Oceanologia (2017) 59, 283—299

Available online at www.sciencedirect.com

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journal homepage: www.journals.elsevier.com/oceanologia/

ORIGINAL RESEARCH ARTICLE

Spatio-temporal pattern of phytoplankton and pigment composition in surface waters of south-eastern Black Sea

Ertugrul Agirbas *, **Lutfiye Koca, Ulgen Aytan**

Recep Tayyip Erdogan University, Faculty of Fisheries, Rize, Turkey

Received 9 November 2016; accepted 7 March 2017
Available online 28 March 2017

KEYWORDS
Chlorophyll-*a*;
Pigment;
Phytoplankton;
HPLC;
Black Sea

Summary Phytoplankton community, diatom to dinoflagellate ratio and pigment composition in surface waters with nutrient data from April 2013 to March 2014 were monitored in the south-eastern (SE) Black Sea using high performance liquid chromatography (HPLC) and microscopic analyses. Microscopic examination revealed a total of 71 species that consist of dinoflagellate (58%), diatoms (25%) and other groups (17%). Microscopy and HPLC-based pigment analyses revealed almost similar results which suggest that the phytoplankton community is mainly composed of diatoms, dinoflagellates and coccolithophores. Fucoxanthin (mean 0.35 $\pm$ 019 $\mu g\ L^{-1}$), peridinin (mean 0.18 $\pm$ 0.14 $\mu g\ L^{-1}$) and 19-hexanoyloxyfucoxanthin (mean 0.24 $\pm$ 0.15 $\mu g\ L^{-1}$) are prominent pigments which showed significant correlation with Diatom-C (r^2 = 0.63—0.71, $p < 0.05$), Dinoflagellate-C (r^2 = 0.49—0.80, $p < 0.05$) and Coccolithophore-C (r^2 = 0.72—0.82, $p < 0.05$), respectively. Mean carbon biomass of diatoms (36.50 $\pm$ 9.72 $\mu g\ L^{-1}$) was higher than that of dinoflagellates (33.32 $\pm$ 9.05 $\mu g\ L^{-1}$). Significant differences were also observed in nutrient ratio (N:P and Si:N) (One-way ANOVA, $p < 0.05$). Results illustrate that HPLC-based pigment approach can be used for taxonomic characterisation of phytoplankton groups in the SE Black Sea. Moreover, relatively high dinoflagellate species dominancy and significant correlations between Phyto-C and marker pigments indicate that phytoplankton community composition is shifting towards much smaller groups in SE coasts of the Black Sea.

* Corresponding author. Tel.: +90 4642233385; fax: +90 4642234118.
E-mail address: eagirbas@gmail.com (E. Agirbas).
Peer review under the responsibility of Institute of Oceanology of the Polish Academy of Sciences.

Production and hosting by Elsevier

http://dx.doi.org/10.1016/j.oceano.2017.03.004

1. Introduction

Phytoplankton contribute at least one quarter of the biomass of the world's vegetation and constitute the base of food web in the aquatic ecosystems (Jeffrey and Vesk, 1997). They have crucial role in modulating the total CO_2 concentration, pH of the ocean and global carbon cycle (Brewin et al., 2010; Takahashi et al., 2002). Phytoplankton also impact the pelagic ecosystem throughout changing trophic transfer, food web and nutrient dynamics (McQuatters-Gollop et al., 2007; Nagata et al., 1996; Pedersen et al., 1999). Identifying changes in phytoplankton community composition and diversity is essential to improve our understanding of the responses to climate forcing (Rykaczewski and Dunne, 2011). Among the phytoplankton groups, diatoms and dinoflagellates have important roles in the ecosystem. Diatoms constitute the food web between the copepod and fish whereas dinoflagellates are generally considered trophic dead ends (McQuatters-Gollop et al., 2007; Verity and Smetacek, 1996). Additionally, shifts in phytoplankton community composition affect the abundance and diversity of marine organisms, eutrophication and food web structure in the ecosystem (Leterme et al., 2006; Micheli, 1999; Oguz, 2005; Richardson and Schoeman, 2004). Moreover, phytoplankton quickly responds to environmental disturbance, and can be used as indicator for trophic levels, eutrophication and different environmental circumstances (Brettum and Andersen, 2005; Margalef, 1978).

Studies on phytoplankton are classically conducted by using microscopy (Booth, 1993; Eker-Develi et al., 2008; Hasle, 1978; Utermöhl, 1958), which needs taxonomic expertise and time for counting samples. In addition, it is not possible to identify some small sized groups (e.g. picoplankton) with microscopy (Jeffrey and Vesk, 1997). Alternatively, some photosynthetic pigments (e.g. fucoxanthin, peridinin, 19-hexanoyoxifucoxanthin, Chl *b*, and zeaxanthin, etc.) for specific phytoplankton groups derived from high-performance liquid chromatography (HPLC) provide information about the composition of the phytoplankton community (Mantoura and Llewellyn, 1983; Wright and Jeffrey, 2006). In this method, a large number of samples can be processed, and it allows fast and easy separation of marker pigments and examination of the structure of phytoplankton assemblages based on pigments (Schlüter et al., 2000). Chl *a* is generally used as a convenient proxy for phytoplankton biomass. Additionally, other accessory pigments (e.g. carotenoids) can be evaluated for the chemotaxonomic association of phytoplankton assemblages (Gibb et al., 2000). Photosynthetic pigments are also considered as indicators for the physiological condition of a phytoplankton community, which indicates environmental condition and trophic status for a given area (Roy et al., 2006). The majority of phytoplankton carotenoids are photosynthetic. While photosynthetic carotenoids (PSC) absorb light energy and transfer it to chlorophyll, photoprotecting carotenoids (PPC) protect the organism against stressful high light conditions. PPC are capable of quenching excited radicals, and converting their excess energy to heat and dissipating it harmlessly. Moreover, the ratio of PSC to PPC may be used to provide some additional characterisation of transitions in phytoplankton community composition across biogeochemical province boundaries and hence the identification of these boundaries (Gibb et al., 2000). Furthermore, PPC and PSC absorb light in different remote sensing spectral bands (e.g. SeaWiFS). Thus, variability in their relative abundances has the potential to affect the performance of algorithms used to retrieve Chl *a* values from remotely sensed ocean colour data (Gibb et al., 2000).

The Black Sea is one of the largest anoxic marine ecosystems in the world (Tolmazin, 1985). It is a semi-enclosed and isolated environment, which has suffered from severe ecological deteriorations over the last three decades (Oguz, 2005). A considerable amount of chemicals, organic matter and nutrients via surrounding rivers (especially in the western Black Sea form the River Danube) affect the Black Sea ecosystem (Eker-Develi and Kideys, 2003; Yilmaz et al., 2006). Surface salinity never exceeds 17 psu, and excess precipitation together with run-off from the rivers Danube, Dniester, and Don creates a surface with low salinity layer overlying a halocline at about 100 m (Longhurst, 2007). Sea surface temperature (SST) exhibits typical seasonal characteristic with the highest in August and the lowest in February (Agirbas et al., 2015).

Studies on the phytoplankton in the Black Sea are mainly conducted along the north-western parts of the Black Sea, and substantially constituted by microscopic examinations (e.g. Bodeanu, 1989, 1993; Bologa, 1986; Cociasu et al., 1997; Ivanov, 1965; Moncheva and Krastev, 1997; Moncheva et al., 2001; Zaitsev and Alexandrov, 1997). Despite significant roles of phytoplankton communities in the Black Sea, information about their pigment composition, distribution and comparative studies using HPLC pigment analysis are limited (Agirbas et al., 2015; Ediger et al., 2006; Eker-Develi et al., 2012). Therefore, in this paper, particular attention has been paid to reveal the temporal pattern of phytoplankton community composition, diatom to dinoflagellate ratios, and pigment composition derived from HPLC analysis along SE coasts of the Black Sea. The objectives of this study are (i) to reveal whether or not diatom to dinoflagellate ratios and pigment composition have been similar in all stations throughout the year, (ii) to explore changes in the phytoplankton community composition, (iii) to investigate whether or not similar changes occur in pigment composition and (iv) to test applicability of HPLC technique in monitoring studies along the SE Black Sea.

2. Material and methods

Samplings were carried out monthly from April 2013 to March 2014 at four stations located in the SE coast of the Black Sea (Fig. 1). The sampling stations were determined by considering bottom topography and fisheries activities. For this purpose, we chose four coastal stations (Iyidere station, Derepazari station, Rize station and Gundogdu station), located one nautical mile from the shore with $<$50 m water depth. The study area is affected by intensive fisheries and anthropogenic activities. Seawater samples for pigment characterisation, phytoplankton and nutrient analyses were taken from surface (0.5 m) by using 5-L Niskin bottle.

2.1. Nutrient analysis

A 250 mL seawater samples for dissolved inorganic nutrients (NO_3-N, NO_2-N, PO_4-P and SiO_2-Si) were filtered through 0.45 μm cellulose acetate filters. The filtrate was collected