

## Surface chlorophyll in the Black Sea over 1978–1986 derived from satellite and in situ data

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### Abstract

Absolute values of chlorophyll *a* concentration and its spatial and seasonal variations in the Black Sea were assessed by using satellite CZCS and in situ data. Since the satellite CZCS had operated for the 1978–1986 period, CZCS data was used for assessing the past state of the Black Sea just before the onset of drastic changes observed in late 1980s. The approach used for the calculation of the absolute values of chlorophyll *a* concentration from CZCS data was based on the direct comparison of in situ chlorophyll *a* data and those of CZCS and by applying the algorithm developed for the transformation of CZCS data into chlorophyll *a* values. CZCS Level 2 data related with pigment concentration having a spatial resolution of 1 km at nadir were used. The daily Level 3 files were derived by binning Level 2 values into 4-km grid cells and the monthly and seasonal Level 3 files were created by averaging the daily Level 3 files over the corresponding period. In situ chlorophyll *a* data were obtained by spectrophotometric and fluorometric methods in 15 scientific cruises over the 1978–1986 period. Total number of ship-measured data used for the comparison with those CZCS values was 590.

Chlorophyll *a* concentration (Chl) was derived from CZCS values (*C*) with regression equations  $\text{Chl} = kC$ ; the coefficient of transformation *k* was calculated from six different data sets by taking into account distinctions between subregions and seasons. The reasons for difference in the *k* values have been analyzed.

Statistical comparison of the chlorophyll *a* values measured in situ and those derived from CZCS data was based on log-transformed data and gave the following results: regression slope = 0.842, regression intercept = −0.081, coefficient of determination ( $R^2$ ) = 0.806, root-mean-square error = 0.195. The mean monthly chlorophyll *a* distributions derived from CZCS data over 1978–1986 have been constructed and the mean seasonal chlorophyll *a* values in different regions have been calculated and analyzed. The significant difference in chlorophyll concentration between the western shelf regions and the open part of the Black Sea has been demonstrated, especially in warm season. At almost all seasons, the highest chlorophyll concentration is observed in the western interior shelf region which is under strong influence of Danube. The summer mean chlorophyll concentration in this region is ~18 times higher than that in the open parts and about nine times higher than in the eastern shelf region. The greatest seasonal variations are observed in the open part of the Black Sea: chlorophyll concentration in cold season is four to six times higher than in summer and three to five times higher than in April and October. To the contrary, in the western interior shelf regions, the concentration is higher in May–October (about twice than that in November–

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March). Seasonal variations in the western outer shelf regions are smoothed out as compared with both the western interior shelf and the open regions.

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## 1. Introduction

The Black Sea ecosystem, suffering ecological deteriorations through long-term changes induced by natural and anthropogenic factors, needs to be continuously monitored for its environmental state and ecological processes. The most practical and appropriate parameter which can be used for monitoring the marine ecosystems is chlorophyll *a* concentration. Its level correlates well with primary production and it is widely accepted as an index of phytoplankton biomass. It has been monitored in the Black Sea for several decades and a large volume of data is available at present (Yunev et al., 1987; Berseneva, 1993; Vedernikov and Demidov, 1993; Yilmaz et al., 1998; Yunev et al., 2002). Chlorophyll *a* concentration is a unique property of marine ecosystems which can be measured at synoptic scales by using satellite ocean-colour data. Today, satellite ocean-color sensors have become a standard tool for the determination of spatial distribution and temporal changes in the chlorophyll *a* concentration. Several types of ocean-color sensors are on operation at present and new ones are planned to be launched in the nearest future (IOCCG, 1999).

The first-generation ocean-color sensor was Coastal Zone Color Scanner (CZCS) launched on the NASA satellite Nimbus-7. CZCS sensor provided a great deal of useful information about the ocean colour for the October 1978–June 1986 period (Acker, 1994). CZCS had operated within the period during which the Black Sea ecosystem was rather stable. Shortly thereafter, the drastic changes in the Black Sea ecosystem were observed which coincided with outbreak of the accidentally introduced ctenophore *Mnemiopsis leidyi* since about summer of 1988 (Shushkina and Vinogradov, 1991). Therefore, the analysis of the available CZCS data for the 1978–1986 period is critically important for the assessment of the early conditions of the Black Sea ecosystem and to understand the subsequent changes.

Attempts for using CZCS data to study seasonal and interannual changes in the Black Sea were made by Nezlin and Dyakonov (1998) and Nezlin et al. (1999). Unlike the earlier studies, the present study is focussed on deriving the absolute values of chlorophyll *a* concentration directly from the CZCS data. Two important aspects of the CZCS data should be kept in mind:

- CZCS data is not a direct measure of chlorophyll *a* concentration, but the so-called “pigment concentration” (sum of chlorophyll *a* and phaeopigments).
- CZCS values can differ essentially from a true sum of chlorophyll *a* and phaeopigments due to errors in atmospheric correction and biooptical algorithm.

The empirical equations for CZCS biooptical algorithm were derived by applying statistical regression for the radiance–chlorophyll data set which contained less than 60 stations near the western and eastern coasts of the USA and in the Gulf of Mexico (McClain et al., 1992). Application of these equations for another body of water having different relationship between absorption of phytoplankton pigments and coloured organic matter (“yellow substance”) can result in appreciable errors (Burenkov et al., 1999).

Our approach for the assessment of absolute values of chlorophyll *a* concentration by using the CZCS data is based on the direct comparison of CZCS and in situ chlorophyll *a* data for the Black Sea.

## 2. The satellite and field data used for the study

### 2.1. The partition of the Black Sea into subregions

Since the relationship between CZCS values and in situ chlorophyll *a* concentrations depends on the water characteristics, comparison between these two data

sets was performed separately for eight subregions (Fig. 1). These subregions were distinguished with respect to bathymetry, spatial distributions of CZCS values, surface currents and anthropogenic impacts (USGOFSO, 1989; Mee, 1992; Zaitsev, 1993; Sur et al., 1994; Cociasu et al., 1996; Ozsoy and Unluata, 1997). The shelf area was considered separately by subdividing it into three interiors: the inner shelf region (1–3) having depth of less than 50 m, the outer one (4 and 5) lying between 50 and 200 m depth contours of the western part and the common shelf (depth less than 200 m) for the rest of the shelf area (8). Open waters were divided into western (6) and eastern (7) subregions. The inner shelf region was separated into three subregions, of which region 1 is under the strong influence of water discharge of the

Dnepr, Dnestr and Bug rivers, whereas region 2 is influenced mainly by the Danube river. Noticeable differences in CZCS values were observed between the inner and outer shelf regions of the northwestern and western parts of the Black Sea (USGOFSO, 1989; Sur et al., 1994, 1996), as well as between the northern (4) and southern (5) parts of the outer shelf region. Since there was no pronounced distinction observed between the southern, eastern and northeastern shelf regions of the eastern part of the basin, they are combined and evaluated as a single region (8).

The general circulation of the Black Sea consists of the strong Rim Current (Oguz et al., 1993) following the narrow continental slope. The current limits water and material transfer from the coastal zone to the open part of the Black Sea. The interior of the Rim Current

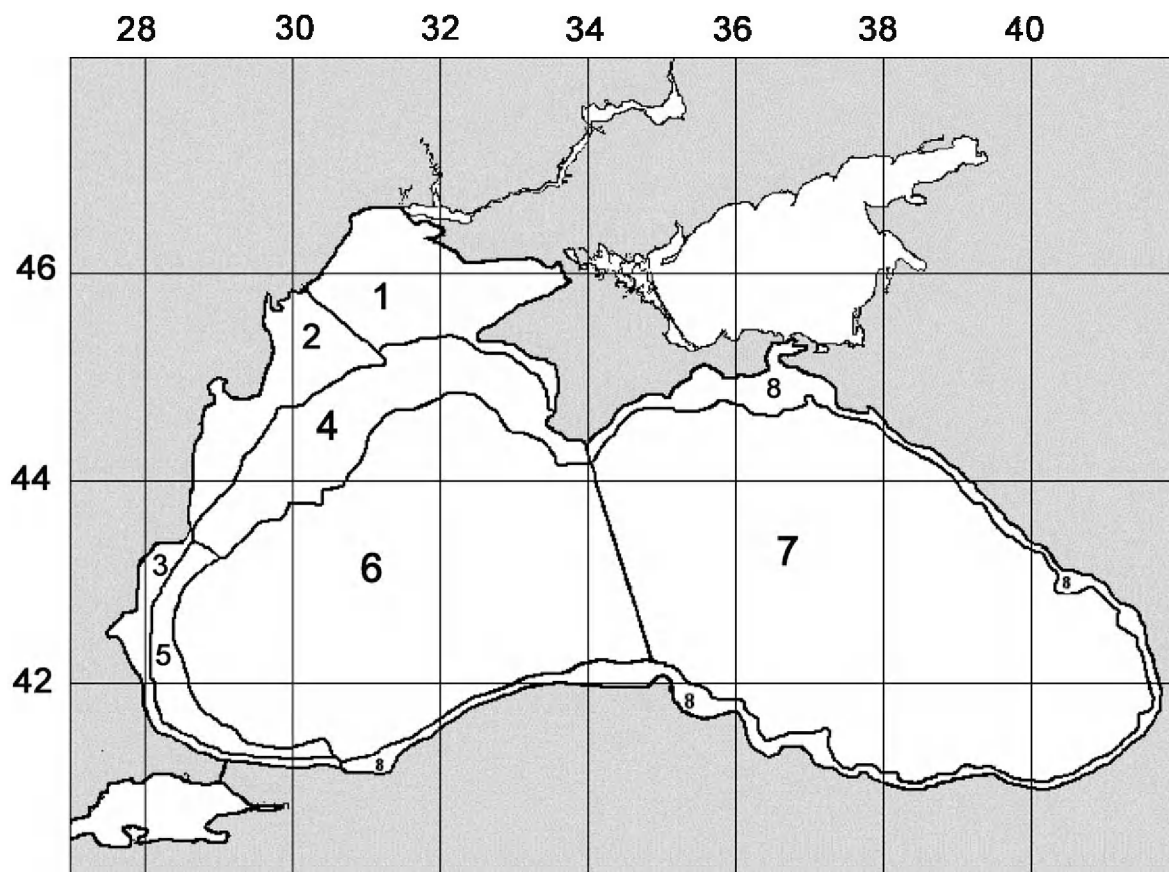


Fig. 1. The partition of the Black Sea into subregions (explanation in the text).

zone is formed by two cyclonic cells occupying the western and eastern halves of the basin. With this in mind, the western (6) and eastern (7) open parts of the Black Sea were considered separately.

## 2.2. CZCS pigment concentration data

The Coastal Zone Color Scanner (CZCS) is a scanning radiometer launched on Nimbus-7 in October 1978. The mission was designed as a proof-of-concept experiment with a limit of 2 h of coverage per day and 1-year demonstration lifetime. Despite its limited designed lifetime, CZCS data were collected until June 1986. Unfortunately, a coverage of the Black Sea by CZCS data was not at a desirable level, especially in cold periods (Nezlin et al., 1999).

CZCS Level 2 data obtained from DAAC GSFC NASA on the pigment concentration with spatial resolution of 1 km at nadir were used in the analysis. The whole region of the Black Sea, bounded by the curvilinear rectangle of 40–48°N and 27–42°E, was broken into  $296 \times 222$  elementary rectangles (“bins”) such that a grid cell of about  $4 \times 4 \text{ km}^2$  size at 44°E was obtained. Since part of the data was totally contaminated by clouds, 356 files were rejected out of total 885 files which were compiled from CZCS Level 2 data and dumped into the rectangle.

The daily Level 3 files were created by averaging CZCS Level 2 values within a given bin and for a given day. Monthly and seasonal (for every year or averaged over 1978–1986) Level 3 files were created by averaging the daily Level 3 files for the corresponding period.

The mean monthly and seasonal CZCS values, evaluated in Sections 3 and 4, were calculated by applying the following procedure. Using the corresponding Level 3 file, the superficial integral,  $I = \int_{\Gamma} C dS = \sum_i C_i dS_i$  was obtained, where  $C$  denotes CZCS pigment concentration,  $\Gamma$  is a contour of the area of interest,  $i$  is the number of a bin with pigment concentration  $C_i$  and an area  $dS_i$ . The summation was taken over the bins with values of CZCS pigment concentration (“bins with data”). The mean values  $\langle C \rangle$  was calculated as  $I/S$ , where  $S$  is the total area of the bins with data. Similarly, the standard deviation  $s$  were calculated from the equation,  $s^2 = \int_{\Gamma} [C - \langle C \rangle]^2 dS / S$ . The mean chlorophyll  $a$  values, discussed in Section 4, were calculated by applying the same procedure,

but using the daily Level 3 files derived from the CZCS values with the algorithm described below (Section 3).

## 2.3. In situ data

Surface chlorophyll  $a$  sampled from 0 m was used in this study. The data were obtained from two sources: Joint International Black Sea Database (TU-BS DB) created at the Institute of Marine Sciences (Erdemli, Turkey) and Database of the Department of Ecological Physiology of Phytoplankton at the Institute of Biology of the Southern Seas (Sevastopol, Ukraine). List of the cruises from which chlorophyll  $a$  data were used in this study is given in Table 1. About 70% of the available Chl- $a$  data were obtained by the standard fluorometric method (JGOFS Protocols, 1994) and the remaining by the standard spectrophotometric method (Jeffrey and Humphrey, 1975; SCOR-UNESCO, 1966).

The detailed experiments for comparing the different techniques used in chlorophyll  $a$  and total phaeo-

Table 1  
The cruises which chl  $a$  data were used in this study

Year	Month	R/V <sup>a</sup>	Method <sup>b</sup>	Source <sup>c</sup>
1978	September, October	Vityaz	Sp	TU-BS DB
1980	August, September	PV	Sp	IBSS DB
1981	April, May	AK	Fl	IBSS DB
	June, July	Orbeli	Sp	TU-BS DB
1982	May	PV	Sp	IBSS DB
	July, August	Aitodor	Fl	IBSS DB
	October, November	Orbeli	Sp	TU-BS DB
1983	September, November	PK	Fl	IBSS DB
1984	May	Vityaz	Sp	TU-BS DB
	September	ML	Fl	IBSS DB
1985	July	PV	Fl	IBSS DB
	September	PK	Sp	IBSS DB
	September, October, November	Rift	Sp	TU-BS DB
1986	January, March	PV	Fl	TU-BS DB
	May, June	Rift	Sp	TU-BS DB

<sup>a</sup> Research vessels: PV, Professor Vodyanitsky; AK, Academician Kovalevsky; PK, Professor. Kolesnikov; ML, Mikhail Lomonosov.

<sup>b</sup> Sp, Fl: spectrophotometrically and fluorometrically measured surface chl  $a$ , respectively.

<sup>c</sup> TU-BS DB: Database of NATO TU-Black Sea Project. IBSS DB: database of the Department of Ecological Physiology of Phytoplankton of the Institute of Biology of Southern Seas (Sevastopol, Ukraine).

pigments *a* measurements, including the high performance liquid chromatography (HPLC), were made by two expert working groups (Neveux et al., 1990; Mantoura et al., 1997).

In almost all tests, the spectrophotometric, fluorometric and HPLC methods resulted in a good agreement for chlorophyll *a* measurements, except for the data having high phaeopigments *a* concentration (usually >50% of chlorophyll *a* and phaeopigments *a* sum) for the Jeffrey and Humphrey (1975) spectrophotometry, and high chlorophyll *b* concentrations given by the JGOFS Protocols (1994) fluorometry. Since the surface layer of the Black Sea is characterized by low phaeopigments *a* content, usually less than 30% of total chlorophyll *a* and phaeopigments *a* (Yunev et al., 1987; Berseneva, 1993; Vedernikov and Demidov, 1993) and small contribution from chlorophyll *b* containing phytoplankton (Georgieva, 1993), good agreement between spectrophotometric and fluorometric Chl-*a* values should be expected for the basin.

Direct comparison between the Jeffrey and Humphrey (1975) spectrophotometric and the JGOFS Protocols (1994) fluorometric techniques in the Black Sea was conducted during the March–April 1999 cruise of RV *Professor Vodyanitsky* (Yunev et al., 2002). Parallel water samples taken from different depths of the shelf and deep-water regions of the Black Sea were measured using the above-mentioned techniques. The comparison has shown that the spectrophotometric chlorophyll *a* values (Chl-Sp) were very close to the fluorometric chlorophyll *a* values (Chl-Fi) with the regression equation  $[\text{Chl-Fi}] = 1.02[\text{Chl-Sp}] + 0.0001$ ,  $r^2 = 0.84$ , S.D. =  $0.077 \text{ mg m}^{-3}$ , CV = 19%,  $n = 9$ . These experimental data and the results of above-mentioned two expert working groups (Neveux et al., 1990; Mantoura et al., 1997) allowed us to pool the Chl-*a* data obtained by these two methods in the Black Sea and treat them as a single data set without any further correction.

The available in situ Chl-*a* data for the 1978–1986 period are presented in Table 2 (with coverages of

Table 2

Mean monthly in situ chlorophyll *a* concentrations with standard deviations (upper line) and coverage of each subregion (lower line) by ship (total number of in situ measurements) and CZCS data (a covered part) over 1978–1986

Month	Regions							
	1	2	3	4	5	6	7	8
January	1.81 ± 0.30 2; 0.623	1.48 ± 1.02 3; 0.956	— 0; 0.960	2.90 ± 2.55 4; 0.788	— 0; 1.0	1.36 ± 0.82 15; 0.964	— 0; 0.328	— 0; 0.427
February	— 0; 0.876	— 0; 0.932	— 0; 0.970	— 0; 0.946	— 0; 1.0	— 0; 0.944	— 0; 0.405	— 0; 0.484
March	— 0; 0.156	— 0; 0.706	— 0; 0.966	— 0; 0.454	— 0; 0.998	1.19 ± 0.59 17; 0.754	0.98 ± 0.61 12; 0.484	1.07 ± 0.92 3; 0.351
April	— 0; 0.952	— 0; 0.932	— 0; 0.988	0.59 ± 0.46 8; 0.996	— 0; 1.0	— 0; 0.999	0.20 ± 0.00 1; 0.962	— 0; 0.908
May	— 0; 0.993	2.98 ± 3.28 2; 0.997	3.43 ± 2.38 11; 0.959	2.66 ± 4.66 17; 0.998	0.72 ± 0.60 31; 0.991	0.27 ± 0.27 23; 0.987	0.18 ± 0.07 8; 0.966	0.40 ± 0.00 1; 0.936
June	— 0; 0.986	— 0; 0.984	5.90 ± 1.70 2; 0.970	— 0; 1.0	1.40 ± 0.00 1; 1.0	0.18 ± 0.10 4; 1.0	0.29 ± 0.21 5; 1.0	— 0; 0.989
July	0.76 ± 0.83 4; 0.988	— 0; 0.990	— 0; 0.990	0.24 ± 0.18 28; 1.0	0.24 ± 0.00 1; 1.0	0.14 ± 0.10 42; 1.0	— 0; 1.0	— 0; 0.988
August	2.50 ± 2.20 7; 0.989	— 0; 0.987	0.44 ± 0.13 2; 0.994	— 0; 1.0	0.29 ± 0.10 9; 1.0	0.12 ± 0.20 17; 1.0	— 0; 1.0	— 0; 0.997
September	2.25 ± 3.73 6; 0.995	2.61 ± 3.13 15; 0.994	0.28 ± 0.00 1; 0.997	0.80 ± 1.32 61; 1.0	0.15 ± 0.05 4; 1.0	0.19 ± 0.14 76; 1.0	0.14 ± 0.14 64; 1.0	0.27 ± 0.19 10; 1.0
October	2.00 ± 0.00 2; 0.990	2.60 ± 0.00 1; 0.995	1.64 ± 1.31 8; 0.981	— 0; 1.0	0.60 ± 0.00 1; 1.0	0.38 ± 0.08 5; 1.0	0.17 ± 0.05 9; 1.0	— 0; 1.0
November	1.50 ± 0.52 11; 0.926	1.59 ± 0.59 8; 0.915	— 0; 0.945	0.85 ± 0.54 16; 0.965	— 0; 1.0	0.46 ± 0.10 8; 0.991	0.55 ± 0.35 2; 0.991	0.64 ± 0.05 2; 0.853
December	— 0; 0.436	— 0; 0.622	— 0; 0.990	— 0; 0.922	— 0; 1.0	— 0; 0.998	— 0; 0.996	— 0; 0.979



each region in a given month by CZCS data). Total number of in situ measurements, most of which was for September (237), May (93) and July (75), were 590. As is seen from Table 2, in situ data were available for less than half of the total number of cells “subregion/month,” particularly there were no measurements for February and December.

Even though the data coverage of the Black Sea by CZCS is much better than the ship data, (i.e., all cells are covered), it is not so good for winter period. The data coverage for the eastern part of the basin (regions 7 and 8) for January–March, for region 1 in March and December, and for region 4 in March is less than 50%.

### 3. Transformation of CZCS data into chlorophyll *a* concentration

As was mentioned before, the approach used in this study for transforming the CZCS data into values of chlorophyll *a* concentration was based on the direct comparison of CZCS and available ship-measured chlorophyll *a* data. Ideally, it would be better to compare the ship and satellite data measured concurrently for the exact pixel at which the ship is located or, at least, for the exact bin on the same day. Unfortunately, “the-same-day-measured” data were only available for August–September 1980 (RV *Prof. Vodyanitsky*) and August 1982 (RV *Aidotor*), but not for all regions. The ship and satellite data measured in the same month were available only for the May–November period, but not again for all regions.

The use of the whole data set over the 1978–1986 period (Table 2) was the only way for a comprehensive comparison between ship and CZCS data for the Black Sea. However, its use is restricted by the assumption that no influence of interannual variations was the case.

#### 3.1. Interannual variations

The available historical data implied that the Black Sea was in a ecologically well balanced and, thus, stable state in 1978–1986. Yunev et al. (2002) reported that the mean surface chlorophyll *a* concentration in the deep Black Sea for May–September interval over the 1964–1986 period was  $0.15 \pm 0.04$

$\text{mg}\cdot\text{m}^{-3}$ . Thereafter, its average value increased regularly at a rate of  $0.06 \text{ mg}\cdot\text{m}^{-3}/\text{year}$  during 1988–1991, and then increased rapidly to the peak value of  $0.99 \pm 0.7 \text{ mg}\cdot\text{m}^{-3}$  in 1992. After 1992, its value decreased down to  $0.26 \pm 0.08 \text{ mg}\cdot\text{m}^{-3}$  in 1993, and continued to decrease regularly at a rate of  $0.02 \text{ mg}\cdot\text{m}^{-3}/\text{year}$  during the 1993–1996 period. Relative stability in the deep parts of the Black Sea over the 1978–1986 period is also supported by the available data on Secchi disk depth ( $15.0 \pm 0.8 \text{ m}$ ) which varied from 14.5 to 17.6 m. Its value have decreased profoundly down to 6.2–13.3 m ( $10.3 \pm 2.9 \text{ m}$ ) in the 1988–1992 period, and increased again up to 10.8–17.7 m ( $12.2 \pm 2.1 \text{ m}$ ) in the 1993–1995 period (Mankovsky et al., 1996).

Analysis of the interannual variations of CZCS data by Nezlin and Dyakonov (1998) and Nezlin et al. (1999) implied that there were no observable changes in open parts of the Black Sea during the warm season of 1978–1986. On the other hand, the same authors have reported a pronounced interannual changes for the cold season. However, they did not evaluate the statistical significance of their conclusions, even though the dispersion of the monthly medians presented in their figures was rather great for most of the years.

The present analysis for the Black Sea coverage of CZCS data in different years has led us to the conclusion that available CZCS data did not provide a possibility for studying interannual variations for cold period of the year. This conclusion can be explained by adducing open western region 6 (Fig. 1), where Nezlin and Dyakonov (1998) and Nezlin et al. (1999) have found appreciable interannual variations.

Years, in which the CZCS coverage of the basin is not less than 10% during cold months, are presented in Table 3. It can easily be seen that the mean values of CZCS concentration are dictated by different months for different years. The mean value for 1978 is determined by the November–December data; 1983—by January; 1984—by October–November; 1985—by October and April; 1986—by April data. It is clearly evident that the observed differences between the annual means are also controlled by the monthly differences in the mean values. It is worth to note that different parts of the region can have a dominant role in the years when the coverage is less than 50% or so. Our calculations have shown that the

Table 3

The years with a coverage of region 6 by CZCS data in cold months not less 10%

Months	October	November	December	January	February	March	April
Years	1979–1982, 1984–1985	1978–1981, 1984	1978–1980	1979–1983	1979, 1981–1982	1980	1979–1980, 1982, 1985–1986

coefficients of variation of CZCS values in many regions of the Black Sea are more than 100% in cold months of the most years partly due to the strong spatial inhomogeneity. The available CZCS data for cold seasons over 1978–1986 do not allow one to distinguish the interannual changes from the monthly

differences and spatial inhomogeneity within a given region.

It should be emphasized that the approach used in here does not demand an absence of interannual variations of chlorophyll concentration, but rather requires interannual stability of the relationships

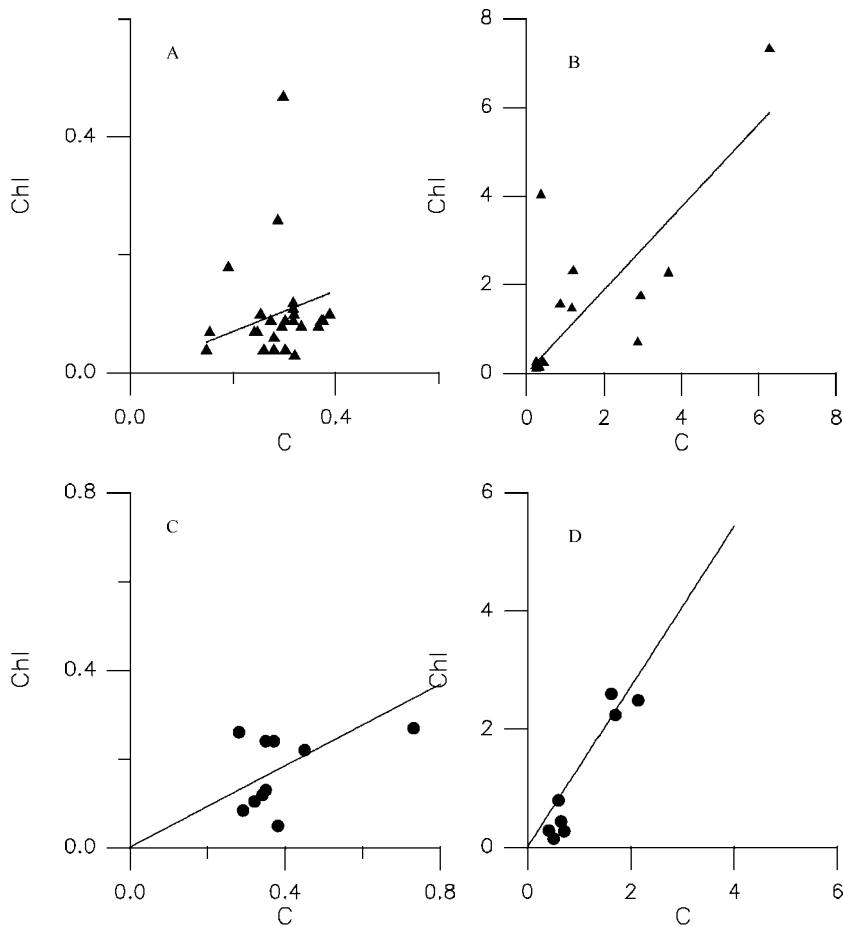


Fig. 2. The lines of regression through origin derived from different subsets in August–September. (A, B) The-same-day-measured data. (C, D) From the whole data set. (A, C) Data from regions 6–8. (B, D) From regions 1–5. Chl: ship-measured chlorophyll *a* concentration ( $\text{mg} \cdot \text{m}^{-3}$ ). C: CZCS pigment concentration ( $\text{mg} \cdot \text{m}^{-3}$ ).

between chlorophyll *a* and CZCS concentrations. Since the available data do not allow us to check such kind of stability directly, we compared indirectly the relationships derived from “the-same-day-measured” data and from the whole set over the 1978–1986 period. Similarly, the chlorophyll *a* values derived from CZCS data by our algorithm were compared with the in situ measured values.

### 3.2. Relationships between CZCS data and ship-measured chlorophyll *a* derived from “the-same-day-measured” data and the whole set

As mentioned earlier, “the-same-day-measured” data were only available in August–September 1980 and August 1982. Suetin et al. (2000) used the data of 1980 for chlorophyll retrieval for only five stations in the northwestern part of the Black Sea. In this study, 40 pairs of ship-measured chlorophyll *a* concentration (Chl-ship) and daily Level 3 CZCS value (*C*) for the bin where the ship was located were used. A linear relationship was assumed between these two parameters:  $\text{Chl-ship} = kC$ , where *C* is CZCS pigment concentration.

The regression slope *k* was calculated by using the formula  $k = (\sum \text{Chl}_i C_i) / \sum C_i^2$ , which is based on the minimization of sum of squares of difference between chlorophyll *a* concentration (Chl-ship) and *kC*, i.e.  $\sum (\text{Chl}_i - kC_i)^2 = \min$ . The standard error of regression ( $s_{\text{regr}}$ ) was calculated as the square root of the residual mean square:

$$s_{\text{regr}} = \sqrt{\sum (\text{Chl}_i - kC_i)^2 / (N - 1)},$$

where *N* is the number of pairs.

Preliminary analysis showed a weak correlation between Chl-ship and *C* when the regression was calculated for all pairs. A detectable difference in the slope *k* was observed for the open and western shelf regions. The correlation became stronger when the regression was calculated separately for these two subsets: one set including the western shelf regions 1–5 (*N* = 15), and the other including open regions 6, 7 and eastern shelf 8 (*N* = 25).

The lines of regression through origin derived separately for the above subsets are shown in Fig. 2A and B. It is seen that the slopes of the regression curves in the studied regions differ significantly (0.356

in regions 6–8 and 0.937 in 1–5). The regression errors were 0.092 and 1.32 mg·m<sup>−3</sup>, and the coefficients of variation were 0.88 and 0.86, respectively.

Fig. 2C and D shows the lines of regression through origin derived from the whole set of data in August–September (Table 2). In this case, the mean monthly values of chlorophyll *a* ( $\langle \text{Chl}_i \rangle$ ) and CZCS concentration ( $\langle C_i \rangle$ ) for different regions were used. The regression slopes and standard error of regression were calculated as weighted estimates by taking numbers of ship measurements into account:  $k = (\sum n_i \langle \text{Chl}_i \rangle \langle C_i \rangle) / \sum n_i \langle C_i \rangle^2$ , where *n<sub>i</sub>* is the number of the in situ measurements in the *i*th subregion;

$s_{\text{regr}}$

$$= \sqrt{\sum n_i (\langle \text{Chl}_i \rangle - k \langle C_i \rangle)^2 / (N - 1)}, N = \sum n_i.$$

Values of *N* were 105 for the western shelf regions 1–5, and 167 for the open part and eastern shelf 6–8.

The relative positions of two regression lines displayed in Fig. 2C and D are similar to those in the previous case. The regression slope for regions 6–8 was equal to 0.461, whereas for regions 1–5, it was 1.357 with regression errors of 0.058 and 0.244 mg·m<sup>−3</sup>, and

Table 4

The coefficients *k* for transformation of CZCS values into chlorophyll *a* concentration (mg·m<sup>−3</sup>)

Months	Regions	<i>k</i>
December–March	All	0.682
April–November	6–8 (open and eastern parts)	0.400
April–June	1–5 (western shelf)	0.400, if <i>C</i> < 0.3 <i>C</i> + 0.1, if 0.3 ≤ <i>C</i> ≤ 1.0 1.10, if <i>C</i> > 1.0
July	1–5 (western shelf)	0.400, if <i>C</i> < 0.3 − 0.272 <i>C</i> + 0.482, if 0.3 ≤ <i>C</i> ≤ 0.9 0.237, if <i>C</i> > 0.9
August–October	1–5 (western shelf)	0.400, if <i>C</i> < 0.3 3.15 <i>C</i> − 0.546, if 0.3 ≤ <i>C</i> ≤ 0.6 1.344, if <i>C</i> > 0.6
November	1–5 (western shelf)	0.400, if <i>C</i> < 0.3 − 0.012 <i>C</i> + 0.403, if 0.3 ≤ <i>C</i> ≤ 2.0 0.379, if <i>C</i> > 2.0

*C* is CZCS pigment concentration (mg·m<sup>−3</sup>).



the coefficients of variation of 0.33 and 0.21, in respective order.

These results have led us to conclude that:

- relationships between CZCS values and chlorophyll *a* concentration in regions 6–8 (the open and eastern part of the Black Sea) and in regions 1–5 (the western shelf) were quite different;
- use of different sets of data (“the-same-day-measured” and the whole set) gave slopes which do not differ significantly from each other;
- standard deviations derived from “the-same-day-measured” data were very high, whereas the use of data from the whole set resulted in reasonable standard deviations.
- use of a greater number of data in the whole set would give more trustworthy regression slopes.

### 3.3. The regression equations

As it is seen from Table 2, the available in situ data did not cover all regions and all months. Lack of the data is most pronounced for winter and spring seasons. There are no in situ data in December and

February, whereas the data for April are available only for regions 4 and 7. In order to transform the CZCS data into chlorophyll concentration over the whole area and in all months, we combined the available data for different regions and months by assuming an uniformity in the oceanological conditions. Then, the calculated slopes of the regression lines were assumed to be common for all parts of the integrated region–season, including the ones with no data. In particular, we were forced to combine all available data for December–March period.

The equations of regression through origin were calculated by applying the formulae given above. The significance of difference between the slopes in different regions–months were evaluated with Student’s *t*-test. The level of significance of  $\leq 0.05$  is the most commonly employed criteria in which the hypothesis of “no difference” is false (Zar, 1984). When the level of significance was more than 0.05, the hypothesis of “no difference” was assumed to be true, and the data sets were combined. Application of this test to the available data sets led us to differentiate six sets of regions–months couples. These were, namely, December–March–all regions; April–

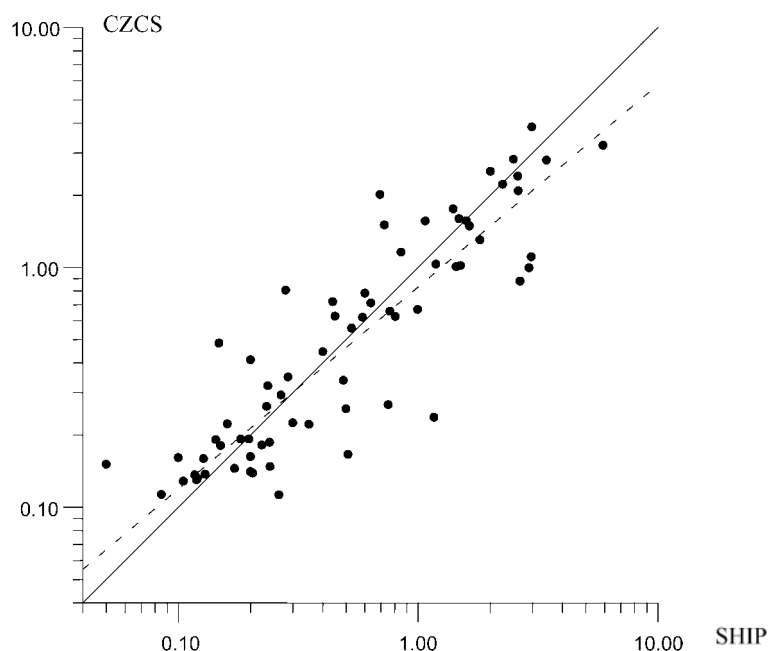


Fig. 3. Scatterplot of Chl-CZCS versus Chl-ship concentration ( $\text{mg} \cdot \text{m}^{-3}$ ). Solid line corresponds to the regression slope equal to 1; dash line is the statistical result.

November—regions 6–8 (the open and eastern parts); April–June—regions 1–5 (the western shelf); July—regions 1–5; August–October—regions 1–5; November—regions 1–5.

In performing the global transformation of CZCS data into chlorophyll *a* concentrations, one should keep in mind that the above regions are a matter of convention, and real lines of demarcation between waters of different types can depart from the border lines between the selected regions, i.e. the areas of different waters types can vary depending on the season (see, for example, Fig. 4A and B). For this reason, the transition formulae were derived for the western regions. The final set of the transformation coefficients used to calculate the absolute values of *a* concentration from CZCS values are presented in Table 4.

### 3.4. The algorithm evaluation

Statistical comparison between the chlorophyll *a* values measured in situ (Chl-ship) and those derived from CZCS data (Chl-CZCS) was based on the available log-transformed mean monthly data for different regions ( $N=69$ ). The scatter-plot of Chl-CZCS versus Chl-ship is shown in Fig. 3. Statistical results of the algorithm evaluation are as follows: regression slope = 0.842, regression intercept =  $-0.081$ , coefficient of determination ( $R^2$ ) = 0.806 and the root-mean-square error (RMS) = 0.195.

These results are not so good when compared with the criteria established by O'Reilly et al. (1998) for SeaWiFS algorithm evaluation which has a regression slope of  $1 \pm 0.01$ , regression intercept of  $0 \pm 0.01$  and  $R^2 > 0.9$ ,  $\text{RMS} < 0.185$ . It should be noted here that there are no algorithms which meet all their criteria for the model evaluation. The statistical results obtained in this study are acceptable, since the coefficient of determination  $R^2$  and the root-mean-square error RMS slightly depart from the criteria values. Our algorithm overestimates the lowest chlorophyll concentration (of order  $0.1 \text{ mg} \cdot \text{m}^{-3}$ ) about 20%, and underestimates the mid ( $\sim 1 \text{ mg} \cdot \text{m}^{-3}$ ) and highest ( $\sim 10 \text{ mg} \cdot \text{m}^{-3}$ ) concentrations corresponding to about 20% and 40%, respectively. It appears to be the best that could be done with the available in situ and CZCS data, quality of which leaves much to be desired especially in cold season.

## 4. Results and discussion

### 4.1. Analysis of the regression slopes *k*

As it was mentioned earlier, CZCS data is a measure of sum of Chl-*a* and phaeopigments. The regression equation between Chl-*a* and sum of Chl-*a* and phaeopigments (*C*) takes the form of  $C = 1.34[\text{Chl-}a]^{0.983}$  (O'Reilly et al., 1998), which may be approximated by the linear equation,  $\text{Chl-}a \approx 0.75C$ . It assumes that the coefficient *k* would be equal  $\sim 0.75$  if there were no errors associated with atmospheric correction for CZCS data and biooptical algorithms used, and if the above equation were valid in the Black Sea. The value of 0.682 for *k* for December–March (Table 4) is in reasonable agreement with the above mentioned value of 0.75, but for other cases the *k* values can be three times less, as well as two times higher. There can be three possible reasons for the observed differences between the value of 0.75 and the values of *k* given in Table 4: (i) variation of the relationship between Chl-*a* and phaeopigments, (ii) errors associated with the atmospheric correction and (iii) errors in the biooptical algorithm. It is unlikely that the first one can explain the observed differences, since Chl-*a* in the Black Sea usually makes up more than 0.7 of total chlorophyll *a* and phaeopigments *a* (see Section 2.3) and is less than 1.0. It is difficult to analyze the errors associated with the atmospheric correction, even though an attempt to clear up them was made by Suetin et al. (1997). The results of validation of SeaWiFS algorithm in the Black Sea (Burenkov et al., 1999) suggest that the main reason of the difference is in the biooptical algorithm, although the other two reasons are not totally rejected.

As was mentioned earlier, CZCS values were derived by applying the regression equations obtained from in situ measurements near the western and eastern coasts of the USA and in the Gulf of Mexico. These equations assume that a definite correlation exists between three main factors that determine the spectral water reflectance: absorption by phytoplankton pigments, absorption by yellow substance, and backscattering by suspended particles. In fact, the interrelationships between the above mentioned factors depend on oceanological conditions. Burenkov et al. (1999) compared Chl-*a* values in the Black Sea derived by SeaWiFS empirical algorithm and those measured in situ.

Their study was performed for the open parts of the Black Sea in October 1997 at three stations. The mean ratio of the measured (“true”) and SeaWiFS Chl-*a* was found to be equal  $\sim 0.46$  which agrees with the values of the coefficient *k*, 0.40, given in Table 4 for the open and eastern parts of the basin for the April–November period. Burenkov et al. (1999) explained the difference between SeaWiFS and measured chlorophyll *a* concentration by the predominance of gelbstoff absorption over that of pigments. Therefore, the low values of *k* in the open regions in April–November and in the western shelf in July and November can be due to the enhanced contribution of the yellow substance, whereas high values of *k* in the western shelf in April–June and August–October indicated the predominance of absorption by phytoplankton pigments. It should be noted that the *k* values in regions 6–8 differ much less than those in regions 1–5. The latter value was found to be equal to 0.682 in December–March, 1.10 in April–June, 0.237 in July, 1.344 in August–October and 0.379 in November. It can be suggested that these changes are due to the processes associated with seasonal variability in the river discharges, especially from the Danube. Of course, this has yet to be investigated, and further validation studies are needed for the Black Sea basin.

#### 4.2. Spatial and seasonal variability of chlorophyll *a* concentration over 1978–1986

The mean monthly distributions of chlorophyll *a* values derived from CZCS data (Chl-CZCS) averaged over the 1978–1986 period are shown in Fig. 4A and B. The distributions reveal a clear difference between the western shelf regions and the open part of the Black Sea, whereas the eastern shelf alone stands out as a narrow zone along the coast. The distributions are quite variable in the western shelf regions and display a rather homogeneous pattern within the open parts. The distributions in the open parts are very similar from April to October. Unfortunately, the quality of CZCS data does not allow one to make comparisons between different months of cold season extending from November to March.

For the analysis of seasonal changes in absolute values of chlorophyll *a* concentrations within different regions of the basin, four seasons were selected in accordance with Vedernikov and Demidov (1993):

cold—from November to March, warm—from May to September, and two transition months—April and October. These authors have summarized the surface chlorophyll *a* data of the open regions of the Black Sea over 1978–1991 and reported the following mean chlorophyll *a* concentrations: cold season— $0.97\text{--}1.52\text{ mg}\cdot\text{m}^{-3}$ , April— $0.61$ ; warm season— $0.28\text{--}0.38$ , October— $0.43\text{ mg}\cdot\text{m}^{-3}$ . As can be seen from Table 5, seasonal variations in Chl-CZCS in open parts 6 and 7 are in good agreement with the results presented by Vedernikov and Demidov (1993): the highest concentration is observed in cold season ( $0.70\text{--}0.83\text{ mg}\cdot\text{m}^{-3}$ ), the lowest in summer ( $0.14\text{--}0.15\text{ mg}\cdot\text{m}^{-3}$ ) and intermediate values of  $0.19\text{--}0.21\text{ mg}\cdot\text{m}^{-3}$  for April and  $0.18\text{--}0.25\text{ mg}\cdot\text{m}^{-3}$  for October. The lower absolute values of chlorophyll concentrations given in Table 5 compared to those given by Vedernikov and Demidov (1993) can be explained by the fact that the latter values included 1988–1991 data (see Section 3.1). On the other hand, chlorophyll *a* concentration for the open parts in warm season (Table 5) is in good agreement with the mean chlorophyll concentration in May–November over the 1964–1986 period presented by Yunev et al. (2002).

The open western 6 and eastern 7 subregions did not differ from one another by their mean annual and summer concentrations. Mean concentration for the cold season in the eastern part was  $\sim 19\%$  higher than that of the western part, being  $\sim 10\%$  and  $\sim 28\%$  lower in April and October.

The eastern shelf region 8 had a higher mean concentration than the open parts for all seasons. From April to October, the mean values differed more than twice, whereas in the cold season the difference exceeded by 40%, with the annual difference being about 80%. The seasonal changes in the open parts and the eastern shelf region were similar. chlorophyll *a* concentrations in these regions were found to be four to six times higher in cold season as compared to that for the summer, and three to five times higher when compared to those for April and October.

Chlorophyll *a* concentrations within the western interior shelf regions 1–3 differed significantly from those in the open and eastern regions 6–8, especially for warm season. The highest chlorophyll concentration was observed at almost all seasons in the western interior shelf region 2 which is under strong influence of the Danube. The summer mean chlorophyll concen-

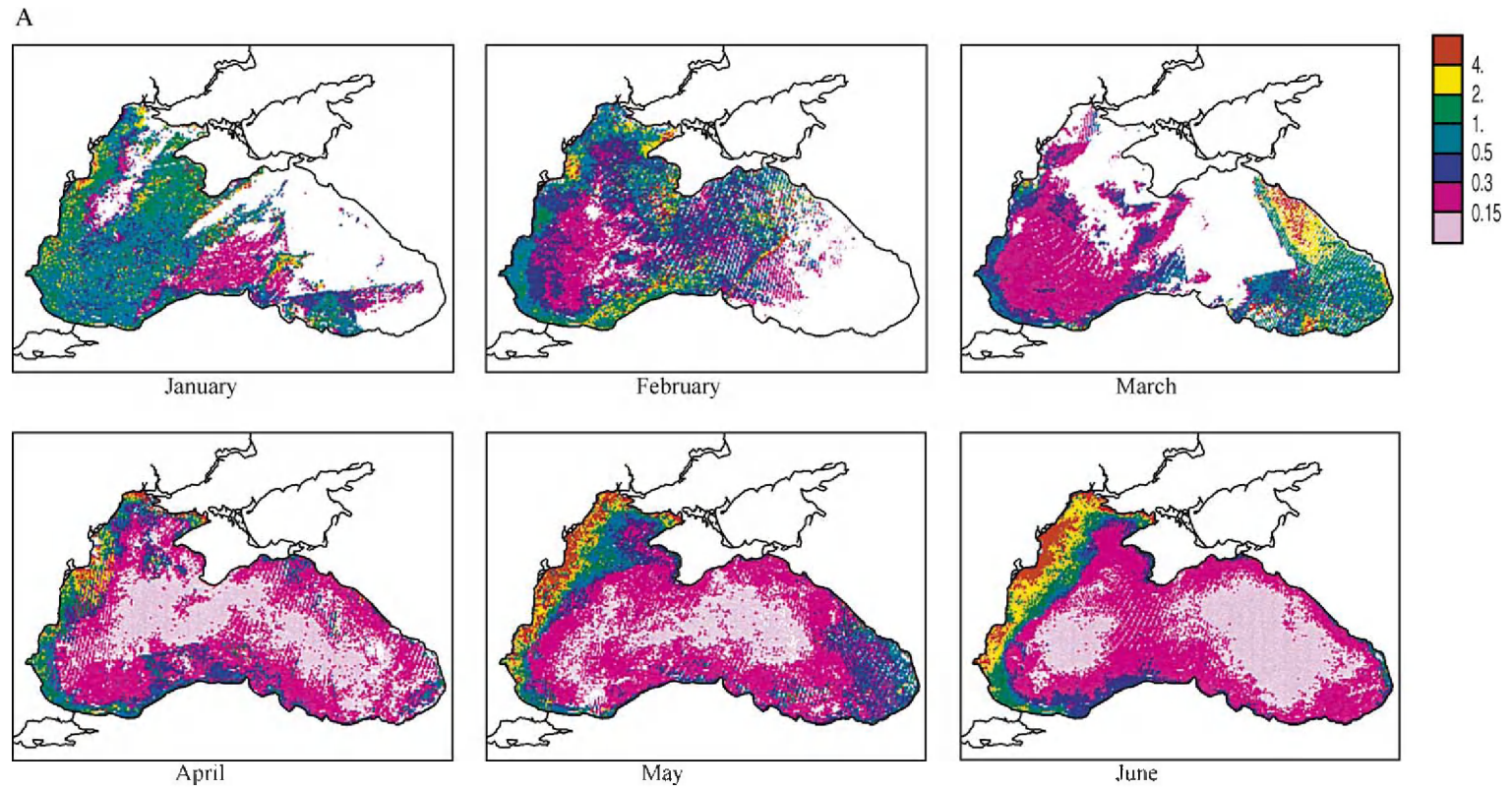


Fig. 4. The mean monthly chlorophyll *a* distributions ( $\text{mg}\cdot\text{m}^{-3}$ ) derived from CZCS data over 1978–1986. (A) January to June. (B) July to December.



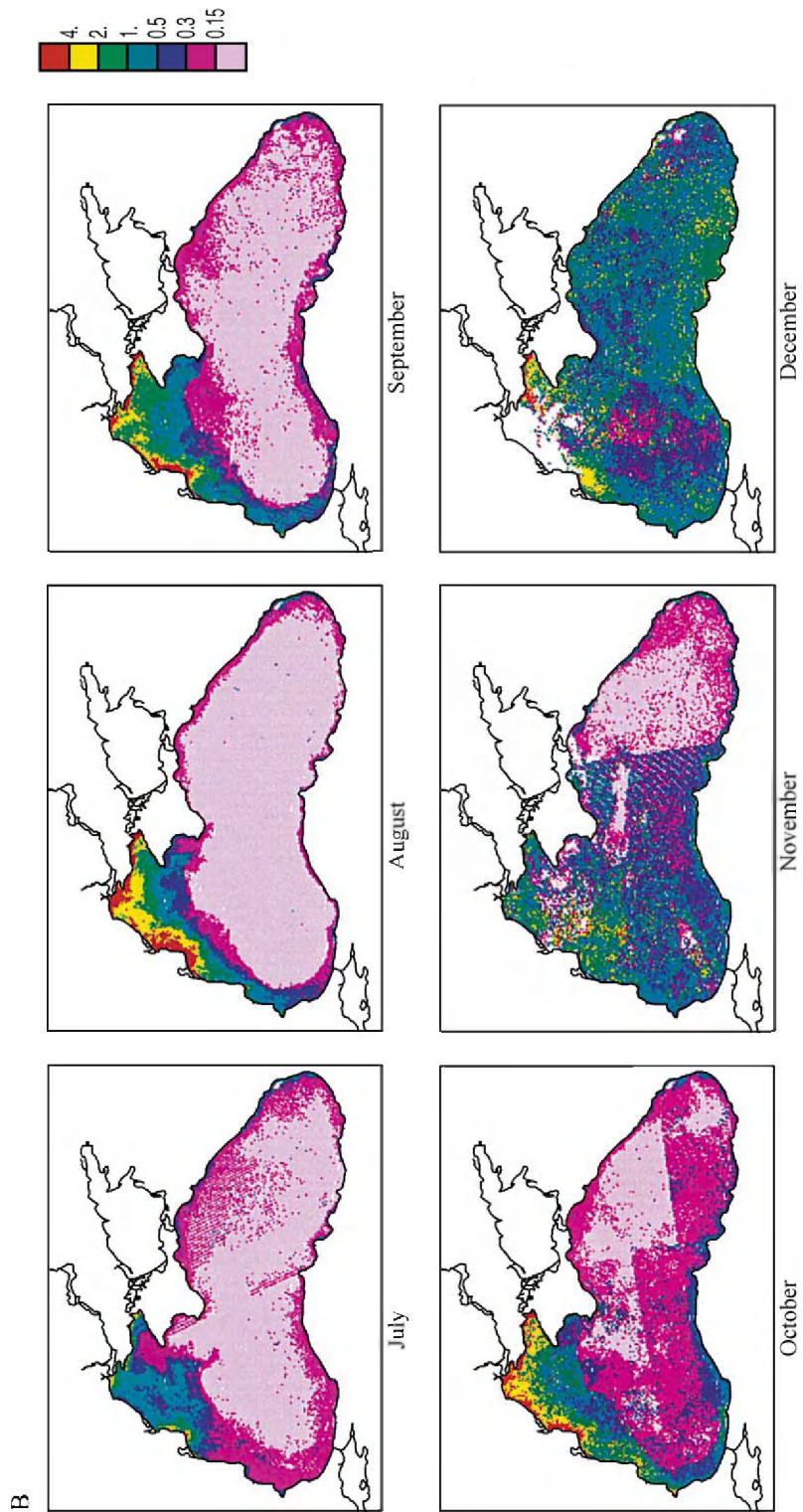


Fig. 4 (continued).

Table 5

The mean chlorophyll *a* concentrations ( $\text{mg}\cdot\text{m}^{-3}$ ) with their standard deviations derived from CZCS data over 1978–1986 for different regions and seasons

Season	Regions								Whole basin
	1	2	3	4	5	6	7	8	
November–March	1.32	1.39	1.06	0.90	0.90	0.70	0.83	1.20	0.87
	0.94	0.72	0.37	0.50	0.26	0.35	0.50	0.66	0.55
April	1.17	1.97	1.77	0.62	1.05	0.208	0.188	0.46	0.41
	2.54	1.64	1.31	1.03	0.74	0.194	0.167	0.46	0.90
May–September	1.97	2.63	1.20	0.58	0.67	0.149	0.144	0.29	0.41
	1.87	1.86	0.77	0.38	0.28	0.044	0.040	0.22	0.86
October	2.52	2.40	1.50	0.80	0.78	0.247	0.177	0.40	0.51
	1.83	2.17	1.13	0.58	0.55	0.155	0.085	0.25	0.94
Annual	1.92	2.49	1.22	0.62	0.75	0.228	0.224	0.41	0.48
	1.65	1.68	0.43	0.35	0.23	0.069	0.075	0.22	0.78

tration in this region was  $\sim 18$  times higher than that in the open parts and about nine times than that in the eastern shelf region. In winter, due to the increased homogeneity in the water column, the mean values in regions 2 and 6–7 differed less than two times, while only a slight difference was observed between regions 2 and 8.

The western outer shelf regions 4–5 appeared to be a transition area between the interior shelf and the open regions. Seasonal variations in these regions were smoothed out as compared with both the western interior shelf and the open regions.

The Black Sea, as a whole, is most homogeneous in cold season, but its open parts are most homogeneous in summer: the coefficients of variation is only  $\sim 28$ –30% (Table 5).

It makes no sense to compare absolute values of chlorophyll *a* in Fig. 4 with the ones derived from current SeaWiFS data because the SeaWiFS chlorophyll *a* concentrations need to be corrected for this particular basin (Burenkov et al., 1999). The relative spatial distributions of chlorophyll concentration derived from CZCS and SeaWiFS data are similar to each other in their general terms.

## 5. Conclusion

The present work gives an example of retrospective joint analysis of satellite and in situ data. This type of analysis allows one to derive absolute values of chlorophyll concentration and to study their spatial and seasonal variations. The proposed approach can

be used with satellite data from other ocean-color sensors such as OCTS and SeaWiFS. This approach can be considered as some kind of “recalibration” of satellite data product with in situ data. Recalibration exercise is important for practical purposes especially for Case 2 waters, where the relations between the absorption by phytoplankton pigments and yellow substance differs significantly from waters where the regression equations for chlorophyll retrieval were derived. Of course, such an approach requires a good coverage of the study area by satellite data and sufficient number of ship measurements in different seasons.

As a result of the present study, reliable estimates of chlorophyll *a* concentration in different seasons and regions of the Black Sea over the 1978–1986 period have been obtained. Conclusions derived through this exercise can be used to make comparisons in Chl-*a* values in different years for assessing changes in the Black Sea ecosystem due to natural and anthropogenic factors.

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