

Distribution of free carbonic acid
in the Baltic Sea water

by

E.N. Tchernovskaja

Summary.

1. The report is based on the information secured from the regular seasonal observations over the hydrochemical conditions of the sea water, carried out on the network of the stationary and provisional research stations during the International Geophysical Year and International Geophysical Cooperation Period by the Soviet research expeditions in the Baltic Sea.
2. Values of pressure of the free carbonic acid and its other forms have been calculated by methods adopted in the international practice in accordance with the observed values of pH, alkalinity, chlorinity and temperature of the sea water.
3. The major deficiency of works on the conditions and distribution of the free carbonic acid in the Baltic Sea is the insufficient information referring to the central and southern parts of the sea, and especially the lack of winter observations which are necessary for a complete characteristic of sea conditions.
4. The distribution of the free carbonic acid pressure (pCO_2), as well as the distribution of other hydrochemical ingredients, depends mainly on the fact that the Baltic Sea water is divided into two layers (which is characteristic of the Baltic Sea) owing to the limited depth of convection current penetration.
5. Seasonal variations of carbonic acid pressure in the upper layer follow the general regularities observed in other seas and depend mainly on the direction of biological processes. The effect of temperature is but of minor importance. In spring, the value of pCO_2 in the productive layer is considerably lower than the mean partial pressure of carbonic acid in the atmosphere which is due to the flowering of phytoplankton (April-May).
6. Following factors are typical of the Baltic Sea:-
 - (a) rather high values of pCO_2 at the surface in the autumn-winter period, and
 - (b) long duration of the period when carbonic acid pressure at the surface is higher than its pressure in the atmosphere, and the sea gives off carbonic acid to the atmosphere.
7. Vertical distribution of the free carbonic acid pressure is comparatively uniform in the layer of 0-40-60 m; maximum gradients are observed at depths of 60-80 m; at 80-100 m depths, the values of pressure are 10 times (and more) higher than those observed in the upper layers of water.
8. Analysis of relation of forms of carbonic acid made for some Baltic Sea research stations, shows that the surface water of the Baltic Sea contains larger quantities of free and hydrocarbonate carbonic acid and smaller quantities of carbonate carbonic acid than the Caspian Sea and the Barents Sea waters.

Extensive research work carried out by Soviet scientific expeditions in the Baltic Sea in 1957-1960 makes it possible to collect considerable information on the active reaction and alkalinity of the Baltic Sea water.

The northern and central parts of the Baltic Sea and the Gulf of Finland are those areas which have been investigated mainly.

The hydrochemical material had been collected seasonally on the base of the network of the stationary and provisional international research stations.

From the analytical data obtained, it was possible to calculate the partial pressure of the carbonic acid (pCO_2) to conclude about its distribution and annual variability.

Values of the carbonic acid partial pressure were calculated from the relations between the values of pH and those of alkalinity determined in 1931 by the special committee of the International Council for the Exploration of the Sea (Buch, Harvey, Wattenberg and Gripenberg (7)).

For calculation they used the formulae:-

$$\log p\text{CO}_2 = pC - pH + \log \text{Alk}_k - \log \text{kHCO}_3'$$

Values of pC and $\log \text{kHCO}_3'$ were determined from the tables compiled by the above authors; the value of pK_2' was determined from the table composed later by Buch on the basis of the more specific values of K_2' (5).

The value of pH was determined by means of a colorimeter against Palitzsch borate buffer solutions and Sørensen phosphate buffer solutions in compliance with the special extended sea-scale of the range 6.8-9.0. To obtain the "true" values of pH the corresponding temperature and salt corrections have been introduced into the observed values.

The alkali reserve (or titration alkalinity) was found by titrating 0.01 normal HCl with a mixed reagent of methyl red + methyl blue. Carbonate alkalinity was determined by the formulae:-

$$A_k - A_{\text{titr.}} = \alpha ;$$

The value of α was taken from the table given by Buch (6).

The character of the free carbonic acid distribution (in terms of $p\text{CO}_2$) in the Baltic Sea as well as the distribution of oxygen and biogene elements depend on the following factors:-

- (a) intercontinental position of the sea;
- (b) almost completely closed cycle of biogene matter;
- (c) vertical zonality of water typical of the sea;
- (d) stagnant effects at the depths of 100 m and more which depend on the rate of penetration of the Kattegat waters into these depths.

The annual variability of pressure of the free carbonic acid in the Baltic Sea is shown by isopleths in the chart (fig.1).

The boundary of vertical seasonal variations of pressure lies approximately at 60-80 m depth which corresponds to the isoline 20. However, within the active layer of water the pressure does not exceed $5-10 \times 10^{-4}$ at. The most distinct seasonal variations of $p\text{CO}_2$ (determined mainly by the change of biological seasons) takes place in the productive layer of water at a depth of 0-10-20 m, the maximum range being in the Gulf of Finland.

Mean values obtained for the period of observations are shown in Table 1.

These values refer to the various seasons of the sea areas and hold for the layer of water of 0-10 m which is in contact with the atmosphere all the year round and which is biologically active and practically uniform in the vertical direction. Though this layer of water is well mixed and is in permanent contact with the atmosphere, the pressure of carbonic acid in it is but rarely equal to the CO_2 pressure in the atmosphere the mean value of which is roughly equal to 3×10^{-4} at. The minimum values are naturally observed in spring when diatoms are flowering (April-May).

At this time of the year the distribution of $p\text{CO}_2$ values on the surface (fig.2) within the sea area is most non-uniform. The minor values refer to the Gulf of Finland and the Gulf of Riga which agrees with the fact that these areas are those showing the most intense flowering of phytoplankton in May. It is noteworthy that the minimum values observed in the Gulf of Finland in 1959 fall in a period of unusually intense growth of phytoplankton (spring 1959). In spring and in summer the pressure of the free carbonic acid is always followed by the overoxygenation and is below its pressure in the atmosphere almost all over the sea surface. Thus the sea absorbs carbonic acid from the air and this carbonic acid is then constantly consumed by the growing phytoplankton.

By autumn $p\text{CO}_2$ in the productive layer of water is considerably increased owing to the cessation of phytoplankton flowering and to the process of dissociation of the dying off organisms.

In 1957-1960 mean values of $p\text{CO}_2$ in the 0-10 m layer of sea water had been changing from the minimum values of $1.8-3.2 \times 10^{-4}$ at. in spring to the maximum ones of $4.9-5.3 \times 10^{-4}$ at. in winter. The summer and autumn values approached mean values for 1927-1938 given by Buch (6); a certain disagreement of the spring values is possibly the result of later periods of observations.

The maximum values of $p\text{CO}_2$ are observed in winter which fact is very interesting because in winter the activity of biological processes is very low, frequent storms contribute to a good contact of the upper layers of water with the atmosphere and (which is important) the very fact of temperature reduction should bring about a decrease of the carbonic acid partial pressure in the sea water.

The increase of $p\text{CO}_2$ values in winter is apparently the result of penetration of large quantities of carbonic acid into the upper layers of water from the lower ones (where the concentration of carbonic acid is high) owing to the deep convection mixing in winter.

Fig. 3 shows the variation of actual and calculated values of $p\text{CO}_2$ during one year (1958-1959) with changing of temperature and salinity but with the constant initial value of pH (for the initial value is taken the value of pH observed in August 1958 when the free carbonic acid pressure in the surface was approximately equal to the mean atmospheric pressure). Obviously the character of the seasonal variations of $p\text{CO}_2$, the actual values of $p\text{CO}_2$ is opposite to the variations of the calculated values of $p\text{CO}_2$, and is consequently opposite to the temperature regime of the sea water during the whole year with the exceptions of periods of intense heating of the sea surface (May-August). Thus, the annual variations of the free carbonic acid in the Baltic Sea (even in the surface) depend mainly not on the temperature variations but on the biological processes of absorption and excretion of carbonic acid reflected in pH values, and on the conditions of interchange between the upper and lower layers of sea water.

Comparison of the data obtained and those determined for other intercontinental and outlying seas shows that summer values of $p\text{CO}_2$ for the upper layer of water are very similar. According to Schultz (8), for instance, the pressure of the free carbonic acid in the North Sea surface water (as determined by means of the Krogh apparatus), with pressure variations from 2.6 to 4.5×10^{-4} at. was on average equal to 3.3×10^{-4} at., and in the Kattegat and in the southern part of the Baltic Sea, with pressure variations from 2.6 to 4.4×10^{-4} at., it was equal to 3.4×10^{-4} at.

Proceeding from the investigations performed by Chigirin, Dobrjanscaja (3) quotes values within 3.5 - 5.5×10^{-4} at. for the Black Sea; Brujevitch (2) states that in summer 1934 $p\text{CO}_2$ in the 0-50 m layer of the Caspian Sea was on an average equal to 4.0 - 4.3×10^{-4} at. According to the information presented by Chigirin (4), the summer values of $p\text{CO}_2$ in 0-10 m layer of the Kara Sea and Greenland Sea are 1.7 - 2.7×10^{-4} at., and 1.8 - 2.6×10^{-4} at. respectively, i.e. considerably lower than the above given values. For the Barents Sea Brujevitch (1) gives values of 2.3 - 2.8×10^{-4} at.

Rather high pressure of the free carbonic acid in the active layer of the Baltic Sea in winter is obviously a characteristic feature of its hydrochemical regime. As a result, the period when the sea gives off the excessive carbonic acid to the atmosphere is rather long. Approximate calculations (fig.1) performed on the base of 4 years of observations show that in the 0-10 m layer of water, the partial pressure of carbonic acid is on an average below the CO_2 pressure in the atmosphere or closely approaches the equilibrium pressure during 3-4 months in a year only; the rest of the time the sea gives off carbonic acid to the atmosphere.

The vertical distribution of $p\text{CO}_2$ values in the active layer of water is comparatively uniform; the thickness of the productive layer of water in which the maximum values of $p\text{CO}_2$ are observed in summer amounts to 20 m; in the more fresh waters such as the Gulf of Finland and the Gulf of Riga it amounts to 10-15 m. In the deep-water areas of the open sea the thickness of the layer in which $p\text{CO}_2$ values in summer are below 3×10^{-4} at., sometimes amounts to 30-35 m. The layer of water characterized by a temperature jump and sharply pronounced during the warm period of the year at depths of 10-15 m, affects but very little the vertical distribution of $p\text{CO}_2$.

The jump in the distribution of the free carbonic acid pressure is well pronounced at depths from 40-80 m, still better at depths from 60-80 m, and is most pronounced in winter. Its position coincides in general with the boundary for the penetration of the convection currents into the deep layers in autumn and winter, i.e., with the lower boundary of the active layer of sea water. Table 2 shows mean gradients of the $p\text{CO}_2$ increase with depth; maximum values of $p\text{CO}_2$ are observed in the 60-80 m layer of water, where they can be very high.

In the deep-water area of the Baltic Sea the quantity of the free carbonic acid is very great. Below 80-100 m gradients $p\text{CO}_2$ values varying within the range of 25 - 50×10^{-4} at. are 10 (and more) times higher than the values obtained in the uppermost layer of water.

The relation between $p\text{CO}_2$ values for the active zone and those for the deep-water area of the Baltic Sea is very close to the relation found by Dobrjanscaja (3) for the Black Sea.

Considering the approximate character of the calculations of pressure of the free carbonic acid it is possible to conclude that in general its value in the deep-water zone is comparatively uniform (fig.1). This is also proved by very negligible gradients of pCO_2 increase below 80-100 m depth (table 2). The distribution of pCO_2 in the water layer near to the bottom as well as the distribution of oxygen and other hydrochemical ingredients nicely contour the boundaries of areas of stagnation and the distribution of the latter over the sea area (fig.2).

It should be pointed out that values of pCO_2 of the more or less same order are observed in the most stagnant areas, for example, at the depths of Gotland Deep as well as in the Landsort Deep in the mouth of the Gulf of Finland etc. However, the concentration of oxygen and especially biogenes in the above mentioned regions differs greatly which determines the degree of stagnation of these regions. Comparison of data obtained for the Gotland Deep during 1957-1960 with the mean values obtained for it during 1927-1938 by Buch (6) shows that in either case pCO_2 values are nearly similar though stagnant effects at the depths of the Gotland Deep² in 1927-1938 were much weaker than in 1957-1960 which is proved by the mean content of oxygen at 200-230 m levels:

0.81-2.42 mg/l and 0.00 mg/l, respectively.

Such constancy of the amount of free carbonic acid in the Gotland Deep area or, in other words, a certain limit of its accumulation there, is apparently related to the fact that with oxygen completely absent and in presence of hydrogen sulfide (i.e. in the reductive medium) a certain quantity of the free carbonic acid can be assimilated during the oxidation of oxygen and ammonia, during the transition of ferric salts into the soluble protoxide form and during other chemical processes. In connection with the above said it could be mentioned that a slight reduction of pCO_2 values was almost constantly observed at the lowest levels of the Gotland Deep. Mean values obtained by Buch show this reduction.

Approximate calculations of carbonic acid forms had been carried out on the basis of values of alkalinity, pH, salinity and temperature according to the tables given by Buch, Harvey, Wattenberg and Gripenberg (7) for the two research stations in the Baltic Sea having different degree of stability of the hydrochemical conditions. The total amount of carbonic acid in mols per litre was determined by summation of the obtained values. When compared, these values proved to be very much like those determined by means of the Buch nomogram (6).

Comparing the values calculated for the Baltic Sea surface water with the corresponding values for the Caspian Sea and the ocean (table 3) it is possible to reveal those peculiarities of correlation between various forms of carbonic acid which are characteristic of the Baltic Sea.

The content of carbonates (in %) in the Baltic Sea water is considerably lower and the content of hydrocarbonates and free carbonic acid is considerably higher than in the Caspian Sea and in the Barents Sea waters.

Table 1

Mean values of pCO₂ in the 0-10 m layer of water observed during 1957-1960

| Time of observations | <u>Gulf of Finland</u> | | | <u>Northern Part</u> | | | <u>Central Part</u> | | | <u>Southern Part</u> | | | <u>Entire Sea</u> |
|----------------------|------------------------|------|----------------|----------------------|------|----------------|---------------------|------|----------------|----------------------|------|----------------|-------------------|
| | extreme | mean | No. of observ. | extreme | mean | No. of observ. | extreme | mean | No. of observ. | extreme | mean | No. of observ. | mean |
| February-March | 3.9-7.5 | 5.3 | 6 | 4.0-6.9 | 5.3 | 12 | 4.0-6.3 | 4.9 | 27 | 4.6-6.5 | 5.2 | 16 | 5.0 |
| May | 0.5-3.6 | 1.8 | 32 | 1.3-3.4 | 2.3 | 32 | 1.6-4.0 | 2.3 | 56 | 1.7-5.4 | 3.2 | 20 | 2.3 |
| August | 2.0-8.1 | 4.0 | 18 | 2.2-4.9 | 3.1 | 34 | 1.2-4.2 | 2.6 | 62 | 4.2-5.0 | 4.6 | 2 | 3.0 |
| October-November | 4.0-7.9 | 5.7 | 30 | 3.0-5.8 | 4.8 | 22 | 3.1-5.9 | 4.5 | 62 | 3.1-4.2 | 3.6 | 10 | 4.8 |

Table 2

Mean gradients of increase in pCO₂ values for 10 m depth

| Layer of water in m | <u>extreme values</u> | | | | <u>On an average throughout the sea</u> | | | |
|---------------------|-----------------------|----------|----------|------------------|---|----------|--------|------------------|
| | March | May-June | August | October-November | March | May-June | August | October-November |
| 0-10 | 0.0-0.9 | 0.0-1.1 | 0.0-0.5 | 0.0-0.7 | 0.2 | 0.3 | 0.3 | 0.2 |
| 10-20 | 0.0-0.6 | 0.1-2.2 | 0.7-3.0 | 0.0-0.7 | 0.2 | 0.7 | 1.8 | 0.3 |
| 20-60 | 0.2-1.5 | 0.6-3.3 | 0.3-2.9 | 1.7-3.7 | 0.6 | 1.2 | 1.7 | 2.4 |
| 60-80 | 0.8-12.5 | 5.8-11.8 | 7.9-19.1 | 0.6-11.1 | 7.6 | 9.1 | 12.1 | 7.5 |
| 80-100 | 3.0-8.4 | 1.5-6.7 | 0.5-3.4 | 1.2-5.0 | 4.2 | 4.0 | 1.7 | 2.7 |
| 100-200 | 0.0-0.6 | 0.4-2.2 | 0.0-0.4 | 0.0-0.7 | 0.4 | 1.0 | 0.2 | 0.3 |
| 200-300 | 0.0-2.8 | 0.0 | 0.0 | 0.0-0.1 | 1.4 | 0.0 | 0.0 | 0.0 |
| 300-bottom | 0.0 | 0.1 | 0.1 | 0.1 | 0.0 | 0.1 | 0.1 | 0.1 |

Table 3

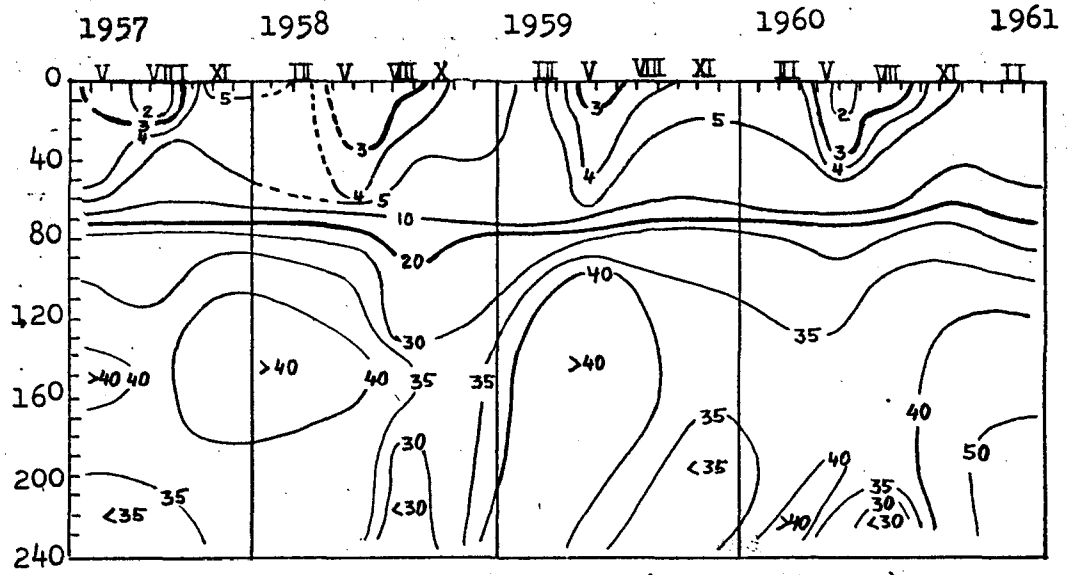
- 6 -

Forms of carbonic acid in the surface water of
the Baltic Sea (57°22'N, 19°57'E.)
the Caspian Sea (38°52'N.) and
the Barents Sea (73°N., 33°34'E.)

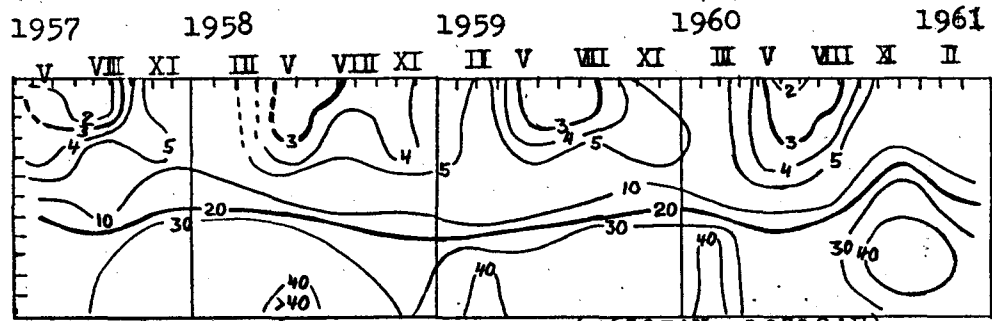
| Date | <u>Baltic Sea</u> | | <u>Caspian Sea</u> | <u>Barents Sea</u> |
|------|-------------------|-----------------|------------------------|--------------------|
| | March, 11 1959 | May, 20 1959 | September, 7-9 1934 | June, 7 1930 |
| | 2.38 | 8.07 | 25.24 | 3.8 |
| | 4.13 | 4.09 | 5.36 | 19.38 |
| | 7.48 | 7.41 | 12.74 | 34.99 |
| | 7.91 | 8.31 | 8.42 | 8.37 |
| | 1.509 | 1.480 | 3.62 | 2.38 |
| | 0.037 | 0.012 | 0.013 | 0.008 |
| | 1.464 | 1.354 | 2.76 | 1.55 |
| | 0.021 | 0.064 | 0.428 | 0.416 |
| | 1.522 | 1.430 | 3.201 | 1.974 |
| | 2.4 | 0.8 | 0.4 | 0.4 |
| | 96.2 | 94.7 | 86.2 | 78.4 |
| | 1.4 | 4.5 | 13.4 | 21.2 |

Bibliography

1. Brujevitch, S.V.; Hydrochemical research work of the State Bathygraphic Institute in the Barents Sea in 1921-1930 - Reports on the 1st session of the State Bathygraphic Inst. No.1, 1931.
2. Brujevitch, S.V.: Hydrochemical processes in central and southern parts of the Caspian Sea (from data obtained in 1934) USSR Acad. of Science Publish.House, M. 1937).
3. Dobrjanscaja M.A.: Principal characteristics of the hydrochemical conditions in the Black Sea - Works of Sevastopol Biological Station, v.13. USSR Acad. of Science Publish. House, M. 1960.
4. Chigirin, N.J.: Carbonic acid system in the North Polar Basin Waters and in the Greenland Sea. Works of the first high-latitude expedition of the ship "Sadko" in 1935 - Issue I v.I. GLAVSEVMORPUT. L. 1939.
5. Buch, K.: New determination of the second dissociation-constant of carbonic acid in the sea water - Acta Academ. Aboensis, Math. et Phys., Vol. XI, No.5, Abo, 1938
6. Buch, K.: Kolsyrejämnvikten i Baltiskahavet - Fennia, Vol. 68, No. 5.
7. Buch, K., Harvey H., Wattenberg, H., and Gripenberg, S.: Über das Kohlensäuresystem im Meerwasser - Rapports et Procès-Verb. des Reun. Cons. Perm. Int.p.Explor.de la Mer, Vol. 79, Copenhagen 1932.
8. Schulz, B.: Hydrographische Beobachtungen insbesondere über die Kohlensäure in der Nord-und Ostsee im Sommer 1921. Aus dem Archiv der deutsch. Seewarte, Vol. XL, No. 2, Hamburg, 1922.



Station 8. Depth 230 m. (Gothland Deep).



Station 6. Depth 120 m. (56°05'N, 19°10'E)

Figure 1. Variations from year to year of free carbonic acid pressure in the central part of the Baltic Sea.

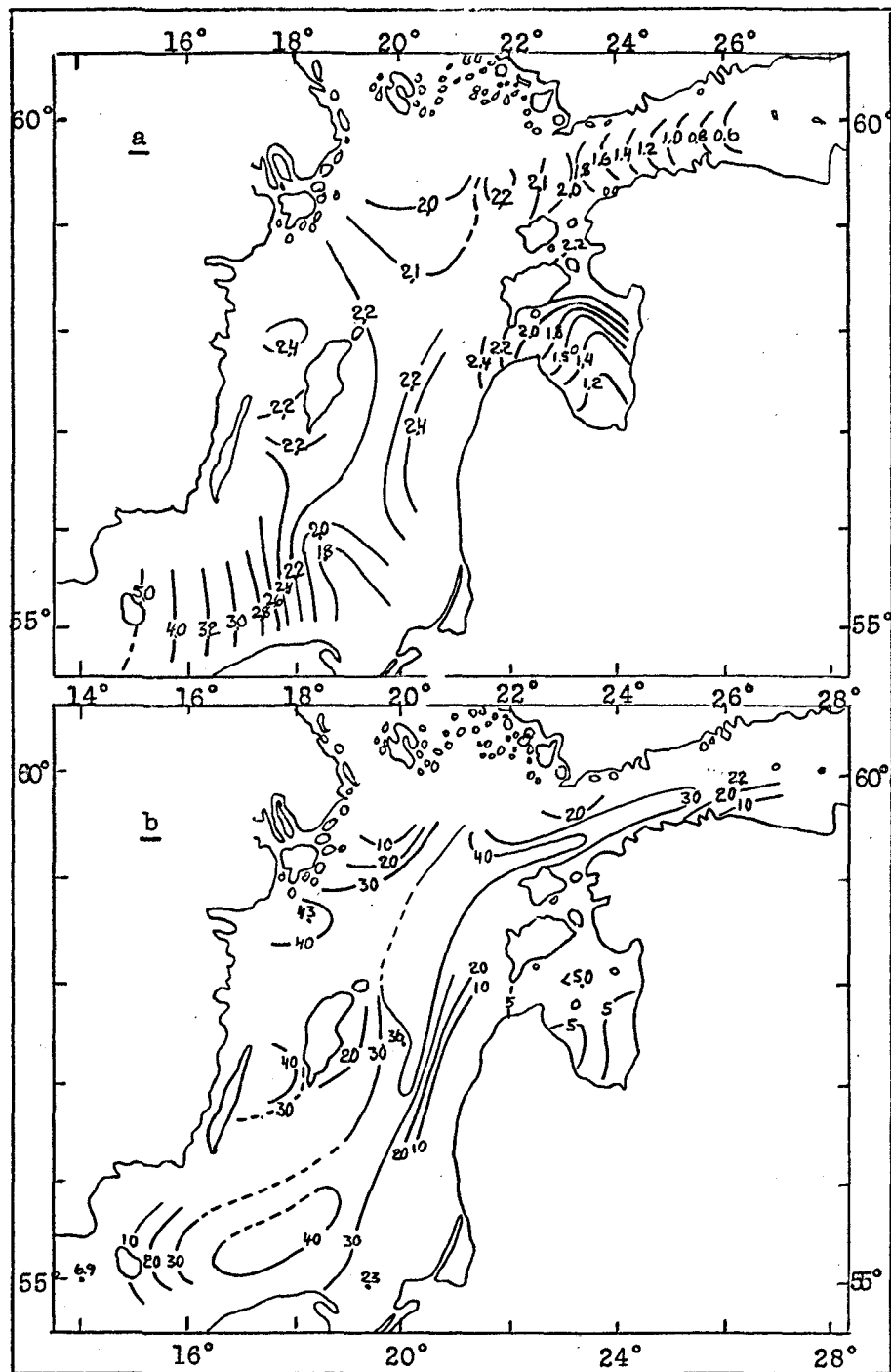


Figure 2. Distribution of free carbonic acid in surface water (a) and in the water layer close to the bottom (b) in May, 1959.

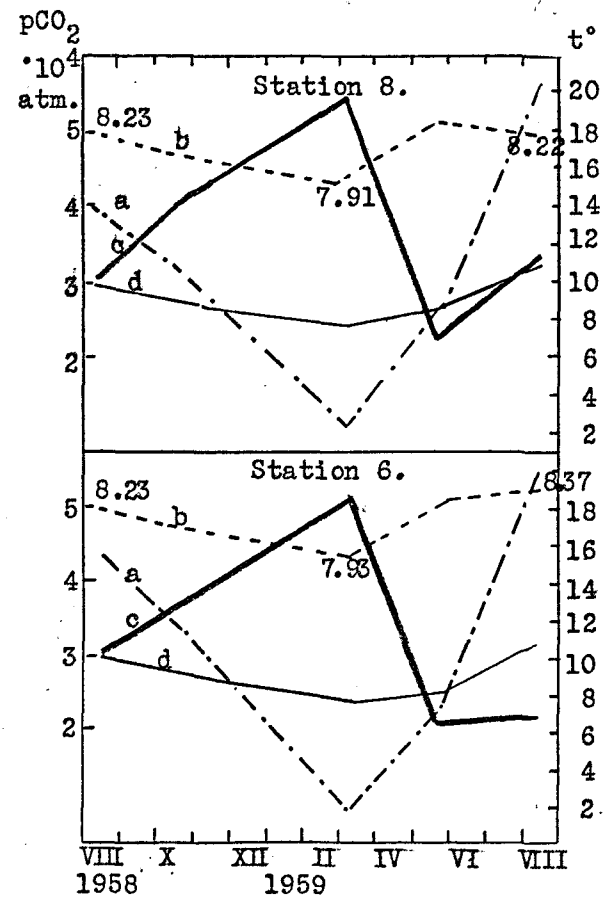


Figure 3. Seasonal changes of temperature of water (a), pH (b), pCO₂ actual values (c) and pCO₂ calculated values (d).