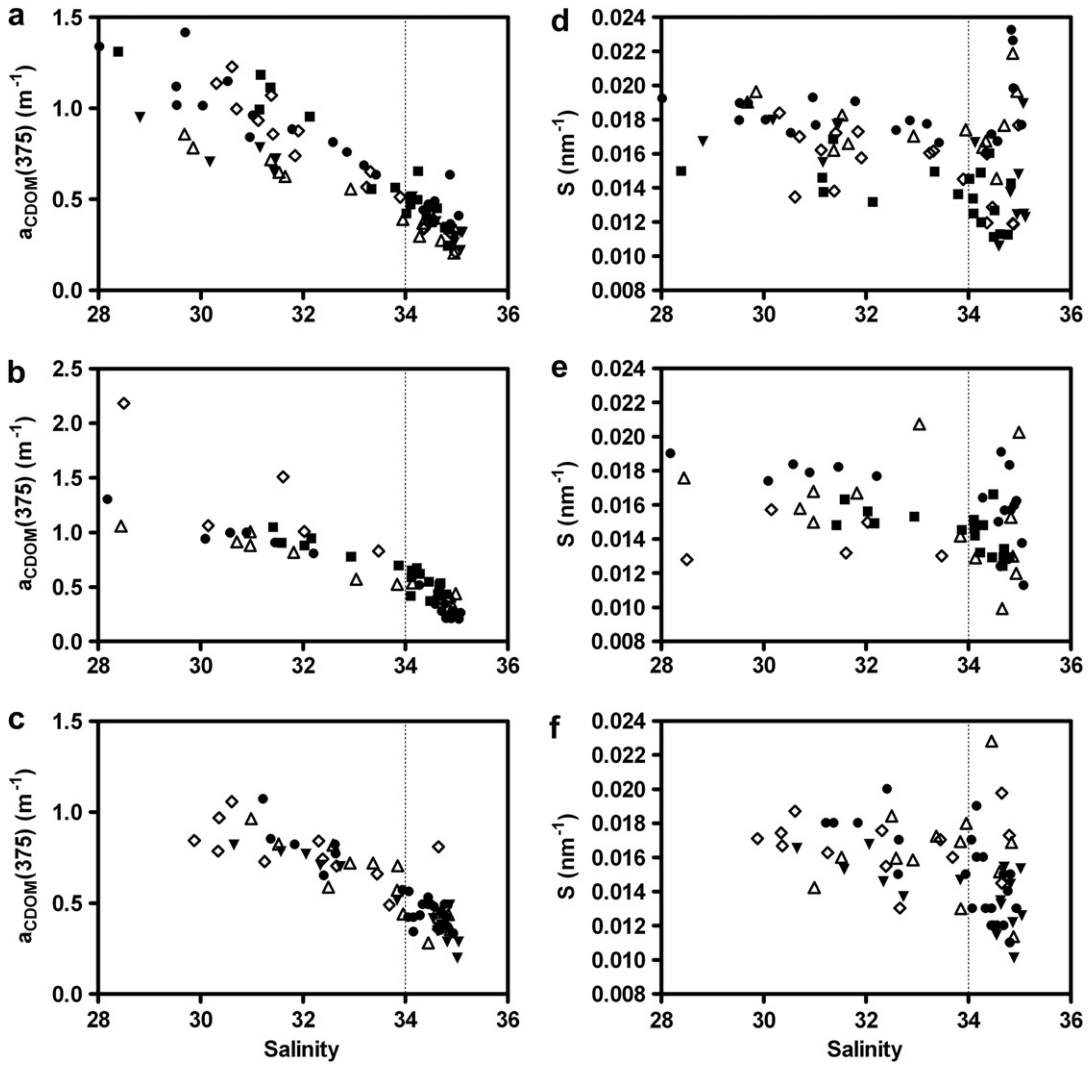

Fig. 4. Variation in $a_{CDOM}(375)$ (a, b, c) and S (d, e, f) as a function of salinity for spring (a,d; filled square, April–May 2004; open triangle, April 2005; filled triangle, April 2006; open diamond, April 2007; filled circle, April 2007), summer (b,e; filled square, July 2004; open triangle, June 2005; open diamond, July 2007; filled circle, July 2008) and late summer (c,f; open triangle, September 2005; filled triangle, September 2006; open diamond, September 2007; filled circle, September 2008) in the BCZ. Salinity 34 is shown with a dotted line.

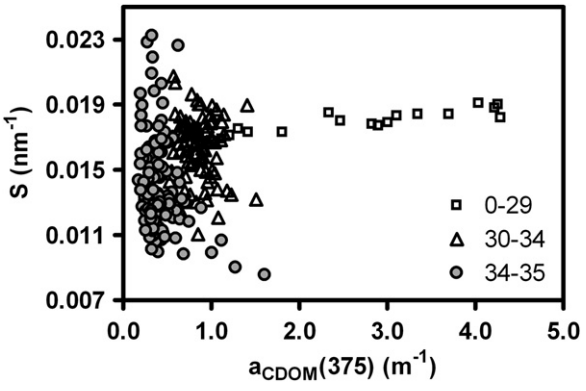

Fig. 5. Relationship between S and $a_{CDOM}(375)$ for all marine and river data collected in the BCZ and the Scheldt estuary, sorted for different salinity ranges: 0–29, 30–34, 34–35.

ranged between 0.0113 and 0.0232 nm^{-1} and between 0.20 and 0.63 m^{-1} respectively, and during the decay phase showed S and $a_{CDOM}(375)$ values from 0.0085 to 0.0177 nm^{-1} with one exception at 0.0203 nm^{-1} and 0.20–1.61 m^{-1} respectively (Fig. 8). The mean S during the growth stage (0.0169 ± 0.0032 nm^{-1}) was significantly higher than during the decay phase (0.0132 ± 0.0023 nm^{-1}; t-test $t = 7.72$, $p < 0.0001$).

4. Discussion

4.1. Variability of a_{CDOM} and S in estuarine and nearshore waters

In this study, values of $a_{CDOM}(375)$ recorded in the marine nearshore and offshore waters of the BCZ ranged between 0.20 and 1.31 m^{-1}. This variation corresponds to the range (0.25–1.00 m^{-1}) reported by Warnock et al. (1999) in the Belgian and Dutch waters along a nearshore transect under Scheldt influence. When considered at 443 nm our CDOM absorption values (0.05–0.48 m^{-1}) compare very well with $a_{CDOM}(443)$ obtained by Babin et al. (2003) in the adjacent German and Dutch waters of the Southern North Sea (0.05–0.50 m^{-1}) and by Boudesseul (2005) in the Eastern

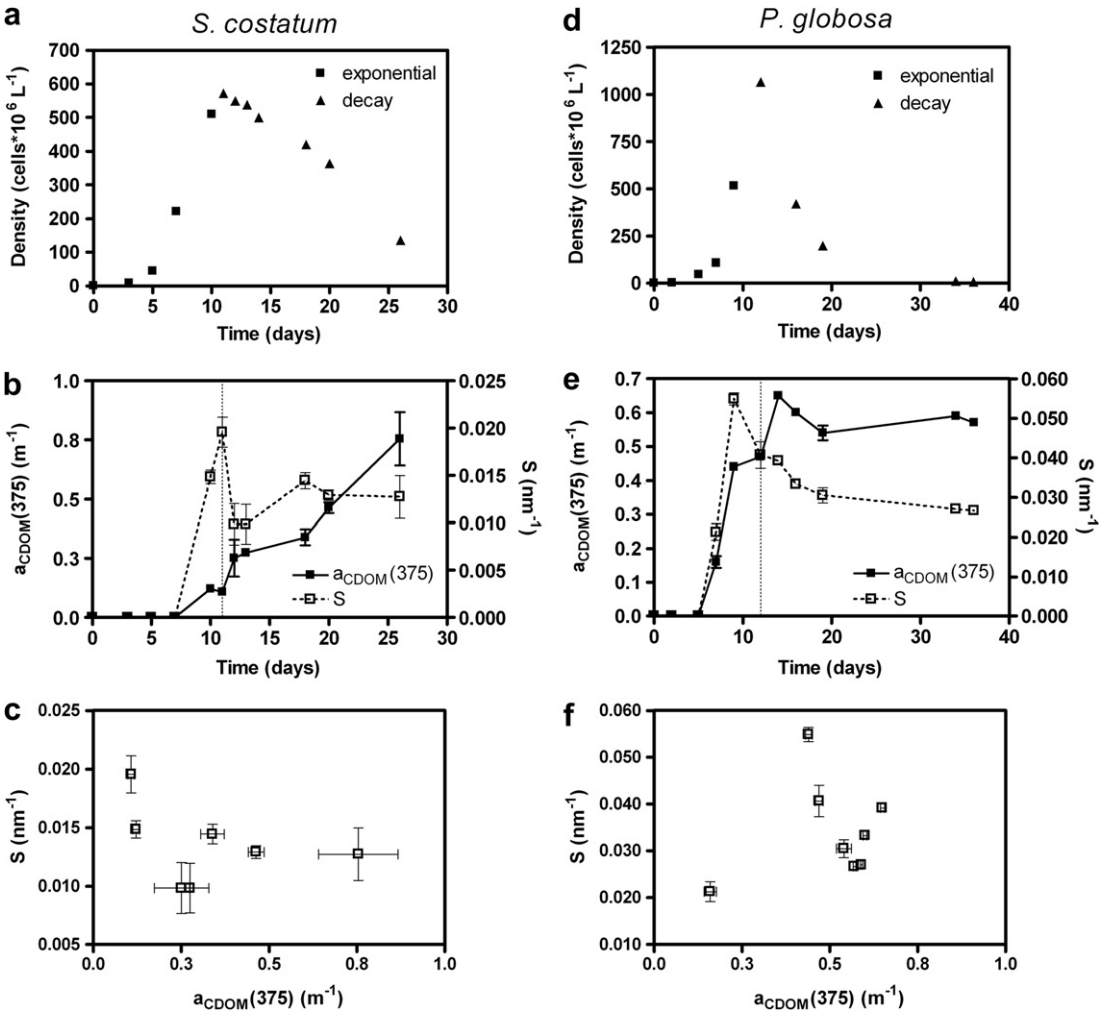

Fig. 6. Results of CDOM production in cultures for *Skeletonema costatum* (left panel) and *Phaeocystis globosa* (right panel): phytoplankton cell density (a,d), $a_{CDOM}(375)$ and S evolution with time (b,e), relationship between S and $a_{CDOM}(375)$ (c,f). Error bars are included for panels b, c, e and f.

Channel French coastal waters (0.01–0.47 m^{-1}). Altogether this suggests that the range of $a_{CDOM}(375)$ between 0.20 and 1.31 m^{-1} is characteristic of Eastern Channel and Southern North Sea nearshore waters.

No clear seasonal variability of a_{CDOM} is found in the BCZ with the exception of high $a_{CDOM}(375)$ recorded in July 2007 and low $a_{CDOM}(375)$ recorded in February 2005 (Table 1). Our low winter results contradict the higher winter but lower spring nearshore values of $a_{CDOM}(375)$ found in Belgian and Dutch waters (Warnock et al., 1999) and in the Eastern Channel influenced by the rivers Seine and Somme (Boudesseul, 2005), suggesting a higher river delivery of CDOM in winter during those studies.

Table 3 compares S values obtained in different estuarine and nearshore-offshore waters for different locations around the world computed using a similar wavelength range to that considered in our study. The computation of S is however highly dependant of the wavelength range considered with an increase of S when curve fitting extends towards shorter wavelengths (Warnock et al., 1999). Considering this, all original S values were recalculated with the wavelength range used in our study to allow comparison. Scheldt estuary values of S are higher than the range for other estuarine systems like Tampa Bay and much higher than those reported for the Mississippi and Orinoco river plumes (Table 3). The range of variation of S found in the BCZ (0.0101–0.0203 nm^{-1}) is similar to

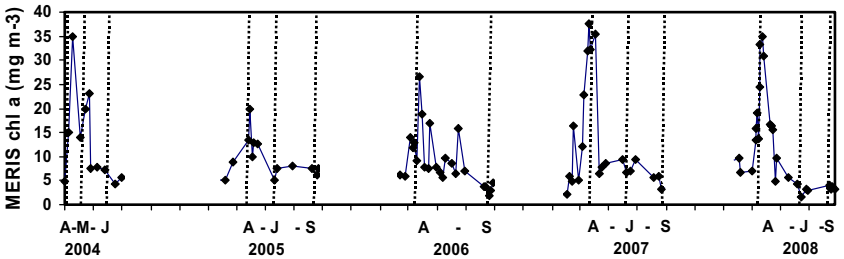

Fig. 7. MERIS chl *a* time series for the BCZ. Superimposed in dotted lines are the dates of cruises performed in the area: A stands for April, M for May, J for June–July and S for September.

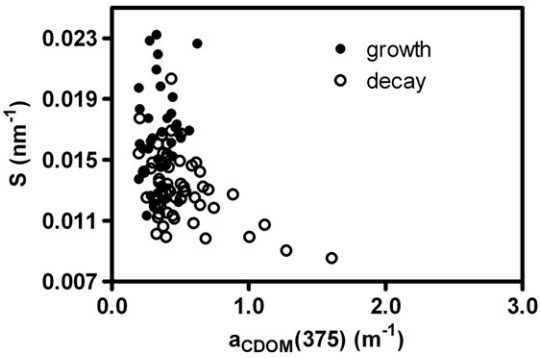

Fig. 8. Relationship between S and $a_{CDOM}(375)$ for all marine offshore data collected in the BCZ, sorted for growth or decay phase of the phytoplankton bloom. For sorting refer to the text.

that found by Babin et al. (2003) for the German and Dutch waters (0.0116–0.0188 nm^{-1}) but broader than that found by Warnock et al. (1999) for samples covering the Southern North Sea (0.014–0.018 nm^{-1}). The range of S values reported by Carder et al. (1989) for the Gulf of Mexico is also narrower (0.0115–0.0172 nm^{-1}).

4.2. Sources of CDOM in the BCZ

The different optical characteristics of CDOM in the Scheldt estuary, the nearshore and the offshore marine waters of the BCZ suggest the existence of at least two main CDOM pools in the marine waters, one terrestrial and one autochthonous marine pool released and processed by phytoplanktonic organisms.

The relation between S and $a_{CDOM}(375)$ has been used in previous studies to differentiate between sources of CDOM, namely terrestrial from marine origin (Stedmon and Markager, 2001; Kowalczuk et al., 2006). A constant terrestrial source shown by a low S variation ($\sim$0.018 nm^{-1}) and a variable marine source characterized by a range of low S values ($S \sim 0.009$ nm^{-1}) to high S values ($S \sim 0.027$ nm^{-1}) was found by Stedmon and Markager (2001) in the Greenland Sea.

4.2.1. Terrestrial source

The inverse linear regression between $a_{CDOM}(375)$ and salinity established for the Scheldt estuary suggests a conservative mixing of terrestrial CDOM with the seawater of the Southern North Sea, as observed in other estuarine systems (Blough and Del Vecchio, 2002; Del Vecchio and Blough, 2004; Chen et al., 2007). In these waters, dilution of continental CDOM is a significant process. The terrestrial origin of the CDOM in nearshore waters of the BCZ is also suggested when comparing the slopes (A) and the terrestrial end-member (B) of the $a_{CDOM}(375)$-salinity regressions (Table 2) observed in marine nearshore waters with those in the Scheldt estuary which are significantly similar with those found by Warnock et al. (1999) for freshwater inputs in front of the Scheldt estuary mouth ($A = 0.145$, $B = 5.38$). This terrestrial origin is also confirmed by the S value of 0.018 nm^{-1} for Scheldt estuarine CDOM, i.e. close to the value found for fulvic acids (0.019 nm^{-1}; Carder et al., 1989).

4.2.2. Marine source

Our results for marine offshore waters contrast with most previous findings where S increases with increasing salinity and decreasing a_{CDOM} as a result of the alteration of terrestrial CDOM (Blough and Del Vecchio, 2002 and references therein, S: 0.018–0.030 nm^{-1} for salinities 30–35). The decrease in S reported for offshore BCZ waters (salinity 34–35) is explained by the presence of phytoplankton-derived CDOM further processed by bacteria and/or by photo-oxidation. Laboratory-controlled studies of CDOM accumulation in phytoplankton cultures of the dominant species in the BCZ show higher S and lower $a_{CDOM}(375)$ for the exponential growth phase and then a decrease in S and increase in $a_{CDOM}(375)$ for the declining phase of cultures (Fig. 6b,e) which could explain the variability in S found for marine offshore waters. It is interesting to note that low S values of $\sim$0.012 nm^{-1} i.e. similar to ours (Fig. 6) have been reported for CDOM accumulated during the decaying phase of diatom cultures (Poulet, 2005). Also in agreement with our results, Zhao et al. (2009) reported higher CDOM absorption during a bloom development and lower values for a non-bloom period. For salinity > 34 some stations with $S > 0.019$ nm^{-1} can be identified in the offshore area. The increase in S at offshore stations has been related to processes like photo-degradation of terrestrially derived CDOM (Vodacek et al., 1997). Without excluding photodegradation, we argue that the S increase is due to biological activity which is seasonal and very dynamic. However, mixing of water masses of different origin cannot be excluded in these coastal areas (Lacroix et al., 2004). Indeed, the significant differences in S found during the growing and decaying phases of the phytoplankton bloom support the idea that the CDOM released along the bloom has its own chemical composition which changes as the bloom ages, thus decreasing the value of S.

Comparison of the results of laboratory cultures $S - a_{CDOM}(375)$ for both species show higher values of S for *P. globosa* (Fig. 9). Although these higher S values are not found in the field, the same trend of variability in $S - a_{CDOM}(375)$ is observed for cultures as in the field (Fig. 8), with higher growth S values and lower decay S values. This is consistent with the fact that *P. globosa* is the dominant species during the bloom in the BCZ while during the decay phase of the bloom diatoms become dominant (Rousseau, 2000).

Our results from cultures and field data show clearly that the phytoplankton-derived CDOM appears during the growth phase but increases mostly during the decaying phase of the bloom as

Table 3
S values from literature and for this study. λ-range shows the range of wavelengths used for S calculation. Only S values calculated using a λ-range close to the one used in our study are shown for comparison. S (350–500) shows the recalculations of original S using the range 350–500 nm.

Location	Water type[a]	λ-range (nm)	S range (nm^{-1})	S (350–500) (nm^{-1})	Source
Mississippi plume	Estuarine	370–440	0.0128–0.0141	0.0134–0.0147	Carder et al. (1989)
Orinoco plume	Estuarine	400–500	0.0148–0.0159	0.0141–0.0152	Del Castillo et al. (1999)
Tampa Bay	Estuarine	350–440	0.014–0.017	0.0143–0.0173	Chen et al. (2007)
Scheldt estuary	Estuarine	350–500	0.0167–0.0191	0.0167–0.0191	This study
Gulf of Mexico	Nearshore	370–440	0.0115–0.0172	0.0120–0.0177	Carder et al. (1989)
Orinoco plume	Nearshore-offshore	400–500	0.010–0.0158	0.0095–0.0153	Del Castillo et al. (1999)
German and Dutch waters	Nearshore-offshore	350–500	0.0116–0.0188	0.0116–0.0188	Babin et al. (2003)
Belgian and Dutch waters	Nearshore-offshore	360–440	0.014–0.018	0.0145–0.0185	Warnock et al. (1999)
Tampa Bay	Offshore	350–440	0.016–0.018	0.0165–0.0185	Chen et al. (2007)
Belgian waters	Nearshore-offshore	350–500	0.0101–0.0203	0.0101–0.0203	This study

[a] Estuarine refers to salinity < 29, offshore to salinity > 34, nearshore to salinities between 30 and 34.

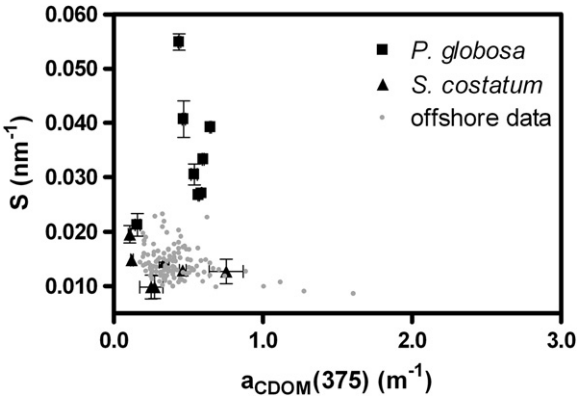

Fig. 9. Relationship between S and $a_{CDOM}(375)$ for CDOM production in cultures of *P. globosa* and *S. costatum* (including error bars). The field offshore data from the BCZ is shown in grey dots.

a result of phytoplankton degradation, and subsequent changes in the chemical composition of the molecules as denoted by the variability in $S - a_{CDOM}(375)$ with time. This result supports the hypothesis that CDOM can be produced/released by phytoplankton and that in marine environments they can account for a large proportion of the CDOM variability observed.

Chemical identification of CDOM molecules from terrestrial and autochthonous origin as proportions of fulvic and humic acids, low or high molecular weight, could help understand the high variability of S found in cultures and in the field. For this purpose, fluorescence techniques have been proved successful (Coble, 1996; McKnight et al., 2001) and could be a potential perspective in the study of CDOM sources.

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