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ОБЩ ОРГАНИЧЕН ВЪГЛЕРОД В ПОВЪРХНОСТНИ ВОДИ НА БЪЛГАРСКАТА ЧЕРНОМОРСКА КРАЙБРЕЖНА ЗОНА

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TOTAL ORGANIC CARBON IN THE SURFACE WATER OF THE BULGARIAN BLACK SEA COASTAL ZONE

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Summary: *Total organic carbon in the surface water in front of the Bulgarian Black Sea coast was investigated episodically over the period 2014-2016. During 13 expeditions conducted with R/V Akademik, samples were collected at stations located in the one-mile zone along the coastline. The results obtained varied from values of the limit of quantification (LOQ) <1 to 10 mg/l. In spring TOC concentrations were lower than in summer and autumn.*

Keywords*: Bulgarian Black Sea coastal zone, TOC, surface water*

Introduction

Total organic carbon (TOC) is the amount of carbon contained in organic compounds. TOC in seawater is mainly composed of organic substances in dissolved and suspended state, including living microorganisms, where its dissolved fraction prevails. Much of the organic matter in seawater is of autochthonous origin, less comes from river runoff, from the atmosphere and from the coast. Part of it is mineralized, precipitated or is exported from the sea basin [1]. An indication of the amount of organic matter present can be obtained by measuring related properties, principally the biochemical oxygen demand (BOD), chemical oxygen demand (COD), turbidity (function of light scattering by suspended particles), colour (related to the quantity of dissolved and particulate substances present) [2] and permanganate oxidation [1].

The total organic carbon in marine water can be a useful indication of the degree of pollution and is often used as a non-specific indicator of water quality. It is referred to as a physico-chemical quality element of the marine environment under the Water Framework Directive (WFD) [3] for establishing a framework for Community action in the field of water policy, but is still not involved in the environmental assessment of our sea water. According to the Marine Strategy Framework Directive (MSFD) which aims at achieving good environmental status of EU marine waters and protecting the resource base on which economic and social activities related to maritime space depend, the state of the environment is assessed on the basis of 11 quality descriptors [4]. TOC is included as an additional primary indicator in the monitoring program Descriptor 5 - Eutrophication, D5C1 – Primary: Nutrient concentrations are not at levels that indicate adverse eutrophication effects. [5].

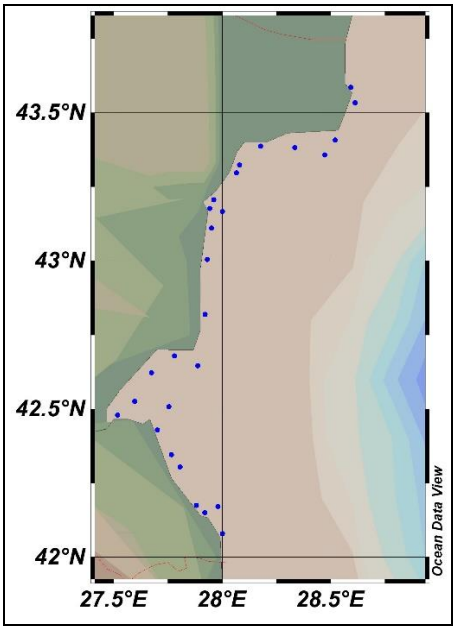
The main objective of the present work is to trace the dynamics of TOC depending on time and space and to determine the influence of other factors on the amount of the studied indicator.

Material and Methods

The subject of this article is total organic carbon in surface seawater. The survey was a part of the national monitoring program for 2014, 2015 and 2016. The monitoring network consisted

of 20 stations located in the one-mile zone along the Bulgarian Black Sea coast (Fig. 1). In 2016, the number of stations increased to 25 and their location moved closer to coast in order for the status of biological quality elements and physico-chemical quality elements could reflect with a higher degree probability the impact of point sources of pollution. TOC data were collected from 13 research expeditions with R/V *Akademik* during three seasons: spring, summer and autumn.

The samples were collected with SBE 911plus CTD from a surface water layer. Temperature, salinity, pH, dissolved oxygen, biochemical oxygen demand and nutrients were measured on board the vessel. TOC samples were fixed with hydrochloric acid (HCl) to pH 2, stored in the dark at 4°C and transported cooled for analysis in an accredited laboratory. The method applied is catalytic combustion of the organic components in a sample at 680°C and measurement of the amount of the produced carbon dioxide (CO2) by an infrared detector using a Shimadzu TOC-L analyzer [6].



Station Code	Station Name	Long	Lat	Depth,m
MS001	Krapets	28.5914	43.5863	15
MS102	Shabla	28.6119	43.5344	14
MS002	Rusalka	28.5198	43.4088	16
MS003	Kaliakra	28.4723	43.3586	14
MSRev1	Kavarna	28.3336	43.3832	16
MS104	Balchik	28.1763	43.3875	15
MS105	Albena	28.0796	43.3247	14
MSRev2	Zlatni pyasatsi	28.0645	43.2981	14
MS005	Varna Bay North	27.9600	43.2064	14
MS006	Varna Bay South	27.9414	43.1778	15
MS004	Galata	28.0000	43.1667	23
MS117	Priboi	27.9370	43.1111	19
MS007	Kamchia	27.9004	43.0053	15
MS008	Dvoinica (stara Obzor)	27.8992	42.8200	18
MS109	Cocketrice	27.8868	42.6465	18
MS009	Elenite	27.7797	42.6990	15
Rev4	Ravda	27.6729	42.6224	18
MS010	Pomorie	27.5955	42.5266	15
MS011	Rosenets	27.5169	42.4635	14
MS012	Burgas 2	27.7529	42.5086	36
MS111	Sozopol	27.6841	42.4298	13
MSRev5	Ropotamo 1	27.7649	42.3463	35
MS110	Maslen nos	27.8054	42.3047	45
MSRev7	Tsarevo 1	27.9790	42.1707	50
MSRev6	Tsarevo 2	27.8797	42.1746	38
MS112	Varvara	27.9191	42.1197	47
MS013	Veleka	27.9820	42.0797	14

Fig.1 Map of the research area

Results and discussion

In 2014, the autumn season was mainly observed. The established TOC concentrations ranged between 2 and 6 mg/l with the average, median and mode for this data set being 3 mg/l. The results obtained in September are comparable to those in the autumn months. Maximum TOC concentration was measured once at Cocketrice station (MS109) in October. Minimum values were registered in September at three stations: Balchik (MS104), Maslen nos (MS110) and Veleka (MS013) and in the autumn - at Sozopol station (MS111).

In 2015, the autumn season was again observed. The established TOC concentrations varied from below the method's quantification limit <1 to 10 mg/l. In the processing of the data below the limit of quantification was applied the principle to translate the result into a figure corresponding to 50% of the method's quantification limit [7]. Minimum TOC concentrations were measured at half of the stations mainly in December (median 2, mode 0.5) and in September, at almost all stations, maximum concentrations were recorded for the period studied (median 5, mode 6).

In 2016, the observations covered two seasons: spring (April and May) and summer (July, August and September). The established TOC concentrations ranged from below the method's quantification limit <1 to 4 mg/l in spring and to 5 mg/l in summer. The dynamics of change was insignificant for both seasons, with minimum concentrations prevailing in April (median 1, mode 2) and maximum in September (median 3, mode 3).

The data collected allow us to trace the dynamics of TOC in time and space.

When comparing the two autumn seasons of 2014 and 2015 (Fig. 2.) we see that in 2014 there was no dynamics unlike 2015. In November 2015, almost at all stations were measured higher TOC values than the other autumn months and in December these values decreased up to 6 times, making it the poorest month of both 2014 and 2015 autumn seasons. This may be due both to the difference in weather conditions during sampling and to productive-destructive processes of the organic matter. In 2014, air and water temperatures were slightly lower and wind-wave higher than in 2015. Comparing the respective months of the two years according to surface water layer data obtained from the CTD fluorescent sensor, chlorophyll *a* values were higher in October 2014 and lower in December 2015 [8]. In November 2015, absolute maximums of nitrate and nitrite nitrogen were recorded at Varna Bay station (MS006) and oxygen saturation was observed, which was caused by blooming of dinoflagellate *Prorocentrum cordatum* (2937.268 mg/l), accompanied by an extremum in the quantitative development (chlorophyll *a* 17 mg/l in surface horizons). In November 2015, blooming concentrations (over 1 mln cells/l) of the seasonally typical diatom *Skeletonema costatum* were also recorded in Burgas Bay [9].

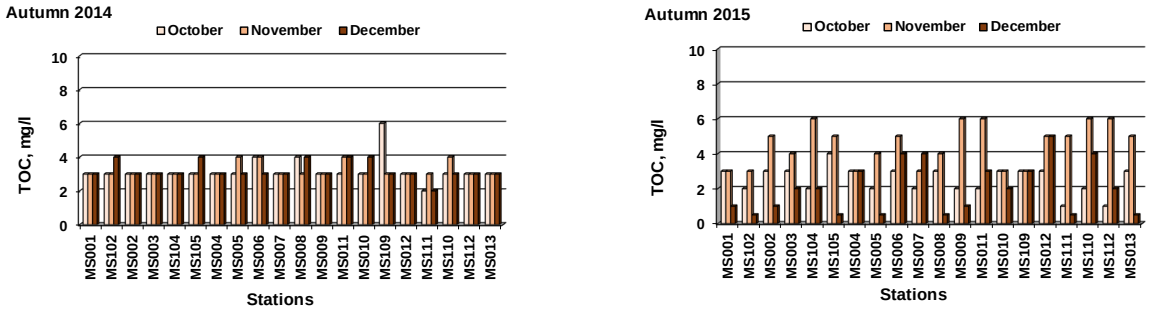


Fig. 2. Distribution of TOC in the surface seawater layer along the Bulgarian Black Sea coast in autumn 2014 and 2015

TOC data collected in 2016 covered five months of two seasons - spring and summer, with the results reported in Fig. 3. In the spring only at five stations the concentrations of organic carbon were greater than 2 mg/l, while in the summer their number increased to 29. Nevertheless, the maximum values did not exceed 5 mg/l for the study period and the median and mode for the richest month of TOC – September, were 3 mg/l. In 2016, according to the classification system for assessing the status of coastal waters [10] and on the basis of physicochemical quality elements, eight of the seventeen water bodies observed did not meet the criteria for "good" status and were assessed as "moderate". The reason for this is the disturbed oxygen regime in both seasons at most monitoring stations, as well as the recording of high values of nutrients at some of them. In the spring of 2016, a long-lasting, covering a large part of the Black Sea basin, bloom of the coccolithophore *Emiliania huxleyi* (Prymnesiophyceae) was registered, determined by the peculiarities of the hydrodynamic processes and water transfer from the northwest shelf. Blooming of the indicator species dinoflagellate *Prorocentrum minimum* in Varna Bay water body was also reported [11].

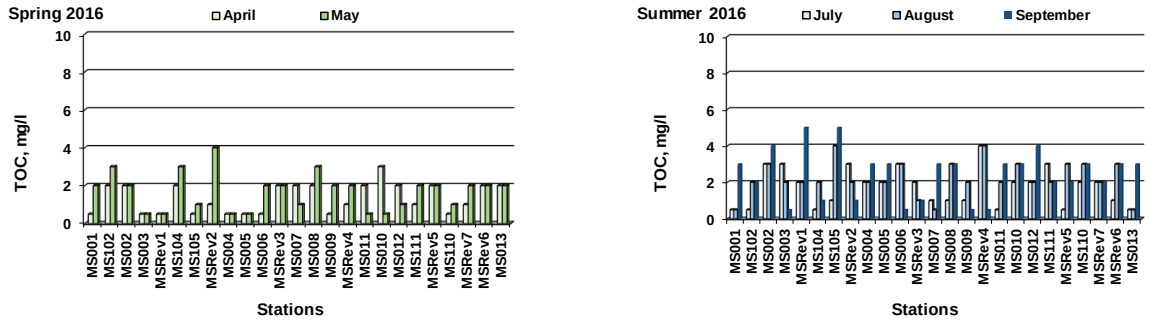


Fig.3 Distribution of TOC in the surface seawater layer along the Bulgarian Black Sea coast in spring and summer 2016

During this study, TOC was observed consecutively for three years in September. Fig. 4 illustrates its spatial distribution in the surface seawater layer along our coast for each year. When comparing the data of 2014 with 2016, it was found that although the two times higher standard deviation (1.34) in concentrations in 2016 and the presence of values below and at the limit of quantification, the two years were comparable (median and mode are 3 mg/l). In September 2015, TOC content was significantly higher at most stations than in September of the other two years. Rozhdestvenski has published long-term data on permanganate oxidation which gives a satisfactory idea of the content of the organic matter, as well as of BOD5, mainly related to living microorganisms and perishable organic matter. According to these studies, both indicators have a similar seasonal distribution with naturally higher values in the hydrological spring and summer [1]. September belongs to the summer season and data were collected about BOD5 and TOC content on seawater surface layer. According to our data, the maximum quantity for both indicators was measured in 2015 (BOD5 - 1.80mg/l, TOC - 10mg/l) and the minimum in 2016 (BOD5 - 0.20mg/l, TOC - 0.5 mg/l), which was actually the limit of determination of the methods.

The measured TOC concentrations are comparable to those reported by Agatova of dissolved and suspended organic carbon measured in the eastern part of the Black Sea (between 2-8 mg/l) in the summer of 2003 [12]. Sapozhnikov et al. reported an increase in the anthropogenic pollution and a change in the composition of the allochthonous inflow into the sea. The construction of numerous reservoirs along the riverbanks results in a decrease in the amount of phosphates and nitrates. The amount of organic nitrogen and phosphorus inputs increases. This in turn leads to an increase in microheterotrophs which mineralize the organic matter and regenerate the nutrients. Data for blooms in the northwestern and western parts of the Black Sea is numerous [13].

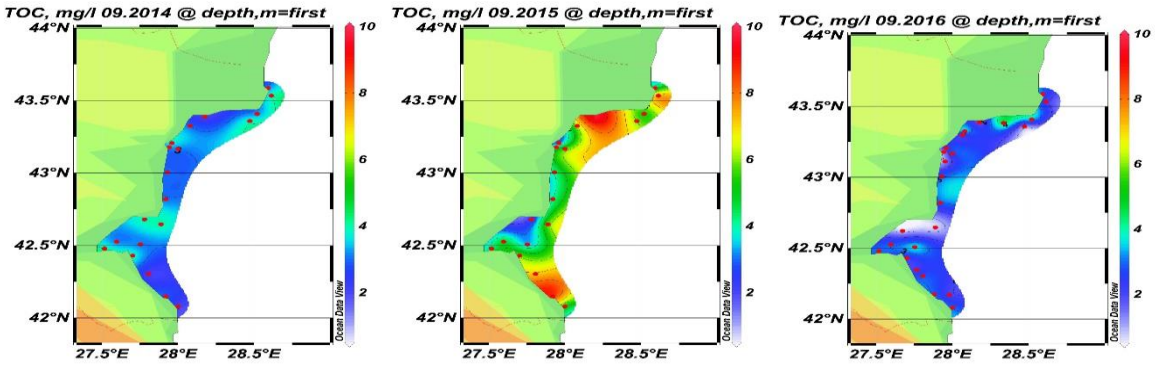


Fig. 4. Distribution of TOC in the surface seawater layer along the Bulgarian Black Sea coast in September 2014, 2015 and 2016

Conclusions

The first results of regular monitoring of total organic carbon in surface seawater in front of the Bulgarian Black Sea coast were obtained, covering three seasons: spring, summer and autumn.

The distribution of TOC in the surface seawater layer, both in time and in space, was monitored. The TOC samples analyzed during the study period were 284 and the test results showed concentrations from below the method's limit of quantification (1 mg/l) to 10 mg/l. In September 2015, TOC featured a maximum concentration during the entire period along the coast and in April 2016, its concentrations were minimal. Seasonal average values of TOC were 1 - 3.5 mg/l in spring, 1.1 - 5.4 mg/l in summer and 1.9 - 4.8 mg/l in autumn.

TOC was correlated with the physical characteristics of the environment, oxygen regime, nutrients, chlorophyll *a*, phytoplankton and other factors, but no dependencies were derived due to episodic or complete lack of accompanying TOC data throughout the period.

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