

# Total Alkalinity and pH in the Black Sea Waters in 2010-2011

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Based on the data of the expeditionary researches of Marine Hydrophysical Institute in 2010-2011, the total alkalinity  $TA$  and pH distributions in the Black Sea waters including the Danube estuary region and the changes in the  $TA$  vertical distribution since 1988 are analyzed. It is shown that the coastal and deep-sea water  $TA$  is strongly influenced by the river flow. In the Black Sea aerobic zone,  $TA$  does not change virtually with depth and does not depend on pH. In the anaerobic zone, it weakly depends on pH, but its dependence on the hydrogen sulfide concentration is of a linear character. Comparison with the data obtained in 1988 shows that in course of the last 20 years no noticeable changes in the  $TA$  values in the Black Sea aerobic and anaerobic zones took place, whereas on the sulfide zone upper boundary the total alkalinity increased by  $0.04 \text{ mg-eq}\cdot\text{l}^{-1}$ .

**Keywords:** total alkalinity, pH, aerobic and anaerobic waters, the Black Sea coastal and deep-sea areas.

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**Introduction.** In course of the whole period of hydrochemical studies in the World Ocean, a few tens of definitions of the term "seawater alkalinity" have been proposed [1]. It is explained by the fact that this parameter is a complex function of the contents of several components which are, in most cases, not conservative. In other words, relative abundance (in relation to the salinity value) of different components varies in a different manner. At the same time, importance of this parameter for assessing the marine environment state explains constant attention of the oceanographers studying both distribution and nature of this index. Moreover, in course of the last decade the parameter acquired a special significance due to its stupendous role in regulating the processes conditioning the  $\text{CO}_2$  flows on the atmosphere-ocean boundary and also the carbon cycle in the marine environment.

According to [2], the seawater alkalinity is treated as the value characterizing predominance of the "base efficiency" over the "acid efficiency". Having been examined, balance of the charges shows that the sum of the weak acids (carbonic, boric, phosphoric, silicic etc.) anions in seawater basically equalizes excess of the conservative cations ( $[\text{Na}^+] + [\text{K}^+] + 2[\text{Ca}^{2+}] + 2[\text{Mg}^{2+}]$ ) over the anions ( $[\text{Cl}^-] + 2[\text{SO}_4^{2-}]$ ) thus constituting the alkaline reserve or alkalinity.

For a simple system consisting of water and the products of dissociation of the carbonic acid and its salts, the (carbonate) alkalinity value is equal to  $[\text{HCO}_3^-] + 2[\text{CO}_3^{2-}]$  i. e., it is equivalent to the strong acid amount that is to be added in order to neutralize completely the solution alkaline potential by transforming all the forms of the carbonic acid into the free carbon dioxide.

At present determination of the titrated, or total alkalinity (*Total Alkalinity – TA*) of seawater given in [3] is the most precise: "The value of natural water total alkalinity is defined as a number of gram-ions  $\text{H}^+$  which is equivalent to the excess

of the protons' acceptors (the bases, formed by weak acids at the dissociation constants  $K \leq 10^{-4.5}$  at 25 °C and a zero ionic strength of solution) over the protons' donors (the acids with  $K \leq 10^{-4.5}$  at 25 °C and a zero ionic strength of solution) calculated per a kilogram of the analyzed sample".

According to the methods used to analyze the Black Sea waters [4], alkalinity implies the amount ( $\mu\text{g-eq}$ ) of hydrochloric acid required to change the seawater pH from the observed values 8.2-8.6 up to the value 5.4, at which the anions of all the weak acids, except for the intermediate forms of the phosphoric acid ( $[\text{H}_2\text{PO}_4^-]$ ) dissociation, will be bound to the acids' non-dissociated forms by the  $\text{H}^+$  ions. Analysis of the international inter-calibration [3] showed that application of this method yields the result which exceeded the standard by not more than 1  $\mu\text{g-eq/l}$ .

The expression for the Black Sea total alkalinity  $TA$  can be represented by the following equation

$$TA = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B}(\text{OH})_4^-] + [\text{HPO}_4^{2-}] + 2[\text{PO}_4^{3-}] + [\text{H}_3\text{SiO}_4^-] + [\text{HS}^-] + 2[\text{S}^{2-}] + [\text{NH}_3] + [\text{OH}^-] - [\text{H}^+] - [\text{H}_3\text{PO}_4] - [\text{HSO}_4^-] - [\text{HF}], \quad (1)$$

which shows that  $TA$  contains carbonate (the sum of carbonate and hydrocarbonate ions) and non-carbonate components. In the aerobic waters of the World Ocean, carbonate alkalinity comprises 96-99 % of the total alkaline reserve [1]. At the pH range 7.5-8.2,  $TA$  of the open ocean waters is conditioned practically by the carbonate  $[\text{HCO}_3^-] + 2[\text{CO}_3^{2-}]$  and borate  $[\text{B}(\text{OH})_4^-]$  alkalinity. In the Black Sea anaerobic zone, among all the non-carbonate components, the sulfide alkalinity  $[\text{HS}^-] + 2[\text{S}^{2-}]$  growing with depth, makes the largest contribution to  $TA$ . On the depth 2000 m, the sulfide alkalinity of the Black Sea water constitutes about 6 % of the total one and exceeds the borate alkalinity by a few times [5]. The role of the other non-carbonate components is insignificant.

It is important to note that one of the characteristics of the  $TA$  value is stable. It means that mixing of two volumes of water with  $M_1$  and  $M_2$  masses, and  $TA_1$  and  $TA_2$  values, respectively, yields the total alkalinity equal to  $TA = (M_1 \cdot TA_1 + M_2 \cdot TA_2) / (M_1 + M_2)$  in the resulting water mass. The same feature is inherent to the value of the total inorganic carbon content. Unlike the general alkalinity, the ratios of its individual components possess are not stable and can change being accompanied by proportional variation of the contents of the basic and acid components. Just for this reason the values of total alkalinity, pH and total inorganic carbon are basic for subsequent calculating the state of the inorganic carbon cycle. At the same time, studying of the Black Sea water general alkalinity was not systematic; among the papers published in the 1980ies, one should note [6-11].

However, the recent years were noticeable for the increased interest to this problem. It is connected, primarily, with studying the ocean carbonate system which regulates and reflects the following feature: behavior of the processes of carbon dioxide exchange between the ocean and the atmosphere; variation of the acid-base equilibrium in the marine environment accompanied by the pH; transfer and accumulation of inorganic carbon in the sea deeper layers. The applied aspects of the problem are the following: how long the ocean will be able to absorb carbon dioxide, the amount of which in the atmosphere increased from 280 to 390  $\mu\text{atm}$  in course of the previous 50 years, (i. e., it increased by 1.4 times and continues to

grow following fuel combustion [12]), and what changes in the hydrochemical structure and what ecological consequences will result from this process.

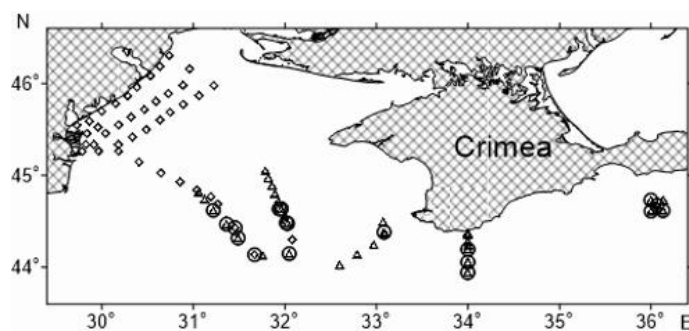
The problems of intra-annual and long-term changes in the carbonate system of the Black Sea aerobic zone in 1932-1933 were considered in [13] which showed the changes both in the pH distribution and in the carbonate system state (primarily, in content of free carbon dioxide CO<sub>2</sub>). The intra-annual changes in the carbonate system state are explained, first of all, by influence of the seasonal temperature variation upon the CO<sub>2</sub> solubility (similar to temperature dependence of the oxygen (and other gases) solubility [14]), and by seasonal changes of intensity of production and destructive processes regulating direction of transition between the carbon of CO<sub>2</sub> and the carbon of organic matter. The long-term variations in the carbonate system state are explained by the processes of the increasing CO<sub>2</sub> partial pressure in the atmosphere that results in growth of its content in the sea surface waters, and also by more intensive carbon vertical transfer. At that the inorganic carbon CO<sub>2</sub> in the sea surface layer transforms into the particular organic matter (POM) gradually sinking to the deeper layers, oxidizing and releasing CO<sub>2</sub>:



These processes naturally result in increase of the free carbon dioxide CO<sub>2</sub> and the total inorganic carbon contents, and in decrease of the pH value. At the same time, *TA* remains invariable since the CO<sub>2</sub> admission and removal do not affect it directly (equation (1)). Constancy of the alkalinity value was discussed in [13] as a proof of this statement, whereas its formation and long-term variations of its distribution in the Black Sea waters were examined neither in this paper nor in other publications.

Just for this reason the present paper is aimed at analyzing the features of the general alkalinity distribution in the Black Sea waters at present and also the processes conditioning its formation and spatial-temporal changes.

**Materials and methods.** The state of the pH and *TA* values in the Black Sea waters was studied by the scientists of the Marine Hydrophysical Institute in October, 2010 and in August, 2011 (the 67<sup>th</sup> and the 69<sup>th</sup> cruises of the R/V “Professor Vodyanitsky”). Hydrochemical observations were carried out using the network of stations shown in Fig. 1.



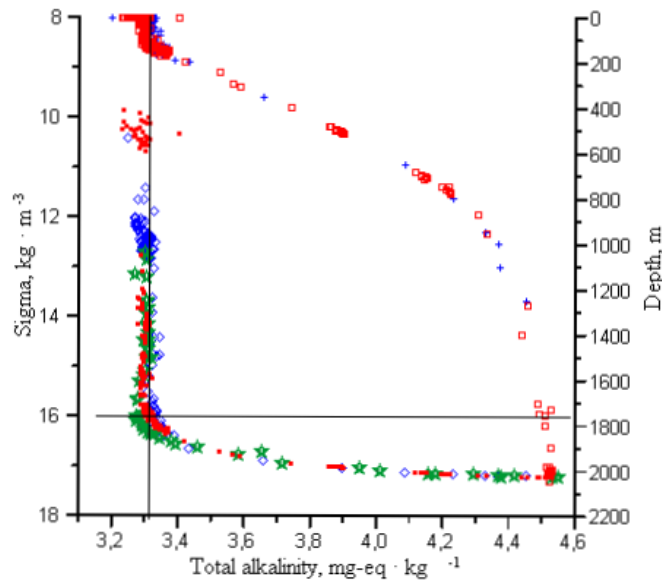
**Fig. 1.** Scheme of the stations in the 67<sup>th</sup> (◇) and the 69<sup>th</sup> (Δ) cruises of the R/V “Professor Vodyanitsky”: ○ are the stations where the *TA* value and the hydrogen sulfide content were determined

Seawater was sampled by 12 plastic bathometers of the *Sea-Bird 911 plus* probing complex (produced by the *Sea-Bird Electronics*). On each of the horizons two samples were taken in a sealed glass bottle with a section for making two parallel analyzes in course of which, according to the procedure in [4], alkalinity was determined by the method of potentiometric titration by the 0.02 M hydrochloric acid to pH = 5.4.

TA in the hydrogen sulfide waters was defined directly on the R/V and immediately after sampling since the maximum term of a sample storage before it is analyzed does not exceed four hours. All in all, in August, 2011, 121 samples were concurrently analyzed in the aerobic zone (up to the isopycnal surface  $\sigma_t = 16.0 \text{ kg/m}^3$ ) and 54 ones – in the anaerobic zone (below  $\sigma_t = 16.0 \text{ kg/m}^3$ ). Average divergence between the hydrochloric acid volumes in two titrations is 0.005 ml for the aerobic zone and 0.003 ml for the anaerobic one that constitutes 0.2 and 0.1 % of the determined values, respectively.

**Results and discussion. Vertical distribution of TA in the Black Sea thickness.**

It is more convenient to start examining the features of the TA spatial distribution in the Black Sea regions under study from its vertical profiles throughout the whole water thickness using the depth and the relative density scales. The data of 1988 (in the density scale) [7] are given in Fig. 2 for comparison.



**Fig. 2.** TA vertical profiles relative to depth (+ – 2010, o – 2011) and density (◇ – 2010, ● – 2011 and ★ – data from [7])

The presented vertical profiles permit to distinguish four zones differing in the slopes relative to the scales: the aerobic zone extending from the surface to the isopycn  $\sigma_t = 15.8 \text{ kg/m}^3$ ; the anaerobic zone located below the isopycn  $\sigma_t = 16.3 \text{ kg/m}^3$ ; the transition one situated between the isopycns  $\sigma_t = 15.8$  and  $\sigma_t = 16.3 \text{ kg/m}^3$ , and the deep-sea zone the depths of which exceed 1800 m.

**Aerobic zone.** It is seen from Fig. 2 that in the aerobic zone, almost homogeneous vertical distribution of total alkalinity is observed. The statistical analysis (Table) has confirmed very small deviations of the *TA* values obtained by the authors and in [7] from the arithmetic mean one up to the isopycn  $\sigma_t = 15.8 \text{ kg/m}^3$  (depths are around 100 m). However, the surface horizon (1 m) was excluded from the considered array because of rather high *TA* variability in the surface waters (see below).

**Average value of total alkalinity (mg-eq/l) in the upper (about 100 m) aerobic zone of the Black Sea**

Date	Quantity of samples	Arithmetic mean	Standard deviation, $\sigma$
June, 1988 [7]	23	3.300	0.013
October, 2010	48	3.308	0.017
August, 2011	53	3.296	0.009

It is seen from the Table that difference between the *TA* mean values in October, 2010 (3.308 mg-eq/l) and in August, 2011 (3.296 mg-eq/l) is 0.012 mg-eq/l or 0.4 %. It follows from Fig. 2 that differences between the *TA* values in the denoted seasons in 2010 and 2011 are observed not only in the surface layer, but also throughout the whole water column up to the anaerobic zone. However, the *TA* variations could hardly take place in the whole aerobic zone during the period between the surveys. It provides the grounds to conclude that the difference between the obtained values – 0.4 % – should be treated as an analytical error of the applied method. Such an error could be most likely caused by the errors resulting from the calibration of sodium carbonate solution by hydrochloric acid, since the error of an individual titration did not exceed 0.2 % (see above).

The value of the applied method error – 0.4 % – includes also the difference between the data obtained by the authors in 2010-2011 and those in [7] obtained in 1988. The foresaid makes it possible to assume that from 1988 to 2011, the *TA* value in the aerobic zone of the sea did not change.

It follows from Fig. 2 that uniformity of the *TA* distribution in the aerobic zone does not change in such an important point in hydrochemistry as the oxycline onset on the isopycnal surface  $\sigma_t = 14.0\text{-}14.2 \text{ kg/m}^3$  (depending on the features of the cold intermediate layer formation). Below this point, uniformity of vertical profiles of many hydrochemical characteristics (nitrogen compounds, silicic acid) is violated [15]. If the fact that the carbonate alkalinity constitutes 96-99 % of the *TA* value (see above) is taken into account, one can conclude that in the Black Sea aerobic zone, the processes of carbonates formation and dissolution are in equilibrium.

For the ocean waters, the basic source of carbonates is a river runoff the alkalinity of which is higher than that of the ocean waters. As for the Black Sea, its water alkalinity exceeds that of the ocean water by approximately 1.5 times; therefore the pattern for the Black Sea is somewhat different. Depending on the season, alkalinity of the Danube waters constituting about 80 % of the whole river runoff to the sea, may be lower or higher than that of the sea surface waters. In other words,

in a spring-summer period, the river runoff reduces and in autumn-winter – increases alkalinity of the surface waters [8].

Transition zone in the isopycn interval  $\sigma_t = 15.8-16.3 \text{ kg/m}^3$ . The *TA* variations as the aerobic conditions transit into the anaerobic ones are of particular interest. At that, on the vertical profiles of many hydrochemical components (on their density scale), there appear such characteristic features as, for example, minimum and maximum of phosphates on  $\sigma_t = 15.9$  and  $\sigma_t = 16.2 \text{ kg/ m}^3$ , or the S-like fragment on the pH profile in the isopycn interval  $\sigma_t = 15.5 - 16.5 \text{ kg/ m}^3$  [15]. The obtained in August, 2011 data on the vertical pH distribution has confirmed existence of the S-like fragment on the density scale (Fig. 3). As for another component of the carbonate system, i.e. total carbon  $C_{\text{tot}}$ , the data from [16] show that one or two minima appear on the vertical profile in the intervals  $\sigma_t = 15.8 - 16.0$  and  $\sigma_t = 16.2-16.6 \text{ kg/ m}^3$ , whereas no extremums are revealed on the vertical *TA* distribution (Fig. 2).

On the upper boundary of the hydrogen sulfide zone, a break on the *TA* vertical profile should take place due to the fact that (besides the above-mentioned components) it is supplemented with the summand conditioned by the content of the sulfide ( $\text{S}^{2-}$ ) and the hydrosulfide ( $\text{HS}^-$ ) ions. The moment of transition from the aerobic zone to the anaerobic one observed on the *TA* profile is very interesting since it can explain due to what process it is increased. It is seen in Fig. 2 that in 2010-2011 within the isopycns  $\sigma_t = 15.8-16.3 \text{ kg/m}^3$ , a smooth transition from a uniform distribution to a monotonic increase with no extremums is observed; though, according to the data in [7], in 1988 small minimum was observed in this isopycn interval. The more important issue consists in increase of *TA* in this transition zone in 1998-2011 by approximately 0.04 mg-eq/l that exceeds the above-defined method error which is 0.4 %. The reason of such a growth is, most likely, the pH decrease in the transition zone during past 20 years [13] that made the carbonate system equilibrium drift to the left:



It led to partial dissolving of calcium carbonate to compensate the carbonate ions' loss. As for the reason for the pH decrease, proceeding from [13], it is related to increase of the organic substance content on the boundary of the hydrogen sulfide zone.

Hydrogen sulfide zone. Just as in the aerobic zone, in 1988-2011 in the anaerobic one the *TA* value below  $\sigma_t = 16.3 \text{ kg/m}^3$  remained unchanged. It is interesting to note that in the aerobic zone, as pH decreases from 8.4 to 7.8 with depth, the *TA* value remains almost unchanged (Fig. 2); whereas in the hydrogen sulfide zone the situation is quite different: as the depth grows up to 2000 m, the pH value changes only by 0.2 (Fig. 3), while the *TA* value increases monotonically (Fig. 2).

It was to be expected that addition of the sulfide component to *TA* would result in its linear dependence upon the hydrogen sulfide concentration (Fig. 4). Two equations of linear dependence were obtained:

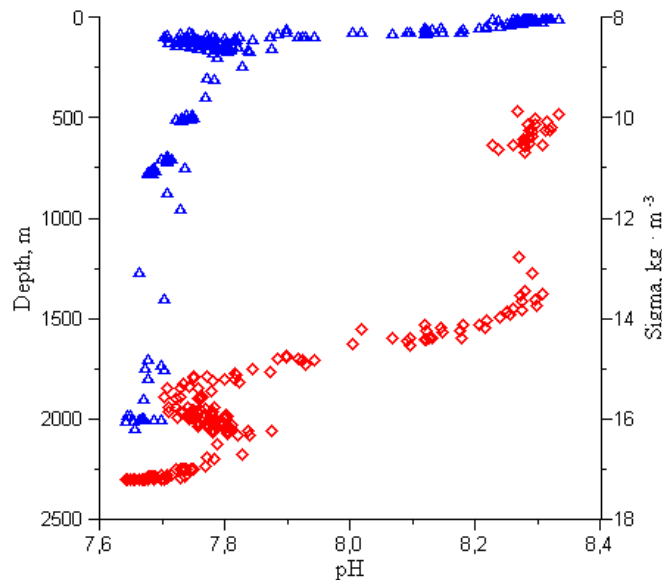
for October, 2010

$$TA, \text{ mg-eq/l} = 3.325 + 3.275 \cdot 10^{-3} [\text{H}_2\text{S}], \mu\text{M (number of samples) and}$$

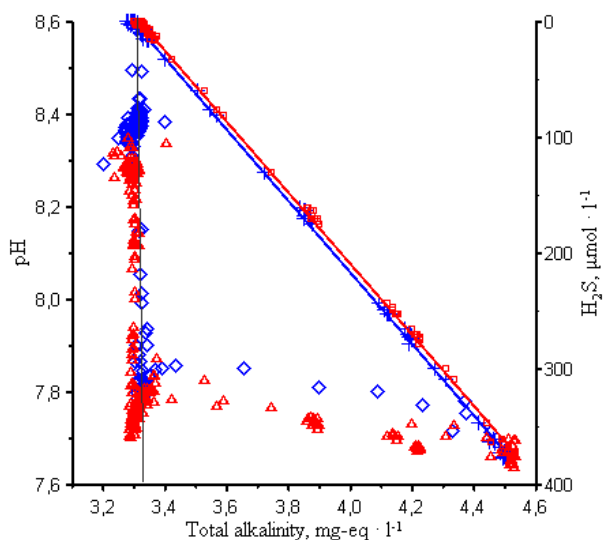
for August, 2011

$$TA, \text{ mg-eq/l} = 3.318 + 3.260 \cdot 10^{-3} [\text{H}_2\text{S}], \mu\text{M (number of samples)}$$

with high coefficients of determination 0.9991 and 0.9994, respectively, where  $[H_2S]$  is the hydrogen sulfide concentration. Since the studies were performed in one and the same region of the Black Sea, and in course of the period between the expeditions the  $TA$  value in the hydrogen sulfide zone and on its upper boundary could not change significantly (this value is conditioned by the free term in the linear equations), it is reasonable to conclude that the linear equations should be completely identical.



**Fig. 3.** Vertical profiles of the pH value in the depth ( $\Delta$ ) and relative density ( $\diamond$ ) scales

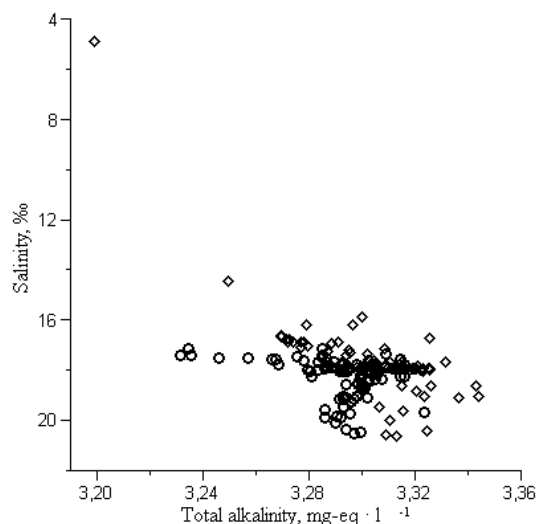


**Fig. 4.** Linear dependence of the  $TA$  value on hydrogen sulfide concentration ( $+ - 2011$ ,  $\circ - 2010$ ) and pH ( $\diamond - 2010$ ,  $\Delta - 2011$ )

High determination coefficients in two equations testify to high accuracy of individual titrations in each of the expeditions. The differences between the values of the free terms 3.325 and 3.318 mg-eq/l, and the coefficients at the hydrogen sulfide concentrations 3.275 and 3.260 are 0.2 and 0.5 %, respectively. The latter value should be considered to be a real error of the measurements carried out in the hydrogen sulfide zone which, as it was noted above, has resulted from the problem of calibration by hydrochloric acid.

Deep-sea part of the anaerobic zone. Vertical profiles of many hydrochemical characteristics in the Black Sea below 1700-1800 m demonstrate their homogeneous distribution caused by uniform dispensation of the hydrological parameters that, in its turn, was induced by thermal activity of the bottom bed [5]. The data on TA obtained in August, 2011 (in 2010 the depth of sampling did not exceed 1300 m) showed that its values did not change below the 1700 m horizon and equaled 4.521 mg-eq/l (18 samples, SD = 0.012 mg-eq/l).

General alkalinity of the Black Sea waters in the region of the Crimea and the Danube mouth. To consider the TA spatial distribution in the Black Sea surface waters, one should preliminary reveal its dependence on salinity. It is seen from Fig. 5 that during the both surveys TA grew with increase of salinity; and in October, 2010 this dependence was more pronounced since the samples were taken in the Danube mouth. Consequently, the Danube water TA was lower than that of the Black Sea water; possibility of such a situation is confirmed by the data in [8].

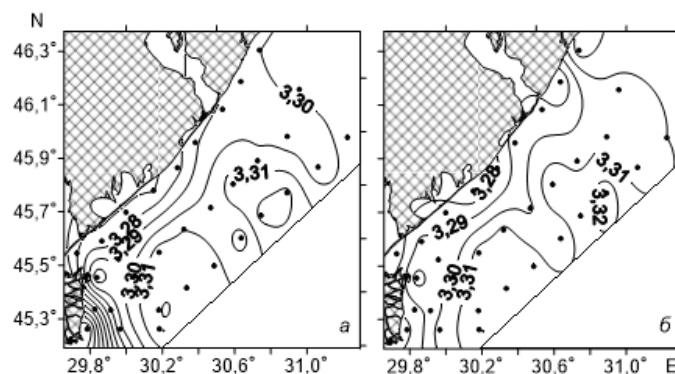


**Fig. 5.** TA dependence on salinity in the 100 m layer of the Black Sea in October, 2010 (◇) and August, 2011 (○)

The TA distribution in the surface and bottom waters in the area between the Danube and the Dniester mouths was similar (Fig. 6). It was caused by fact that the survey was carried out during the onset; as a result, the entire thickness of the test area was occupied by the Black Sea waters that came from the open part of the shelf. Izohaline 17 ‰ taken as a boundary of the Danube transformed runoff on the northwestern shelf, in the surface waters was located along the coastline at a dis-



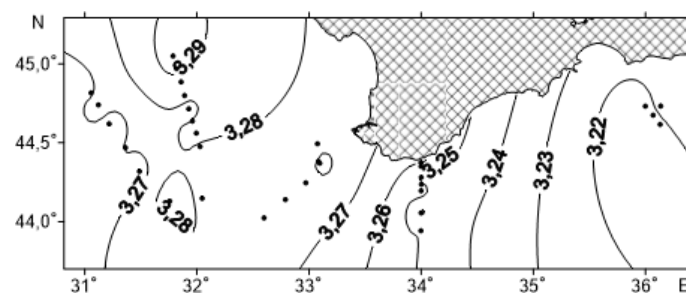
tance not exceeding two or three miles from the coast and was moved up to 10 miles off the coast just opposite the Dniester estuary and the Danube delta. The effect of the Danube runoff upon the bottom waters of the test area was practically zero. The Dniester runoff reduced the bottom water salinity near the estuary only on a small water area close to the coast (<17 ‰) [17].



**Fig. 6.** TA distribution (mg-eq/l) on the surface – *a*, and the bottom (up to the 50 m depth) – *b* horizons in October, 2010

This circumstance explains similar TA spatial distributions in the surface and bottom waters; it confirms the earlier-drawn conclusion on its uniform vertical distribution in the aerobic zone. Fig. 6, *a*, *b* shows gradual decrease of TA as it approaches the coast; at that locations of the isolines in the interval 3.29-3.32 mg-eq/l almost coincide. Only in the immediate proximity to the Danube delta, the surface water TA becomes lower than 3.28 mg-eq/l and achieves its minimum 3.20 mg-eq/l at a distance of two miles from the Danube mouth.

The TA spatial distribution in the surface waters near the Crimea coast in August, 2011 is shown in Fig. 7. It is seen that it monotonically increases to the westward from 3.22 mg-eq/l near the Feodosiya Bay to its maximum 3.29 mg-eq/l on 32° E. To the west off this meridian, the surface water TA decreases to 3.27 mg-eq/l on the test area boundary. The reasons of such changes are related to the river runoff effect upon the seawater composition: low-salinity waters of the Azov Sea flowed through the Kerch Strait to the eastern part of the test area, and the Danube runoff – to its western part [18].



**Fig. 7.** TA distribution (mg-eq/l) on the surface (1 m) horizon in August, 2011

To assess influence of the autumn and summer seasons upon the *TA* value in the surface water, one can compare the data obtained in October, 2010 and in August, 2011 at two stations with the same coordinates – 44°30' S and 32 °E. The surface water salinity in two surveys differed insignificantly (17.94-18.00 ‰ in 2010 and 17.91-17.93 ‰ in 2011). In other words, in both cases just the Black Sea waters, but not the partially transformed freshwater runoff, were examined. At the insignificantly differing salinity, in autumn the *TA* value on the surface was higher: 3.315-3.318 mg-eq/l in October as compared to 3.275-3.280 mg-eq/l in August; this exceeds the method error (0.4 %). Consequently, decrease of the photosynthesis and, hence, consumption of the dissolved inorganic carbon in autumn has resulted in increase of the *TA* value.

**Conclusion.** The expeditionary research carried out by the scientist of the Marine Hydrophysical Institute in 2010-2011 have provided the following results on distribution of total alkalinity and pH in the Black Sea waters:

- since 1988 in the aerobic and anaerobic zones of the sea, practically no changes in the *TA* vertical distribution took place;
- in 1988-2011 in the transition zone within the isopycn interval  $\sigma_t = 15.8-16.3 \text{ kg/m}^3$  *TA* increase by approximately 0.04 mg-eq/l;
- in the anaerobic zone, the *TA* linear dependence upon the hydrogen sulfide concentration is revealed;
- the *TA* distribution in the surface waters of the coastal and shelf regions located from the Danube mouth to the Feodosiya Bay, is significantly effected by the river runoff.

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