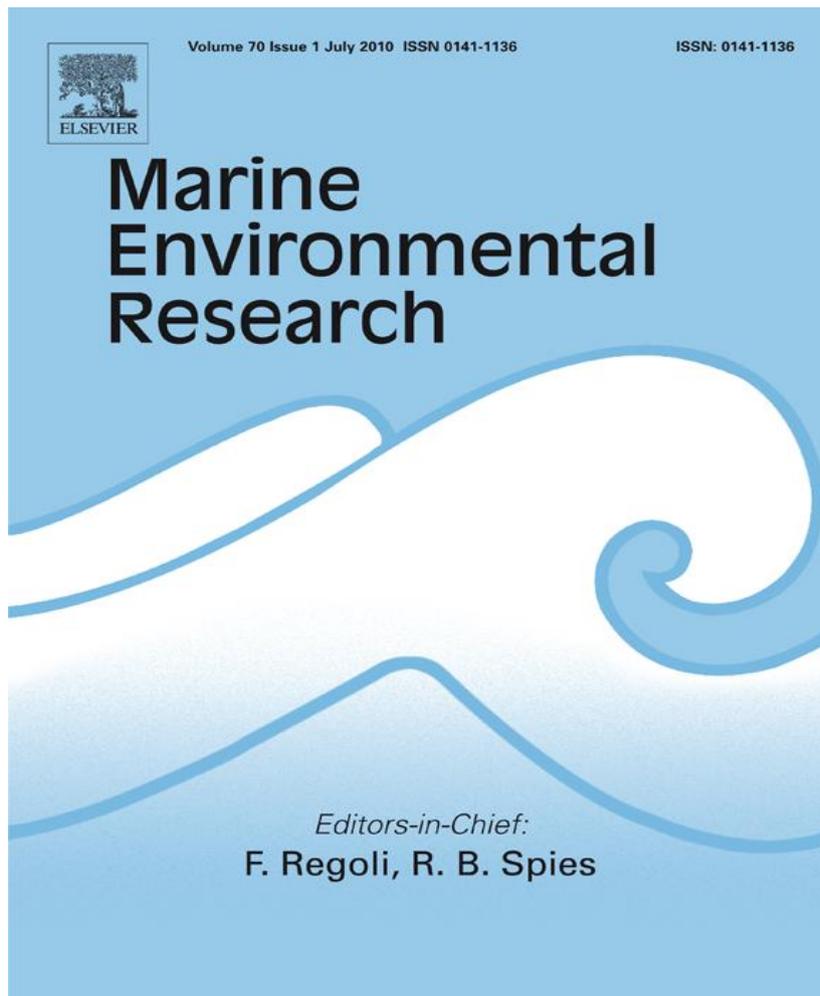


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Winter to spring variations of chromophoric dissolved organic matter in a temperate estuary (Po River, northern Adriatic Sea)

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ABSTRACT

The light absorbing fraction of dissolved organic carbon (DOC), known as chromophoric dissolved organic matter (CDOM) showed wide seasonal variations in the temperate estuarine zone in front of the Po River mouth. DOC concentrations increased from winter through spring mainly as a seasonal response to increasing phytoplankton production and thermohaline stratification. The monthly dependence of the CDOM light absorption by salinity and chlorophyll *a* concentrations was explored. In 2003, neither DOC nor CDOM were linearly correlated with salinity, due to an exceptionally low Po river inflow. Though the CDOM absorbance coefficients showed a higher content of chromophoric dissolved organic matter in 2004 with respect to 2003, the spectroscopic features confirmed that the qualitative nature of CDOM was quite similar in both years.

CDOM and DOC underwent a conservative mixing, only after relevant Po river freshets, and a change in optical features with an increase of the specific absorption coefficient was observed, suggesting a pre-vailing terrestrial origin of dissolved organic matter.

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1. Introduction

The general circulation in the Northern Adriatic Sea (NA) is characterized by a northward current along the eastern coast and a Western Adriatic Current (WAC) flowing southwards along the western coast. Near the Po River delta the stratification persists throughout most of the year (Artegiani et al., 1997). The structure of the plume depends on the discharge rate and the stratification of the water column, resulting in maximum offshore extension under high runoff, strong Bora wind forcing and summer stratification (Mauri and Poulain, 2001). The Po River freshwater may flow southward along the shelf strengthening the WAC (Malanotte-Rizzoli and Bergamasco, 1983) or cross the shelf extending toward Istria in the central basin (Mauri and Poulain, 2001). In particular, during periods of weak stratification, in absence of wind forcing, vortices constrain fresh Po river waters to a southward flow along the Italian shelf (Orlić et al., 1992). In contrast, during periods of stratification, particularly in spring–summer, the Po freshwater

plume spread across the basin to the Istrian coast to form a front that divides the northern basin (Franco and Michelato, 1992; Jeffries and Lee, 2007). The extent of Po River inflow and wind forcing, therefore, modulate fresh water (FW) penetration in the NA (Kourafalou, 1999; Jeffries and Lee, 2007). Dilution processes are the main factor controlling dissolved and particulate organic matter concentrations in the mixing zone of Po River (Pettine et al., 1999 and references therein).

Many efforts have been devoted to understand the dissolved organic carbon (DOC) cycle and the role of chromophoric dissolved organic matter (CDOM) in the marine environment (Blough and Del Vecchio, 2002 and references therein). The coastal zone, especially in areas adjacent to the estuaries of major rivers, is a marine environment where key biogeochemical processes occur (Hansell and Carlson, 2002). DOC represents the major fraction (60%) of riverine organic matter (Spitzzy and Ittekkot, 1991); in addition, a local source of autochthonous DOC from phytoplankton and bacterial activity may be observed in the region influenced by freshwaters (Sempéré et al., 2000; Raymond and Bauer, 2001). The estuaries are often characterized by high mixing rates that make it difficult to discriminate between different DOC sources (e.g.: Stedmon and Markager, 2003). As CDOM is the most important sunlight-absorbing substance in the sea especially in the UV and blue region of the spectrum (Ferrari, 2000 and references therein)

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its optical properties provide information on DOM as a whole and on DOC fractions which are fundamental for studies on organic matter and carbon fluxes in aquatic ecosystems (Bacastow and Maier-Reimer, 1991). A fraction of CDOM consists of a mixture of aliphatic and aromatic substances deriving from the degradation of terrestrial and aquatic plants (Kirk, 1994). This material contributes to form the light absorbing fraction of DOM and its absorption is strongest in the UV region, restricting the penetration into surface waters of biologically damaging UV radiation and protecting phytoplankton and other aquatic organisms (e.g.: de Mora et al., 2000) but, at the same time, limiting the in depth production because of its shading effect (Stedmon et al., 2000).

The aim of this work was to investigate the winter to spring variations of dissolved organic matter and its chromophoric fraction in the temperate estuarine zone of the Northern Adriatic in two periods (during 2003 and 2004) characterized by significantly different Po river inflows, in order to elucidate its origin and composition. Correlations among DOC, CDOM and physical–chemical parameters were also discussed in terms of processes involved.

2. Material and methods

2.1. Sampling

Water samples were collected at 6 stations on a transect from the Po Prodelta eastwards (Fig. 1) from February to May 2003 (ten cruises) and from February to June 2004 (ten cruises). Surface waters were sampled using 5 L Niskin bottles. Water samples for DOC and POC analyses were filtered through Whatman GF/F, precombusted at 480 °C for 4 h, 100 µL of HgCl₂ (1 g L⁻¹) were added to 10 ml of the seawater sample for DOC conservation (Cauwet, 1999). About 2 L of seawater were filtered on Whatman GF/F for chlorophyll *a* (Chl *a*) analyses. All samples were stored at –20 °C until analysis.

2.2. Analytical procedures

Temperature, depth and salinity were determined by a CTD probe (Conductivity, Temperature, Depth, SEA Bird Electronics - SBE 25). Vertical CTD profiles were performed at all stations during cruises in 2003 and 2004.

DOC concentrations of seawater samples were measured using a Shimadzu TOC 5000 Analyzer and a 1.2% Pt on silica catalyst at 680 °C. Potassium hydrogen phthalate was used as standard. The reproducibility of the analytical procedure was within 2–3%.

POC was determined with a CHN Elemental Analyzer Carlo Erba Mod. EA1110, after acidification with HCl (1 N), to remove the

inorganic carbonate fraction. Acetanilide was used as standard. The reproducibility of the analytical system was lower than 2%.

Chl *a* was extracted in acetone 90% and determined by UV–VIS ATI Unicam UV2 double beam spectrophotometer (Parson et al., 1984).

UV–Visible spectra of CDOM in waters were recorded from 280 to 800 nm by UV–VIS ATI Unicam UV2 double beam spectrophotometer with quartz cells (5 cm) using Milli-Q water as blank. Data were expressed as absorption coefficients: $a_{\lambda} = 2.303A_{\lambda}/L$, where A_{λ} is the absorbance at a given wavelength and L is the path length in meters. A baseline correction was applied by subtracting the absorbance average value at 650 nm.

The absorption coefficient of CDOM at 355 nm ($a_{CDOM355}$) was chosen (Blough and Del Vecchio, 2002), as the specific wavelength of 355 nm coincides with the pulsed frequency tripled Nd:YAG excitation laser currently used in shipborne and airborne laser fluorescence spectroscopy sensing (Ferrari and Dowell, 1998).

$a_{CDOM280}$ at 280 nm was chosen because it is the spectral region where aromatic substances (Traina et al., 1990), which are mainly of terrestrial origin as lignin, absorb.

The slope of the absorption spectra, S_{CDOM} , describing the rate of decrease of CDOM absorption with increasing wavelength, was extracted from the absorption data using an exponential decay curve fitted to the plot of absorption coefficient (a_{λ} , m⁻¹) versus wavelength (λ) over the range 350–480 nm. The S_{CDOM} parameter was calculated according to Green and Blough (1994):

$$a(\lambda) = a(\lambda_0)e^{-S_{CDOM}(\lambda-\lambda_0)}$$

where $\lambda_0 = 480$ nm is the initial wavelength, and S_{CDOM} is the fitted parameter (nm⁻¹) for the exponential decay of a_{λ} with increasing λ .

Nutrients (ammonium-NH₄⁺, nitrite-NO₂⁻, nitrate-NO₃⁻, orthophosphate-PO₄³⁻ and orthosilicate-Si(OH)₄, were analysed spectrophotometrically (Parsons et al., 1984) by a Technicon TRAACS 800 autoanalyzer. Dissolved inorganic nitrogen (DIN) was calculated as the sum of the NH₄⁺, NO₂⁻ and NO₃⁻ concentrations.

The salinity is expressed on the basis of the UNESCO practical salinity scale (PSS 1978).

For the graphical representations Grapher 7 (Golden Software Inc, USA) was used. Statistical analyses were performed using Statistica 6 (Statsoft, USA).

3. Results and discussion

3.1. Po river inflow

During the period 1918–2004 it has been observed that the Po river flow regimen was generally characterized by two main

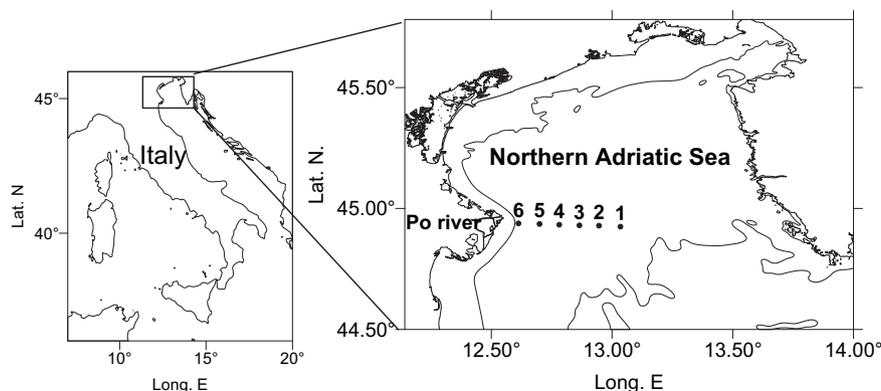


Fig. 1. Sampling stations.

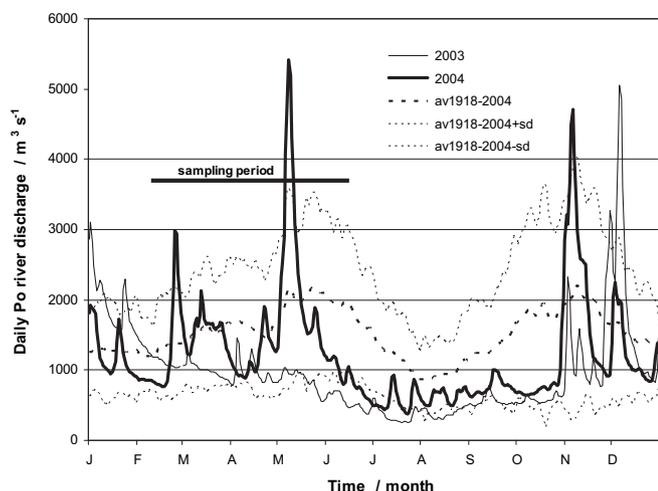


Fig. 2. Daily average inflow of Po River in 2003 and 2004. Av 1918–2004 = average inflow in the period 1918–2004; av 1918–2004 \pm sd = average inflow in the period 1918–2004 \pm standard deviation.

periods of high rate in late spring (May–June) and autumn (October–November) and by a minimum in summer (July–August). These variations are due to the seasonal rainfall in the drainage basin and to the melting of snows on the mountains in late spring. The mean daily inputs of the Po River in 2003 and 2004 are reported in Fig. 2 along with the average flow in the period 1918–2004.

During 2003, except in January and February, the Po river flow was lower than the 1918–2004 average, whereas in 2004 there were two main freshets in February ($\sim 3000 \text{ m}^3 \text{ s}^{-1}$) and May ($>5000 \text{ m}^3 \text{ s}^{-1}$): this implied that higher salinities were observed during 2003 than in 2004.

The stratification in front of the Po mouth was limited to the coastal waters during the winter–spring period of 2003, whereas in 2004 the plume reached the centre of the NA basin and the discontinuous discharges caused the advection of FW pools offshore. Therefore the salinity vertical gradients (Fig. 3) were more marked in 2004 ($\Delta S = 7 \pm 4$) than in 2003 ($\Delta S = 3 \pm 4$). The situation observed in front of Po delta is in accordance with the stronger warming of stratified surface waters observed in spring 2004 in the NA with respect to 2003, which determined also a higher stability (De Lazzari et al., 2008). Moreover, the higher river discharge of 2004 caused a more relevant eastwards spreading of the plume than in 2003 and lower salinities (<35 psu) were observed near the Po prodelta. Lower rainfall precipitation and higher salinities during spring–summer of 2003 were observed also in other areas of the Adriatic (Celio et al., 2006; Grbec et al., 2007) and are supported by the more than 50% lower than average (1918–2004) Po inflows in spring of 2003 (Fig. 2) and by the lower content of fresh waters observed in the station in front of Po delta (Fig. 4a).

The surface water temperatures ranged between 7.3 and 18.2 °C in 2003 and between 5.5 and 21.8 °C in 2004. The colder temperatures were observed in February in the less saline waters of the Po river plume as usually observed in the Northern Adriatic (Russo et al., 2005). The highest temperatures due to the seasonal warming were recorded on May 2003 and June 2004 in the shallowest coastal station. The descriptive statistics for the parameters measured in surface waters are summarized in Table 1.

3.2. Chlorophyll *a* and nutrients

The average and standard deviation of Chl *a* concentrations with statistically significant differences between the two years are reported in Table 1.

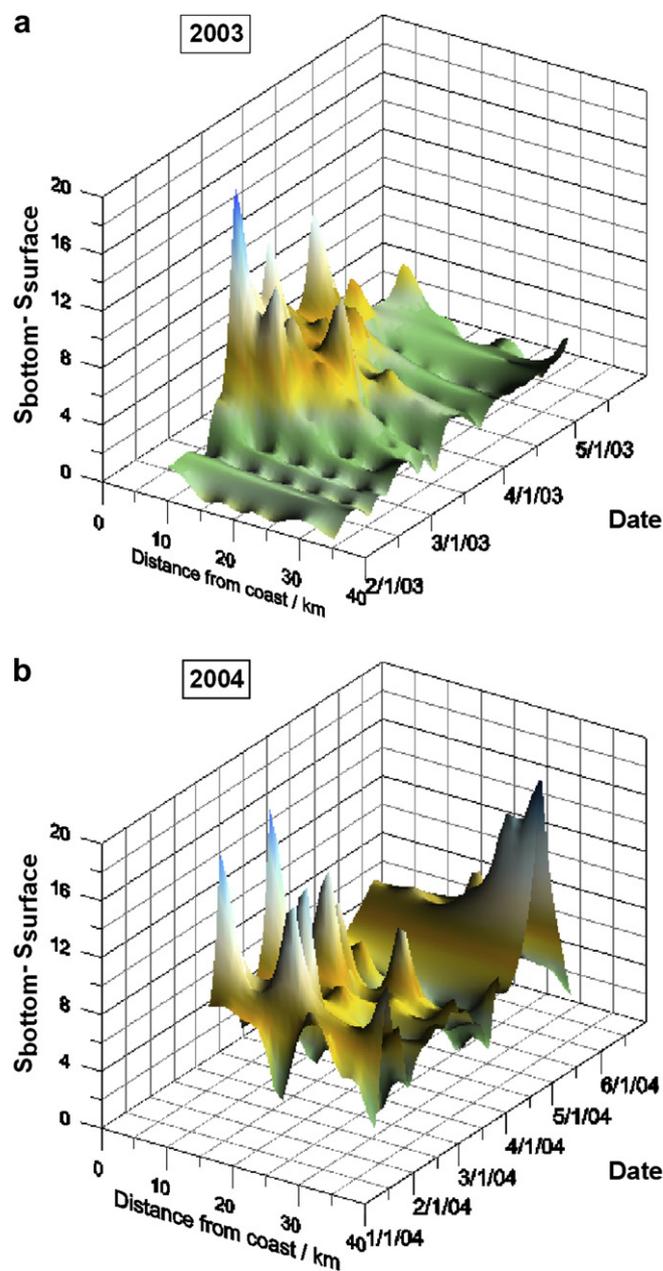


Fig. 3. Variation of the vertical salinity gradient (between bottom and surface) at increasing distances from the coast.

Chl *a* concentrations were on average 4 fold higher in 2004 than in 2003 when an increased nutrient availability sustained a more relevant phytoplankton biomass (Table 1). The monthly distribution of Chl *a* in the 2003 and 2004 (Fig. 4b) years showed high concentrations in the last period of 2004. The highest value of the Chl *a* in the last period of 2004 was probably due to a phytoplankton bloom of *Cerataulina pelagica*, stimulated by the nutrients carried by the Po river (Socal et al., 2008). The monthly Chl *a* concentrations plotted as a function of salinity in 2003 and 2004 (Fig. 5) showed a negative linear relationships between Chl *a* and salinity in March 2003 and 2004, April 2004 and May–June 2004. This situation is typically observed in the NA when the spring runoff determines an increase of Chl *a* concentrations (Barale et al., 2005; Mauri et al., 2007).

Relevant relationships were found between Chl *a* and orthosilicate concentrations in March, April and May–June 2004 (Table 2)

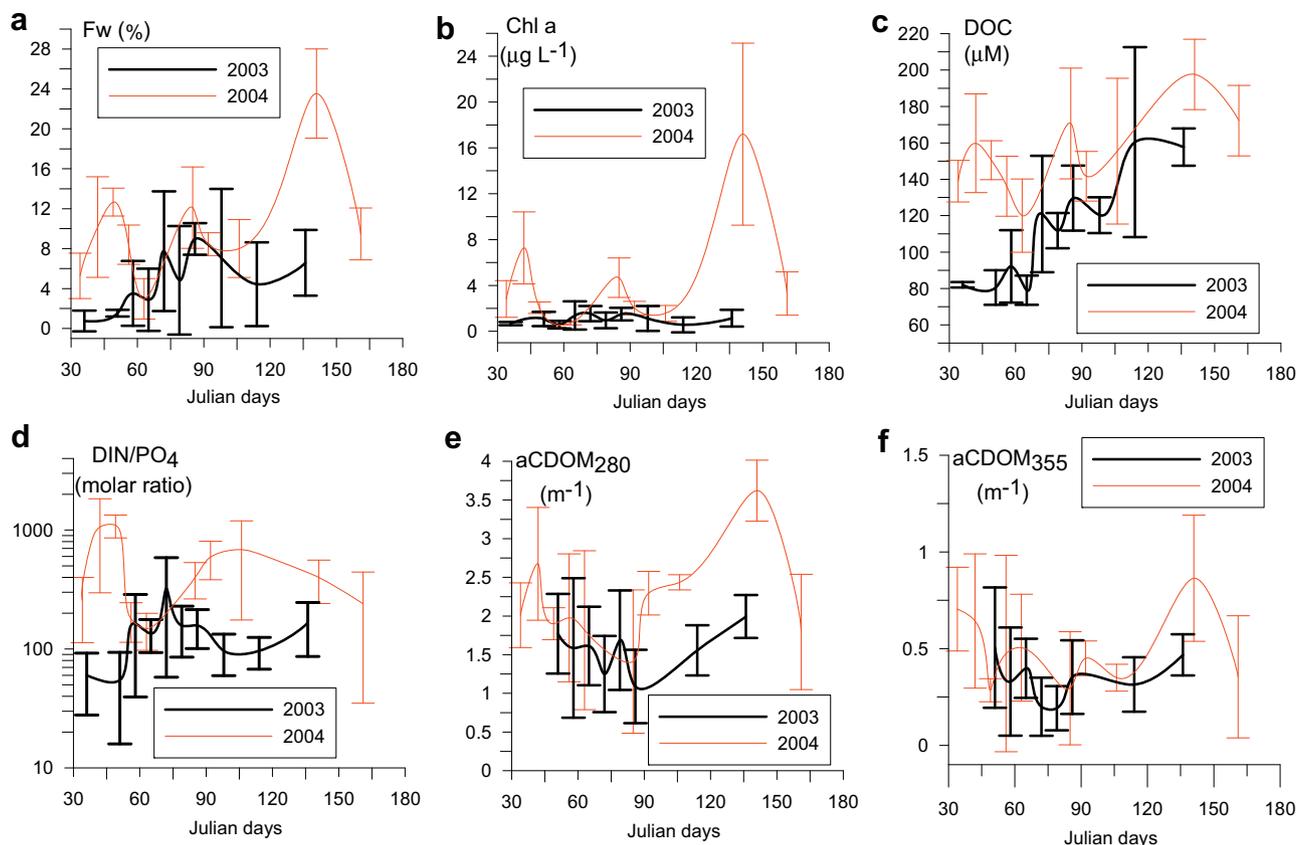


Fig. 4. The seasonal distribution of Fw, DOC, Chl a, DIN/PO₄, aCDOM₂₈₀, aCDOM₃₅₅ in 2003 and 2004.

but were not observed in 2003. Considering that the influence of the Po River was weaker in 2003 than in 2004, the river inputs significantly increased the primary production and consequently the amount of organic matter in the basin.

The concentration of dissolved inorganic nitrogen (DIN) was on average higher in 2004 than in 2003, reaching the highest values in winter 2004: DIN had the same trend of NO₃⁻, which was >76% of

the nitrogen forms. Higher NH₄⁺ concentrations were found in 2003 (Table 1) which could be due to a more intense bacterial degradation, enhanced by the higher winter temperatures. A significant negative relationship (*p* < 0.05) has been found between DIN concentrations and salinity showing that the major amount of nutrients was transported by riverine waters.

3.3. Dissolved organic carbon

The main fraction of total organic carbon in the waters was the dissolved form both in 2003 (mean: 86%; range: 67–95%) and in 2004 (mean: 78%; range: 45–95%); the lowest values in 2004 were observed in February when the Po flow was low. Monthly variations in DOC concentrations in 2003 and 2004 showed lower concentrations in winter and higher in spring (Fig. 4c) following a trend typical for the northern Adriatic Sea (Giani et al., 2005). The gradual build up of DOC accumulation proceeds from spring to summer when sub basin scale seasonal circulation structures link the eutrophic western part with the oligotrophic central part of the basin. The cyclonic re-circulation cause the transport of DOC produced in the coastal areas to the offshore regions where the system has low bacterial growth efficiency and long DOC utilization time (Polimene et al., 2007). Significantly higher DOC concentrations in 2004 with respect to those observed in 2003 (Table 1) could be a consequence of the major input of Po River as well as of the exudation/release from the more intense phytoplankton blooms associated with a higher retention of FW in the NA.

Mixing diagrams of concentrations along the salinity gradient were used to infer the net effect of estuarine processes. Concentrations of DOC were plotted as a function of salinity for the different

Table 1
Average values for salinity (S), freshwater (Fw), temperature, dissolved organic carbon (DOC), chlorophyll *a* (Chl *a*), nutrients and spectroscopic characteristics of CDOM in 2003 and 2004, highlighting the significant differences between the two years.

Parameter	Units	2003			2004			<i>t</i> test
		<i>n</i>	Average	SD	<i>n</i>	Average	SD	
S		59	36.3	4.4	60	34.6	2.3	<0.001
Fw	%	59	4.9	4.6	60	10.1	6.0	<0.001
T	°C	59	10.3	3.0	60	10.8	4.9	ns
DOC	μM	59	114	36	60	155	31	<0.001
POC	μM	59	18.3	9.7	60	50.6	43.7	<0.001
Chl <i>a</i>	μg L ⁻¹	59	1.06	0.76	60	4.27	5.49	<0.001
P-PO ₄ ³⁻	μM	59	0.08	0.06	59	0.05	0.07	<0.05
Si-Si(OH) ₄	μM	59	3.80	2.53	60	6.65	5.25	<0.001
N-NH ₄ ⁺	μM	59	1.47	1.35	60	0.71	0.90	<0.001
N-NO ₂ ⁻	μM	59	0.41	0.23	60	0.76	0.37	<0.001
N-NO ₃ ⁻	μM	59	8.86	8.90	60	14.92	10.83	<0.001
DIN	μM	59	10.74	9.52	60	16.39	11.16	<0.001
aCDOM ₂₈₀	m ⁻¹	56	1.6	0.6	56	2.2	0.9	<0.001
aCDOM ₃₅₅	m ⁻¹	47	0.3	0.2	56	0.5	0.3	<0.05
a [*] CDOM ₂₈₀	m ⁻² gC ⁻¹	48	1.2	0.6	55	1.2	0.4	ns
a [*] CDOM ₃₅₅	m ⁻² gC ⁻¹	48	0.3	0.2	55	0.3	0.2	ns
S _{CDOM} × 10 ³	nm ⁻¹	31	20.4	5.9	34	20.7	5.2	ns

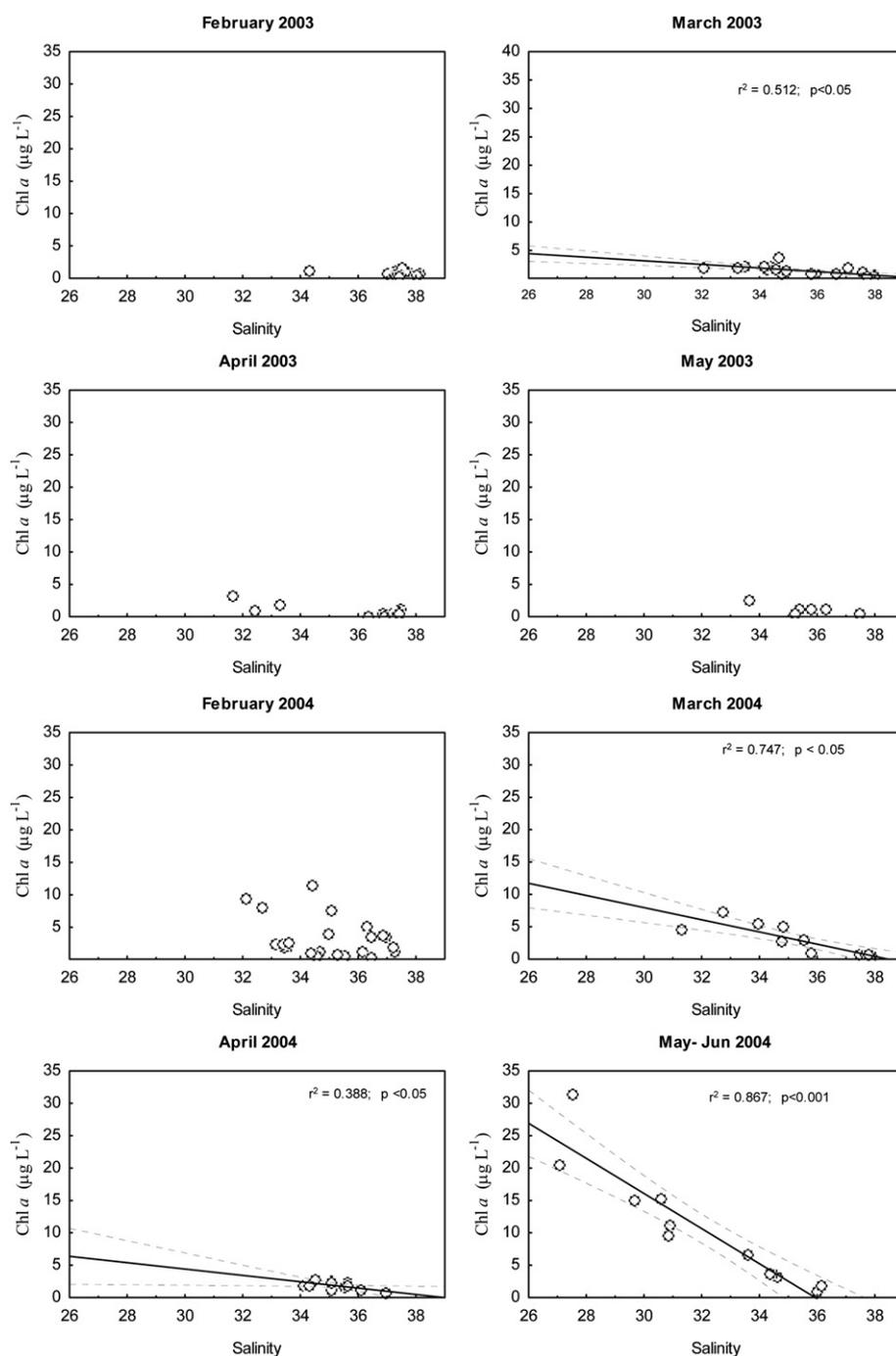


Fig. 5. Plots of chlorophyll *a* (Chl *a*) vs salinity (2 m) in different months of sampling in 2003 and 2004.

periods of sampling (February, March, April and May–June) in 2003 and 2004. The fairly linear plots corresponding to March 2003, March 2004 and May–June 2004 indicate a conservative mixing of the dissolved organic matter during these periods (Fig. 6).

A positive correlation between DOC and Chl *a* in February, March and May–June 2004 (Table 2) highlights the contribution of the intense phytoplankton biomass, following which extracellular polysaccharides probably represent a relevant fraction of dissolved organic carbon (Decho, 1990). This is supported also by the increase of dissolved carbohydrate concentrations which are observed during diatom blooms in the NA (Ahel et al., 2005 and references therein).

3.4. Chromophoric dissolved organic matter

Values of chromophoric dissolved organic matter in 2004 were on average higher than those found in 2003 (Table 1), with the highest values in May–June 2004. The absorption coefficients showed a significant statistical difference between the two years (Table 1). The mean aCDOM₂₈₀ absorbance coefficients significantly ($p < 0.001$) increased from 1.6 m^{-1} in 2003– 2.2 m^{-1} in 2004; these aCDOM₂₈₀ values were similar to those found in coastal waters of Tuscany by Seritti et al. (1998). Similarly the mean aCDOM₃₅₅ absorbance coefficients also increased from 0.3 m^{-1} in 2003 to 0.5 m^{-1} in 2004 (Table 1). These values for aCDOM₃₅₅ fall in the

Table 2
Linear correlation coefficients between Chl *a*, DOC, salinity (*S*) and absorption coefficients (aCDOM) during winter-spring of 2003 and 2004. Significant correlation ($p < 0.05$) is in bold.

	February 2003			March 2003			April 2003			May 2003		
	<i>n</i>	<i>r</i>	<i>p</i>	<i>n</i>	<i>r</i>	<i>p</i>	<i>n</i>	<i>r</i>	<i>p</i>	<i>n</i>	<i>r</i>	<i>p</i>
aCDOM ₃₅₅ vs <i>S</i>	12	0.101	n.s.	24	-0.042	n.s.	6	-0.153	n.s.	6	-0.382	n.s.
aCDOM ₂₈₀ vs <i>S</i>	12	-0.218	n.s.	24	-0.345	n.s.	6	-0.799	n.s.	6	-0.965	<0.005
DOC vs aCDOM ₃₅₅	12	0.017	n.s.	24	-0.317	n.s.	6	0.046	n.s.	6	-0.423	n.s.
DOC vs aCDOM ₂₈₀	12	0.174	n.s.	24	-0.116	n.s.	6	0.004	n.s.	6	0.013	n.s.
Chl <i>a</i> vs aCDOM ₃₅₅	12	-0.292	n.s.	24	0.285	<0.05	6	0.084	n.s.	6	0.344	n.s.
Chl <i>a</i> vs aCDOM ₂₈₀	12	-0.177	n.s.	24	0.410	<0.005	6	0.407	n.s.	6	0.598	<0.05
DOC vs Chl <i>a</i>	17	-0.469	n.s.	24	0.202	n.s.	12	0.307	n.s.	6	0.357	n.s.
Chl <i>a</i> vs P-PO ₄ ³⁻	16	-0.449	n.s.	25	0.442	<0.05	12	0.421	n.s.	5	0.612	n.s.
Chl <i>a</i> vs Si-Si(OH) ₄	16	0.495	n.s.	25	0.524	n.s.	12	0.416	n.s.	5	-0.800	<0.05
Chl <i>a</i> vs N-NH ₄ ⁺	16	-0.373	n.s.	25	0.263	n.s.	12	0.159	n.s.	5	-0.043	n.s.
Chl <i>a</i> vs N-NO ₂ ⁻	16	-0.407	n.s.	25	0.354	n.s.	12	0.594	<0.05	5	0.06	n.s.
Chl <i>a</i> vs N-NO ₃ ⁻	16	-0.507	<0.05	25	0.507	<0.05	12	0.650	<0.05	5	0.011	n.s.
aCDOM ₃₅₅ vs DIN	11	-0.260	n.s.	25	0.212	n.s.	6	-0.143	n.s.	6	0.520	n.s.
aCDOM ₃₅₅ vs N-NH ₄ ⁺	11	-0.353	n.s.	25	0.513	<0.01	6	-0.652	n.s.	6	0.180	n.s.
	February 2004			March 2004			April 2004			May–June 2004		
	<i>n</i>	<i>r</i>	<i>p</i>	<i>n</i>	<i>r</i>	<i>p</i>	<i>n</i>	<i>r</i>	<i>p</i>	<i>n</i>	<i>r</i>	<i>p</i>
aCDOM ₃₅₅ vs <i>S</i>	19	-0.307	n.s.	12	0.026	n.s.	10	1.608	n.s.	12	-0.853	<0.001
aCDOM ₂₈₀ vs <i>S</i>	19	-0.443	n.s.	12	-0.023	n.s.	10	-0.150	n.s.	12	-0.946	<0.001
DOC vs aCDOM ₃₅₅	19	2.975	n.s.	12	-0.275	n.s.	10	-0.365	n.s.	12	0.546	<0.005
DOC vs aCDOM ₂₈₀	19	0.346	<0.05	12	0.138	n.s.	10	0.185	n.s.	12	0.544	<0.005
Chl <i>a</i> vs aCDOM ₃₅₅	19	0.355	<0.05	12	-0.370	n.s.	10	0.492	<0.05	12	0.564	<0.005
Chl <i>a</i> vs aCDOM ₂₈₀	19	4.969	<0.001	12	-0.059	n.s.	10	0.141	n.s.	12	0.590	<0.001
DOC vs Chl <i>a</i>	23	0.577	<0.05	12	0.886	<0.001	11	-0.638	<0.05	12	0.649	<0.05
Chl <i>a</i> vs P-PO ₄ ³⁻	24	-0.025	n.s.	12	0.128	n.s.	11	-0.029	n.s.	11	-0.050	n.s.
Chl <i>a</i> vs Si-Si(OH) ₄	24	0.134	n.s.	12	0.705	<0.05	11	0.728	<0.05	11	0.858	<0.05
Chl <i>a</i> vs N-NH ₄ ⁺	24	-0.251	n.s.	12	0.636	<0.05	11	-0.016	n.s.	11	0.822	<0.05
Chl <i>a</i> vs N-NO ₂ ⁻	24	0.649	<0.005	12	0.599	<0.05	11	0.604	<0.05	11	0.926	<0.05
Chl <i>a</i> vs N-NO ₃ ⁻	24	0.578	<0.005	12	0.140	n.s.	11	0.517	n.s.	11	0.241	n.s.
aCDOM ₃₅₅ vs DIN	22	-0.174	n.s.	12	0.364	n.s.	5	-0.013	n.s.	11	0.723	<0.05
aCDOM ₃₅₅ vs N-NH ₄ ⁺	22	-0.188	n.s.	12	0.142	n.s.	5	-0.445	n.s.	11	0.888	<0.001

n.s. = not significant.

range (0.4–1.1 m⁻¹) reported by Rochelle-Newall and Fisher (2002b), for coastal areas in the Chesapeake Bay.

Sub-monthly variations in aCDOM₃₅₅ in 2003 and 2004 (Fig. 4f) could reflect the presence of considerable amount of chromophoric dissolved organic matter of continental origin derived from fluvial input. Nevertheless the contribution of bacterially transformed algal exudates, especially in the April and May–June, during the strong river flows (Fig. 2) and intense phytoplankton growth, cannot be excluded.

The analysis of monthly data revealed significant correlations in May–June 2004 among salinity, DOC, aCDOM₂₈₀, aCDOM₃₅₅ and Chl *a* samples collected after the Po freshets (Table 2). The same was not observed in the previous months (February–April, Table 2). The trend of aCDOM₃₅₅ is related to land proximity as the highest aCDOM₃₅₅ is usually observed in freshwaters and estuaries and decreases in coastal and offshore waters (Blough et al., 1993). aCDOM₂₈₀ and aCDOM₃₅₅ were inversely correlated with salinity in May–June 2004 (Table 2). The linear dependence between aCDOM and salinity (Fig. 6) could be interpreted as the result of the conservative mixing of terrestrial CDOM. A similar behaviour is usually observed in periods of higher river input, lower solar irradiance and stratification breakdown (Blough and Del Vecchio, 2002).

Despite the fact that a significant fraction of the DOC is not associated with CDOM, a positive correlation was observed between DOC values and aCDOM in May–June 2004 (Table 2). This observation was also reported by several authors (Vodacek et al., 1995, 1997; Chen, 1999). The amount of non-absorbing DOC in May–June 2004, extrapolated by the intercept on the DOC axis from the positive correlation between aCDOM₃₅₅ and DOC at aCDOM₃₅₅ = 0, contributed to 86%, of the average DOC concentration of this period.

Therefore the incidence of the absorbing fraction was assumed to be 14%. The estimation from aCDOM₂₈₀ gave a 23% of incidence of the chromophoric fraction on total dissolved organic carbon in the same period of 2004.

Considering all of the monthly cruises, there was no significant relationship between CDOM concentration and Chl *a* concentration in almost all periods of 2003 and 2004, except for May–June 2004 when both aCDOM₂₈₀ and aCDOM₃₅₅ were correlated with Chl *a* (Table 2) and salinity ($r = -0.932$, $p < 0.001$). These strong relationships were probably a consequence of the mixing process, both due to the input of fluvial-terrestrial chromophoric organic matter and possibly to bacterial reprocessing of the algal organic matter produced by the phytoplankton. Recent research pointed toward a microbial source of CDOM in the aquatic environment and led to the hypothesis that phytoplankton is not a direct source of CDOM but that bacterial reprocessing of DOM of algal origin is an important source of CDOM (Rochelle-Newall and Fisher, 2002a). The lack of observed relationships between aCDOM and Chl *a* concentration has been reported in other works (Nelson et al., 1998; Rochelle-Newall and Fisher, 2002b) and this supports the hypothesis that CDOM is not directly released by phytoplankton.

Whereas in both years a seasonal increase of DOC from winter to spring is evident (t test, $p < 0.05$), the same is not true for aCDOM which has a stronger variability on the ten days and monthly time scale (one way ANOVA, $p < 0.05$). This suggests that there is probably no seasonal accumulation of CDOM in the surface waters as this fraction is more labile than most of bulk DOM.

The specific UV absorption at 280 nm can be used as an index of the proportion of humic compounds as a strong linear relationship exists between the molar absorptivity at 280 nm and the aromatic content of water-soluble fulvic and humic acids (Chin et al., 1994).

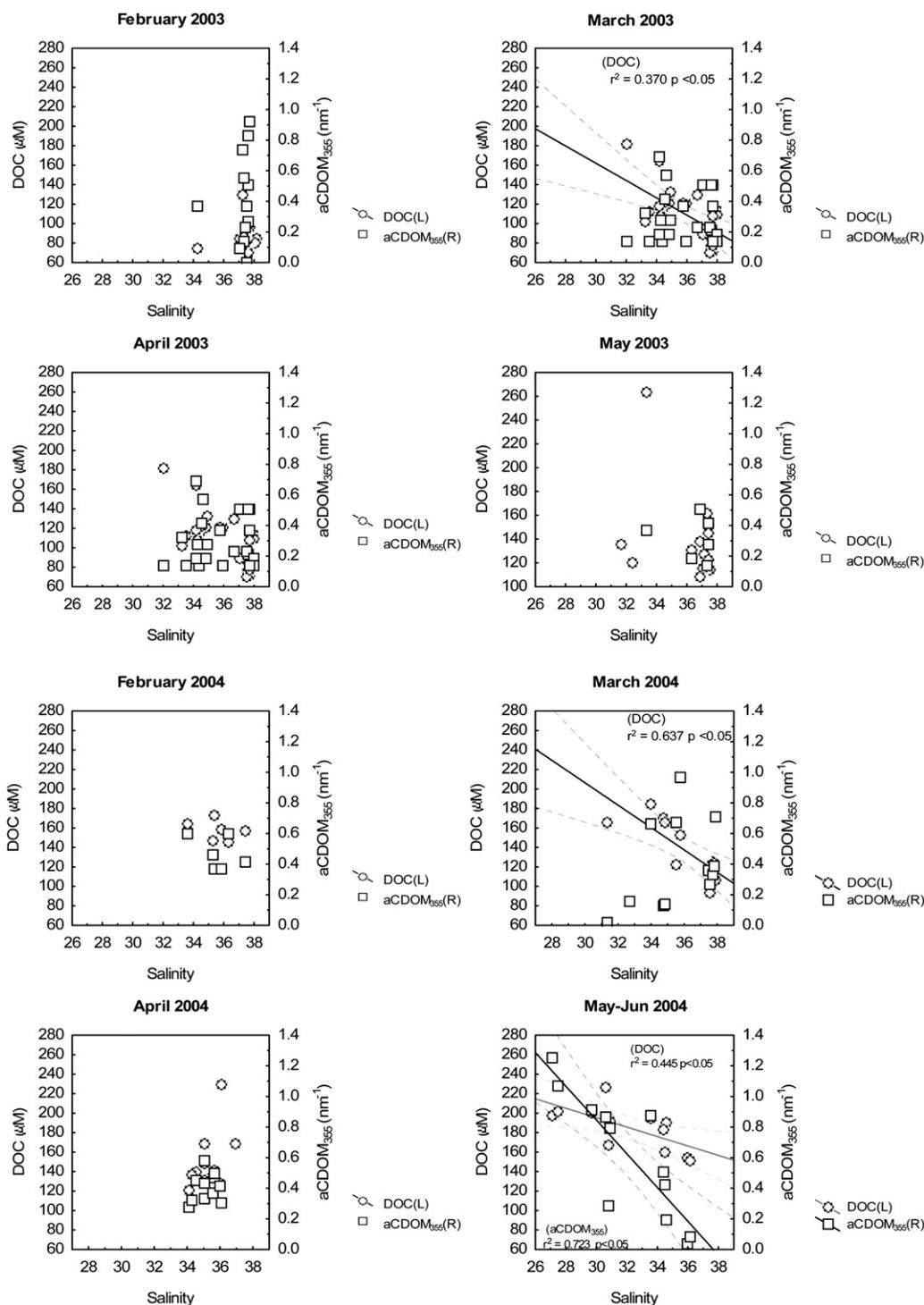


Fig. 6. DOC (L-left) and aCDOM₃₅₅ (R-right) plotted as a function of salinity in the different period of sampling (February, March, April and May–June) in 2003 and 2004.

On this basis, the riverine transport of terrestrially derived CDOM from Po River was probably the dominant delivery mechanism by which CDOM entered in estuarine and coastal waters of northern Adriatic Sea. Also in other marine environments, the contribution of chromophoric matter could derive from a large fraction of humic compounds of fluvial or terrestrial origin (Blough et al., 1993), even if the role of bacteria in reprocessing DOM of algal origin and producing CDOM is not excluded. According to Twardowski et al., (2004) *in situ* production of CDOM in terrestrially dominated

waters may be evident only under a relatively stable water mass containing a high level of phytoplankton but a relatively low background of terrestrial CDOM.

A significant positive relationship between aCDOM₃₅₅ and DIN (Table 2) found in May–June 2004, could derive from DOM photoproducts (Moran and Zepp, 1997) or by intense microbial degradation (Coble et al., 1998 and references therein). CDOM, when photolytically degraded, can be a source of dissolved organic and inorganic compounds such as NH₄⁺ and PO₄³⁻ (Bushaw et al.,

1996): actually a strong relationship between aCDOM and NH_4^+ (Table 2) was observed in May–June 2004. The absence of linear relationship between CDOM and phosphate in all the investigated periods of 2003 and 2004 could be due to the low concentrations of phosphate in both years. Though the riverine inflow was higher in 2004, the orthophosphate concentrations did not increase as they were probably immediately taken up by phytoplankton. In 2004 the DIN/ PO_4 ratio (Fig. 4) was much higher than in 2003 probably because the phosphate consumption limited the assimilation of the DIN. The reduction of the phosphorus load in the Po River water (Pagnotta et al., 1995) and a significant increase in the DIN/ PO_4 ratio in the NA surface waters was observed by different authors (Rinaldi et al., 1998; Degobbis et al., 2000). Earlier research indicated that phosphorus was also the primary limiting element in the NA prior to the reduction of its load (Chiaudani and Vighi, 1982; Degobbis and Gilmartin, 1990). The lack of PO_4^{3-} could play a role in the CDOM accumulation by limiting its microbial degradation, as it was shown that phosphorous exerts a limiting role on bacterial DOC degradation in the NA (Zoppini et al., 2005 and references therein) or, by favouring, its transformation due to the enhanced alkaline phosphatase (Ivančić et al., 2009).

Probably a concerted action of phytoplankton and bacteria concur to form CDOM as phytoplankton provides substrates that heterotrophic bacteria process into coloured compounds (Rochelle-Newall and Fisher, 2002a,b). Moreover, the presence of biological by-products (e.g. nutrients) could stimulate primary production (Bricaud et al., 1981) and secondary productivity (Nelson et al., 2004).

The spectral slope (S_{CDOM}) was determined to improve the information about the nature of DOM chromophores and quite similar values in 2003 and 2004 were observed (Table 1). The values in the study area are similar to those reported by Babin et al. (2003) for the Adriatic Sea. The high variability of S_{CDOM} values in the two years and the absence of linear relationship between S_{CDOM} and salinity suggest a non conservative behaviour of S_{CDOM} . This type of wide variability in S at low CDOM concentrations has also been reported in earlier studies (Blough et al., 1993; Stedmon et al., 2000). Possible reasons for the increase in standard deviation in the slope coefficients S are photodegradation and bacterial utilization of CDOM, as both these processes have been reported to have a flattening effect on the slope (Stedmon et al., 2000 and references therein).

The low values of specific absorption coefficients ($a^*\text{CDOM}$), at 280 and 355 nm, obtained by normalizing the absorbance at the specific λ per unit of DOC (Table 1), could be due to the occurrence of low molecular weight compounds and low aromatic carbon content as found by several authors (Chin et al., 1994). Similar values of $a^*\text{CDOM}$ at 280 and 355 nm have been reported by Seritti et al. (1998) for the estuarine and coastal waters of the Tyrrhenian Sea. Changes in the optical properties become evident only in May 2004 when the low salinity of waters determined a 30% increase in specific absorption coefficient of DOM ($1.5 \pm 0.1 \text{ m}^{-2}\text{gC}^{-1}$ for $a^*\text{CDOM}_{280}$ and $0.4 \pm 0.1 \text{ m}^{-2}\text{gC}^{-1}$ for $a^*\text{CDOM}_{355}$, respectively).

4. Conclusions

The Northern Adriatic waters in front of Po River are characterized by variations in hydrological and physical processes which strongly influence the dissolved organic matter dynamics on a monthly and sub-monthly time scale. A seasonal increase from winter to spring of DOC was evident in both years of study, whereas the chromophoric fractions did not show a seasonal trend similar to that of DOC, possibly because of its lability.

The relatively scarce riverine input in 2003 may account for the less significant relationship found between DOC and nutrients

concentrations, whereas the high values of DOC were probably a consequence of the increased freshwaters inputs. The marked depletion of inorganic phosphorus probably limits the microbial degradation of DOC, favouring its accumulation. CDOM values were much higher in 2004 than in 2003 and the spectroscopic features showed that the average qualitative nature of CDOM was quite similar in both years. Only after relevant freshets can an increase of the specific absorption coefficient take place.

The contribution of UV–VIS absorbing DOC in May–June 2004, after the Po freshet, was estimated to be 14–23% of DOC. The lack of relationships between CDOM and Chl a concentrations in both years, with the exception of May–June 2004, could imply that the phytoplankton is not a direct source of CDOM, whereas bacteria could play a relevant role in the CDOM production.

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