RECENT DATA CONCERNING THE VERTICAL DISTRIBUTION OF CHLOROPHYLL *a* IN THE WESTERN BLACK SEA

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ABSTRACT

This paper presents chlorophyll *a* data collected in 2008 from nine sampling stations along a south-east transect, from the front of the Danube mouths to the Black Sea abyssal plain waters.
The chlorophyll *a* concentrations ranged from 0.02 to 6.30 µg/l, highest values being recorded at shallow stations. In early spring (April), the vertical distribution of chlorophyll *a* was rather homogeneous in the photic zone. A weak pronounced DCM layer was found at 10 m depth in outer shelf and slope shelf waters (chl *a* 0.74 µg/l – 0.96 µg/l) and it descended to 30 – 40 m in abyssal plain waters (chl *a* 0.59 µg/l – 0.91 µg/l).
In September, the vertical distribution of chlorophyll *a* showed a well developed DCM (chl *a* 1.0 µg/l - 4.88 µg/l) at 21 – 28 m over the entire transect due to a stronger seasonal thermocline.

KEY WORDS: Western Black Sea; chlorophyll *a*; DCM.

INTRODUCTION

Chlorophyll *a* concentration is considered to be the main measure of phytoplankton biomass and has been intensively discussed as applied to the Black Sea in a variety of aspects including patterns of spatial distribution, seasonal and inter-annual variability (Vedernikov and Demidov, 1993; Oguz *et al*., 2002; Kopelevich *et al*., 2002; Yunev *et al*., 2002; Moncheva, 2003).

The seasonal cycle of chlorophyll *a* is not spatially uniform across the Black Sea. According to some authors, the open Black Sea experiences its maximum of chlorophyll *a* during the autumn and winter with minimum levels occurring during the summer (Vinogradov *et al*., 1999). The blooming cycle begins near the NW shelf slope during September and progresses eastward, covering the entire basin in October and November. This is the phytoplankton response to seasonal pycnocline erosion in autumn, which replenishes the photic zone with nutrients from the mixed layers (Vinogradov *et al*., 1999). The bloom ends as stratification occurs, nutrients are depleted and grazer pressure increases (Vinogradov *et al*., 1999).

Unlike the central basin of the Black Sea, in NW shelf waters, the seasonal cycle of phytoplankton exhibits two blooms (Sorokin, 2000). The spring bloom, strongly related to the Danube flow, begins during April and May, the months of maximum Danube discharge, when the nutrient – rich shelf waters are enough warm for phytoplankton growth (Cociaşu and Popa, 2005; Yunev *et al*., 2007). The decline of the spring bloom is most likely the consequence of a combined action of two factors: nutrient depletion and increasing of zooplankton grazing pressure (Chu *et al*., 2005). An autumn bloom also occurs in shelf waters due to seasonal thermocline erosion and decreasing of zooplankton grazing pressure, but is not as intense as the spring bloom. The chlorophyll *a* minimum occurs during the winter, when the Danube discharge is lowest and shelf waters are well mixed and cool (McQuatters-Gollop *et al*., 2008).

This paper aims to emphasize spatial distribution of chlorophyll *a* in the western part of the Black Sea, based on data gathered in 2008 both from shelf and open waters.

STUDY AREA

In April and September 2008, two cruises were organized in the western part of the Black Sea onboard R/V *Mare Nigrum*. There were sampled nine stations (Table 1) distributed along a transect South-East, starting from the front of the Danube River mouths (Sf. Gheorghe arm) and ending in the Balck Sea abyssal plain waters (Fig.1).

Table 1 - Coordinates of the stations performed in April and September 2008, during R/V *Mare Nigrum* cruises

Station	Coordinates		Bottom depths (m)	Observations
	Latitude-North	Longitude-East		
S-01	44°45.00	29°36.00	15	Inner shelf
S-02	44°38.00	29°40.00	50	Inner shelf
S-03	44°01.00	30°03.00	100	Outer shelf
S-04	43°58.00	30°04.00	150	Outer shelf
S-05	43°45.00	30°13.00	500	Continental slope
S-06	43°36.00	30°18.00	1000	Abyssal cones area
S-07	43°30.00	30°22.00	1500	Abyssal plain
S-08	43°01.00	30°40.00	2000	Abyssal plain
S-09	42°30.00	31°00.00	≈2200	Abyssal plain

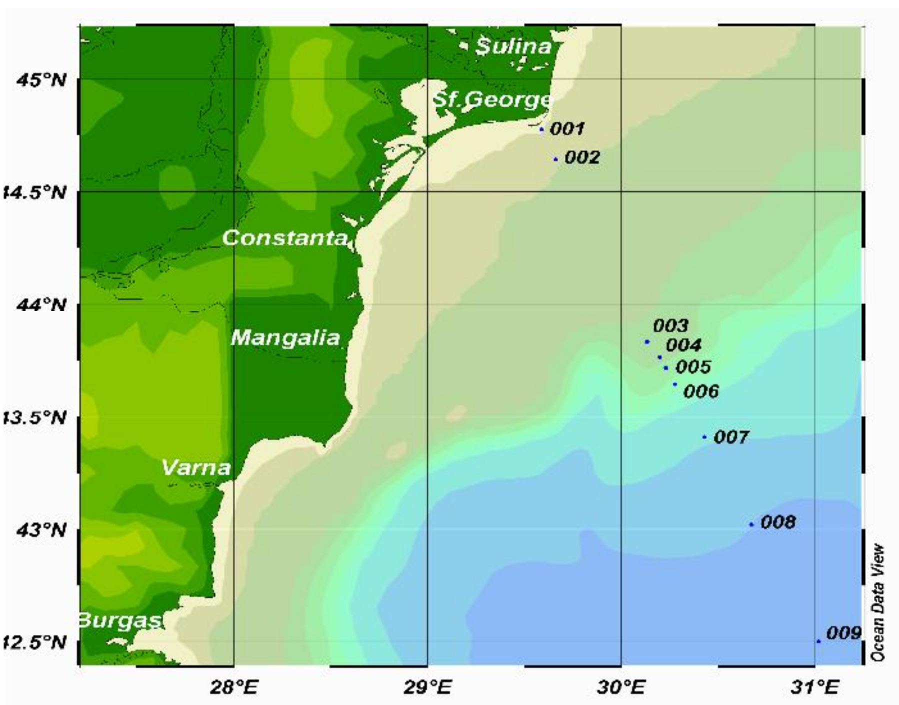

Fig. 1 - Map of sampling stations performed in April and September 2008, during R/V *Mare Nigrum* cruises

MATERIALS AND METHODS

The sampling depths, from surface to 100 m, were selected according to CTD profiles. Pressure, temperature, salinity, Sigma-T, and dissolved oxygen (DO) were measured by CTD sensors. Water samples were collected by a Seabird CTD-Rosette system in 5 l plastic bottles during the upcast, for nutrients and biological (chlorophyll *a* and phytoplankton) analyses. Nutrient samples were frozen and kept at -20ºC for subsequent analyses. PO_4-P, SiO_4-Si, NO_3-N, NO_2-N, NH_4-N were measured according to standard methods (Grasshoof *et al*., 1999). Some dissolved oxygen measurements were done onboard by Winkler titration method (Grasshoff *et al*., 1999), just to check the oxygen probe values.

For chlorophyll *a* measurements, variables volumes (1-5 l) of seawater were filtered onboard through 0.7μm GF/F Whatman filters. The filters were preserved at -20ºC until subsequent analyses. In the laboratory, the pigment was extracted with 90% acetone and measured spectrophotometrically (CECIL CE-2020 spectrophotometer), concentrations being calculated using the SCORE - UNESCO equations (UNESCO, 1966).

Phytoplankton samples were preserved in 4% formaldehyde seawater buffered solution. Qualitative and quantitative phytoplankton determinations were made according to standard methods (Morozova-Vodyanitskaya, 1948, 1954; Bodeanu, 1987-1988).

Physical-chemical and biological data were processed with the program Ocean Data View 4 (Schlitzer, 2009).

RESULTS AND DISCUSSION

In April 2008, chlorophyll *a* ranged between 0.02 and 5.00 μg/l, the highest concentrations being recorded in shallow water stations (S-01 and S-02), in front of Sf.Gheorghe mouth.

The vertical distribution of chlorophyll *a* in the inner shelf stations showed relatively high concentrations both in the surface layer (2.55 μg/l at S-01, 2.29 μg/l at S-02 respectively), and especially in the near bottom waters (2.72 μg/l at S-01, 5.00 μg/l at S-02 respectively) (Fig.2). Unlike the station S-01, where the pattern of chlorophyll *a* vertical distribution was relatively homogeneous and almost similar with the pattern of phytoplankton total biomass, at station S-02, chlorophyll *a* maximum was found near the bottom, while the biomass revealed its minimum (1.05284 mg/l) (Fig.3).

Due to light limited conditions in inner shelf waters (the Danube turbid water discharge is higher during this period), the phytoplankton total biomass recorded quite low values (0.105 – 1.6284 mg/l), although the nutrient regime was favorable. Higher chlorophyll *a* values found in bottom waters were probably the result of the presence of chlorophyll *a* degradation products from resuspended detrital material.

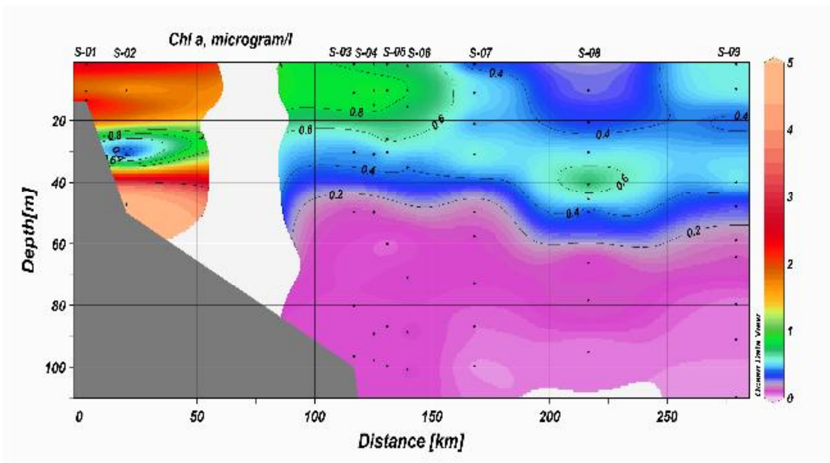

Fig. 2 - Spatial distribution of chl *a* along the Sf.Gheorghe profile (NW Black Sea) in April 2008

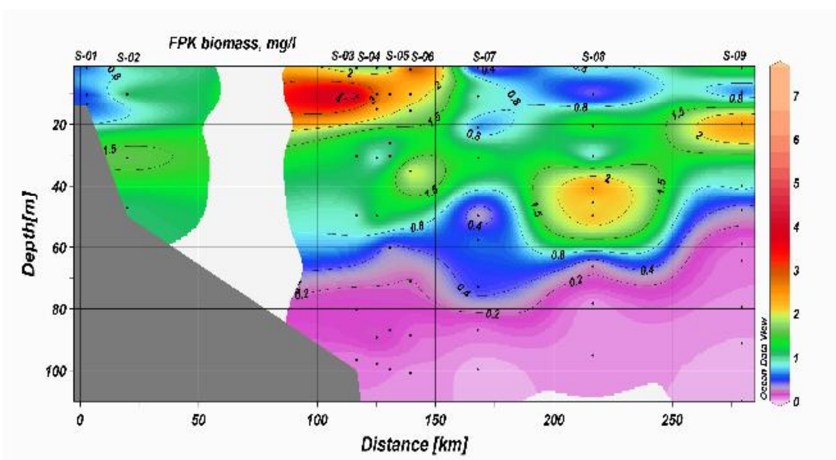

Fig. 3 - Spatial distribution of phytoplankton biomass along the Sf.Gheorghe profile (NW Black Sea) in April 2008

Chlorophyll *a* distribution pattern is the result of quantitative and qualitative interrelations of some physical – chemical state parameters of the reference ecosystem.

In early April, in the waters above continental shelf and slope, the temperature gradient was very low (Fig.4), thus the upper mixed layer descend to 50 – 60 m (upper boundary of permanent pycnocline) (Fig.5) favoring the vertical transport of nutrients from deep to surface waters.

The photic zone waters are well oxygenated, DO ranging between 9.88 and 10.45 mg/l (Fig. 6); the upper boundary of oxycline was found at 35 – 40 m depth. In the outer shelf and slope waters, the organic matter decomposition was more intense below the upper boundary of pycnocline (50 - 60 m), most part of resulted nutrients remaining unused within pycnocline. Therefore, only a small part of regenerated nutrients can be transported to the surface and near surface layers and supporting the phytoplankton growth.

In early spring, in outer shelf and shelf slope waters, the nutrient stock in the photic zone is provided by „new" nutrients brought from deep waters, due to intensive mixing processes during winter (Chu *et al*., 2005), as well as by the high nutrient discharge from the Danube River.

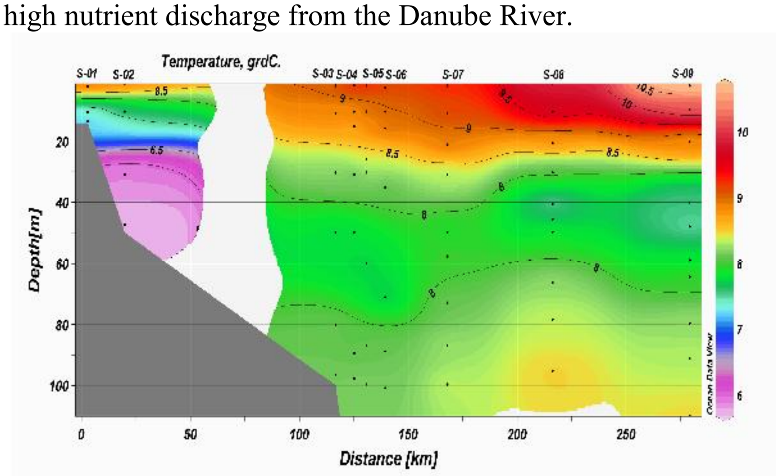

Fig. 4 - Spatial distribution of temperature along the Sf.Gheorghe profile (NW Black Sea) in April 2008

Nutrient vertical distribution patterns exhibited a relatively homogeneity in the upper mixed layer. PO_4-P ranged from values below detection limit to 0.38 μM, NO_3-N from 1.04 to 4.47 μM, NH_4-N from 0.87 – 2.34 μM and silicate from 3.4 to 11.1 μM. Outer shelf and shelf slope waters were P- limited in the upper layer, N/P ratio ranging between 24 and 560 (Fig.7). Si/N ratio ranged between 0.8 and 1.7 (Fig.8), which suggests there was no Si limitation.

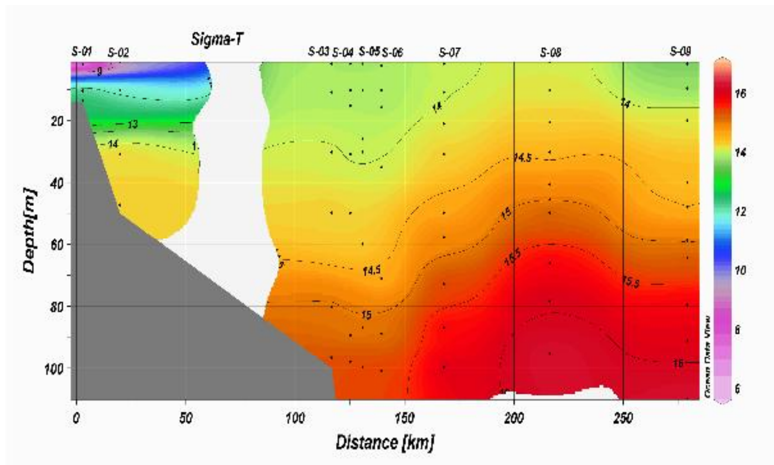

Fig. 5 - Sigma-T spatial distribution along the Sf. Gheorghe profile (NW Black Sea) in April 2008

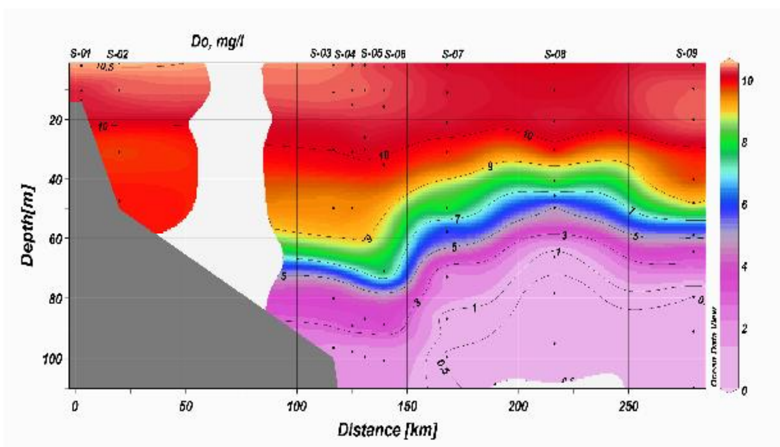

Fig. 6 - Dissolved oxygen (DO) spatial distribution along the Sf. Gheorghe profile (NW Black Sea) in April 2008

In outer shelf and continental slope area, chlorophyll *a* exhibited a low vertical variability in upper 0 – 20 m layer, its values ranging within 0.29 and 0.96 µg/l. The highest concentrations (0.74 µg/l at S-06 and 0.96 µg/l at S-04) were found at 10 m depth, suggesting a slightly developed deep chlorophyll maximum (DCM) layer at this depth (Fig.2).

The pattern of phytoplankton biomass vertical distribution was almost similar to chlorophyll *a* (Fig.3). The maximum total biomass was found also in 10 m layer (between 1.8454 mg/l at S-06 and 6.6283 mg/l at S-03).

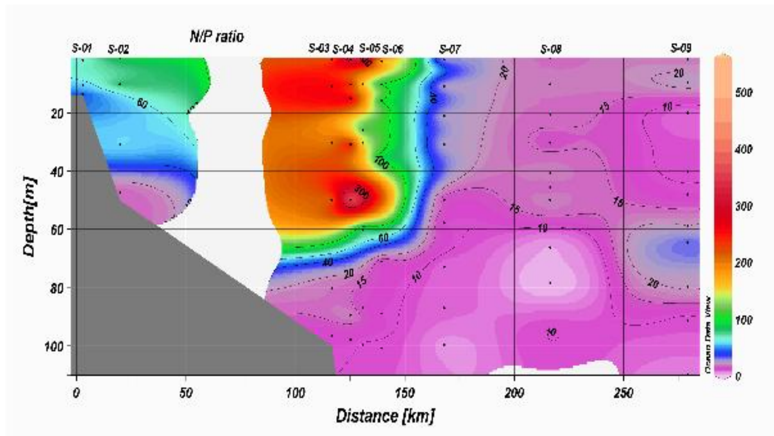

Fig. 7 - Spatial distribution N/P ratio along the Sf. Gheorghe profile (NW Black Sea) in April 2008

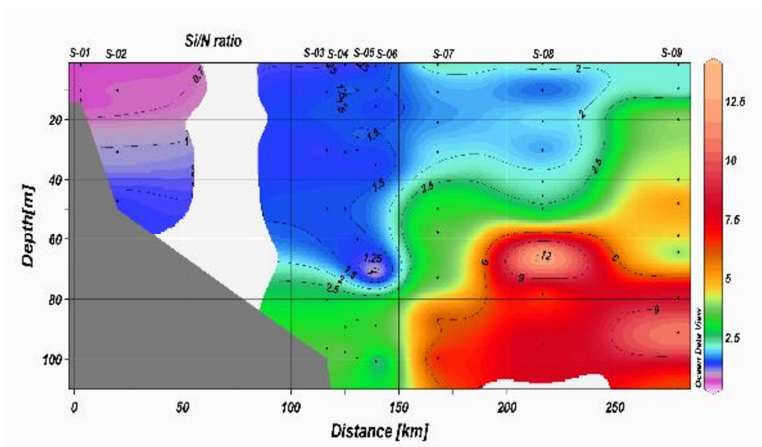

Fig. 8 - Spatial distribution Si/N ratio along the Sf. Gheorghe profile (NW Black Sea) in April 2008

In the abyssal plain waters (S-07 – S-09), the vertical distribution of chlorophyll *a* was governed by the occurrence of seasonal pycnocline (Fig.5). The seasonal pycnocline formation led to a reduction in nutrient supply from deep waters (Vedernikov and Demidov, 1997). The organic matter resulting from winter/spring bloom was „detained" within pycnocline and was subject to decomposition processes (upper boundary of oxycline corresponding to upper boundary of seasonal pycnocline). The upward flux of nutrients resulted from these processes towards the upper mixed layer was limited, thus the stock of available nutrients increased within pycnocline (Fig.7, 8). Unlike the shelf and continental slope waters which were P – limited, molar ratios (N/P 8.5 – 17.1 and Si/N 1.5 – 3.9) (Fig.7, 8) in the abyssal plain area suggest a weak nitrogen limitation in the photic zone.

Chlorophyll *a* vertical distribution in the central basin (depth > 1500 m) emphasized a deeper DCM (30 – 40 m depth), but its values (0.48 – 0.59 μg/l) were relatively close to the surface values (0.22 – 0.55 μg/l).

Also quite high values (0.13 -0.58 μg/l) were measured beneath DCM, at depths of 45 – 50 m (Fig.2), but this fact was probably the consequence of chlorophyll *a* degradation products in particles residing below thermocline.

With reference to phytoplankton biomass, at stations S-07 and S-08 the highest values were determined at DCM (1.4133 mg/l at S-07, 3.1982 mg/l at S-08 respectively), unlike the station S-09, where total phytoplankton biomass (2.5569 mg/l) was found shallower, above thermocline (20 m depth) (Fig.3).

Therefore, in April, unlike the shelf and shelf slope waters, where DCM was nutrient limited (P – limited) and primary production appeared to be supported mainly by "new" nutrients, in abyssal plain waters DCM was light limited, primary production being supported most likely by regenerated nutrients.

In September 2008, chlorophyll *a* ranged from 0.02 to 6.30 μg/l, the highest values were recorded in shallow waters.

At shallowest station (S-01) chlorophyll *a* registered higher value in near bottom layer (6.30 μg/l) as compared to surface waters (3.96 μg/l) (Fig.9). Unlike chlorophyll *a*, phytoplankton biomass was about two times higher in surface waters (1.7805 mg/l) than in near bottom waters (0.6898 mg/l) (Fig.10). As shown above, this fact could be explained through the presence of chlorophyll a degradation products in resuspended detritus particles.

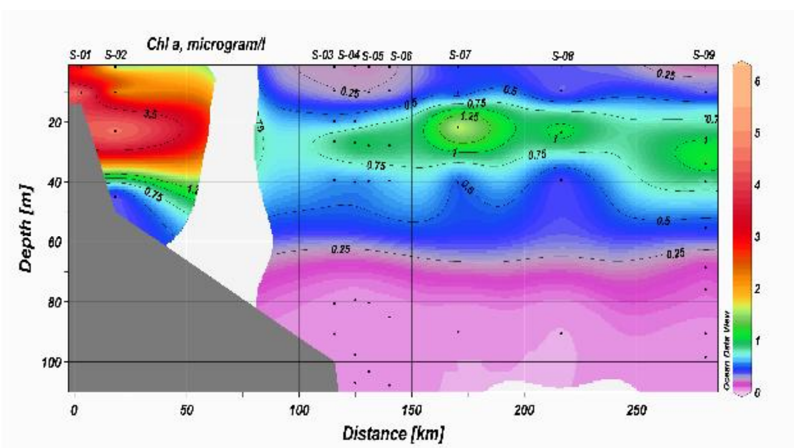

Fig. 9 - Spatial distribution of chl *a* along the Sf.Gheorghe profile (NW Black Sea) in September 2008

At all other stations (both in shelf and open waters), the seasonal thermocline was strongly pronounced in late summer (Fig.11) and governed the vertical distribution of chlorophyll *a*.

The seasonal thermocline restricts the upward flux of nutrients from the deep nutrient – rich waters. In upper mixed layer, above thermocline (0 – 20 m), there were recorded quite low nitrate and silicate concentrations (NO_3-N 1.64 – 2.47 µM, SiO_4-Si 0.61 – 2.97 µM respectively). N/P (5.7 – 17.6) and Si/N (0.23 – 1.05) ratios showed quite strong N and P limitation in upper mixed layer (Fig.11, 13). Thus, nutrient limitation conditions contributed, probably together with inhibitory effect of light in surface waters, to low chlorophyll *a* values (0.16 - 0.45 µg/l) above thermocline (Fig. 9).

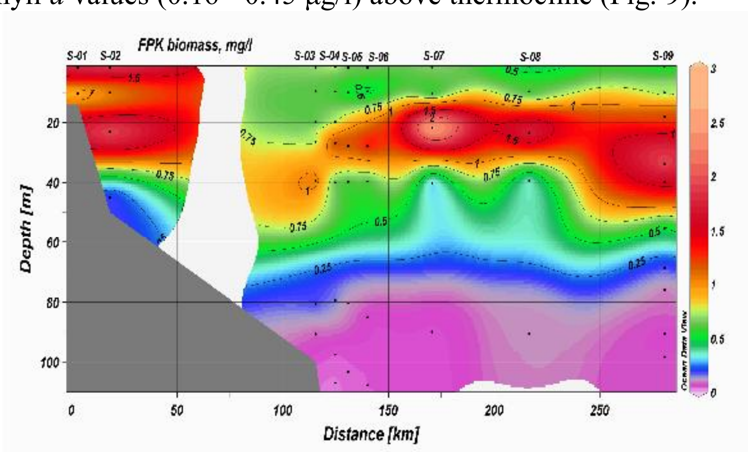

Fig. 10 - Spatial distribution of total biomass along the Sf. Gheorghe profile (NW Black Sea) in September 2008

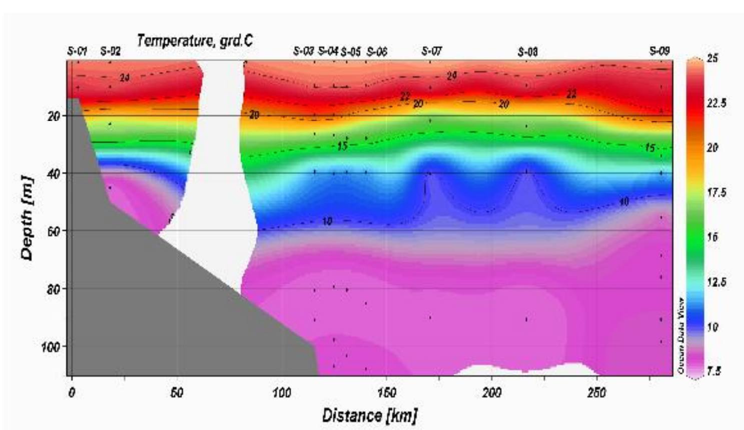

Fig. 11 - Spatial distribution of temperature along the Sf.Gheorghe profile (NW Black Sea) in September 2008

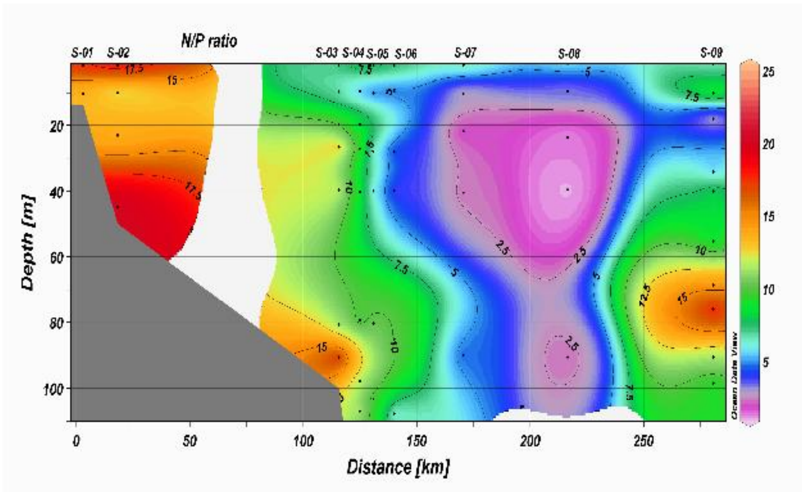

Fig. 12 - N/P ratio spatial distribution along the Sf.Gheorghe profile (NW Black Sea) in September 2008

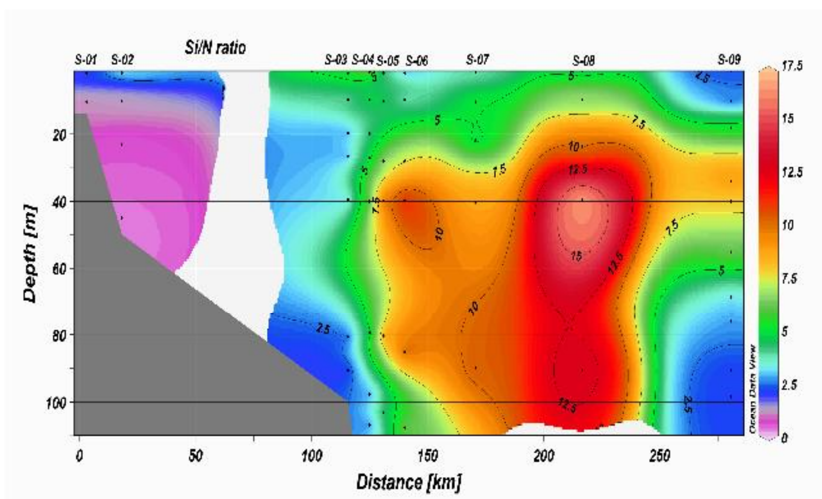

Fig. 13 - Si/N ratio spatial distribution along the Sf.Gheorghe profile (NW Black Sea) in September 2008

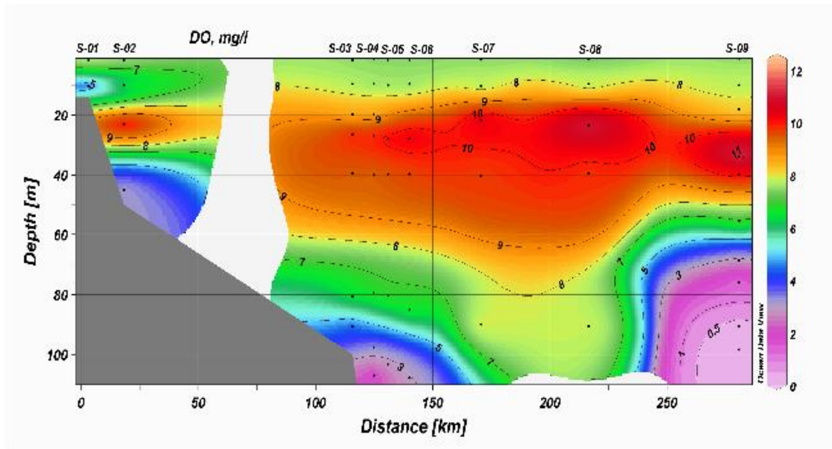

Fig. 14 - DO spatial distribution along the Sf.Gheorghe profile (NW Black Sea) in September 2008

On the other hand, the sharp decrease of DO from just below the upper boundary of thermocline suggests intense organic matter decomposition processes, leading to an increase in nutrient stock within thermocline which could support the primary production. Therefore, at depths of 20 – 30 m, light conditions and regenerated nutrients favored intense photosynthetic processes, DO reaching maximum at these depths, over the entire transect (between 11.05 mg/l at S-05 – 12.59 mg/l at S-09) (Fig.14). However, molar ratios shown in Fig. 12 and 13 revealed a strong N – limitation within thermocline along the profile.

The vertical distribution of chlorophyll *a* revealed, excepting station S-01, a well pronounced deep chlorophyll maximum (DCM) layer at 20 – 30 m depth. The concentrations in this layer were much higher than those recorded in upper mixed layer (above thermocline), ranging between 1.03 μg/l at S-03 and 4.88 μg/l at S-02 (Fig.9).

Chlorophyll *a* and phytoplankton total biomass displayed nearly similar depth distribution patterns. Phytoplankton total biomass recorded values between 0.0144 and 3.0232 mg/l, the highest values being recorded within the thermocline (Fig.10). The vertical distribution of phytoplankton biomass exhibited maximum values in DCM layer (between 1.2628 mg/l at S-05 and 3.0232 mg/l at S-07), excepting station S-03 where the maximum (1.62925 mg/l) was found at lower boundary of thermocline (Fig.10).

Maximum values of chlorophyll *a*, DO and phytoplankton total biomass found at similar depths (20 – 30 m) strongly suggest that in late summer/early fall, primary production peaked in DCM layer.

CONCLUSIONS

In 2008, chlorophyll *a* concentrations ranged between 0.02 and 6.30 µg/l. The highest values were measured in front of Sf.Gheorghe mouth, both in April (2.29 – 5.00 µg/l) and September (3.96 – 6.3 µg/l).

In early spring, except for shallow stations (S-01 and S-02), chlorophyll *a* values were low, but the vertical distribution was nearly uniform within the upper 0 – 20 m layer. In shelf and continental slope waters, DCM was found at 10 m depth, chlorophyll *a* ranging between 0.74 and 0.96 µg/l. Towards the central basin (depth > 1500 m), where the seasonal pycnocline occurred, it descend to 30 – 40 m depth, but the chlorophyll *a* concentrations in this layer remained below 1 µg/l (0.59 – 0.91 µg/l).

In late summer, the vertical distribution of chlorophyll *a* revealed a well developed DCM at depths of 21 – 28 m, chlorophyll *a* values ranging between 1.03 and 4.88 µg/l in this layer and being much higher than values measured in the surface layer (0.16 – 0.45 µg/l).

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