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NW Adriatic Sea biogeochemical variability in the last 20 years (1986–2005)

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Abstract. This paper presents a long-term time series (1986–2005) of hydrological and biogeochemical data, both published and unpublished. Data were collected in the north-western area of the Adriatic Sea, at two stations that are considered hydrodynamically and trophically different. The time series have been statistically and graphically analysed on a monthly scale in order to study the annual climatologies, links between the concentrations of chlorophyll-*a* and the variability in the environment, trophic differences between the two areas and chlorophyll-*a* trends over time. Basically, the two areas have similar hydrological features, yet they present significant differences in the amount of nutrient inputs: these are in fact higher at the coastal site, which is characterized by a prevalence of surface blooms, while they are lower at the offshore station, which is mainly affected by blooms at intermediate depths. Nonetheless, throughout the whole water column, chlorophyll-*a* concentrations are only slightly different. Both areas are affected by riverine discharge, though chlorophyll-*a* concentrations are also driven strongly by the seasonal cycle at the station closer to the coast. Results show that the two stations are not trophically different, although some controlling factors, such as zooplankton grazing in one case and light attenuation in the other, may further regulate the growth of phytoplankton. In both cases no significant trends are detected in either the average chlorophyll-*a* values or in dispersion of the data, in contrast with significant trends in temperature and salinity.

1 Introduction

The Northern Adriatic Sea (Fig. 1) is a shallow shelf basin with an average depth of 35 m and a prevalent cyclonic circulation of water masses (Artegiani et al., 1997a). The area is largely affected by riverine inputs that provide the basin with a significant flow of freshwater and land-derived nutrients. The Po river is by far the largest Italian river: in the last 20 years it attained a mean discharge of 1465 $m^3 s^{-1}$ with high intra- and inter-annual variability (st. dev.=1056 $m^3 s^{-1}$), with peaks in May, mainly due to snow melting, and in October–November, because of high precipitation (Fig. 2). Furthermore, the Northern coast has several smaller rivers that contribute to the overall flow. Consequently, the hydrodynamics of the Northern Adriatic Sea are quite complex and strongly affected by large variations in heat fluxes and the volume of incoming freshwater (Artegiani et al., 1997a). Generally, a temporal succession of two different hydrodynamic patterns has been recognized: between November and March, the westernmost waters are diluted mainly by the Po River outflow and remain separated from the highly saline and vertically-mixed offshore waters thanks to a frontal system located 8–16 km from the coast. The dissolved and particulate matter, coming from the land, therefore remains more or less confined. Between April and October, warmer waters diluted by freshwater inflows are confined to the surface layer and reach almost all of the Northern basin. During that period, one or more pycnoclines separate the water masses of intermediate density, while the high-density waters are confined near the bottom (Artegiani et al., 1997a). Recently, Jeffries and Lee (2007) have shown that the location of the frontal system is highly dependent on the type of physical forcing affecting the Po plume. Grouping historical data of Po rates, wind velocity and ambient stratification into dominant dynamics, instead of seasonal scale, they found that fresh filaments extend across the Northern Adriatic during Bora events and that Po waters spread extensively offshore also during high-discharge, strongly stratified periods.

The northern Adriatic is one of the most productive Mediterranean regions (Fonda Umani et al., 2005). Phytoplankton abundance and distribution is largely dependent on

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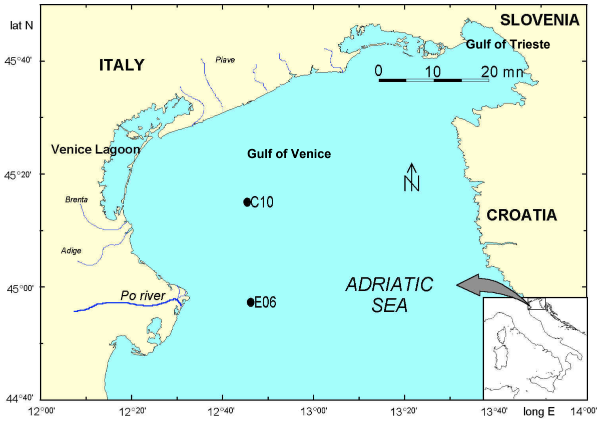


Fig. 1. Study area and location of the sampling stations C10 and E06.

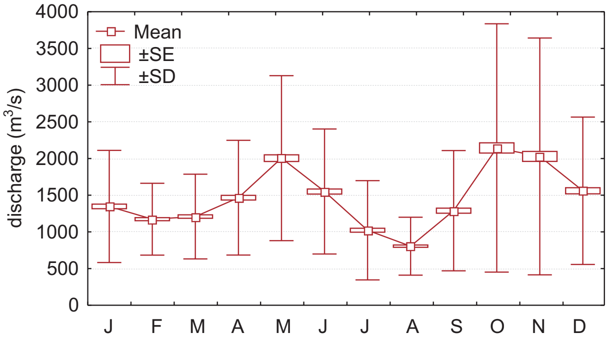


Fig. 2. Monthly mean and variability of the Po river discharge (daily data from “Magistrato del Po”, Parma, Italy).

nutrients and light availability, but also on the stability of the water column. The large periodic modification in the structure and dynamics of the Northern Adriatic Sea causes large spatial and temporal distribution of phytoplankton species composition, biomass and production (Fonda Umani, 1996). A general west-to-east decreasing gradient in the phytoplankton standing crop and production has been recognized in winter, while during summer stratification the lateral advection of river run-off in surface layers and the presence of marked pycnoclines result in vertical heterogeneities and local variations in primary productivity (Franco and Michelato, 1992). Primary productivity, representing the immediate result of interactions among physical, chemical and biological variables, gives a dynamic overview of the environment, and is therefore a valuable tool for following the complex effects of freshwater inputs in the Northern Adriatic system (Socal et al., 2002). Although there have been some previous large-scale spatial and temporal studies that focused on the hydrological (e.g., Artegiani et al., 1997a,b; Raicich, 1996) and biogeochemical (Zavatarelli et al., 1998) characteristics of the Adriatic Sea, research into the inter- and intra-annual variability of the Northern basin productivity related to its hydrology is still scarce.

In a short-term study, Mauri et al. (2007) related MODIS chlorophyll concentration (chla_a2) in the northern Adriatic Sea to Po discharge rates and local wind forcing. They found a significant correlation between the North Adriatic optical properties and both the Po river discharge and the local wind forcing. In particular, the Western Coastal Layer (WCL) width, the structure of the Po river bulge, and the plume extension were significantly affected by both factors. Since MODIS includes also the the contribution of CDOM and mineral particles, their results are, however, of difficult interpretation, as the authors also mentioned in their paper.

Over the past years the North Adriatic has been negatively affected not only by eutrophication phenomena (Degobbis et al., 2000), but also by the apperance of massive mucillage aggregates and anoxic episodes (Precali et al., 2005). Recent studies have reported a rise in water temperature (e.g., Corti et al., 1999), in the Mediterranean Sea (Rixen et al., 2005) and in the Northern Adriatic basin (Russo et al., 2002). Not much data analysis, apart from model experiments (Vichi et al., 2003a), has been done, however, on the quantification of chlorophyll-*a* response to the changing meteorological conditions in the Northern Adriatic Sea.

We present here the analysis of 20 years (1986–2005) of physical, chemical and biological data, both published and unpublished, collected at two stations, that have operated since the beginning of the twentieth century (Fig. 1). Many authors (e.g., Alberighi et al., 1997; Pugnetti et al., 2003, 2004; Bernardi Aubry et al., 2006) have classified E06 as a station that is influenced by the Po river run-off and characterized by meso-eutrophic waters, while they have represented C10 as a meso-oligotrophic station that is only partially influenced by the Po river discharge; the latter occurs particularly during intense stratification periods, when the Po plume eventually turns north-eastwards. In particular, whereas Alberighi et al. (1997) referred to the two stations as trophically different, Pugnetti et al. (2003) could not typify a significant difference in community composition, because a prevalence of tolerant species is observed in the whole area of the North Adriatic Sea. Bernardi Aubry et al. (2006) concluded that the hydrological and trophic variability seemed mainly to affect phytoplankton abundance and biomass rather than species composition.

The main objectives of this work are:

(i) to compare C10 and E06 annual climatologies, with particular regard to chlorophyll-*a* variability, in order to confirm or reject the hypothesis of two very different trophic areas.

(ii) to relate chlorophyll-*a* to other hydrological and biogeochemical variables so as to identify the principal factors influencing phytoplankton dynamics in both areas.

(iii) to analyse long-term variations in chlorophyll-*a* dynamics at the two stations, either highlighting or excluding possible trends related to climate change and/or to anthropogenic pressures.

Studying the phytoplankton biomass, using the chlorophyll-a concentration as an indicator of the standing biomass, we aim at providing a further contribution for better understanding the northern Adriatic biogeochemical variability, its effects on the productivity of the rest of the Mediterranean basins, and a statistical methodology that can be used in other areas of the Mediterranean Sea.

2 Sampling and methods

The sampling stations C10 (45°15′ 00″ N, 12°46′ 00″ E), and E06 (44°57′ 50″ N, 12°46′ 20″ E) are located about 20 and 10 nautical miles from the Italian coast and have a maximum depth of 29.5 and 32 m, respectively (Fig. 1). Chlorophyll-*a*, dissolved inorganic nutrients and oxygen samples were taken at fixed depths of 0, 5, 10, 15, 20, 25 m (standard levels, SL). Samples were collected monthly from April 1986 to August 2005, during different cruises and supported by different project funding. Because of the high short-term variability of the Adriatic environment, we decided to analyse the data on the smallest available scale (monthly), even if, in doing so, the winter months are less represented (Fig. 3). The data frequency shows a different amount of samples for each month, while in the same month the number of samples from both C10 and E06 is comparable. For each station we analysed, at every SL: temperature, salinity and density, obtained using a CTD probe; samples of nutrients (N-NH_3, N-NO_2, N-NO_3, Si-SiO_4, P-PO_4), dissolved oxygen and chlorophyll-*a* using Niskin and Nansen bottles. Dissolved inorganic nutrients were analysed according to the methods described by Strickland and Parsons (1972) and Grasshoff et al. (1999), dissolved oxygen by the Winkler method (Winkler, 1914), while chlorophyll-*a* was assessed according to Holm-Hansen et al. (1965). In the end, 564 samples from C10 and 530 from E06 were fluorometrically analysed.

Statistical analyses (descriptive, non-parametric, principal component analysis and partial regression) were performed using commercial software (Statistica by Statsoft). Test results were considered: significant at p–level <0.05, very significant at p–level <0.01 and highly significant at p–level <0.001. The powerful non-parametric Wilcoxon Matched Pairs test was used to compare the biogeochemical features between the two sampled sites. A comparison between the vertical distribution of chlorophyll-*a* in the water column at the C10 and E06 stations was carried out by Whisker plots and the significance of the results was tested by the non-parametric Wilcoxon Matched Pairs test. The correlation between chlorophyll-*a* and other physical and hydrochemical variables was studied using parametric tests, after the normalization of some of the non-normal distributions by the Shapiro-Wilk test. A normal distribution was significantly obtained at both sites for all the variables, except for phosphate. A principal component analysis (PCA) was then applied to identify the weight of each variable, presenting the results of the first two components. To avoid auto-correlation phenomena between the environmental variables considered independent, we finally applied a Ridge Regression analysis to the normalized data for clarifying the statistically-significant, linear correlation between chlorophyll-*a* and the other variables. Ridge regression is used when the independent variables are highly intercorrelated: a constant bias (λ) is added to the diagonal of the correlation matrix, which is then re-standardized so that all diagonal elements are equal to 1 and the off-diagonal elements are divided by the constant. In this way Ridge regression artificially lowers the correlation coefficients so that more stable estimates (β coefficients) can be computed. The Cox-Stuart test was performed to highlight possible trends in time. Graphic linear interpolations were carried out using commercial software (Surfer 8.0 by Golden Software): the median values of all the variables at every SL have been plotted on a monthly scale by the linear Kriging method.

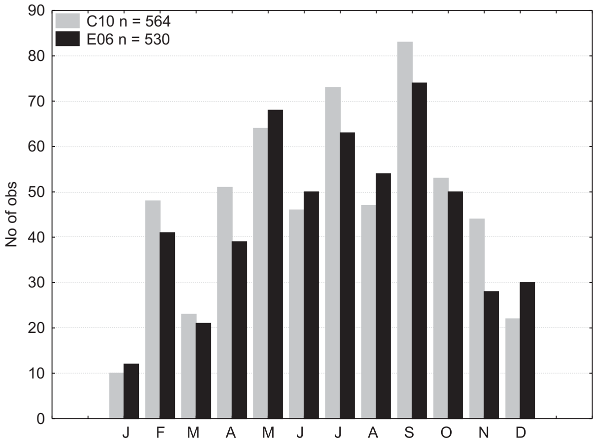


Fig. 3. Number of observations per month.

3 Results

3.1 Hydrological and biogeochemical features

Chlorophyll-*a* data for both stations, are plotted in Fig. 4 for the whole period. Time series plots of the other studied variables are available as supplemental material (see Appendix A, http://www.biogeosciences.net/4/673/2007/bg-4-673-2007-supplement.pdf). In Table 1 we list the number of valid observations, the medians, the ranges and the Wilcoxon Matched Pairs test results of comparison between the two stations for all the available hydrological and

Table 1. Valid Number of samples, Median, Minimum, Maximum and Wilcoxon Matched Pairs test for all the variables at C10 and E06[a].

	C10				E06				Wilc.test				
Variable	N	Median	Min.	Max.	N	Median	Min.	Max.	N	T	Z	p	sig.
Temper.	563	15.8	7.5	28.8	528	15.2	5.8	29.4	527	67738	0.45	0.65	ns
Salinity	563	37.5	31.0	38.6	528	37.6	15.7	38.5	527	64877	1.34	0.18	ns
Density	563	27.6	20.5	29.9	528	27.9	11.2	30.0	527	65164	1.26	0.21	ns
OxSatur	511	99.2	7.7	134.6	485	99.1	13.4	158.1	451	49519	0.52	0.60	ns
$N\text{-}NH_3$	548	0.3	0.0	21.6	507	0.6	0.00	31.7	497	38806	6.98	0.00	***
$N\text{-}NO_2$	549	0.1	0.0	5.0	507	0.1	0.0	4.7	497	52009	1.88	0.06	ns
$N\text{-}NO_3$	547	0.6	0.0	25.5	506	0.9	0.0	93.1	494	47760	4.08	0.00	***
DIN	555	1.3	0.0	27.8	506	2.0	0.0	97.7	503	43553	5.90	0.00	***
$Si\text{-}SiO_4$	548	2.1	0.0	30.1	509	3.3	0.0	54.8	498	47055	4.69	0.00	***
$P\text{-}PO_4$	550	0.04	0.00	1.30	512	0.06	0.00	1.09	503	40285	5.98	0.00	***
Chl-*a*	564	0.9	0.0	11.4	530	1.1	0.0	25.3	530	62886	2.05	0.04	*

[a] ns: not significant, * $p<0.05$: significant, *** $p<0.001$: highly significant.

biogeochemical variables over the 20-year period. Descriptive statistics reveals that the main differences between the two sites are due to the large dispersion in the E06 variable values, rather than to any differences in the trends of the central (median) values. Statistically high significant differences are observed for all the nutrients' concentrations, except $N\text{-}NO_2$ and also, to a less extent ($p<0.05$), for the chlorophyll-*a* values between the two areas.

In order to study time (seasonal) and space (depth) features, which may explain those differences, and in order to provide an helpful analysis for model validation, we analyse the main features that result from all monthly median values, at every SL, shown in time-depth plots in Fig. 5 (C10) and in Fig. 6 (E06). Both sites show similar features in the hydrological variables. The density isolines (panel c) reveal that the water column is mixed between November and March and stratified for the rest of the year. Freshwater inputs, limited to the top 10 m of the water column, affect the salinity fields in different ways from site to site. The salinity (panel b) at C10 begins to decrease in March, so that the minimum of surface salinity (S=34.6) is found in May–June, reflecting the first annual peak of the Po river discharge (Fig. 2). The salinity starts to increase in July, and in autumn the C10 area is less affected by the second peak of the Po river (S=36.3). The salinity at E06 has a much lower value in March, so it reaches a surface minimum earlier, in April (S=31.3), remaining at constant values around 33–34 until August. In October it detects again the effect of the Po river peak with a second minimum surface value of 34.1.

The nutrients' concentrations show similar distributions at both sites, with lower concentrations at C10. Nutrient profiles are generally characterized by higher surface concentrations down to a depth of 5–10 m. In the bottom 15 m of the water column, nutrient concentrations are either uniform (nitrate, phosphate in late summer) or increasing with depth (silicate, ammonium).

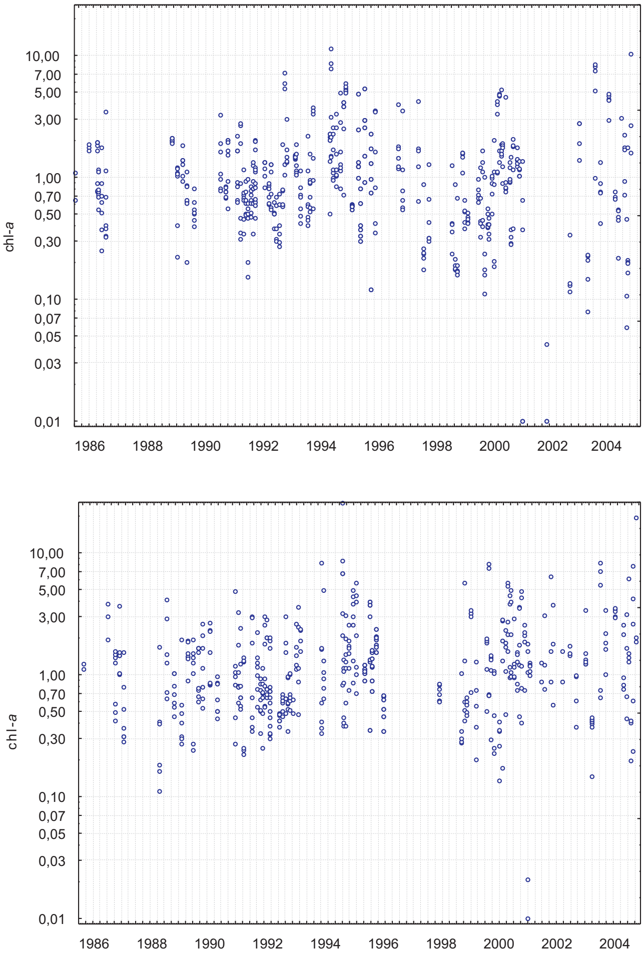
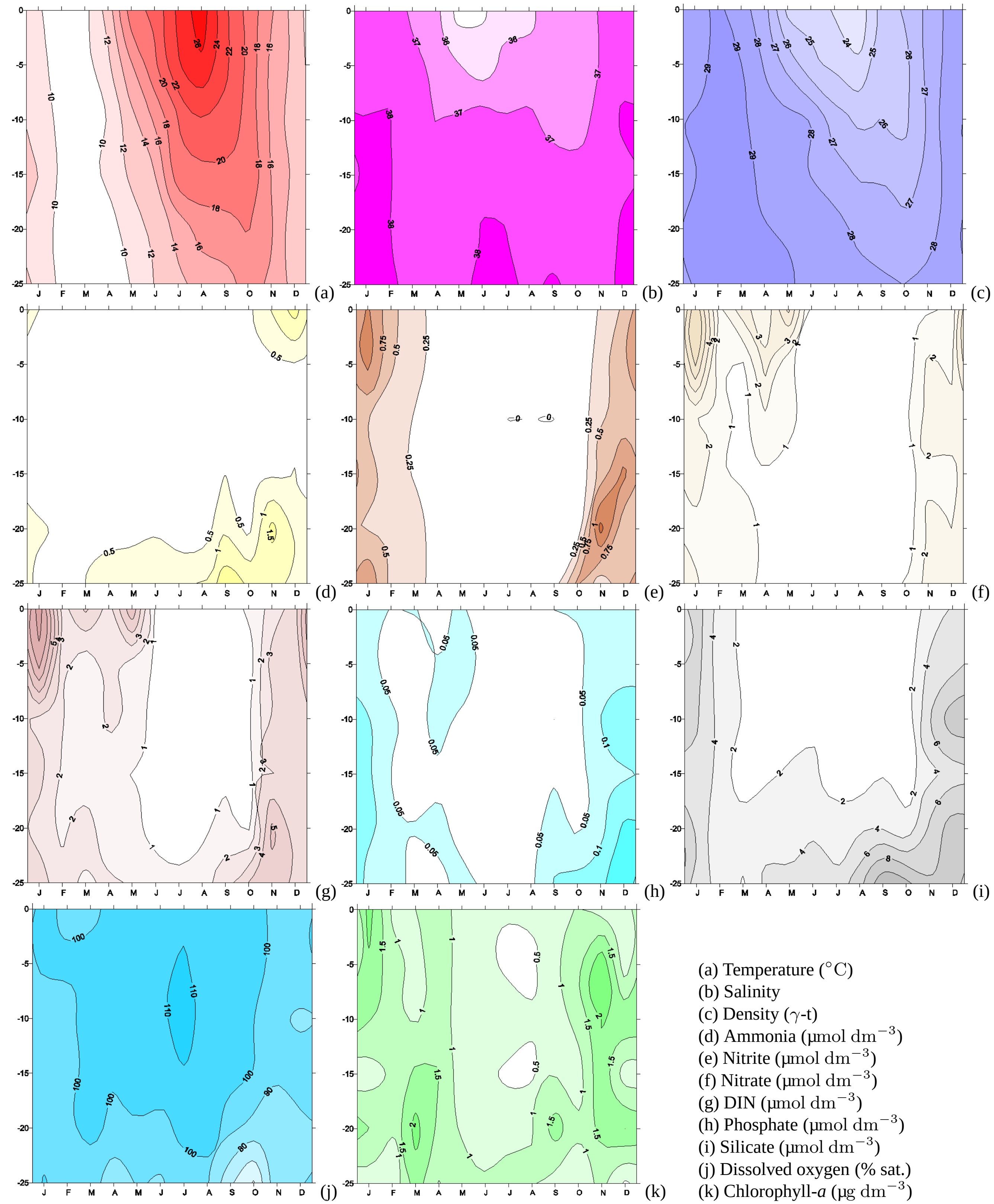


Fig. 4. Chlorophyll-*a* samples ($\mu g\,dm^{-3}$, log scale) collected at C10 (above) and E06 (below).



(a) Temperature (°C)
(b) Salinity
(c) Density (γ-t)
(d) Ammonia (µmol dm^{-3})
(e) Nitrite (µmol dm^{-3})
(f) Nitrate (µmol dm^{-3})
(g) DIN (µmol dm^{-3})
(h) Phosphate (µmol dm^{-3})
(i) Silicate (µmol dm^{-3})
(j) Dissolved oxygen (% sat.)
(k) Chlorophyll-*a* (µg dm^{-3})

Fig. 5. C10 time-depth plots of medians on a monthly scale.

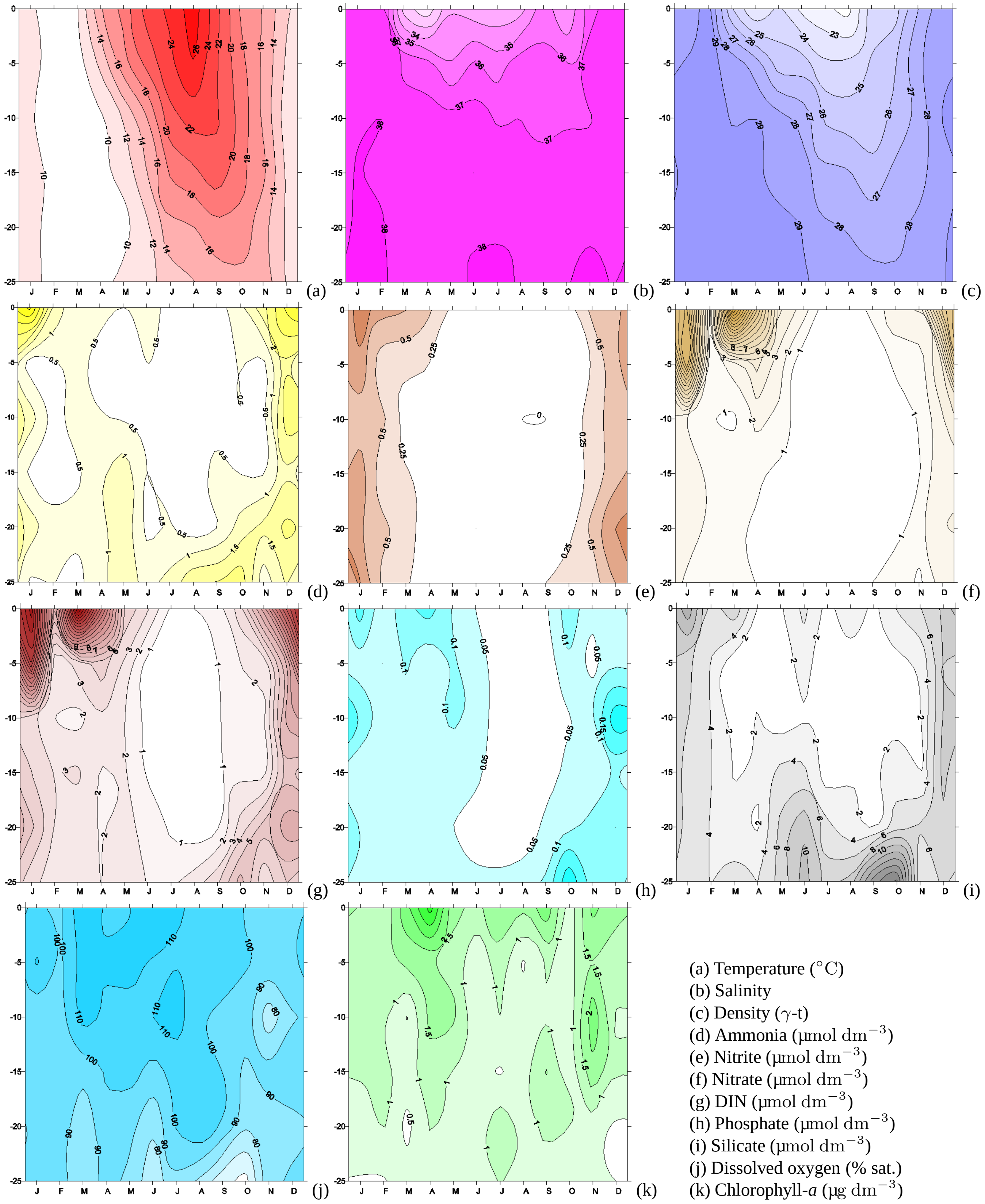


Fig. 6. E06 time-depth plots of medians on a monthly scale.

Table 2. Valid Number of samples, Median, Minimum, Maximum and Wilcoxon Matched Pairs test for chlorophyll-*a* at C10 and E06 on a monthly scale[b].

	C10				E06				Wilc.test				
Month	N	Median	Min.	Max.	N	Median	Min.	Max.	N	T	Z	p	sig.
Jan	10	0.8	0.4	4.2	12	1.0	0.2	2.3	10	20.0	0.764	0.45	ns
Feb	48	1.0	0.1	4.8	41	1.0	0.2	5.7	41	365.5	0.598	0.55	ns
March	23	1.1	0.2	5.2	21	0.8	0.2	4.4	21	113.0	0.087	0.93	ns
April	51	1.2	0.3	4.8	39	1.3	0.4	5.0	39	277.5	1.349	0.18	ns
May	64	0.9	0.3	11.4	68	1.3	0.4	25.3	63	863.0	0.993	0.32	ns
June	46	0.7	0.1	2.5	50	0.8	0.2	8.1	44	407.5	1.021	0.31	ns
July	73	0.6	0.1	5.3	63	1.2	0.2	7.8	63	645.5	2.482	0.01	*
Aug	47	0.7	0.1	10.3	54	0.9	0.2	19.4	46	344.0	2.147	0.03	*
Sep	83	0.8	0.1	4.9	74	0.9	0.3	8.2	72	785.5	2.966	0.00	**
Oct	53	0.9	0.3	7.2	50	0.7	0.0	5.6	47	301.5	2.778	0.00	**
Nov	44	1.7	0.4	5.8	28	1.4	0.1	3.5	28	150.0	1.207	0.23	ns
Dec	22	0.6	0.0	2.1	30	1.1	0.1	2.8	22	103.0	0.763	0.45	ns

[b] ns: not significant, * $p<0.05$: significant, ** $p<0.01$: very significant.

The water column is almost completely depleted in ammonia (panel d) throughout the year at C10, and between March and October at E06. Surface peaks are present at C10 in December, while they are seen at E06 in December and January. Nitrite (panel e) remains at low concentrations at both sites: close to zero between April and October and slightly higher for the rest of the year, reaching a maximum in January. The nitrate time evolution (panel f) indicates that very low concentrations are found between May and October at C10 and between June and September at E06. Because of the second Po river peak and the increase in the vertical mixing processes, which diffuse the bottom-regenerated nutrients, the entire water column shows high values during winter at both sites. Dissolved inorganic nitrogen ($[DIN]=[N\text{-}NO_2]+[N\text{-}NO_3]+[N\text{-}NH_3]$, panel g) reflects mainly the nitrate trend at the surface and the ammonia trend at the bottom.

Phosphate concentrations (panel h) are close to zero at both sites, at all depths, during most of the year. Slightly higher concentrations are present in December and January, although E06 values are generally higher.

Silicate concentrations (panel i) are high throughout the water column at both sites in December and January, because of mixing processes, while are high only at the surface at E06 (e.g. in June), reflecting low salinity concentrations and therefore the Po river's influence.

Dissolved oxygen (panel j) shows comparable concentrations at both sites, as well as a good general oxygenation of the waters and a progressive decrease of concentrations with depth, well revealing an opposite annual pattern compared to the ammonia, phosphate and silicate concentrations (panel d, h, i). Minimum values, well below saturation levels, are found in the deeper SL in September–October at the end of the stratification period. Successively, stratification is broken by surface cooling and wind stirring action, redistributing oxygen and nutrient concentrations throughout the whole water column during the following months (November, December).

Chlorophyll-*a* (panel k) shows a complex annual cycle at both stations. C10 surface waters are characterized by a January peak and low values for the rest of the year. The lowest concentrations are found between May and October, corresponding to the stratified period (panel k) with low DIN and DIP (dissolved inorganic phosphate) concentrations. Subsurface maxima, below a depth of 15 m in March and in the whole water column in November, coincide with the river nutrient inputs. E06 presents the highest chlorophyll-*a* concentrations at the surface throughout the year, a pattern that is exactly opposite to that of salinity. In fact the highest values are registered in March–April, September and November, months that are characterized by very different hydrological and biogeochemical conditions.

3.2 The vertical variability of chlorophyll-*a*

The time-depth plots of Fig. 5 and Fig. 6 give an immediate overview of the median situation characterizing both sites' environment. In this section we focus on an analysis of the variability. Monthly vertical profiles of chlorophyll-*a* concentrations for both sites are shown in Fig. 7, where the Whisker plots represent the median values and the non-outliers ranges (Whisker, coeff.=1) at every SL. Table 2 presents the valid number of observations, the medians, the ranges and the Wilcoxon Matched Pairs test for chlorophyll-*a* on a monthly scale at both stations.

Excluding exceptional values, classified as outliers, median concentrations do not exceed 4 µg dm^{-3}, and the scale is limited to 8 µg dm^{-3}. Similar vertical profiles are found between October and February, when mixing processes prevail. During the rest of the year, which is mainly characterized by strong temperature and salinity stratification, E06 maintains

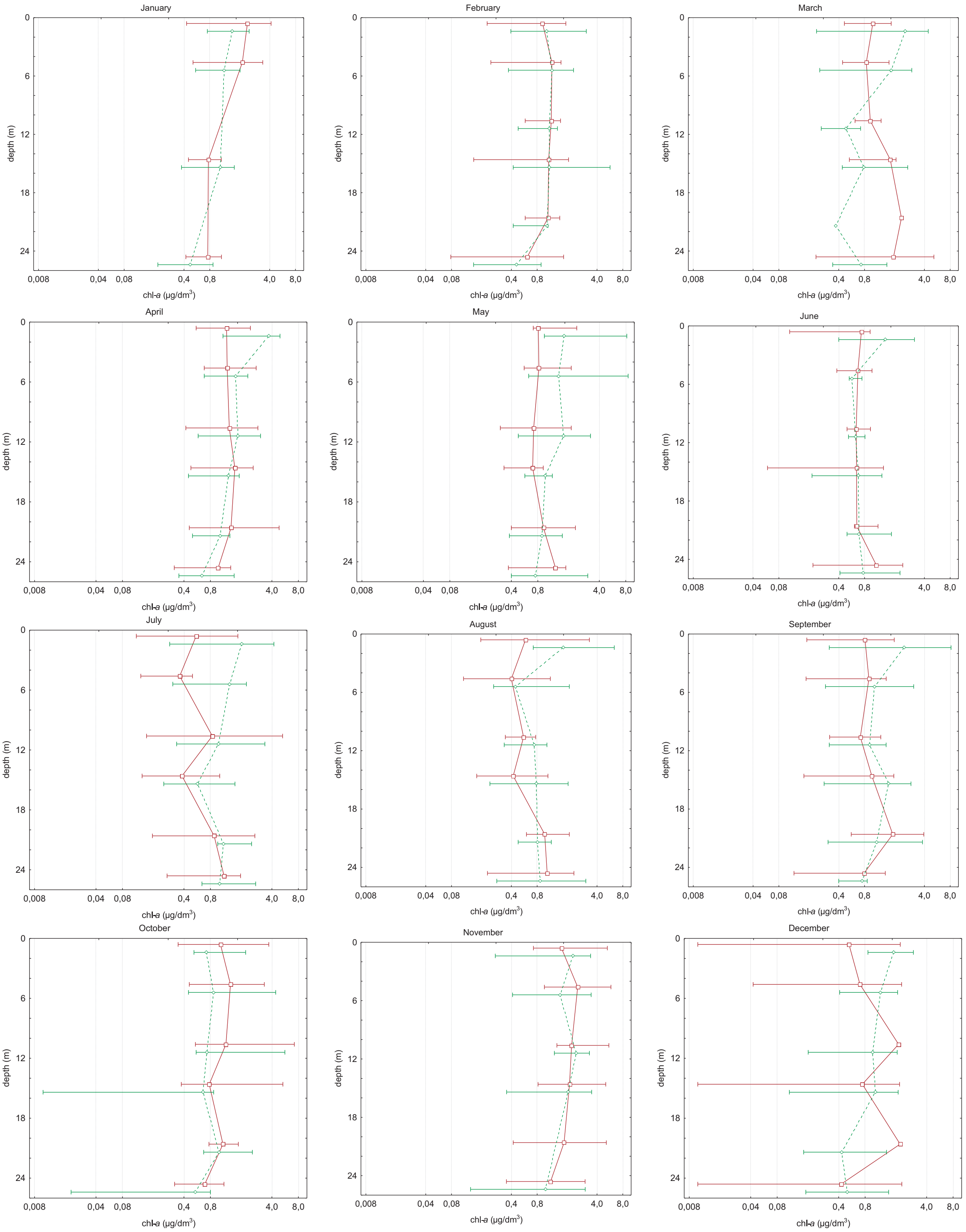


Fig. 7. Monthly vertical profiles of chlorophyll-*a* medians (log-scale) and range of variability at C10 (red continuous line) and E06 (green dashed line).

Table 3. Ridge Regression results for C10 (left) and E06 (right)[c].

	C10								E06						
	Beta	s.e.Beta	B	s.e.B	t(494)	p	sig.		Beta	s.e.Beta	B	s.e.B	t(455)	p	sig.
Intercept	–	–	1.667	0.411	4.057	0.000	–	Intercept	–	–	0.584	0.107	5.436	0.000	–
NO_3	0.248	0.066	0.180	0.048	3.770	0.000	***	Salinity	−0.361	0.055	−0.000	0.000	−6.578	0.000	***
Salinity	−0.258	0.064	−0.043	0.011	−4.023	0.000	***	NO_3	0.130	0.057	0.068	0.030	2.282	0.023	*
Depth	0.195	0.056	0.004	0.001	3.453	0.001	**	NH_3	−0.145	0.051	−0.131	0.045	−2.874	0.004	**
Temper.	−0.113	0.055	−0.004	0.002	−2.055	0.040	*	PO_4	−0.083	0.041	−0.205	0.101	−2.033	0.043	*
%$Ox._{sat}$	0.084	0.048	0.001	0.001	1.759	0.079	ns	$SiSO_4$	0.159	0.060	0.086	0.032	2.671	0.008	**
NH_3	−0.062	0.047	−0.070	0.053	−1.336	0.182	ns	% $Ox._{sat}$	0.138	0.057	0.001	0.001	2.437	0.015	*
NO_2	0.062	0.055	0.126	0.112	1.119	0.264	ns								

[c] s.e.: standard error, ns: not significant, * $p<0.05$: significant, ** $p<0.01$: very significant, *** $p<0.001$: highly significant.

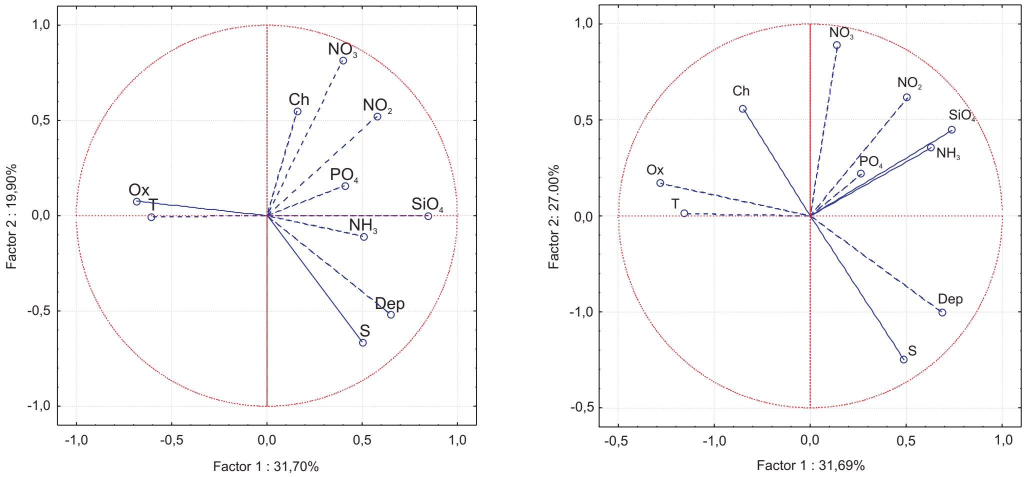


Fig. 8. PCA: projection of the variables (T: temperature, S: salinity, Dep: depth, Ox: oxygen % sat., NH_3, NO_2, NO_3, PO_4, SiO_4, Ch: chlorophyll-*a*) on the factor plane (C10, left and E06, right).

higher concentrations in the surface layer, while C10 does the same mostly at deeper depths.

The annual cycle at C10 is characterized by minimum concentrations between May and October, and maximum ones in November, followed by April, March and May, while the other months have intermediate values. Apart from October and November, E06 is generally characterized by high concentrations limited to the top 5–10 m layer.

Statistically significant differences (Table 2) are found in July, August, September and October. The significant differences detected in July and August and the very significant ones in September are due to sensibly lower concentrations in the top 20 m at C10. October is the only month during which concentrations in the entire water column are very significantly higher at C10 than at E06. For the rest of the year, the chlorophyll-*a* profiles at C10 and E06 have opposite trends and cross each other at different depths between 10 and 20 m.

3.3 Relationships among variables

With the aid of principal component analysis (PCA) we intended to investigate which factors are related to the variability of, and which are the interconnections between, the physical and biogeochemical variables, particularly in relation to the seasonal cycle and the loads of nutrients.

After the normalization of the non-normal distributions, we carried out the PCA and the Ridge Regression tests. The variables' PCA projection on the factor plane is represented in Fig. 8. Among the variables, we also considered depth as an indicator that explains surface/bottom processes. The sum of the first two PC explained 51.61% of the total variance for C10 and 58.68% for E06. The factor plane representation groups the variables in three quadrants for both stations: one quadrant is for salinity-depth covariance, a second one is for oxygen-temperature and a third one is for nutrients. At C10 ammonia is situated in the salinity-depth quadrant, opposite to the oxygen concentration. In this graphical representation chlorophyll-*a* is found in different quadrants: for C10 it is located in the nutrients quadrant, while for E06 it has an intermediate position between nutrients and oxygen-temperature.

The Ridge regression results (Table 3) are listed according to the order in which the variable was introduced in the model equation, together with the consequent p–level of significance. At C10, the first highly significant positively-related variable is nitrate, followed by the highly significant negatively-related salinity, the very significant positive relation with depth and the significant negative relation with temperature. The negative relation with ammonia and the positive one with nitrite are also introduced in the regression equation, although their relation is not significant. At E06, all the variables introduced in the model are at least significant. The first highly significant negative relation is with salinity, followed by the significant positively-related nitrate, the very significant negative relation with ammonia, the significant negative relation with phosphate, the very significant positive relation with silicate and the significant positive relation with oxygen. The nutrient relations were positive or negative depending on consumption or excess. The strongest chlorophyll-*a* dependence is then positive with nitrate at C10, followed by the hydrological variables, while at E06 it is negative with salinity, followed by the nutrients' concentrations.

3.4 Temperature, salinity and chlorophyll-*a* inter-annual trends

In order to analyse long-term variations in chlorophyll–*a* dynamics, we used the Cox-Stuart test for trends (Sect. 2) and we applied it both to the physical variables and to chlorophyll–*a*. The analysis of the surface water temperature (Table 4) shows a significant increase in May and June and a very significant one in July at both sites, in agreement with the rise in air temperature and annual heat fluxes observed in the Northern Adriatic Sea (Russo et al., 2002). Another significant increase is found in December at both sites, indicating a tendency towards milder winters. However, C10 is the only station showing a significant trend in the whole years median values. In fact, between August and November E06 is characterized by a negative temperature trend which, without being a significant value, still agrees with the registered increasing flow of the Po river that causes floods during autumn (Raicich, 2003). The same feature is not found at C10, probably because the freshwater effect is confined to the Northern Adriatic Current region (Artegiani et al., 1997a).

This is further confirmed by the Cox-Stuart test results for surface salinity (Table 4). No significant trend is found at C10, either in spring, or in summertime, when the area may be reached by the Po river plume. Significant trends are instead seen at E06: a very significant decrease in February, a significant decrease in October and a very significant increase in November. In order to understand the relations between the Po discharge and the physical variables, we have performed the Spearman Test for correlations on daily scale with a 1-week time lag between the observed run-off and the observed salinity and temperature (Appendix A). Both stations are generally influenced by the Po river's spreading. C10 is mostly affected by temperature fields, since a larger effect may be detected during spring and summertime, when it feels the effect of the Po maximum in May, due mostly to snow melting, that slakens the thermocline formation. E06 is, instead, equally affected by temperature and salinity fields, since the impact of the river may be detect all year round and it is closer than at C10: thus, salinity and temperature values faster decrease than at C10.

The Cox-Stuart Sign test (Table 5) on chlorophyll–*a* reveals no significant long-term trend in both the median and the dispersion. The weak negative trend in the C10 annual value is considered random, as is the slight increase at E06. On the other hand, C10 shows a significant increase in the central value in April, although this is not really relevant considering the entire annual cycle. The variability is fairly constant, with a small indication of increase for both stations. Any missing result in the Cox-Stuart test is due to an insufficient number of available comparisons.

4 Discussion

The hydrological and biogeochemical evolution presented in Sect. 3.1 shows that the C10 station is directly influenced by high river outflows, when the general circulation and stratification can favour the NE spreading of the Po plume. Conversely, E06 is largely affected by the Po river run-off, irrespective of their magnitude, and also by other smaller rivers, as confirmed by much lower salinity values for all of the non-mixed periods. Generally, the nutrient concentrations are higher in the near-surface region where the lowest salinities are observed. This is consistent with the role of the rivers as the major nutrient sources for the region.

Several works (e.g., Fonda Umani, 1996; Mozetic et al., 1998; Fonda Umani et al., 2005) have showed that the November blooming of the Northern Adriatic is poorly controlled by micro- or meso-zooplankton. Consequently, the surface peaks of winter ammonia are most likely due to bacterial activity on senescent phytoplankton cells. The bottom 5 m of the water columns show concentrations that well reflect a trend opposite to that of the dissolved oxygen in the same period, indicating benthic recycling of ammonia. The role of benthic nutrient remineralization is then an important factor that can be inferred from the monthly analysis.

Low salinity values during periods of low nitrate concentrations suggest that most of the land-derived nitrate is taken up by phytoplankton. However, while C10 is characterized by low concentrations of chlorophyll-*a*, E06 maintains higher values. The absence of a gradient in nitrate and the different response of chlorophyll–*a* at C10 and E06 may not be explained only by consumption. Different controlling factors may affect phytoplankton growth in the two areas. At C10, chlorophyll-*a* concentrations seem to pretty well follow

Table 4. Cox-Stuart test results for surface temperature (left) and salinity (right) at C10 and E06[d].

	Temp										Sal									
	C10					E06					C10					E06				
Month	N	+	–	p	sig.	N	+	–	p	sig.	N	+	–	p	sig.	N	+	–	p	sig.
Jan	6	2	0	–	–	6	3	0	–	–	6	0	3	–	–	6	1	2	–	–
Feb	19	5	4	0.500	ns	16	3	5	0.344	ns	19	2	7	0.090	ns	16	0	8	0.004	**
March	12	3	3	0.656	ns	10	2	3	–	–	12	4	2	0.344	ns	10	5	0	–	–
April	18	5	4	0.500	ns	13	4	2	0.344	ns	18	6	3	0.254	ns	14	4	3	0.500	ns
May	26	11	2	0.033	*	27	11	2	0.011	*	26	4	9	0.133	ns	27	10	2	0.055	ns
June	18	8	1	0.020	*	17	7	1	0.035	*	18	4	5	0.500	ns	17	4	4	0.637	ns
July	32	14	2	0.002	**	27	12	1	0.002	**	18	4	5	0.500	ns	17	4	4	0.637	ns
Aug	20	2	6	0.055	ns	21	3	7	0.172	ns	21	5	5	0.623	ns	21	4	5	0.500	ns
Sep	32	9	6	0.227	ns	25	3	9	0.073	ns	32	11	5	0.105	ns	25	6	6	0.613	ns
Oct	22	5	6	0.500	ns	18	3	6	0.254	ns	22	7	4	0.274	ns	18	1	8	0.035	*
Nov	19	5	4	0.500	ns	15	1	6	0.072	ns	19	7	2	0.090	ns	15	7	0	0.008	**
Dec	12	6	0	0.016	*	12	6	0	0.016	*	11	0	5	–	–	12	0	5	–	–
Sum	236	75	38	0.001	***	207	58	42	0.111	ns	236	60	56	0.384	ns	208	50	48	0.397	ns

[d] +: number of increases, –: number of decreases, ns: not significant, * $p<0.05$: significant, ** $p<0.01$: very significant, *** $p<0.001$: highly significant.

Table 5. Cox-Stuart test results for chlorophyll-*a* at C10 (left) and E06 (right)[e].

	C10									E06								
	cent.					dis.				cent.					disp.			
Month	N	+	-	p	sig.	+	-	p	sig.	N	+	-	p	sig.	+	-	p	sig.
Jan	10	5	0	–	–	2	0	–	–	12	5	1	0.109	ns	1	2	–	–
Feb	48	9	15	0.240	ns	4	4	0.637	ns	40	7	13	0.132	ns	3	3	0.656	ns
March	23	6	5	0.500	ns	4	1	–	–	21	7	3	0.172	ns	3	2	–	–
April	51	22	3	0.006	**	5	4	0.500	ns	38	11	8	0.324	ns	4	5	0.500	ns
May	64	17	15	0.393	ns	5	3	0.363	ns	68	16	18	0.393	ns	10	6	0.227	ns
June	46	13	10	0.365	ns	8	3	0.113	ns	50	14	11	0.368	ns	4	3	0.500	ns
July	73	12	24	0.075	ns	5	4	0.500	ns	62	16	15	0.399	ns	8	2	0.055	ns
Aug	43	10	13	0.365	ns	5	6	0.500	ns	54	18	9	0.122	ns	5	3	0.363	ns
Sep	83	20	21	0.399	ns	5	5	0.623	ns	74	19	17	0.378	ns	4	4	0.637	ns
Oct	53	11	15	0.340	ns	4	4	0.637	ns	50	9	16	0.194	ns	3	5	0.363	ns
Nov	44	6	15	0.058	ns	7	4	0.274	ns	28	5	9	0.212	ns	3	4	0.500	ns
Dec	22	0	11	–	–	3	2	–	–	30	9	6	0.304	ns	3	4	0.500	ns
Sum	278	131	147	0.266	ns	48	37	0.223	ns	262	136	126	0.341	ns	51	43	0.261	ns

[e] cent.: central trend, disp.: data dispersion, +: number of increases, –: number of decreases, ns: not significant, ** $p<0.01$: very significant.

the annual cycle of nutrients. At E06, every period of high concentration is followed by a period of low concentration, indicating that some factor acts successively and regulates phytoplankton abundance. Nutrients have shown to be sufficient and sometimes in excess at this site and are thus not limiting the growth. We suppose that zooplankton grazing, whose annual cycle is usually out of phase with that of phytoplankton (e.g. in the Adriatic, Fonda Umani, 1996) may be one of the main regulating factors of the chlorophyll-*a* pattern.

Phosphate is considered as the principal nutrient limiting primary production in the region (e.g. Gilmartin et al., 1990). Socal et al. (1999) found that the Adriatic Surface Water (ASW) of the photic layer of the Otranto Strait was characterized by an excess of nitrogen (N:P=50). While most of the nitrogen is advected out of the northern basin, phosphorous is efficiently removed from the water column, brought to organic form and possibly buried in the bottom sediments on the Adriatic shelf. However, even though Socal et al. (1999) confirmed the thesis of P-limited Adriatic, the significant presence of diatoms was explained by new production sustained by regenerative processes and DOP and DON as important sources of nutrients. Degobbis et al. (2005) analysed changes in nutrient ratios in relation to mucilage events in the northern Adriatic. While DIN was mostly correlated to the Po river outflow, phosphate was efficiently controlled by phytoplankton assimilation. During a low freshwater input, the increased phytoplankton standing crop was ascribed to more efficient DIN assimilation and faster recycling of phosphate. Our data analysis shows that high concentrations of chlorophyll-*a* are detected during months and at depths at which the phosphate concentrations are close to zero. Following these previous attempts to explain the phoshate behaviour in the Adriatic Sea, we confirm that phosphorus is consumed and rapidly remineralized to sustain abundant biomass production in the Adriatic Sea.

Despite the observed coherent seasonal coupling between physical and hydrochemical features (Figs. 5, 6), chlorophyll-*a* shows a complex annual cycle in both areas. Nevertheless, the chlorophyll-*a* vertical profiles are similar when mixing processes prevail (Fig. 7). For the rest of the year, which is characterized by a strong stratification of temperature and salinity, E06 maintains higher concentrations in the surface layer, where it is mostly affected by riverine loads, while C10 does so mostly at intermediate depths, because a smaller presence of photo-attenuating materials may allow photosynthesis in the entire water column (Vichi et al., 2003b).

This is also confirmed by the PCA (Fig. 8). The first principal component of the PCA captures the effect of periodic stratification, while the second component highlights the effect of river inputs. At C10, chlorophyll-*a* concentrations are mainly correlated to riverine run-off, while at E06, the nutrients being at least sufficient, the correlation with the seasonal cycle is strongly positive and opposite to depth-salinity, because the highest concentrations are found at the surface. A further confirmation comes from the Ridge Regression test results (Table 3). At C10, the only nutrient in the equation is nitrate, which is also the closest variable to chlorophyll-*a* in the PCA projection. The following correlations are with the physical variables and are typical of offshore areas affected by land-derived nutrients and mostly characterized by blooms at intermediate depths. At E06, the Ridge Regression highlights a strongly opposite trend with salinity, which is responsible for the surface blooms and is well-shown in the PCA diagram (Fig. 8). Finally, the test shows a positive correlation with nitrate and silicate, indicating a continuous availability, and a negative correlation with ammonia and phosphate, that are therefore consumed at the site.

The Cox-Stuart test (Sect. 3.4) for the analysis of long-term trends detected significant changes only for the physical variable, but not for chlorophyll-*a*. A possible explanation for this behaviour lies in the different relationship that both stations have with the river run-off. Both areas detect the effect of the warming (Corti et al., 1999; Rixen et al., 2005), but only E06 is likely to show the effects of the increasing precipitation. In fact, both stations are affected by the rise in summer temperature, due to higher heat fluxes. But, while at E06 the rise in temperature is balanced by an autumn reduction, due to the large quantity of freshwater inflow, at C10 this does not happen, since no large effect is detected of the Po water spreading there during autumn. Therefore at C10 the water generally becomes warmer.

The absence of a trend was also found in model simulations (Vichi et al., 2003a). Even if we are not able to assess the climatological change, the Cox-Stuart test agrees pretty well with the Eastern Mediterranean Climatic Transient (EMCT). The EMCT is a global change in the meteo-oceanographic conditions happening over the Mediterranean Sea during recent decades (Rixen et al., 2005), and is defined as a collection of events, such as rising temperature and fewer rainy days with heavier precipitation.

It is interesting to compare our results with other highly productive European regional seas, as the Black Sea and the Baltic Sea. Nehring (1992) analysed a 30-years (1958-1989) biogeochemical data set in the Baltic proper and found that, except for the period 1969–1977, nutrient concentrations no longer increased, remaining at stable, but high levels. During periods of water renewal, a strong correlation was detected between salinity and nutrients. Oxygen was found to increase, although no significant trend was identified. The strong deterioration of oxygen conditions and the phosphate accumulation in central Baltic deep waters were attributed to the absence of water renewal caused by climate changes in the northern emisphere and worsened by the entrance of North Sea polluted waters through the Danish Strait into the Baltic.

Gomoiu (1992) synthetized in her work the ecological changes in the NW Black Sea in the period 1972–1992: increasing quantities of nutrients and organic matter, oxygen imbalance and appearance of hypoxic and anoxic phenomena, mass mortalities of benthic organisms, reduction in diversity at different levels, development of opportunistic species. The author concluded that the ecosystem reflected a regressive evolution and a fragile and unstable phase.

In both cases, and in contrast with our results, positive trends were detected for phytoplankton biomass (chlorophyll–*a*) and primary productivity. We believe that the efficient mixing, especially due to local wind episodes, may prevent the eutrophication of the Adriatic Sea. Furthermore, we analysed a timeseries data postponed to the reduced quantities of phosphorus used in detergents in the late 1980s. Degobbis et al. (2000) and Bernardi Aubry et al. (2004) reported, in fact, a phosporous decrease in their works. Despite this, we are not able to define a possible associated chlorophyll-*a* change on this temporal scale and with this high natural variability. We can then hypothesize that: i) a real change did not happen; ii) the temporal scale of the chlorophyll-*a* processes might have not fit with the other variable trends; iii) the ecosystem evolution might have favoured new species in the composition of the phytoplankton population without changing the total stock; iv) a possible trend might exist at the extreme concentrations, which are not sufficiently represented in the sample.

4.1 Trophic variability of the NW Adriatic

The descriptive statistical analysis presented in Sect. 3.1 indicates that the C10 and E06 areas have significantly comparable hydrological characteristics, while they are differently affected by the river's discharge. However, chlorophyll-*a* only shows a weakly significant difference. High-frequency interconnected physical and biological processes are thus likely to modulate chlorophyll-*a* dynamics, also when the nutrients' availability is dominant. We may thus define these stations as highly variable and varying between meso and meso-oligotrophic characteristics.

There is no international agreement between different indicators and indices regarding the assessment of the trophic status of seawater, mostly due to different criteria, methodologies of data analysis and restrictions to selected regions. For example, Giovanardi and Tromellini (1992) refers to oligotrophic status for the Northern Adriatic waters characterized by chlorophyll–*a* levels $<1.7\,\mu\mathrm{g\,dm^{-3}}$, Ignatiades (2005) for Aegean Sea waters having chlorophyll–*a* values $<0.5\,\mu\mathrm{g\,dm^{-3}}$, while Babin et al. (1996) for Northern Atlantic waters with chlorophyll–*a* concentrations $<0.05\,\mu\mathrm{g\,dm^{-3}}$. We prefer to analyse the trophic status of a certain region as the result of the complex interactions between all the dynamic processes that in time, as seasonal cycle, and space, as dynamic in the water column, bring to specific nutrients and chlorophyll–*a* patterns, oxygen saturation and vertical stability of the water column. Our main interest is thus not an absolute definition of the trophic status of each station, but a relative comparison between the areas to find possible differences or similarities.

The Wilcoxon Matched Pairs test (Table 1) shows that, considering all the data set (in time and space), the two sites are affected by similar hydrodynamics, highly significant different nutrient inputs and slightly significant differences in chlorophyll–*a* concentrations. The same test applied to the intra-annual variability of chlorophyll–*a* (Table 2) shows that those differences are due to significant differences between June and August, when E06 maintains higher concentrations, and vice versa in September. On the other hand, the analysis of the intra-annual variability, considering also the different depths, presented in time-depth plots (Fig. 5 and Fig. 6) shows that, in the same period, both stations are characterized by a reduction in nutrient concentrations, stable oxygenation, stratified waters and chlorophyll–*a* values with the lowest annual values (Fig. 7). Besides, the slightly higher values of chlorophyll–*a* in the deepest layer at both stations are a clear indicator of photosynthetic activity of the bottom SL and thus water transparency. This leads us to consider the areas as trophically much similar than previously reported in literature (e.g., Alberighi et al., 1997; Pugnetti et al., 2003, 2004; Bernardi Aubry et al., 2006).

5 Conclusions

The long-term set of hydrological and biogeochemical data coming from the C10 and E06 stations, located in the NW Adriatic Sea, allowed us to formulate a reasonable picture of the NW Adriatic biogeochemical variability and we are now able to answer to the main questions that guided our scientific work.

(i) Generally, the two stations cannot be considered trophically different, as some previous literature had done. Our data analysis show similarities between the two areas, concerning the chlorophyll–*a* response to different physical and biological features. Nutrients standing stocks cannot be considered a sufficient criterion to characterize conditions and trophic differences between different areas.

(ii) The two stations may be characterized by different controlling factors regarding the chlorophyll–*a* dynamics. C10 chlorophyll-*a* is mainly controlled by periodic river inputs. E06 is strongly correlated with the seasonal cycle, may be efficiently grazed by zooplankton and a high presence of photo-attenuating material may limit the photosynthesis at the deepest SL. We suggest the importance of studying the coupling between the phytoplankton cycle and zooplankton abundance and distribution, since zooplankton is an essential controlling factor in the phytoplankton trend and evolution throughout the trophic chain characterizing an area.

(iii) Data analysis shows that we should review the thesis of phosphorous being a classical growth-limiting factor of phytoplankton abundance in the NW Adriatic Sea. Other phosphorous sources besides orthophosphate, such as organic phosphorous and fast regeneration processes, can contribute to maintaining phytoplankton growth. It is therefore necessary to resolve the fast remineralization processes in the pelagic domain on a higher frequency scale in order to clarify the effective co-limiting factors.

(iiii) The absence of a significant chlorophyll-*a* trend in time at either site, in agreement with model results of scenario simulations (Vichi et al., 2003a), is not sufficient to allow us to assume that the communities or other indicator did not change. Previous studies, based on a shorter time scale (Pugnetti et al., 2003; Bernardi Aubry et al., 2006), could not typify any significant difference in community composition. Our next step will therefore be to couple this study with an analysis of the abundance, biodiversity and distribution of the different species of phytoplankton during the same study period in order to find if an intra- and inter-annual variability is present in the long term.

Appendix A

Time series plots of the studied variables (except chlorophyll–*a*, presented in Fig. 4) and the analysis of the correlation between the physical oceanic variable (temperature and salinity) and the Po river's discharge (data scatterplots and Spearman Test) are available as supplemental material at http://www.biogeosciences.net/4/673/2007/bg-4-673-2007-supplement.pdf.

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