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Optical properties and light penetration in the waters of the Gulf of Trieste (north Adriatic Sea)

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ABSTRACT This is the first systematic study on the relationships between optical properties and hydrological and biological conditions in the Gulf of Trieste, north Adriatic Sea. The inherent and apparent optical properties (IOPs and AOPs) have been regularly monitored since January 2002, together with traditional hydrological parameters, with the aim of investigating the spatial and temporal patterns of bio-optical properties in this shallow coastal area. The results of this two-year monitoring point to high temporal variability of this shallow coastal ecosystem with regard to its optical characteristics, beside the well-known variability in hydrological and biological phenomena. The most prominent physical and bio-optical signals observed were associated to seasonal variability, however, several important events interrupted the seasonal cycle. Continental inputs, and phytoplankton blooms are the dominant sources of optical variability and these events can strongly vary in duration and spatial extent.

1. Introduction

This research focuses on the Gulf of Trieste, north Adriatic Sea, which is the northernmost part of the Mediterranean Sea. Its position, the presence of endemic and endangered species [e.g. *Fucus virsoides, Platictichthys flesus italicus, Cymodocea nodosa*: Castellarin *et al.,* (2002)] and, most of all, its sensitivity to anthropogenic perturbations due to intense harbor, fishing, fish farming and touristic activities make the entire Gulf of Trieste an environmentally significant area and have emphasized the need for an intense and long-lasting multidisciplinary monitoring to track changes in environmental quality. In recent times the Gulf of Trieste has, in fact, experienced several environmental changes such as recurrence of red tides and of toxic algal blooms (Mozetic *et al.,* 1997; Sellner and Fonda Umani, 1999; Cabrini *et al.,* 2000), increased frequency in mucus aggregate formation (Long *et al.,* 1998; Azam *et al.,* 1999), seasonal bottom oxygen depletion (Orel *et al.,* 1993; Malej and Malacic, 1995) and seagrass die off (Odorico and Bressan, 1992; Odorico, 1998). In the frame of a joint research with several local institutions (WWF-Natural Marine Reserve of Miramare, Marine Biological Laboratory-LBM, National Institute of Oceanography and Experimental Geophysics-OGS), physical, chemical and biological parameters are being regularly monitored through a variety of techniques including real-time meteo-oceanographic data from profiling buoys (MAMBO-OGS buoy), weekly CTD casts, discrete water sampling for chemical and biological analysis, acoustic tracking, scuba diving surveys and visual census of marine life (Bussani *et al.,* 2003; Codiglia *et al.,* 2003; Nair *et al.,* 2003; Picciulin *et al.,* 2003), in a time series station at the border of the WWF - Natural Marine Reserve of Miramare (NMRM).

The acquisition of bio-optical data has been recently introduced as a new tool for rapid assessment of seawater properties, of phytoplankton bloom characteristics (Lipizer *et al.,* 2004) and for a possible future comparison with remotely sensed data of ocean color. Optical properties are especially informative because they are determined mainly by three parameters (colored dissolved organic matter, phytoplankton chlorophyll and suspended particulate matter), which are diagnostic indicators of a variety of natural and anthropogenic stressors (Gallegos and Jordan, 2002).

The overall objective of this work is to map the temporal patterns of bio-optical properties in the Gulf of Trieste in diverse seasonal and hydrological conditions.

To approach this objective, weekly acquisitions of continuous profiles of inherent optical properties (IOPs) and of apparent optical properties (AOPs) have been carried out since January 2002, simultaneously with traditional hydrological and biological measurements in a fixed station at the border of the NMRM. According to the definition proposed by Mobley (1994) IOPs (absorption, attenuation and scattering of light) depend only on the substances comprising the water medium; on the other hand, AOPs (irradiance, radiance and their vertical attenuation coefficients) depend both on the medium and on the directional structure of the ambient light field.

2. Materials and methods

The Gulf of Trieste is a semi-enclosed basin, located in the northernmost and shallowest part of the Adriatic Sea, with a maximum depth of 26 m (Mozetic *et al.,* 2002). The hydrodynamical and trophic conditions of the basin are characterized by very large interannual, seasonal and shorter term variability due to the peculiar tidal regime of the area (Malacic *et al.,* 2000; Malacic and Viezzoli, 2000), to the alternation between mixing and stratification processes of the water column, to the strong easterly winds characteristic of the northern area (Bora) and particularly intense in the Gulf of Trieste, and to the variable riverine contributions. The general circulation in the deep layer is usually cyclonic, while it is opposite in the surface layer (Stravisi, 1983a), with an intermediate layer in between; however, local atmospheric forcing (winds) and river plumes can strongly modify this overall scheme (Ursella *et al.,* 2000; Malacic and Petelin, 2001; Malacic, 2003). The whole area is strongly affected by river runoffs (Stravisi, 1983a), especially along the shallow north-western coast (Isonzo river), by the presence of several submarine freshwater springs and by the urban and industrial contributions of the towns (Koper, Trieste, Monfalcone) along the coast (Barbieri *et al.,* 1999). All these factors determine high interannual variability of biological components (Malej *et al.,* 1995*,* 1997; Mozetic *et al.,* 1998).

From January 2002 to December 2003 vertical profiles of hydrological and optical properties were carried out monthly from January 2002 and weekly from May 2002, in general, three times per day, for a total of 98 profiles in 2002 and 91 in 2003, at a time-series station (C1) located at the outer limit of the Natural Marine Reserve of Miramare, in the Gulf of Trieste, northern

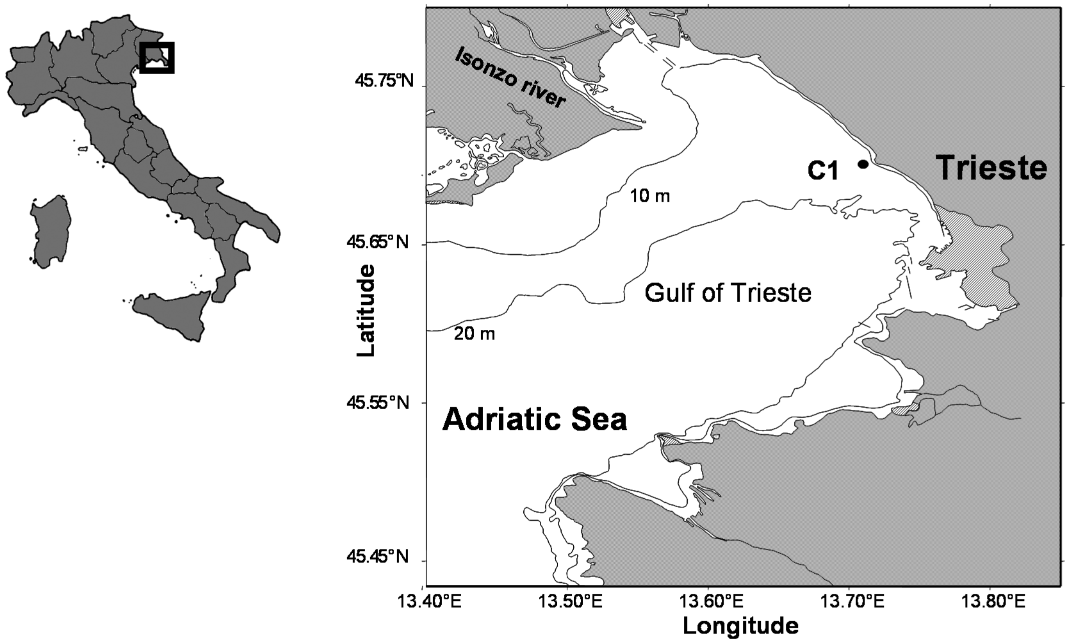

Fig. 1 - Map showing the Gulf of Trieste and the position of the sampling station C1.

Adriatic Sea (Fig. 1). The station is 17 m deep and is located at approximately 300 m from the coast (45° 42' 03.5" N – 13° 42' 36.2" E); it was chosen as a site for a long time-series of observations on physical, chemical and biological properties (Cataletto *et al.,* 1995; Mozetic *et al.,* 1998) and is close to the position of the meteo-oceanographic buoy MAMBO-OGS, which profiles the water column 8 times per day. Although it is close to the coast, this station can be considered representative of the gulf, as its depth corresponds to the gulf mean depth and its general thermohaline properties do not differ remarkably from the center of the Gulf of Trieste (Celio *et al.,* 2002).

Hydrological properties were measured with an Ocean Seven conductivity-temperature-depth profiler (CTD), model 316, manufactured by Idronaut. The CTD probe was equipped with a Seapoint fluorimeter which was calibrated at least seasonally with a series of different concentrations of natural phytoplankton samples, or, alternatively, of phytoplankton cultures. A wide range of concentrations of phytoplankton cells, covering values usually encountered in the gulf, was prepared and measured with the Seapoint fluorimeter; immediately after, samples were filtered and chlorophyll *a* concentration was determined fluorimetrically following extraction in acetone according to Strickland and Parsons (1972), with modifications as reported by Welschmeyer (1994), using a Turner TD-700 fluorimeter calibrated spectrophotometrically with pure Chl *a* (Sigma Chemical Co.). The discrete chlorophyll a samples measured in the laboratory were mainly used as a comparison with the Seapoint fluorescence profiles. The significant correlation between chlorophyll *a* concentration determined from discrete samples and Seapoint fluorimetric data ($R^2 > 0.8$, n = 156) allowed us to use continuous fluorimeter profiles in order to follow the temporal and vertical evolution of chlorophyll *a* concentration with greater resolution.

For hydrological, as well as for optical profiles, mean and standard deviation were calculated for every meter starting from 0.50 m below the surface. Values outside the range determined by $\pm$ 3 standard deviation (3 σ) from the estimated mean were rejected ("common processing").

Vertical profiles of the following IOPs: spectral absorption [$a(\lambda)$] and attenuation [$c(\lambda)$] coefficients were acquired at nine discrete wavelengths (412, 440, 488, 510, 532, 555, 650, 676, 715 nm) using a flow-through absorption-attenuation meter (AC9, WET Labs). The equipment was calibrated on a regular basis at the Oceanographic Calibration Center at OGS (CTO), using optically pure water as a reference (purified by reverse osmosis and subsequently electro-deionized with a Millipore ELIX3 System) and the instrument drift was monitored according to the manufacturer's specifications. Raw data provided by the acquisition software (Wetview 5.0) were corrected for *in situ* temperature and salinity conditions according to Pegau and Zaneveld (1994) and Pegau *et al.* (1997) and, as a final step, absorption data were corrected for the scattering error using method III described by Zaneveld *et al.* (1994). After temperature, salinity and scattering error corrections, spectral scattering coefficients [$b(\lambda)$] were finally derived as the difference between $c(\lambda)$ and $a(\lambda)$.

AOPs [vertical profiles of downwelling irradiance $E_d(z,\lambda)$ and of upwelling radiance $L_u(z,\lambda)$] were measured with a Satlantic spectroradiometer (OCI-200 and OCR 200) equipped with seven spectral wavebands (412, 443, 490, 510, 555, 665 and 683 nm, spectral bandwidth 10 nm). In order to take into account any variations in incident light during instrument deployment, downwelling irradiance at seasurface $E_s(0,\lambda)$ was measured during vertical profiling of E_d and L_u with the Satlantic OCR-507I irradiance sensor mounted on the top of the boat, away from any superstructures (antenna mast and navigation sensors). The radiometers were deployed on the sunny side of the ship with a 1m extension boom to reduce shadowing effects. Particular attention was dedicated to prevent bottom impact and the subsequent sediment resuspension.

The radiometers were factory calibrated by the immersion factor (Mueller and Austin, 1995) and by checking the dark currents at the NMRM Laboratory. Using ProSoft 6.3d software, raw data were converted into engineering units and adjusted for the dark current obtained from the calibration file (Level 1 to level 2 processing).

Radiometric data processing consisted in normalization of underwater irradiance and radiance with the mean values of surface irradiance $E_s(0,\lambda)$ at all seven wavelengths. Missing data and spikes were checked and irregular profiles were rejected. Radiance and irradiance for each meter were obtained by Least Square Linear Regression of the logarithmic profile, after the "common processing", and vertical attenuation coefficients were calculated as the local slope (Smith and Baker, 1984, 1986). Several methods were tested for the sub-surface value estimation. The best results were obtained by discarding the data higher than the probable error (PE = 0.6745 σ) from the estimated first layer mean.

PAR irradiance was calculated by trapezoidal integration of E_d between 400 and 700 nm and PAR attenuation coefficients (K_{PAR}) have been computed at every meter.

Discrete samples for fluorimetric analysis of chlorophyll *a* (Chl *a*) and for filter pad absorption via spectrophotometry were collected from 6 depths (0, 1, 5, 10, 13 and 15 m) using Niskin bottles, collected on GF/F glass-fiber filters and stored at –20°C until they were analysed in the laboratory.

In the laboratory, absorption spectra of the suspended sediment were determined with an HP-8453 diode array spectrophotometer associated with a Labsphere RSA-HP integrating sphere, following the Transmittance-Reflectance method described by Tassan and Ferrari (1995). After optical density measurements on untreated samples, filters were soaked in 15% sodium hypochlorite solution (1% active chloride) for removal of pigment absorption according to Ferrari and Tassan (1999), rinsed with distilled water and subsequently analyzed for absorption of the inorganic fraction. Absorption coefficients due to the extracted phytoplankton pigments were derived as the difference between measurements before and after sample depigmentation.

We will concentrate on the absorption coefficients at 412 and 676 nm, and on downwelling PAR irradiance normalized for surface values within the large optical data set available (total absorption, attenuation and scattering coefficients over 9 wavelengths, inorganic and organic particulate absorption spectra, downwelling irradiance and upwelling radiance over 7 wavelengths and PAR irradiance) . The 412 and 676 nm wavelengths have been selected because they are absorbed, respectively, by color detrital matter (CDM), which is the sum of color dissolved organic matter (CDOM) and nonalgal particles (NAP), and by phytoplankton (Claustre *et al.,* 2000).

3. Results and discussion

3.1. Hydrological properties

Hydrological properties measured at station C1 from January 2002 are presented in Fig. 2.

The seasonal cycle is characterized by large fluctuations between the winter vertical homogeneity, with the coldest temperatures generally measured in February (6.5°C, February 2003) and constant over the entire water column, and the summer stratification, with the highest temperature measured at the surface in August (27.3 °C, August 2003) (Fig. 2a). The haline stratification is strongly dependent upon precipitation and continental inputs, with the greatest dilution usually occurring in late spring and in autumn (Fig. 2b). Freshwater contributions are mainly due to the River Isonzo which strongly affects salinity, inorganic nutrient and terrigenous matter distribution in the upper layer, especially in summer and autumn when abrupt peaks in river discharge rapidly dilute surface salinity at the C1 station (Fig. 2b). The flow pattern of the continental inputs is, however, strongly related to the prevailing surface circulation which can reverse during strong Bora episodes as is often observed in winter when the Isonzo plume exits from the gulf as a narrow coastal jet along the Italian coast (Malej *et al.,* 1995; Malacic and Petelin, 2001). In addition, precipitation and riverine inputs are subject to great interannual variability: for instance, the meteorological situation encountered in 2003 was characterized by extremely low precipitation (Fig. 3), with a pattern close to the minimum annual cumulative precipitation reported in the period 1841 – 2002 (Stravisi, 2005) and a mean annual River Isonzo river discharge (37 $m^3 s^{-1}$ in 2003) was less than half the previous year (76 $m^3 s^{-1}$, from Unità Operativa Idrografica-Udine). In correspondence with this prolonged period of draught, salinity values higher than 37.7 were measured along the whole water column during most of the year, with a maximum of 38.2 in the deeper layer, which indicates the advective flow of high salinity waters from the south, as reported in an earlier study (Celio *et al.,* 2002) in similarly dry

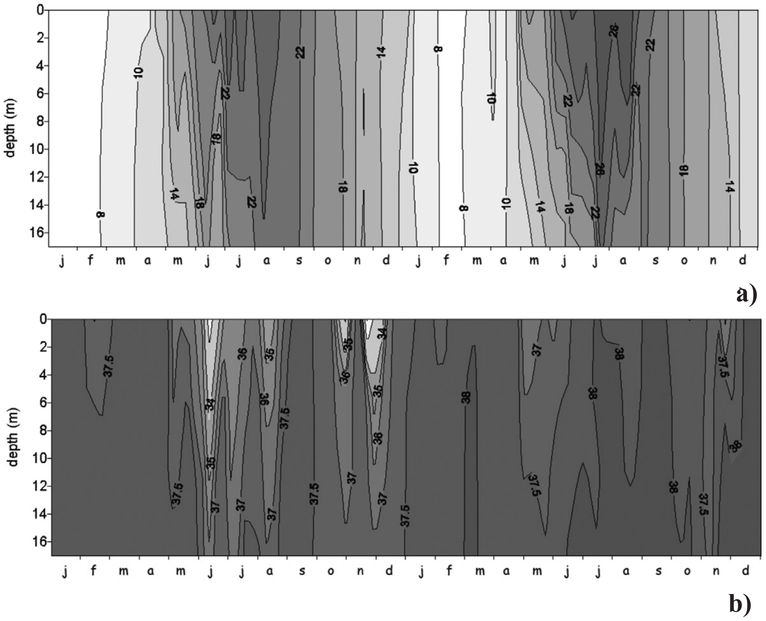

Fig. 2 - Time series of temperature (a) and salinity (b) measured in the C1 station from January 2002 to December 2003.

conditions.

A common feature, observed in both years, is that the stratification gradually brought about by vernal heating and by freshwater inputs is rapidly disrupted due to strong wind mixing events, commonly observed at the end of the summer (Bussani *et al.,* 2003). In both years, in fact, an abrupt change in vertical stratification is observed at the beginning of September.

3.2. Chlorophyll a

The seasonal distribution of chlorophyll *a*, determined by the Seapoint fluorescence sensor, reflects the hydrological structure of the water column. In periods of vertical homogeneity, chlorophyll concentration is constant over the entire water column, while in periods of stratification chlorophyll accumulation is usually detected in the deeper layers (Fig. 4). The onset, the duration and the intensity of the algal bloom show interannual variability which is due to temporal shifts in the establishment of thermohaline stratification, in water column mixing, in differences in riverine contributions and, as a consequence, in nutrient availability, as is typical for mid-latitude temperate coastal areas (Cushing, 1989; Longhurst, 1995; Lucas *et al.,* 1998).

The results of the monitoring carried out in the WWF Natural Marine Reserve of Miramare indicate that the onset of algal biomass accumulation, leading to chlorophyll concentrations higher than 1.0 μg l^{-1}, is a common feature in late autumn and winter, as already reported for the Gulf of Trieste by Mozetic *et al.* (2002), for the coastal waters of the north Adriatic by Totti and Artegiani (2001) and for other coastal and estuarine ecosystems (Labry *et al.,* 2001; Gohin *et al.,* 2003). On the other hand, the typical spring bloom mainly due to Diatoms, which is a general

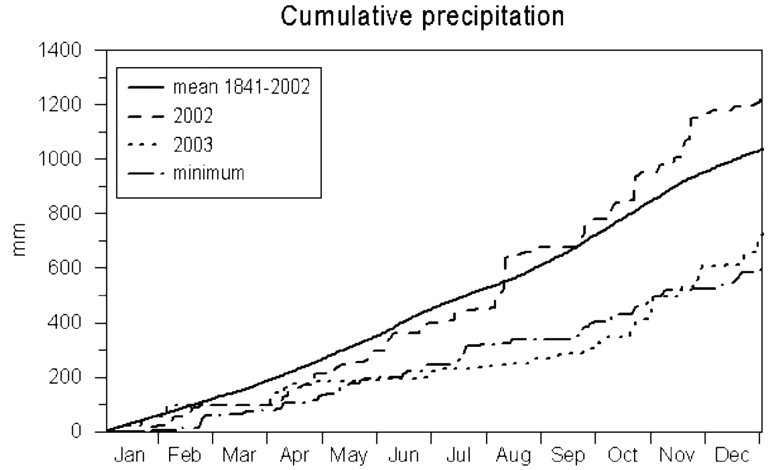

Fig. 3 - Cumulative precipitation measured during the years 2002 (dashed line), 2003 (dotted line), the mean calculated between 1841 – 2002 (solid line) and minimum values of the period 1841 – 2002 (dash-dot line) [data from: Stravisi and Purga, (2003; 2004) and Stravisi, (2005)].

feature of the north Adriatic Sea, was not encountered during this study. In both 2002 and 2003, the highest chlorophyll concentrations were observed during a late summer bloom, with chlorophyll concentrations higher than 8.0 μg l^{-1} in August 2002 and higher than 4.0 μg l^{-1} in September 2003. The August 2002 bloom was the most intense of the whole investigated period; it was, however, a very rapid event which lasted less than a week, as evidenced from three surveys performed within ten days of each other and as revealed by continuous fluorimetric data recorded by MAMBO-OGS profiling buoy (OGS Annual Report, 2003). The lower intensity of algal blooms in 2003 is ascribable to the extremely low freshwater contribution of both riverine and meteorological origin and therefore to the reduced inorganic nutrient input which sustains primary production processes.

The observed difference in the typical bloom dynamic is related to the high inter-annual biological variability due to complex interactions between wind regime, freshwater – nutrient-rich run-off (low in both springs 2002 and 2003), species competition and food web structure (classical versus microbial food web).

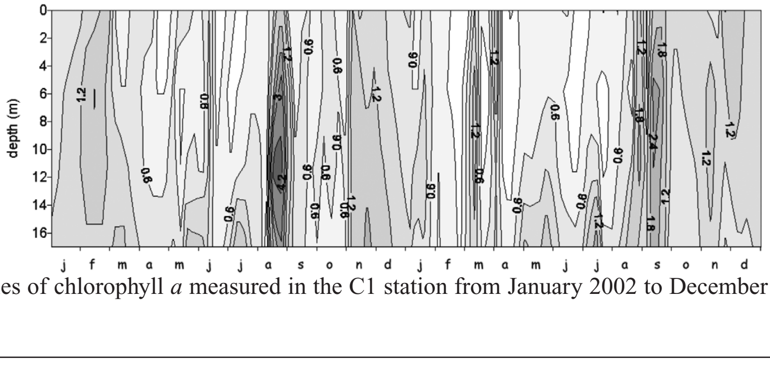

Fig. 4 - Time series of chlorophyll *a* measured in the C1 station from January 2002 to December 2003.

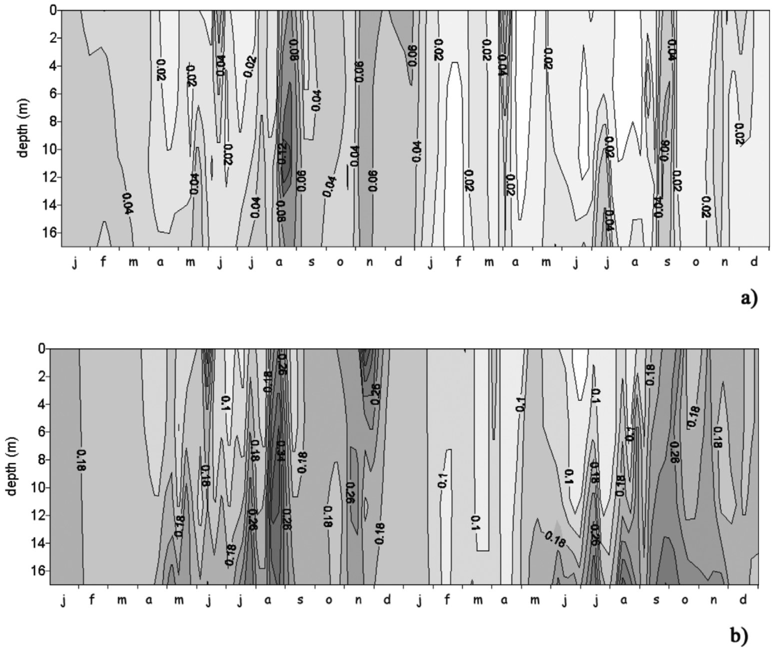

Fig. 5 - Time series of absorption coefficient at 676 nm (a676, 5a) and at 412 nm (a412, 5b) measured in the C1 station from January 2002 to December 2003.

3.3. Optical properties

IOPs and AOPs varied both temporally and spatially (i.e. along the water column) during the monitored period (Figs. 5, 6 and 7). Taking into account the time series of absorption at 676 nm (Fig. 5a), in both years, the lowest values are generally encountered in spring and early summer, with an abrupt increase at the end of the summer which was particularly remarkable in August 2002, when the highest values (a676 = 0.22 m^{-1}) were recorded. This almost tenfold increase in a676 was associated with the most pronounced algal bloom observed during this study (Fig. 4). When considering both the temporal and vertical pattern of a676 (Fig. 5a) and chlorophyll *a* (Fig. 4) it can be seen that the absorption at 676 nm generally covaries with chlorophyll, as confirmed by the relatively good correlation between the two parameters ($R^2 > 0.85$, n = 600). In fact, although any substance present in the water interferes with IOPs, light at 676 nm is selectively absorbed mainly by chlorophyll *a*. As a general pattern, absorption coefficients at 412 nm closely follow those at 676 nm (Fig. 5); some differences between the temporal (last months of 2003) and vertical distribution (bottom layer) may be ascribed to a larger contribution of particulate and dissolved organic matter due to sediment resuspension (bottom layer in May 2002, June and October 2003) and to terrigenous input associated to riverine contribution (surface layer in November 2002), as indicated by the lower surface salinity (Fig. 2b).

In the cases where the strongest difference between a412 and a676 was observed (for instance in early autumn 2003), the spectra of total absorption (particulate and dissolved) measured *in situ* were compared with those of particulate absorption from discrete bottle samples (Fig. 6). As a676 is mainly due to chlorophyll and a412 is an indicator of colored detrital matter (CDM) (Claustre

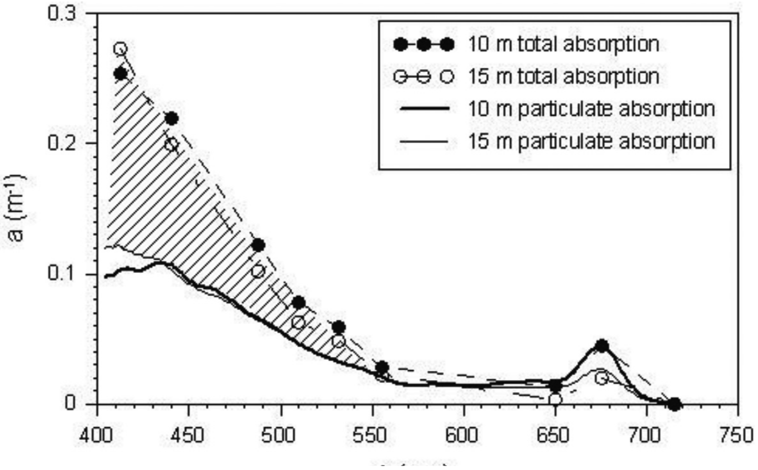

Fig. 6 - Absorption spectra of total (dissolved + particulate) matter (dashed lines with circles) and of particulate (solid lines) matter measured at 10 m (filled circles, and bold solid line), chlorophyll concentration at 3.52 µg l^{-1}, and at 15 m (open circles, thin line), chlorophyll concentration 1.10 µg l^{-1}.

et al., 2000), the comparison allows us to recognize the different contributions of these two important components to the light absorption spectrum. In Fig. 6, dashed lines with circles represent total absorption (dissolved and particulate matter measured with profiling AC9) while solid lines represent the absorption spectrum of particulate matter (discrete bottle data), both at 10 and 15 m depth, respectively. The large difference at shorter wavelengths between total (dashed lines) and particulate absorption (solid lines) indicates the high contribution of color dissolved matter (CDOM) to total absorption (shaded area). In fact, considering a412, absorption of CDOM (total absorption – particulate absorption) at both depths corresponds to 0.16 m^{-1}, which represents 61 ad 57% of the total a412 at 10 and 15 m, respectively. Considering annual mean values of light absorption at 412 nm, the average contribution of CDOM to total color detrital matter (CDM) corresponds to 29% in 2002 and to 42% in 2003. The high load of dissolved organic matter has already been documented for the north Adriatic (Lipizer *et al.,* 1997, 1999; Terzic *et al.,* 1998; Cozzi *et al.,* 1999) and is associated to the major degenerative phenomena observed in the basin such as bottom hyopoxia and mucilage accumulation (Degobbis *et al.,* 1995; Azam *et al.,* 1999). The higher contribution of CDOM in 2003 fits well with the general conditions of low nutrient-rich freshwater inputs, therefore with a shift from the classical towards the microbial food web, mainly fuelled by recycled and organic compounds (Fonda Umani, 2000; Puddu *et al.,* 2000).

On the other hand, the difference in the peaks at 676 nm between 10 and 15 m is correlated with chlorophyll concentration (Figs. 4 and 5a), with a higher peak at 10 m depth, corresponding to 3.52 µg l^{-1} chlorophyll, and a lower peak at 15 m (1.10 µg l^{-1} chlorophyll).

The information provided by the temporal and spatial distribution of downwelling PAR irradiance allows us to understand how light propagates in the waters of the Gulf of Trieste and to determine the quantity of light available for the marine ecosystem. The pattern displayed by normalized PAR irradiance, as a percentage of the surface value, presents an overall seasonal

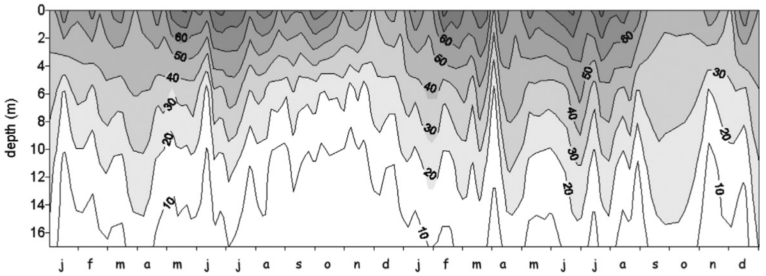

Fig. 7 - Time series of normalized PAR irradiance.

trend: light penetration is generally lower in late autumn and winter, while it reaches the highest values in spring (Fig. 7). Considering the isopleths corresponding to 10% of incident PAR, it deepens from 8 m in January 2002 to 15 m in June and shifts up again at the end of the year to 8 m in November. The same general pattern, but more pronounced and occurring in advance, is recognizable also in 2003 (low light penetration in early winter and high in spring). In both years, however, a short term variability due to meteorological and biological phenomena is clearly recognizable. An uplifting of the 10% isopleth is, in fact, observed in connection with particular events such as the continental inputs in early June 2002 (Figs. 7 and 2b) and the intense algal bloom observed in August 2002 (Figs. 7 and 4).

Finally, the transmittance in percent per meter as a function of wavelength has been calculated for each year in order to classify the water types in the NMRM. Fig. 8 presents the annual mean and standard deviation of the transmittance calculated within the water layer free from bottom reflection effects. Comparing the two monitored years, the mean transmittance in 2003 is higher than in 2002, due to extremely lower continental inputs and precipitations (Figs. 2b and 3). According to the Jerlov classification (Jerlov, 1976), the NMRM waters lie within the first and the third classes of the “coastal waters”, in agreement with the results of an earlier study carried out in the Gulf of Trieste in the period 1951 – 1980 (Stravisi, 1983b).

4. Conclusion

This is the first systematic study on the relationships between optical properties and hydrological and biological conditions in the Gulf of Trieste. The results of the two-year monitoring carried out in the waters of the Natural Marine Reserve of Miramare point at a high temporal variability of this shallow coastal ecosystem with regard to its optical characteristics, beside the well-known variability in hydrological and biological phenomena. In fact, seasonal and interannual variability in the general circulation of the water masses, in precipitation, in continental inputs, in timing of thermohaline stratification and in phytoplankton bloom evolution all contribute in shaping the bio-optical patterns in the Gulf of Trieste. From the comparison between seasonal average values, interannual variability in optical, as well as in biological properties is more than twice that between seasons in the same year. The most prominent bio-optical signals observed were associated with seasonal patterns of hydrodynamical properties,

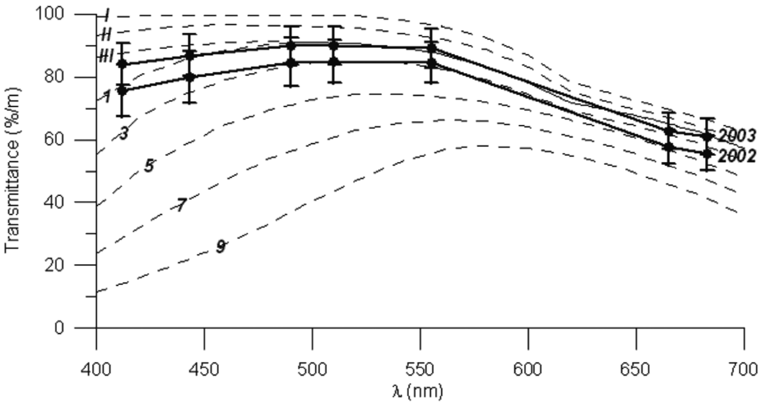

Fig. 8 - Annual mean transmittance calculated for 2002 and 2003, superimposed on Jerlov water types (from Jerlov, 1976).

with high attenuation, thus lower light penetration, during autumn and winter, and higher light penetration in spring and summer; however a shorter term variability due to meteorological and biological phenomena is superimposed on the seasonal signal.

As other coastal environments reported (Chang and Dickey, 2001; Sosik *et al.,* 2001), the timescales of optical variability in the shallow waters of the Gulf of Trieste are generally shorter and episodic, with high-amplitude fluctuations that often mask the seasonal cycles. Continental inputs and phytoplankton distribution are the dominant sources of optical variability, with phytoplankton blooms being the most important factor.

This research has focused mainly on the effect of phytoplankton blooms on optical properties in general, without distinction between different algal species and physiological states. The large data set collected during the monitored period by the several institutions involved will be further investigated to identify optical signatures of different algal blooms (Diatoms, Dinoflagellates), to study relationships with different particulate and dissolved organic compounds (particulate and dissolved organic carbon, nitrogen and phosphorous) and to compare *in situ* data with remotely sensed ocean color information.

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