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Annual variations in bio-optical properties at the 'Estación Permanente de Estudios Ambientales (EPEA)' coastal station, Argentina

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Abstract

Variations in optical properties at a coastal station (EPEA) off the North coast of Argentina (38° 28′ S 57° 41′ W) were studied in 2000–2001. Changes observed in the absorption by three components of seawater (phytoplankton, detritus, and chromophoric-dissolved-organic-matter or CDOM) were analysed in relation to changes in environmental conditions (temperature, stability of the water column, irradiance) and changes in the phytoplankton community structure. An annual cycle typical of temperate seas was observed in the stability of the water column, with a strong thermocline in summer and a vertically homogeneous regime in winter. The proportion of detritus absorption at the surface was related to these changes in stability of the water column, being larger in winter due probably to re-suspension from the bottom. Absorption by phytoplankton and CDOM were not related to temperature or the stability of the water column and there was no covariation in absorption by the three seawater components. On the other hand, absorption by phytoplankton was significantly related to the predominant cell-size. The percentage contribution of ultraphytoplankton ($<5\,\mu m$) to total chlorophyll-*a* concentration varied between 6% and 46% throughout the year, being the highest during summer. Accordingly, the specific absorption coefficient of phytoplankton at 440 nm (absorption/chlorophyll-*a*) varied between 0.01 in July (when there was a bloom of the large diatom *Coscinodiscus wailesii*) and 0.09 m^2 mg $Chla^{-1}$ in February (when *Synechococcus* spp. was predominant). The relationship between in situ and 1 km daily satellite estimated OC4V4 chlorophyll-*a* concentration showed a good correlation ($r^2 = 0.94$ for 9 out of the 19 data points where an exact match up could be made). Marked variations were observed when comparing 8 day-9 km binned data with the 19 points. While some of the differences are due to the highly dynamic hydrography of this region, variations in phytoplankton composition also contribute to the difference between in situ and satellite-derived values.
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Keywords: Coastal waters; Absorption; Phytoplankton; Detritus; CDOM; Satellite chlorophyll; Southwestern Atlantic

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1. Introduction

A great interest exists nowadays in understanding ecological processes occurring in coastal areas. They are usually important from an economical point of view and, moreover, natural phenomena occurring in there affect the nearby land, where some important urban areas are located. In turn, urban activities affect the natural development of these ecosystems. The first link in most trophic webs in the ocean is occupied by phytoplankton. Because of their characteristics, small size (~1–0.001 mm) and mostly free-floating condition, these photosynthetic organisms are extremely dependent on the physical–chemical environment in which they live. There are numerous studies of species succession, distribution, and changes in physiological status of phytoplankton related to environmental changes in the ocean (e.g., Margalef, 1963, 1978; Smayda, 1980; Margalef and Estrada, 1981). These changes, in community structure and in physiological status, are reflected in changes in the optical characteristics of phytoplankton (e.g., Yentsch and Phinney, 1989; Bouman et al., 2003; Bricaud, 2004; Sathyendranath et al., 2004).

The most economical and synoptical way to estimate phytoplankton abundance nowadays is the use of ocean-colour remote-sensing techniques. This satellite estimation relies on knowing how phytoplankton affect the sea-surface reflectance measured by the sensor (e.g., Gordon and Morel, 1983). Some of the most commonly used algorithms to retrieve chlorophyll-*a* concentration from ocean-colour are empirical, and hence biased towards the optical characteristics of the places used to acquire the primary data. Moreover, they have been mainly developed for clear water situations (e.g., open ocean), where phytoplankton is assumed to dominate changes in the reflectance signal (Case 1). It is recognized that these algorithms may not work properly for coastal areas (IOCCG, 2000), where other optically active components present in the seawater (i.e., detritus, and chromophoric-dissolved-organic-matter or CDOM) may dominate changes in the reflectance signal (Case 2). A recent study covering 350 stations on coastal waters around Europe showed marked variations in the absorption properties of water components (Babin et al., 2003).

The development of suitable algorithms for regional coastal areas is, therefore, one of the major focus of bio-optical studies at the moment. The Southern Hemisphere, and South America in particular, remains one of the least studied places of the world ocean (see Partnership for Observation of the Global Oceans—Sao Paulo Declaration, 2000, http://www.ocean-partners.org/documents/docSPD.pdf). Nevertheless, several studies based on remote-sensing analysis alone have shown that the South Atlantic is a very dynamic place, with highly coloured features (Garcia et al., 2004; Gonzalez-Silvera et al., 2004; Romero et al., in press). According to some of these satellite studies, the Argentinian Shelf seems to have important blooms of coccolithophorids along its shelf-break (Brown and Podestá, 1997). Even more, a recent study (Gregg et al., 2005) on global trends in chlorophyll distribution, from SeaWiFS information from 1998 to 2003, predicts that the Patagonian Shelf' (taken it in a broad sense starting–Uruguay at the North) would be the place showing the most rapid increase in chlorophyll concentration (+67.8% over the 6 years analysed). On the other hand, these studies had no field data to corroborate their findings. The few satellite chlorophyll-*a* validation studies carried out in the southwestern Atlantic revealed that there is a need to revise the algorithms used for this area (e.g., Armstrong et al., 2004; Garcia et al., 2005).

The project Dinámica del Plancton Marino y Cambio Climático (DiPlaMCC) is dedicated to study long-term variations in the plankton community (including bacterioplankton, phytoplankton, zooplankton, and ichtyoplankton) in relationship with environmental factors (physical and chemical) at the coastal station EPEA (Estación Permanente de Estudios Ambientales), with the ultimate goal to detect possible extraordinary effects such as those caused by climate change. Station EPEA is located at 38° 28′ S 57° 41′ W approximately 13.5 nautical miles off Miramar and at 27 nautical miles from Mar del Plata (Fig. 1). While its location would correspond to 'Coastal Waters', due to its proximity to the isobath of 50 m, it may at some times be influenced by advection of 'Middle Shelf Waters' of Subantarctic origin, and on particular occasions by fresher water from La Plata river (Carreto et al., 1995; Guerrero and Piola, 1997; Lucas et al., 2005). That makes this station highly dynamic hydrographically. The DiPlamCC project started in February 2000, and the frequency of sampling to the EPEA station has been approximately monthly since then. As part of this time-series project, changes in bio-optical characteristics of the water column are being

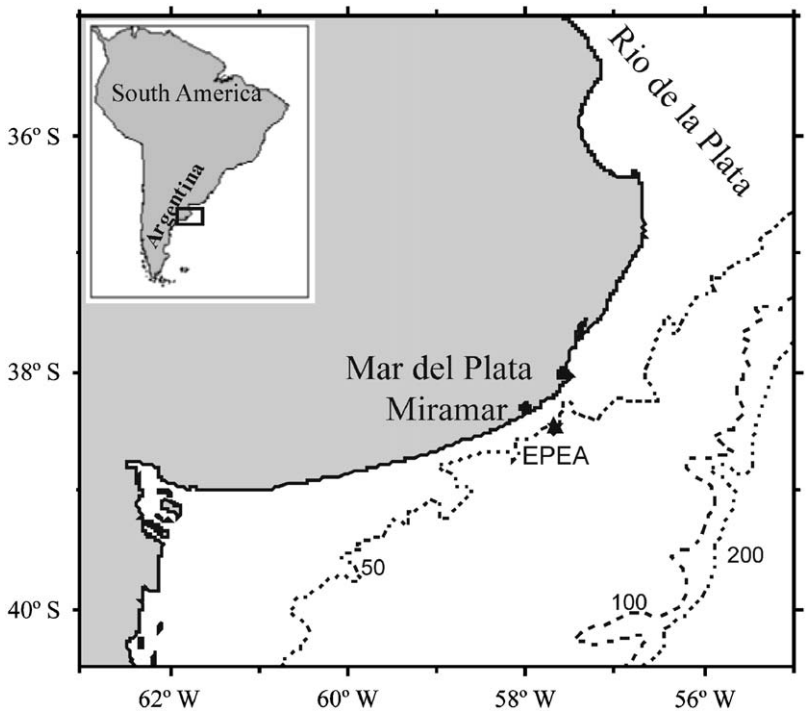

Fig. 1. Location of the time series station 'Estación Permanente de Estudios Ambientales' (EPEA).

studied at the site. EPEA is also one of the foundational stations of ANTARES, a network of time series stations being studied around South America (www.antares.ws).

The aim of the present work is to analyse the first bio-optical results obtained from this time series study. A complete year sampling is analysed to (1) determine if there were any predictable temporal pattern in the optical characteristics of the main seawater components (i.e., phytoplankton, detritus, and CDOM); (2) determine if changes in these bio-optical properties could be related to environmental variables, and to variations in phytoplankton composition; and (3) assess how changes in these bio-optical characteristics affect the estimation of chlorophyll-*a* concentration by remote sensing of ocean-colour.

2. Materials and methods

2.1. Sampling

A total of 19 Cruises (Table 1) to station EPEA took place between February 2000 and 2001, with a frequency of at least once a month, on board the research vessel "Capitán Cánepa" (INIDEP). Sampling was always performed around local noon. During most of the cruises—except cruises: 5, 9, 15, 17, and 18—temperature and salinity profiles were determined by means of a Seabird SBE1901 CTD. Underwater light (PAR: photosynthetically active radiation), natural fluorescence, and temperature profiles were obtained with a PUV-500/510B Biospherical radiometer. Water samples for the determination of nutrients, chlorophyll-*a* concentration, absorption of particulate (in all cruises), and dissolved matter (except in cruises 1 and 2), and identification of phytoplankton composition were taken from surface with a bucket and from different depths using Niskin bottles. Seawater samples for nitrate determination were kept at $-20\,^{\circ}C$ until analysis at the laboratory using a Technicon Autoanalyser.

2.2. Fitting of PAR profiles

PAR profiles obtained from the radiometer were corrected for possible errors due to the movement of the ship, by fitting an exponential function to the actual data. The water column was divided into three layers: (1) from the surface to the depth of 35% surface PAR, (2) from the 35% to the 10% surface PAR, (3) from 10% surface PAR to the bottom. The downwelling attenuation coefficient,

Table 1
Details of the cruises performed at the EPEA station during the period February 2000 and February 2001

Cruise name	Correlative cruise number	Date of cruise	SeaWiFS	Variables measured
CC0400	1	3 February00	X	1, 2, 3, 4, 5, 6, 7, 9
CC0700	2	9 March 00		1, 2, 3, 4, 5, 6, 7, 9
CC0900	3	29 March 00	X	1, 2, 3, 4, 5, 6, 7, 9
CC1100	4	25 April 00		1, 2, 3, 4, 5, 6, 7, 8, 9
CC1300	5	10 May 00	X	2, 3, 4, 5, 6, 7, 8,9
CC1500	6	24 May 00		1, 2, 3, 4, 5, 6, 7, 8, 9
CC1700	7	7 June 00	X	1, 2, 3, 4, 5, 6, 7, 8, 9
CC1900	8	14 July 00		1, 2, 3, 4, 5, 6, 7, 8, 9
CC2200	9	8 August 00		2, 3, 4, 5, 6, 7, 8, 9
OB0900	10	8 September 00		1, 2, 3, 4, 5, 6, 7, 8, 9
CC2600	11	28 September 00		1, 2, 3, 4, 5, 6, 7, 8, 9
CC2900	12	18 October 00	X	1, 2, 3, 4, 5, 6, 7, 8, 9
CC3200	13	3 November 00	X	1, 2, 3, 4, 5, 6, 7, 8, 9
CC3400	14	17 November 00		1, 2, 3, 4, 5, 6, 7, 8, 9
CC3700	15	1 December 00	X	2, 3, 4, 5, 6, 7, 8, 9
CC3800	16	14 December 00	X	1, 2, 3, 4, 5, 6, 7, 8, 9
CC0101	17	9 January 01		2, 3, 4, 5, 6, 7, 8, 9
CC0301	18	29 January 01	X	2, 3, 4, 5, 6, 7, 8, 9
CC0501	19	20 February 01		1, 2, 3, 4, 5, 6, 7, 8, 9

Variables measured: 1 = CTD profile (temperature, conductivity); 2 = temperature profile (sensor on radiometer); 3 = PAR irradiance profile (radiometer); 4 = fluorescence profile (sensor on radiometer); 5 = chlorophyll-*a* total and $<5\,\mu m$ (discrete depths from Niskin bottles); 6 = nitrate (discrete depths from Niskin bottles); 7 = particulate absorption (discrete depths from Niskin bottles); 8 = CDOM absorption (discrete depths from Niskin bottles); 9 = phytoplankton composition (discrete depths from Niskin bottles).

$K_d(PAR)$, correspondent to each one of these layers was calculated and applied in the fitting of the exponential function.

2.3. Depth and strength of the thermocline

The position and degree of strength of the thermocline were estimated by applying the first derivative of temperature with respect to depth. The maximum absolute value of the slope (change in temperature versus change in depth) was taken as a measure of the strength of the thermocline (ΔT), and the depth at which it occurred as the thermocline-depth (Z_T).

2.4. Concentration of chlorophyll-a

A known volume of seawater from each sampled depth was filtered on board onto a GF75 MFS glass-fibre-filter. Another sample was pre-filtered through a 5 μm polycarbonate filter, and the filtrate filtered again onto a GF75 MFS glass-fibre-filter. The chlorophyll-*a* (*Chla*) concentration was determined in the laboratory (on land) for the total sample and for the $<5\,\mu m$ fraction using the fluorometric method (Holm-Hansen et al., 1965). Filters were extracted in 90% acetone, stored overnight at $-20\,^{\circ}C$, sonicated and centrifuged previous to measurement in a spectrofluorometer Perkin Elmer LS3.

2.5. Chlorophyll-a profiles

The continuous vertical natural-fluorescence recordings from the radiometer were converted into '*Chla*' concentration, by calculating the *Chla*/fluorescence factors at depths were discrete samples for in vitro *Chla* were taken, and linearly extrapolating those factors in between sampled depths.

2.6. Phytoplankton composition

Cells were identified and quantified using the Utermöhl method (Hasle, 1978). Epifluorescence microscopy (Verity and Sieracki, 1993) was used for a better characterization of ultraphytoplankton groups ($<5\,\mu m$).

2.7. Particulate absorption

Duplicate samples of seawater were filtered on board onto GF75 MFS glass-fibre-filters, at dim light and low pressure (<35 kPa). Filters were kept at −20 °C on board until arrival to the laboratory (~3 h), where they were kept in liquid nitrogen (−196 °C) until measurement. Optical density of the total particulate material was measured between 350 and 750 nm in a double beam Shimadzu UV-210A spectrophotometer following the quantitative filter technique (Yentsch, 1962; Mitchell, 1990). The blank consisted, in each case, of a glass-fibre-filter through which a volume similar to that of the sample of pre-filtered surface seawater had been filtered. After that filters were washed with hot methanol and detritus optical density was recorded (Kishino et al., 1985). The averaged value of optical density—750 to 710 nm—was subtracted from the whole spectrum in each case (total and detritus). Spectra were corrected for the pathlength amplification factor by applying the quadratic equation of (Mitchell, 1990) using the coefficients reported by Hoepffner and Sathyendranath (1992). Total [$a_p(\lambda)$], detritus [$a_d(\lambda)$], and phytoplankton [$a_{ph}(\lambda) = a_p(\lambda) - a_d(\lambda)$] absorption coefficients (m^{-1}) were estimated by accounting for the factor to convert decimal to natural logarithms, and for the area of the filter and volume of seawater filtered (Mitchell and Kiefer, 1988). Most absorption values reported here (except for cruises 1, 2, and 3) represent the average from duplicate samples. The coefficient of variation of $a_{ph}(440)$ for all samples considered ($n = 59$) was 9.7% ±10.6.

2.8. Chromophoric-dissolved-organic-matter

Absorption by CDOM was measured following, mostly, the protocol described in the "Plumes and Blooms—project" (www.icess.ucsb.edu/PnB/manual/acdom.htm). Seawater samples were filtered through 0.2 μm Nuclepore filters (acid pre-washed) and the filtrate kept in caramel glass bottles in the fridge (~4 °C) for no longer than 2 days. CDOM optical density was measured between 270 and 750 nm using 4 cm cuvettes. Ultra-pure water (NANOpure UV system) was used as a blank. Two measurements were made from each sample. The value of optical density at 700 nm was subtracted from the whole spectrum. Absorption coefficients for CDOM [$a_y(\lambda)$; (m^{-1})] were estimated by accounting for the factor to convert decimal to natural logarithms, and for the pathlength of the cuvette. All absorption values reported here represent the average from the pseudo-replicate samples. The coefficient of variation of $a_y(440)$ for all samples considered ($n = 50$) was 22.2% ±23.8. The relatively high level of noise at this wavelength is due to the fact that the CDOM spectra, increasing exponentially towards the ultraviolet, is very low in the visible.

2.9. Satellite chlorophyll-a

Satellite chlorophyll-*a* concentrations were derived from SeaWiFS measurements of water leaving radiance using the OC4V4 algorithm (O'Reilly et al., 2000). Level 1a data from a few days bracketing each cruise was processed to level II using SeaDAS 4.8 software and the chlorophyll-*a* concentration at the location corresponding to station EPEA was extracted. Level III reprocessing V5.1 global 8 day-9 km binned data was used to extract a time series of chlorophyll-*a* concentration at that location for the period September 1997–June 2005.

3. Results and discussion

3.1. Hydrographic characteristics

The vertical distribution of temperature throughout the 19 cruises at the EPEA station showed a seasonal cycle (Fig. 2). Surface temperatures oscillated between ~23 °C and ~10 °C. A well-established thermocline in summer during Cruise 1 (Cr. 1) separated high surface temperatures (~23 °C) from colder waters at depth (~14 °C). This thermocline started deepening by the end of summer (Cr. 2) until completely disappearing in the early fall (Cr. 3). During fall and winter the water column was well mixed with temperatures progressively decreasing from ~19 °C (Cr. 3) to ~10 °C (Cr. 9). Towards the end of winter (Cr. 10) and the beginning of spring (Cr. 11 and 12, 13, 14) seawater temperature increased and a thermocline started to develop (Cr. 15) until reaching a summer situation again (Cr. 16, 17, 18 and 19).

The *Chla* distribution also showed marked variations throughout the year, although not always following those in temperature (Fig. 2). *Chla* concentrations were low in the mixed layer (<1 mg m^{-3}) in summer (Cr. 1 and 2). Cruise 1 showed a maximum in fluorescence at around 23 m (just above the thermocline), that was not shown in

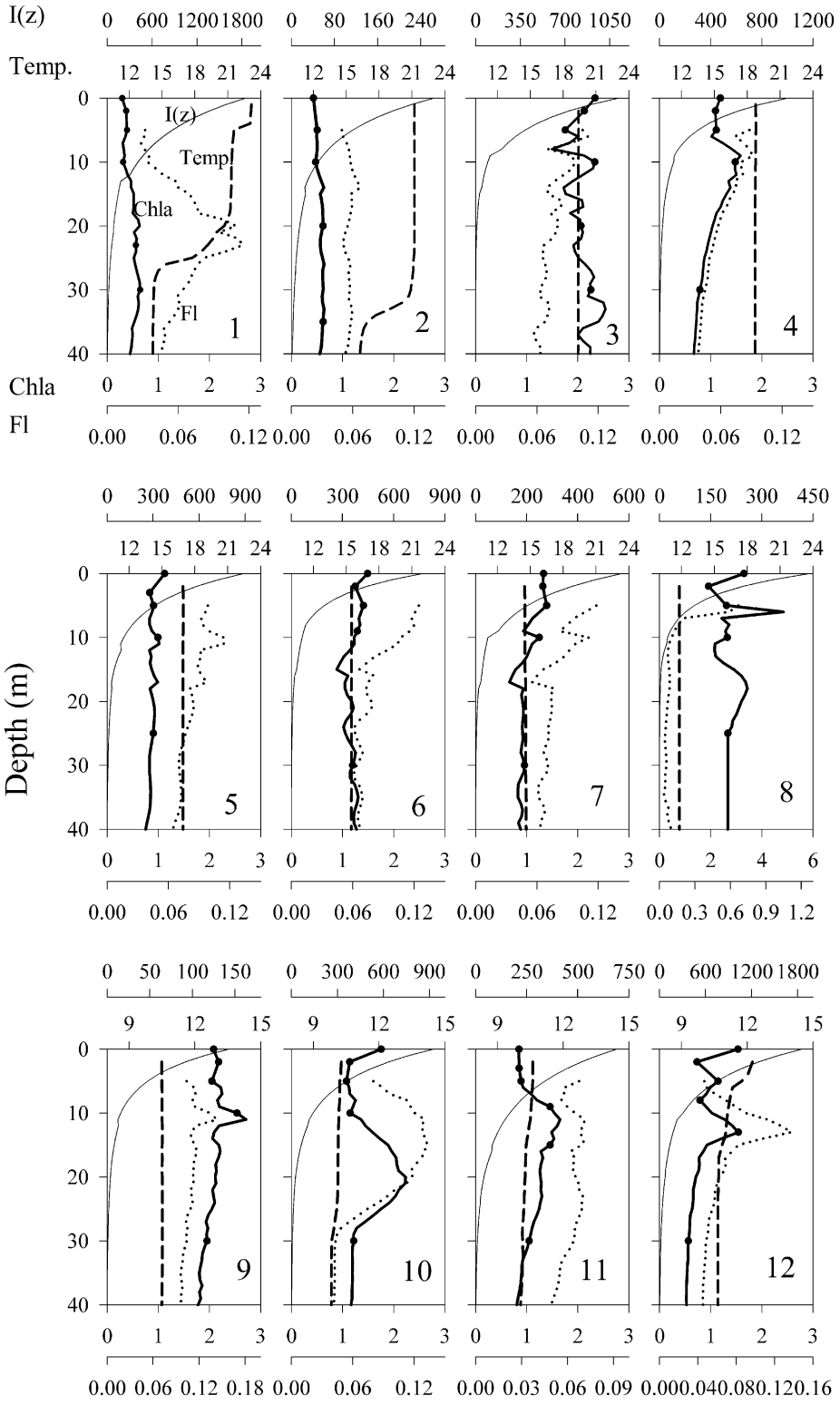

Fig. 2. Vertical profiles of main variables during the 19 EPEA cruises analysed. Temp.: temperature in °C; $I(Z)$: downwelling PAR in μmol quanta $m^{-2} s^{-1}$; *Chla*: chlorophyll-*a* concentration in $mg\,m^{-3}$; Fl: natural fluorescence in relative units.

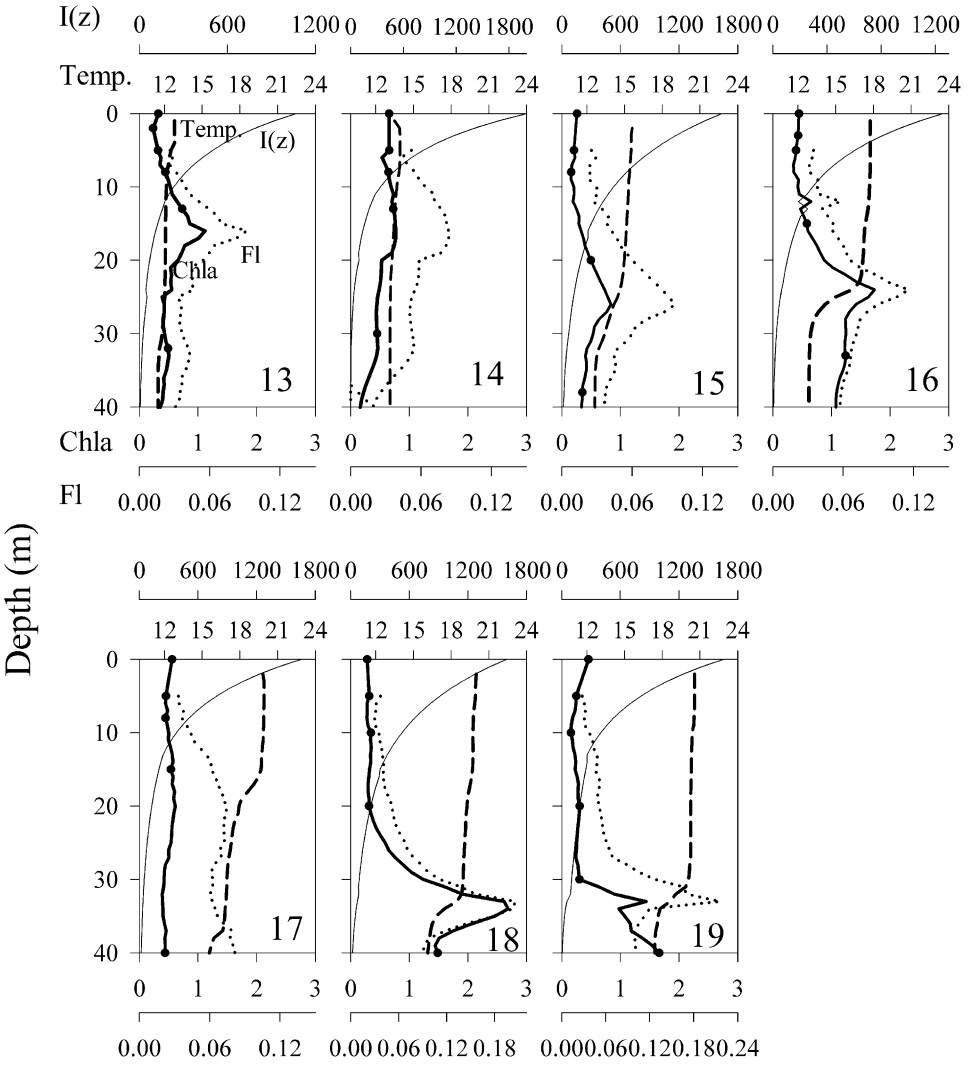

Fig. 2. (*Continued*)

the extracted *Chla* concentration. There are different explanations for this lack of match between the fluorescence and chlorophyll profiles. First of all, a high concentration of phaeophytin was found ($\sim$0.3 mg m^{-3}) at this depth. The fluorometric acidification method here used (Holm-Hansen et al., 1965) is known to overestimate phaeopigments in the presence of chlorophyll-*b* (Trees et al., 1985), and microscopic examination showed that phytoplankton was dominated by small chlorophytes (picophytoplankton) at 23 m. Hence, the high ratio fluorescence to *Chla* could be due, in part, to an artifact of the chlorophyll method. It is also known that fluorescence from cells exposed to high irradiances close to the surface can be inhibited, causing a false fluorescence peak at depth (Cullen, 1982); but here the *Chla* profile was homogeneous not showing a decrease with depth, as it would be expected in the case of surface photoacclimation. The breakdown of the thermocline homogenized the *Chla* profile and gave rise to a fall bloom of phytoplankton with concentrations of *Chla* $\sim$2.5 mg m^{-3} (Cr. 3). After that concentrations dropped to $\sim$1 mg m^{-3} during the end of fall and the beginning of winter (Cr. 4, 5, 6, and 7). The maximum *Chla* concentration, $\sim$3.0 mg m^{-3} at the surface with a peak of $\sim$5 mg m^{-3} at 6 m, was registered in mid-winter (Cr. 8). In August *Chla* concentrations continued to be relatively high and homogeneously distributed

throughout the water column (Cr. 9). At the beginning of September (Cr. 10), although the water column was still homogeneous (with an incipient thermocline at 30 m), the *Chla* profile showed a prominent peak at about 20 m. At the end of September and October (Cr. 11–12) the *Chla* profile showed minor peaks at about 11–13 m, coincident with mild steps in temperature. At the beginning of November (Cr. 13) *Chla* concentrations dropped to $\sim 0.5\,mg\,m^{-3}$, showing a peak at ~15 m. In mid-November (Cr. 14) the *Chla* profile was homogeneous (probably due to a temporary mixing event) with concentrations of $\sim 0.7\,mg\,m^{-3}$. From there on, the development of the thermocline was concomitant with a decrease in *Chla* concentrations in the upper mixed layer ($<0.5\,mg\,m^{-3}$) and the presence of a deep *Chla* maximum (Cr. 15, 16, 18 and 19); except in Cr. 17 where the *Chla* profile was homogeneous coinciding with a notorious change in water temperature and the presence of a shallower thermocline.

It is known that this region of the coast can be influenced by waters from La Plata river during summer (Piola et al., 2005). Nevertheless, during this particular studied period salinity values (data not shown) did not suggest evidence of La Plata river waters at the EPEA station.

3.2. Transparency of the water column according to the distribution of the main absorbing components

Profiles depicted in Fig. 2 show the absolute values of irradiance—exponentially fitted—from in situ measurements. These values are highly dependent on the cloud cover conditions at the time of measurement. Nevertheless, a progressive decrease in light penetration towards winter and an increase in summer were noticeable. This trend could be better seen in the variations observed throughout the year in the depth at which the 1% of surface irradiance (I_0) occurred (Fig. 3). A deeper light penetration in summer (Cr. 1, 2, and from 15 onwards), when solar irradiance was high, was coincident with the presence of a well-defined thermocline. This indicates stratification in the water column with low phytoplankton biomass, due to a depletion of nutrients in the upper layer (nitrate concentrations varied from $<0.2\,\mu M$ at the surface to $>3\,\mu M$ at 30 m). This is evident in the low integrated *Chla* values (Fig. 3) and in the low $a_{ph}(440)$ values (Fig. 4); at the same time the strong density barrier probably impeded the resuspension of sediments from the bottom as evidenced in the low $a_d(440)$ values (Fig. 4). These two effects combined tend to decrease the amount of particulate material in suspension and favour a clear water column.

The breakdown of the thermocline in the fall (Cr. 3) produced a mixing in the water column coincident with an increase in phytoplankton—due to the input of nutrients from depth (nitrate concentrations were ~0.61–0.75 μM throughout the water column)—as evidenced in the integrated *Chla* values (Fig. 3) and in the phytoplankton absorption (Fig. 4). During winter (Cr. 4–10) the water column remained well-mixed, with high

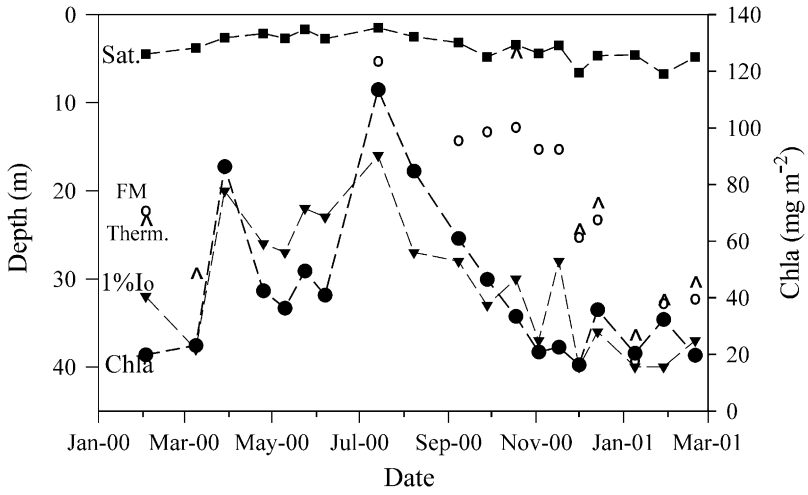

Fig. 3. Variations in some bio-optical characteristics at the EPEA station throughout the year. Therm.: depth of the thermocline, whenever evident; FM: depth of the maximum fluorescence value, whenever evident; 1% Io: depth at which downwelling irradiance was equal to the 1% of surface irradiance; *Chla*: value of the integrated water-column chlorophyll-*a* concentration.

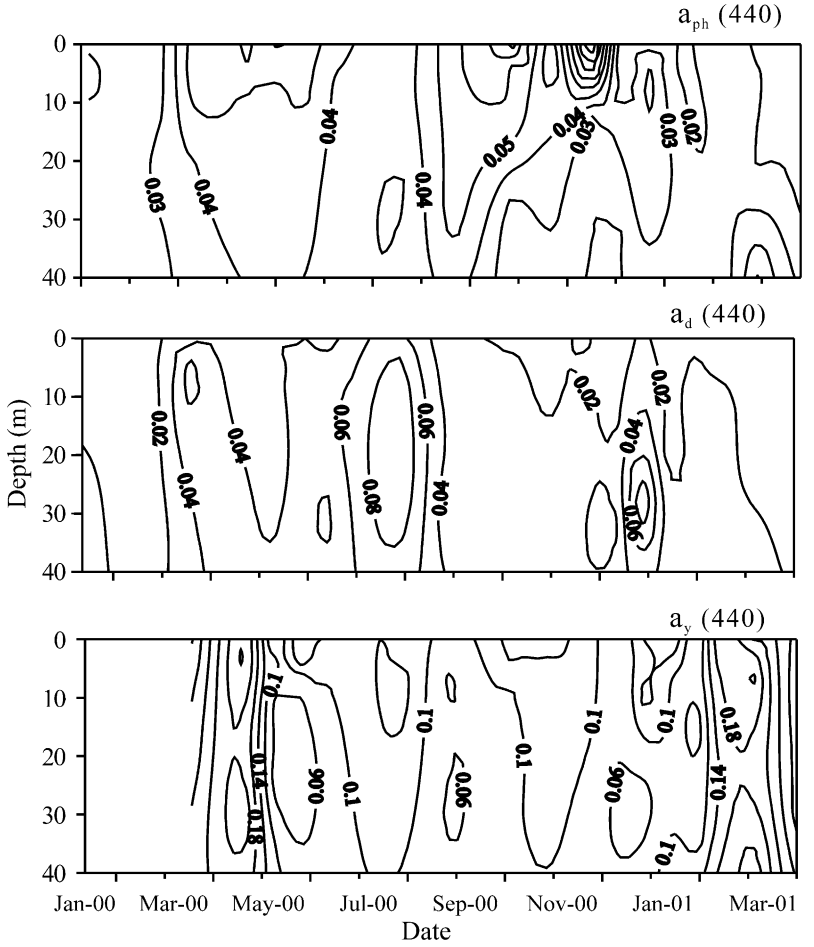

Fig. 4. Vertical distribution of absorption by main water components throughout the year at EPEA. $a_{ph}(440)$: phytoplankton absorption coefficient at 440 nm (m^{-1}); $a_d(440)$: detritus absorption coefficient at 440 nm (m^{-1}); $a_y(440)$: CDOM absorption coefficient at 440 nm (m^{-1}).

nitrate concentrations (>1 μM), integrated *Chla* values were higher than in spring/summer and showed a bloom in July, Cr. 8 (Fig. 3), evidenced also in the phytoplankton absorption (Fig. 4). During the fall/winter the amount of sediments in suspension increased (Fig. 4) showing three peaks in March (Cr. 3), July (Cr. 8), and mid-November (Cr. 14) probably due to stronger mixing events. These variations in the amount of particulate material, making the water more turbid, were also reflected in a shallowing of the depth at which 1% I_0 was found (Fig. 3).

3.3. Variations in the relative absorption by different water components

The contribution of phytoplankton, detritus and CDOM to the sum of absorptions (i.e., total absorption without including seawater absorption) at five of the SeaWiFS bands was estimated at surface for cruises 3–19. Absorption values for each of these components were averaged over a 20 nm interval around the centre of each of the following bands: 1 = 412 nm, 2 = 443 nm, 3 = 490 nm, 4 = 510 nm, and 5 = 555 nm. Fig. 5 shows the percentages of absorption by phytoplankton, detritus and CDOM absorption for band 2 [$a(443)$] during these cruises. CDOM represented the highest percentages of absorption at surface for most of the year (between 36% and 87% of the sum of absorption). The same was true for the vertical distribution of $a_y(440)$, which was always higher than those of $a_{ph}(440)$ (Fig. 4). The high CDOM absorption is not unusual for coastal waters (Kirk, 1994; Blough and Del Vecchio, 2002; Babin et al., 2003).

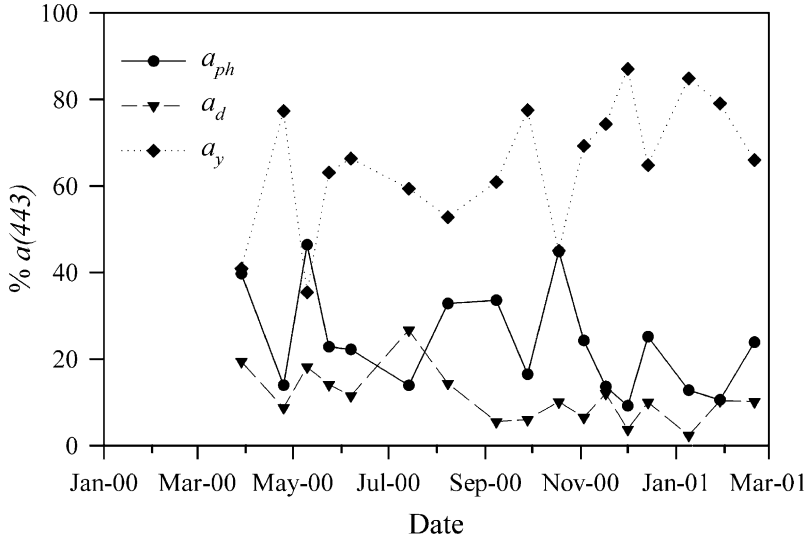

Fig. 5. Temporal variations in the contribution of different water components to the total absorption (water excluded) for band 2 of SeaWiFS (20 nm-binned values centred at 443 nm) at the surface at EPEA. a_{ph}: percentage contribution of phytoplankton absorption; a_d: percentage contribution of detritus absorption; a_y: percentage contribution of CDOM absorption.

There was no correlation among absorption by phytoplankton, detritus, and CDOM at surface. Analysis of correlation among the absorption values of different components at the 5 SeaWiFS bands yielded no significant correlation between any of them. Detritus and CDOM absorptions were neither correlated with phytoplankton absorption, nor were they correlated to each other. This means that detritus and CDOM were not prevalently of phytoplankton origin. At this dynamic coastal environment the concentrations of detritus and CDOM may be influenced by terrestrial outflow, by re-suspension from the bottom, and by advection of shelf waters. These results are contrary to those found by (Babin et al., 2003) showing a covariation between the absorption by phytoplankton, detritus, and CDOM. Although, it should be noticed that in this last case a significantly larger data set (350 points; instead of 17 in our case) was used.

In looking for possible factors affecting the absorption by phytoplankton, detritus and CDOM, we analysed the correlation among the absorption of each one of these components, at each of the 5 binned wavelengths, and several environmental variables at surface. There were no significant correlations among any of the absorption bands of phytoplankton, detritus and CDOM and surface temperature (all 19 cruises) or salinity (for the 14 cruises where CTD measurements were done). Next we checked if there were any relationships between the absorption by different water components at the surface and the stability of the water column. The strength of the thermocline was chosen here as a measure of the stability of the water column instead of density, since in some of the cruises CTD profiles were not performed. Thus, temperature profiles measured by the sensor mounted on the radiometer were used. For cruises in which there were simultaneous measurements performed with both instruments, CTD and radiometer, temperature profiles looked similar (data not shown). Furthermore, for those cruises were CDT casts were recorded the depth of the pycnocline, as well as the order of cruises according to the degree of intensity in the slope of density with depth, were similar to those found for temperature. That means that for the most the stability of the water column was determined by temperature. Statistical analysis showed that absorption by detritus—for bands 1, 2, 3 and 4—was significantly correlated with both the depth and the strength of the thermocline. Deeper and stronger thermocline correlated with lower absorption by detritus at surface. This suggests that one of the major sources of detritus may be re-suspension from the bottom, and that its concentration at surface is regulated by the presence and strength of a vertical barrier. CDOM absorption was not significantly correlated, at any of the 5 bands, with either the depth neither the strength of the thermocline. This

indicates that CDOM was not predominantly coming from the sea floor. Absorption values of phytoplankton showed no significant correlation with either the depth neither the strength of the thermocline, except for absorption at band 5. This last band is centred at 555 nm, where absorption by most pigments is expected to be low except for some phycobilins. Hence, one explanation may be that this relationship with the strength of the thermocline is caused by absorbing material other than pigments in the phytoplankton. When phytoplankton and detritus absorption were plotted against PAR irradiance at surface (I_0) there were no significant correlations, but a clear outlier became evident. This point corresponded to a cruise in mid October (Cr. 12) with high I_0 values. When this point was removed from the analysis, all 5 bands of phytoplankton and bands 1 and 2 of detritus absorption were significantly correlated with I_0. These relationships showed that as I_0 increased, phytoplankton and detritus absorption decreased. This would denote the decrease in phytoplankton abundance towards the summer, probably due to the decrease in nutrients in the upper layer, and the decrease in detritus concentration with the establishment of the thermocline. CDOM absorption did not show significant correlations with I_0 for any of the 5 bands. This is contrary to what has been observed at another time series site (BATS) located in the open ocean (Nelson et al., 1998), where photobleaching of CDOM was a dominant process.

3.4. Relationship between absorption and phytoplankton composition

The specific absorption coefficient of phytoplankton—absorption divided by chlorophyll-*a* concentration—at the blue [$a^*_{ph}(440)$], showed a significant positive correlation with irradiance at surface ($r^2 = 0.33$ for a $P < 0.01$). This could be caused by a succession in species composition, having different optical properties (e.g., Margalef, 1963; Sathyendranath et al., 1987; Bricaud et al., 1995; Sosik and Mitchell, 1995; Lutz et al., 1996; Bricaud, 2004) and by changes in the photoacclimation of the cells, changing their intracellular pigment concentrations (e.g., Mitchell and Kiefer, 1988; Falkowski and LaRoche, 1991; Lutz et al., 2001, 2003). It is expected that the concentration of photoprotective pigments (e.g., zeaxanthin), which absorb strongly in the blue, will increase with an increase in light intensity. Unfortunately, we do not have data on pigment composition to test this hypothesis. However, microscopic observations showed a predominance of *Synechococcus* spp. (<2 μm in size; and known to contain high amounts of zeaxanthin) in the phytoplanktonic community in summer (data not shown). The change in the percentage of chlorophyll-*a* in the fraction <5 μm was coincident with the change observed in $a^*_{ph}(440)$ during the cruises (Fig. 6). As the percentage of chlorophyll-*a* in the fraction <5 μm increased, $a^*_{ph}(440)$ also increased ($r^2 = 0.31$ for a $P < 0.01$) showing the well-known "packaging effect". This predicts that

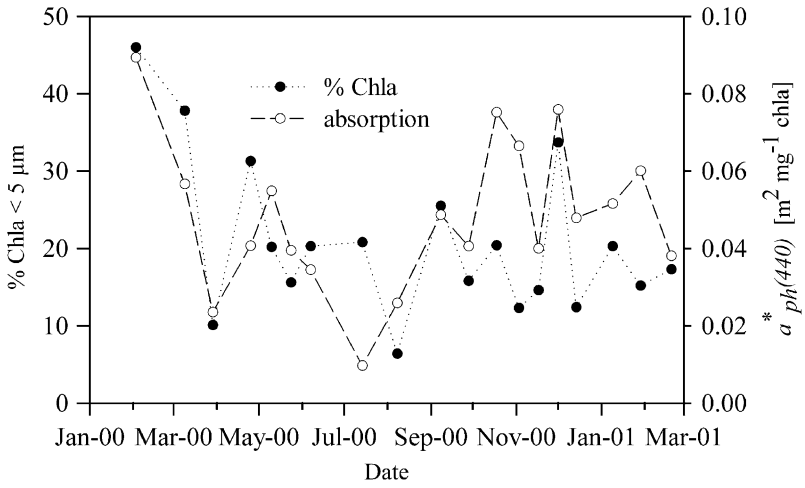

Fig. 6. Variations in the specific absorption coefficient of phytoplankton at 440 nm, $a^*_{ph}(440)$ [$m^2\,mg^{-1}\,chla$], and percentage of chlorophyll-*a* concentration in the <5 μm phytoplankton fraction.

as cell-size decreases or intracellular concentration of pigments increases the efficiency of absorption will increase (Duysens, 1956; Sathyendranath et al., 1987). At the EPEA station the contribution of $<5\,\mu m$ cells to total chlorophyll-*a* at surface varied between ~6% and ~46% throughout the year, highly influencing the absorption characteristics of phytoplankton.

It is interesting to note that in this study the two cases differing the most from the general trend in the relationship between $a^*_{ph}(440)$ and % $Chla<5\,\mu m$, corresponded to the cruises carried out in mid-July (Cr. 8) and in mid-October (Cr. 12). In July (Cr. 8) a bloom of the huge (~300 μm) diatom *Coscinodiscus wailesii* was detected. This was coincident with the lowest value of the specific absorption coefficient [$a^*_{ph}(440) = 0.01\,m^2\,mg\ Chla^{-1}$] and the highest chlorophyll-*a* concentration ($Chla = 3.3\,mg\,m^{-3}$) found for the whole period. In October (Cr. 12) the phytoplanktonic community was dominated by the euglenophyte *Eutreptiella* sp. The value of phytoplankton-specific absorption coefficient [$a^*_{ph}(440) = 0.07\,m^2\,mg\ Chla^{-1}$] at this cruise was higher than what could be expected from these relatively large cells (~40 μm), being closer to the values of $a^*_{ph}(440)$ reported for ultraphytoplankton ($<5\,\mu m$) (Morel et al., 1993; Ciotti et al., 2002). We speculate about three reasons why this species would have a high-specific coefficient in the blue. First, the presence of chlorophyll-*b* may have caused some biased in the *Chla* determination by the fluorometric-acidification method leading to an erroneously low chlorophyll concentration. Nevertheless, if *Chla* concentration were calculated without considering the acidification factor the value of $a^*_{ph}(440)$ would have been $0.06\,m^2\,mg\ Chla^{-1}$, still a clear outlier. Second, the in vivo absorption of chlorophyll-*b* may have increased the total cell absorption in the blue (Hoepffner and Sathyendranath, 1991). Third, microscopic observation revealed that *Eutreptiella* sp. had numerous chloroplasts evenly distributed almost filling its cytoplasm. This particular arrangement of chloroplasts may increase its efficiency of light absorption.

Variations in the relationship between the absorption coefficient of phytoplankton and chlorophyll-*a* concentration have been related to changes in cell size and pigment composition in numerous works (e.g., Sathyendranath et al., 1987; Bricaud et al., 1995; Lutz et al., 1996, 2003; Ciotti et al., 1999, 2002; Stuart et al., 2000; Bricaud, 2004). Furthermore, some of these variations in phytoplankton absorption characteristics have proved to be useful to differentiate phytoplankton groups from the remote-sensing reflectance (Sathyendranath et al., 2001, 2004). As the time series study at EPEA station progresses, we hope to be able to apply some of these models to extract information on phytoplankton composition or 'functional groups' from their bio-optical characteristics.

The value of $a^*_{ph}(440)$, for all cruises all depths considered ($n = 71$), increased significantly with an increase in temperature ($r^2 = 0.20$ for a $P<0.0001$). This is in accordance with previous studies (Sosik and Mitchell, 1995; Bouman et al., 2003), and can be explained by a change in phytoplankton community structure, varying the cell size and the pigment composition with the consequent influence on the packaging effect as explained previously. On the other hand, when only surface samples were selected for the test, there was no significant correlation between the value of $a^*_{ph}(440)$ and temperature. This may be an indication that other factors, not directly related to temperature (e.g., grazing), are contributing to variations on the phytoplankton composition, or on their optical properties (e.g., photoacclimation), at the surface. Whereas, the indirect effect of temperature becomes evident when considering vertical changes embedding probably larger variations in light and nutrient concentrations.

3.5. Grouping of phytoplankton absorption spectra according to their temporal variations

To assess if there were significant differences in the bio-optical and physical properties at EPEA station throughout the year, which could then be used to divide the annual period into a small number of characteristic temporal stages, *K*-means clustering analysis was performed. This method allows to separate the samples in a given '*K*' number of groups (3 was chosen for this exercise) of the greatest possible distinction in the mean of the given variables. The variables chosen to represent variations during the different cruises were: the strength of the thermocline [ΔT], and the absorption spectra of phytoplankton—at the surface—normalized to the value of absorption at 676 nm, taking for the analysis the values at the 5 SeaWiFS bands [$a^n_{ph}(\lambda)$].

Similarities in [ΔT] clearly grouped the profiles into 3 clusters: (1) cruises with the strongest thermoclines, corresponding to the summer 2000 (EPEAs: 1 and 2); (2) cruises with well defined but

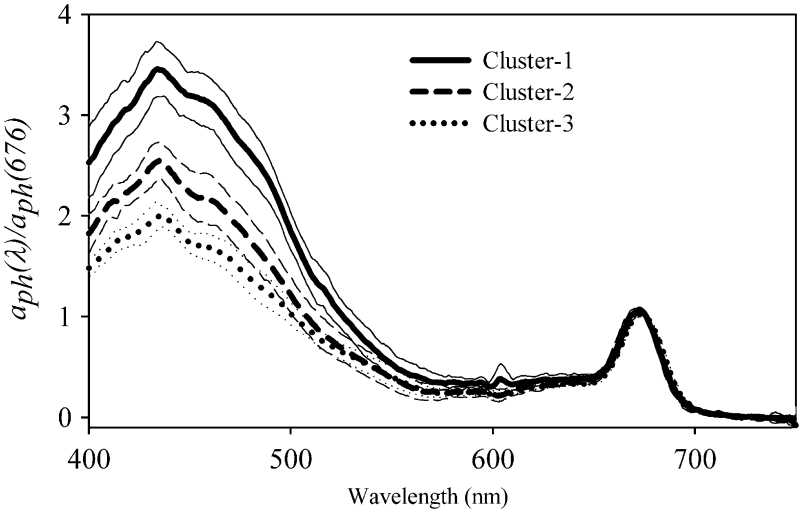

Fig. 7. Averaged and standard deviations of phytoplankton absorption, normalized to 1 at 676 nm, for the three clusters (see text).

milder thermoclines, corresponding to spring/summer 2001 (EPEAs: 16, 17, 18, and 19); (3) the rest of the cruises (EPEAs: 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, and 15) with homogeneous temperature profiles corresponding to autumn and winter (2000).

On the other hand, using similarities in the phytoplankton absorption spectra $[a^n_{ph}(\lambda)]$ as a criteria to group cruises, rendered 3 different sets of clusters (Fig. 7): (1) cruises where the absorption of phytoplankton was significantly higher at the blue (EPEAs: 12, 15, 16, 17, 18, 19); (2) cruises where the ratio blue to red was intermediate (EPEAs: 1, 2, 5, 6, 8, 10, 13, 14); (3) cruises where the spectra were significantly flatter (EPEAs: 3, 4, 7, 9, 11).

The use of a physical characteristic of the water column, such as the strength of the thermocline, to separate temporal cases rendered a define picture. The three clusters obtained could be readily related to seasonal changes in weather provoking the mixing or stability of the water column in this temperate region (Fig. 2). On the other hand, the clusters obtained by similarities in the shape of the phytoplankton absorption spectra grouped different cruises than those discriminated by the stability of the water column.

It is known that the optical characteristics of phytoplankton are related to the environmental conditions to which the cells are exposed, and hence a matching in the groups would have been expected. For example, high surface temperatures are associated to summer conditions when the thermocline is strong (in temperate areas), or to tropical/subtropical oceanic regions, where nutrient concentrations are usually low and irradiance is high, under these conditions the phytoplankton community is mainly dominated by small cells, which in most cases have low intracellular pigment concentrations with high proportions of photoprotective carotenoids. These characteristics of the phytoplankton determine a low packaging effect and a higher absorption in the blue than in the red region of the spectrum (e.g., Stramski and Morel, 1990; Sosik and Mitchell, 1995; Bouman et al., 2000). Therefore, a certain correlation among environmental variables (e.g., temperature and irradiance) and absorption characteristics of phytoplankton can be expected, and indeed have been observed in several studies (e.g., Yentsch and Phinney, 1989; Bouman et al., 2003). Following this, we would expect here to find that cruises showing the highest ratios blue/red in the phytoplankton absorption would coincide with those having the strongest thermocline, and on the other extreme those having the flattest spectra would be the cruises showing homogeneous temperature profiles, with intermediate cases in both variables forming a third group. Nevertheless, we actually found that significant changes in the phytoplankton absorption spectra occurred in some cases independently from changes in the temperature conditions.

Variations in the composition of phytoplankton populations, as well as variations in their physiological status, are complex and depend on a number

of known and most probably some unknown interactions with environmental variables, and with other biological components in the ecosystem. It should also be taken into account that a biological property measured at a given time may represent an acclimation to previous environmental conditions, rather than to those measured at the time of sampling. The fact that living organisms encompass, in a fine regulation, all these complex temporal physical—biogeochemical interactions, make it difficult to discern universal relationships between a given biological property (e.g., absorption coefficient) and a physical variable (e.g., temperature). Thus, some expected trends emerge from large data sets gathering samples from many different environmental conditions (following natural proportions; i.e., not biased to emphasize any peculiar case), where significant—even if sometimes weak- correlations between optical and environmental variables are found (e.g., Yentsch and Phinney, 1989; Bouman et al., 2003). On the other extreme, significant -and sometimes strong- correlations are usually found in confined sets of samples representing a particular situation, such as a defined gradient in a vertical profile or in a horizontal frontal area (Sosik and Mitchell, 1995). These constrained relationships may in some circumstances be of a different trend than the one normally expected representing a particular situation. For example phytoplankton community structure may be regulated by grazing (Goericke, 2002) producing anomalous low ratios $a_{ph}(440)/a_{ph}(676)$ at high temperatures in the Arabian Sea (Bouman et al., 2003). That is why, when dealing with intermediate-size data sets results may be confound, not always showing significant correlations between biological and environmental properties. In this case, it is hoped that more robust patterns may emerge after enough data be gathered through the time series study at the EPEA station.

3.6. Satellite-derived products

The greatest utility of satellite data is to fill in gaps between the in situ sampling and to provide a synoptic picture of the region. The availability of 8 years of satellite ocean colour data allows us to study interannual changes and regional effects on the EPEA time series station. But the satellite data products have to be validated against in situ data before extensive analyses are undertaken. Satellite-derived chlorophyll concentrations can be validated directly by in situ measurements.

A comparison between the in situ measured chlorophyll-*a* concentration and that derived from the satellite showed that while there is a small bias and offset in the correlation between the two, the high r^2 indicates linearity in the relationship ($r^2 = 0.94$, Fig. 8). The largest difference between satellite derived and in situ chlorophyll concentrations was observed on 18 October when *Eutreptiella* dominated the phytoplanktonic community (Fig. 8). However, it is unclear whether the dominance of this species was the cause of this difference in surface optical properties. A careful examination of the satellite imagery (Fig. 9a) shows that the sample location was just at the edge of the bloom and that the adjacent pixel, 1 km away, has a chlorophyll concentration of 1.49, compared to the in situ value of 1.53. If this value were used instead, the regression coefficient improves to 0.995. Currently, clouds limit the number of direct comparisons, especially in the winter. Only 9 of the 19 cruises had corresponding satellite values and there were no matches between June and October. However, both satellite data from days bracketing the in situ sampling day as well as level 3 binned data suggest that there may be large differences between in situ and satellite-derived values in winter (Figs. 10 and 11). Thus more matches from the winter may make a difference to our conclusion that the OC4 algorithm is adequate in these waters.

Regarding the influence of particular phytoplankton groups, the increase of backscattering due to the calcite plaques of coccolithophorids on satellite images of *Chla* is well known (Brown and Yoder, 1994). Different species of coccolithophorids have been recorded in the South Atlantic (Gayoso, 1995), and at the EPEA station in particular (Negri et al., 2003). Nevertheless, coccolithophorids were never found in significant in cell concentrations at the EPEA station during this first studied year.

The 9 km-8 day binned level III data from September 1997 to June 2005 (Fig. 11) was used to derive an annual cycle of the mean and standard deviation of chlorophyll concentration at the EPEA station location. Neither this 8-year mean of 8 day-9 km data nor the daily 1-km data from 2000–01 bracketing the days of the in situ sampling show the clear wintertime peak seen in the in situ data. This could be due to extremely cloudiness during winter

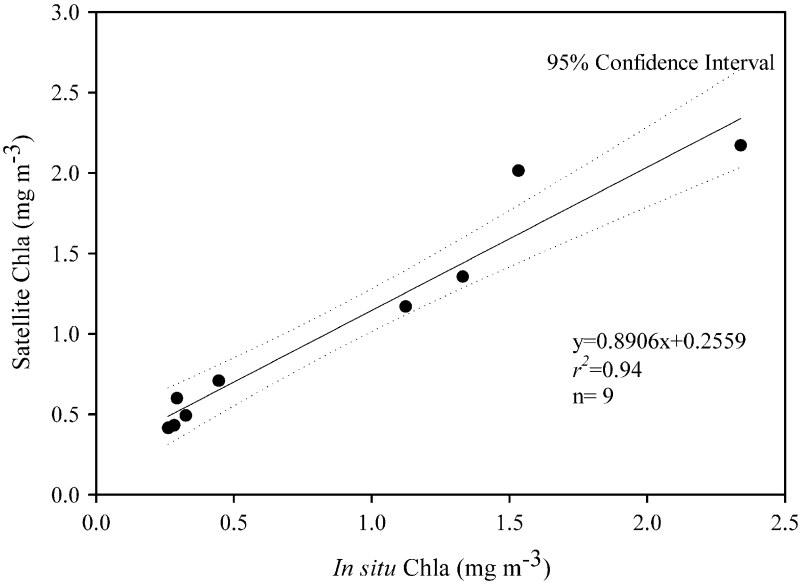

Fig. 8. Regression between chlorophyll-*a* concentration values measured in situ and those estimated by high-resolution remote sensing, for the 9 points where there was a match up.

in this region. We can speculate that at least part of this marked difference between satellite and in situ chlorophyll during winter may be caused by the type of phytoplankton present at the time. Specifically during this year there was a bloom of *Coscinodiscus wailesii* which, as previously mentioned, due to its large size has a very low-specific absorption coefficient deviating from what is normally assumed by the tested satellite algorithms. On the other hand, both sources of satellite data (high and low resolution) show what seems to be a secondary peak in the late spring (mid-December to mid-January) that is not seen in the single year of in situ data available. A comparison of the daily 1-km data and the 8 day-9 km data suggests that the in situ data may have missed this secondary peak because of the spatial patchiness of the blooms. This region is extremely dynamic with many patchy blooms, dramatic examples of which can be seen in Fig. 9a–e. For example, an examination of the 1-day imagery shows that the high standard deviations seen between late September and early December (days 240–330) of the 8-year mean is due to the year to year variability in the location of filaments of high biomass associated with intrusion of Middle Shelf Waters. This work shows that binned data can sometimes be better tool to understand long-term seasonal and inter-annual trends than high resolution spot samples.

4. Concluding remarks

These first results show that this coastal area, one of the most populated along the Argentinean coast, is subjected to a highly dynamic oceanographic regime (Carreto et al., 1995; Lucas et al., 2005) and to high variations in the bio-optical properties influencing the colour of the waters. There were clear patterns of change in the physical conditions throughout the year, as evidenced by the formation and rupture of a seasonal thermocline. These physical variations were accompanied by changes in the transparency of the water column as determined by the detritus absorption. Although CDOM dominated absorption at the surface throughout the year, its variations were not related to irradiance or temperature conditions. There were marked variations in the absorption properties of the phytoplankton, although these were not strictly related to the stability of the water column, but they were related to the light intensity at the surface. Variations in the shape of the absorption spectra of phytoplankton were significantly related to the structure of the phytoplankton community, especially to the cell-size. Evidence is showed that these changes in the phytoplankton composition may significantly affect the remote-sensing estimation of *Chla* in the region.

These results, hence, reinforce the relevance of continuing and strengthen the time series studies, to

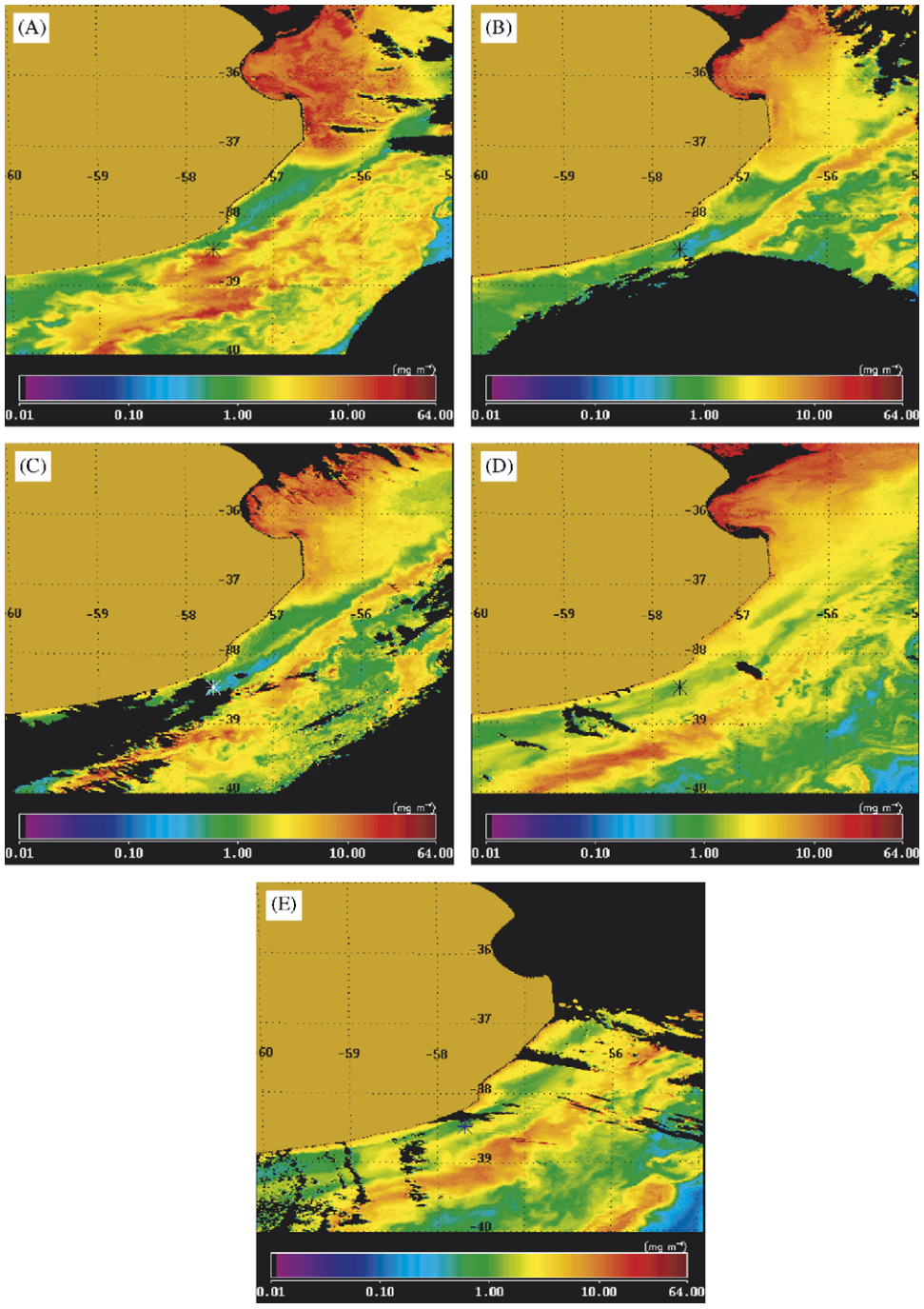

Fig. 9. Level 2, 1-km SeaWiFS imagery of chlorophyll concentration. The location of the EPEA station is marked by *. (A) 18 October 2000—The EPEA station sampled on the same day is at the very edge of the high chlorophyll patch with markedly lower chlorophyll concentration at the adjacent pixel. (B) 2 November 2000—The EPEA station is at the edge of a low chlorophyll region although the satellite derived value at the exact location sampled in situ the next day is higher. (C) 3 November 2000—The low chlorophyll water has drifted closer to the EPEA station and the satellite-derived value is closer to that measured in situ. (D) and (E) 16 and 19 November 2000—day before and two days after the in situ sampling with large changes in chlorophyll values in the region of the EPEA station.

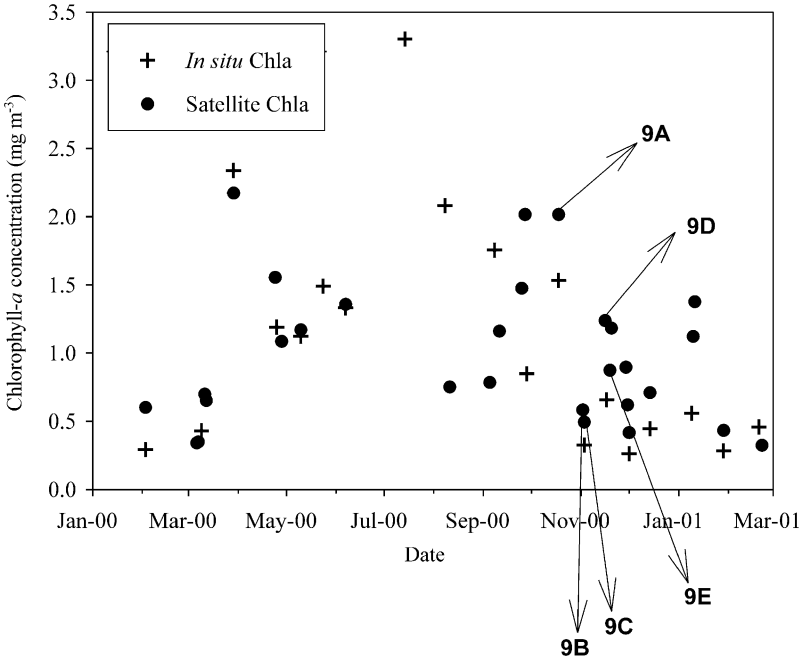

Fig. 10. Level 2, 1-km SeaWiFS-derived chlorophyll-*a* concentrations bracketing the dates of the EPEA in situ sampling. The points corresponding to the images shown in Fig. 9 are marked.

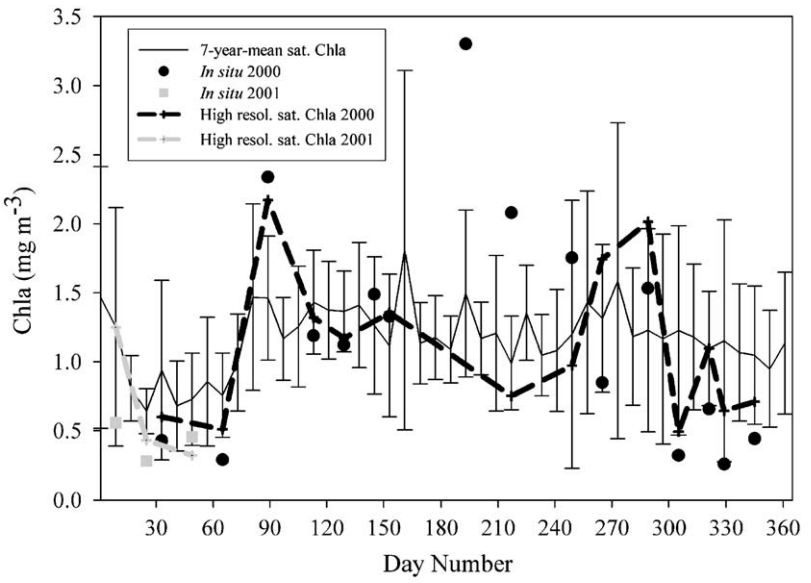

Fig. 11. An annual cycle of chlorophyll-*a* concentration derived from the 7 year average Level 3, 8-day, 9-km binned SeaWiFS data. The error bars mark the standard deviation about the average. The level 2 SeaWiFS data as well as the in situ measurements from the EPEA station for 2000–2001 cycle are also shown.

analyse in more detail variations in in situ optical properties, such as reflectance and absorption at different bands (which can be measured by remote sensing) that could be related to environmental variables, such as temperature or irradiance (which can also be measured by remote sensing). This will help to improve the satellite estimation of *Chla*, by separating the effect of detritus and CDOM, and

also the bias caused by variations in optical properties of different taxonomic groups of phytoplankton allowing the use of more detailed models (e.g., Stramski et al., 2001). The impact of variations in phytoplankton absorption properties, in turn, could be exploited to gain information about phytoplankton composition at different times of the year, and under varying environmental conditions (e.g., Sathyendranath et al., 2004). In the long run, decadal time span, this information can be used to distinguish the effect of normal natural variations on the phytoplankton abundance and composition, and that caused by particular natural (extreme wind mixing, sporadic incursions of other water masses) or anthropogenic generated (increase in land drainage with high contents of organic, toxic or nutrient compounds) phenomena.

This constitutes one of the final goals not only of the study at EPEA station, but also at a regional scale, of the ANTARES network. It is expected that simultaneous progress in in situ time series studies, as well as the possibility to extrapolate in space and time using remote sensing information, would offer the possibility to follow changes along the marine ecosystems around South America.

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