Experimental study of CO_2 gas exchange in the system "atmosphere – water surface" of Lake Baikal (statement of experiment)

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Main problems of the technique for carrying out comprehensive experiments on the study of gas exchange between the atmosphere and water surface of Lake Baikal in the period of open water are considered. The most interesting results available to date are briefly presented.

Introduction

Carbon compounds and their circulation in the Earth system are the main factors determining biomass production on the land and in the World Ocean. The carbon cycle is closely related with climate and the changes occurring in the natural medium.

The carbon-containing gases such as carbon dioxide and methane are among the most important greenhouse gases and, variations of their contents in the atmosphere can essentially affect the change of the radiative budget of the planet.

At present, the most debatable problem of the general problem of the climate change is the reason of the observed steady increase of the carbon dioxide concentration in the atmosphere and its effect on the global warming.

This fact made the researchers to concentrate the main attention on the processes of the regional scale and on the search for earlier ignored natural and anthropogenic sources and sinks determining gas exchange in the system "atmosphere – underlying surface" [Ref. 1].

Most investigations in the hydrosphere are devoted to gas exchange between the atmosphere and World Ocean, but the information about these processes in the atmosphere over fresh water reservoirs is very limited.[2–4]

Lake Baikal is one of the unique natural objects of Siberia, which mainly determines the state of the environment in the region.[5–10]

As to the cycles of the carbon and its compounds, the choice of Baikal as the object under study makes it possible to overcome the limits of regional problems, because Baikal is, in our opinion, the only natural laboratory, in which the majority of processes can be set off in quite clean form.

It is practically impossible to find a standard in natural objects, which would keep its inner properties during several years, because all natural objects are under the effect of increasing anthropogenic loading and constant trend of climate change.

In this aspect, water of Lake Baikal is, likely, the only unique exception. Long-term investigations of water chemical composition of the Lake has shown that real variations in concentrations of main cations and anions do not lie out of the limits ±1%, and, hence, the Lake Baikal water can be considered as natural standard of clean water of the constant composition, "which will not be changed in nearest decades" [Ref. 10].

Based on high cleanness and constancy of the chemical composition of the water, one can suppose that the main seasonal and annual variable in Lake Baikal is the biological component.

Therefore, it is possible to sufficiently correctly select physical, chemical, and biological components in the complex process of gas exchange between water and the atmosphere.

Procedure of the complex experiment

A series of investigations of the chemical composition of Baikal surface water, carried out earlier in its different regions, allowed us to answer some questions about seasonal and partially diurnal variability of the CO_2 content in water.[5–9] As applied to the gas exchange processes, the absence of direct atmospheric measurements or insufficient comprehensiveness of experiments seriously restrict the possibilities of the use of their results for quantitative estimations.

To solve this problem, a series of comprehensive experiments was started in 2002 at the coast of Lake Baikal.

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The west coast of the Southern Baikal in the region of village Bol'shie Koty was selected for measurements. According to a series of measurements of aerosol and gas characteristics of the atmosphere carried out earlier, this part of the territory can be considered as background. The experimental complex was located at the stationary site of the Limnological Institute SB RAS.

Measurements were carried out by 2–3-week cycles in different hydrological seasons. The choice of the regime of measurements was caused by the following circumstances. On the one hand, the alternation of several synoptic cycles falls into this period, the temperature regime is not changed greatly, and, hence, the obtained data in each hydrological season can be meant representative. On the other hand, short series of measurements make it possible to minimize the cost of the experiment.

Taking into account the accuracy characteristics of the available instrumentation and the fact that turbulent exchange over the cold water surface is much lower than over the land, we preferred the method of accumulative chambers to measure the fluxes of CO_2.

Figure 1 shows the developed diagram of the experiment *5*, the chambers and the places of their arrangement (*1*, *2*, *3*, *11*), some devices (*4*, *7*, *10*, *12*), and the general view of the outlying point of the observatory *6*, in which the recording devices were situated.

Two floating semi-immersed chambers *1*, *11* (Fig. 1) were located on the water surface at a distance of about 30 m from the coast. One of the chambers was permanently closed, the second was equipped with the device for automated ventilation. Measurements of the carbon dioxide concentration were carried out by means of the gas analyzer consisting of a sensor, a pump, and 3-position air valves. Gas was sampled in turn from three points and delivered to the gas analyzers through tubes. Air was sampled directly from the atmosphere through the first channel (the height of the sampling was 1 m above the water surface) and from measurement chambers through two other channels.

Controlling the regime of the chamber ventilation, switching air valves for reading from measurement channels, and data recording were computerized.

To monitor the content of CO_2 in water,[11] the floating electrode of the pH-meter "Expert" was placed directly in the chamber, the data from which were also recorded by the computer. The frequency of digitizing the signals from the gas analyzer and polling the pH sensor was 100 Hz with the averaging over 1000 readings.

The chemical analysis of water was carried out in the filed laboratory situated at the coast, where the values of pH, concentrations of dissolved oxygen, hydrocarbonate, nitrate, and phosphate were measured. Measurements of the ions H^+ activity were carried out by means of pH-meter "Expert" with the error of 0.02. The oxygen was measured by Winkler method with relative error of 0.3%, hydrocarbonate was measured by the potentiometer method (a relative error of 1%). Concentrations of nitrate and phosphate were measured by photometric methods with relative errors of 4 and 1.5%, respectively. The content of CO_2 in water was calculated using the value of pH and the concentration of hydrocarbonate.[11]

Some water samples were fixed for subsequent biological analysis. They were processed after the expedition by specialists of Limnological Institute SB RAS.

Obviously, the photosynthesis of phytoplankton plays a key role in the change of concentrations of carbon dioxide, oxygen, and biogenic elements. At the same time, classic methods for taking into account the biomass of plankton water plants and measurements of the photosynthesis intensity are laborious and time-consuming, that seriously hinders their application in the monitoring regime. Corresponding express techniques of fluorescent analysis can partially replace them.[12] Regular measurements of the fluorescent characteristics of water samples were started in 2004.

Development of the experimental technique

Technique for estimation of fluxes

Preliminary experiments have shown that the arrangement of the chambers on the water surface works well practically in all weather conditions, except for storm situations, when their uncontrollable ventilation is possible at high waves.

The flux was calculated based on the rate of the change of the carbon dioxide concentration in the chamber during a certain time interval:

$$F = \frac{\Delta C}{\Delta t}\frac{V_{\text{cham}}}{S_{\text{cham}}}. \quad (1)$$

Here $\Delta C/\Delta t$ is the change of the carbon dioxide concentration during the time interval Δt, V_{cham} is the air volume in the chamber above the water surface, S_{cham} is the area of the chamber bottom.

First measurements were conducted only with the closed chamber *5*. The diurnal behavior of the carbon dioxide concentration changes in the closed chamber, near-water atmosphere, and pH of the surface water are well exemplified by Fig. 2, where the diurnal rhythms of variability of the gas exchange process are well seen. At the same time, at such statement of measurements, correct estimation of the flux is possible only on linear parts of the curve.

In order to increase the time resolution of flux measurements, the second chamber operating in the regime of regular automated ventilation (see Fig. 1, *2* and *3*) was introduced in the experiment since 2004. An example of record of the signals from two chambers is shown in Fig. 3 (Fig. 3*a* shows the period of emission of carbon dioxide from the water surface and Fig. 3*b* relates to its sink).

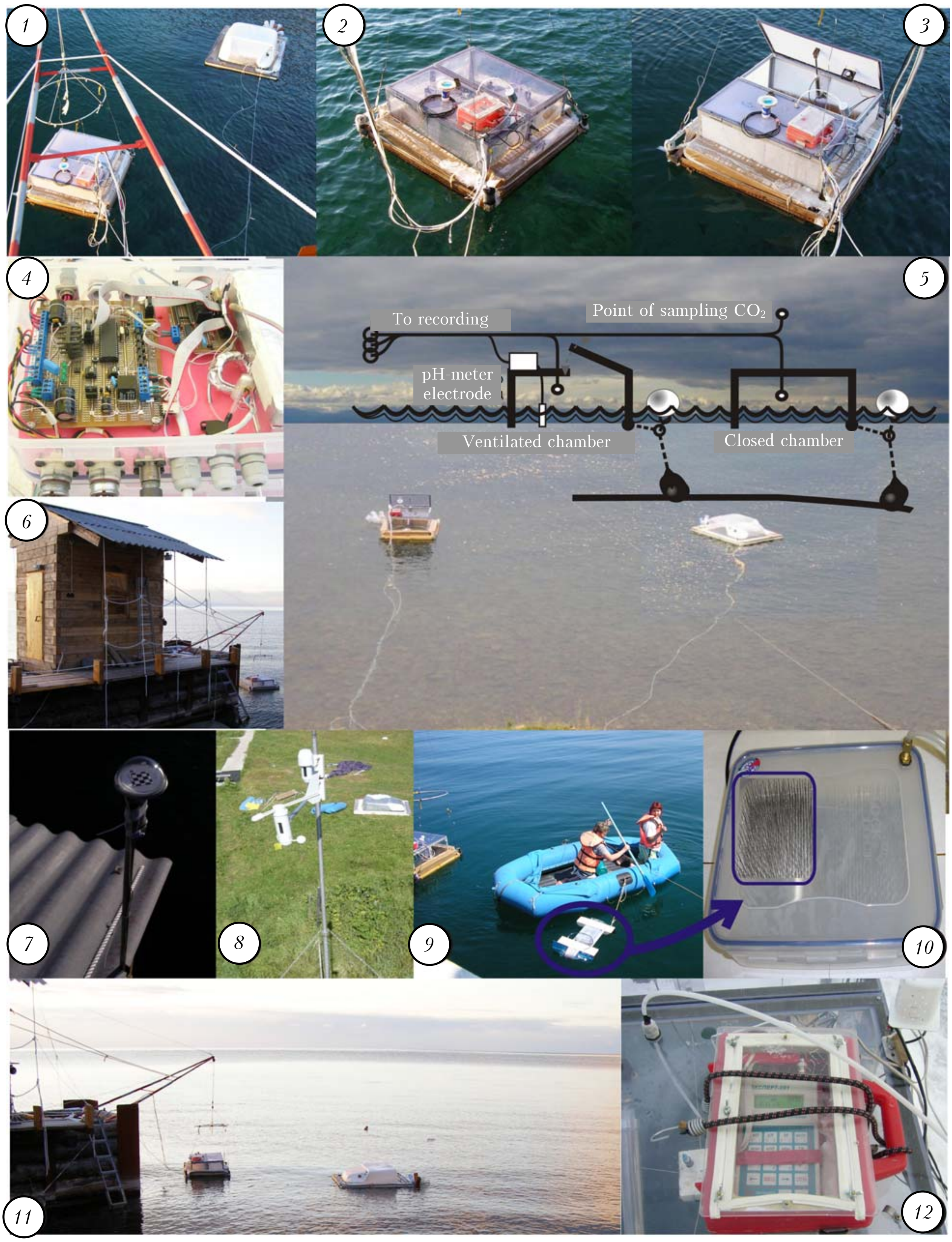

Fig. 1. Main fragments of the comprehensive experiment: lifting device of the chambers when working from the remote site of the observatory (*1*), ventilated chamber in closed state (*2*), ventilated chamber during ventilation (*3*), gas analyzer (*4*), organization of air sampling at three points (*5*), general view of the remote site of observatory (*6*), pyranometer (*7*), meteorological mast (*8*), surface water sampling (*9*), device "hedgehog" for surface water sampling (*10*), chambers in working state (*11*), arrangement of pH-meter "Expert" on one of the chambers (*12*).

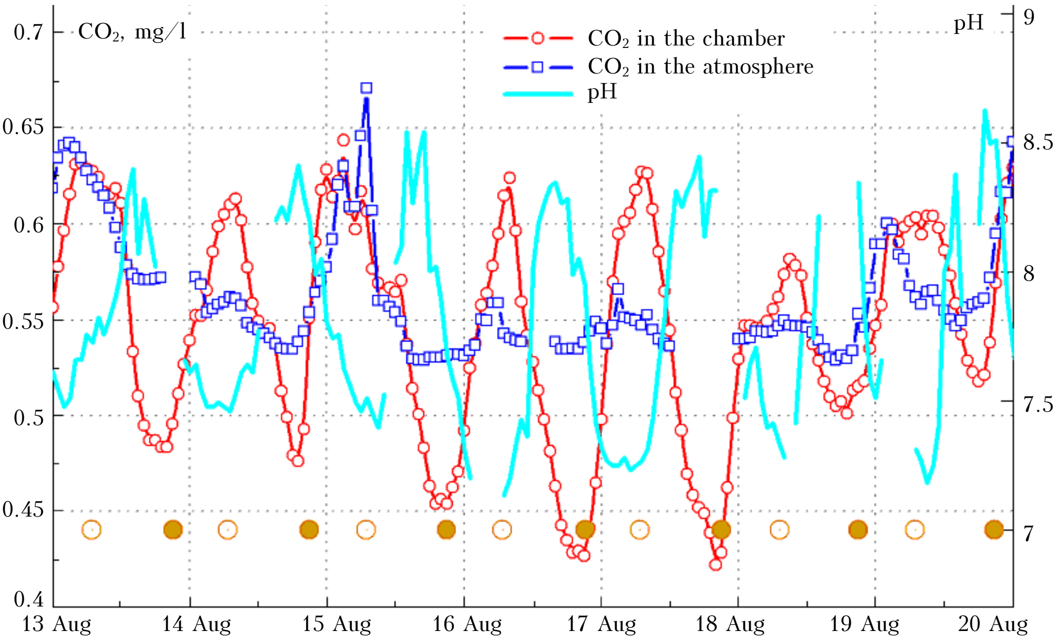

Fig. 2. Example of the behavior of variations of the concentration of carbon dioxide in the closed chamber, near-water atmosphere, and pH of surface water.

As follows from Fig. 3, the increase (Fig. 3*a*) or decrease (Fig. 3*b*) of the carbon dioxide concentration in the chamber is observed after ventilation of the chamber depending on the flux sign.

Thus, application of the ventilated chamber makes it possible to estimate the flux direction in each cycle. It should be noted that in the case of badly pronounced fluxes (as a rule, in the cold season) we failed to obtain a good time resolution, and had to increase the period of keeping the chamber closed.

Improvement of the water sampling technique

The carrying out of experiments close to the coastal line raised some questions about the representativeness of the data obtained by the chemical analysis of water. To which degree the samples of surface water, collected near the chambers, can be burdened by local effects and to which degree they can be expanded to other coastal regions in the littoral of the Lake Baikal?

In order to control possible effect of local processes at the point of measurements of the carbon dioxide fluxes, the following sampling technique was selected. The samples of the surface water were collected from the 1–2 cm thick layer every 3 hours at two points (the moments of sampling and the devices for collection of the surface water are shown in Fig. 1, *9* and *10*). One of the points was placed just near the chambers at a distance of 20–30 m from the coast (at a depth of 1.5–2 m) and another one was located at a distance of 100 m (a 5 m depth) from the costal line.

Complete chemical and fluorescent analysis of water has been carried out for each sample during the whole period of observations. The fragment of the temporal behavior in one of the cycles of simultaneous measurement of the O_2 and CO_2 concentrations is shown in Fig. 4; Figure 5 shows the correlation diagram of the coefficient values of photosynthetic activity (CPA) at the close and far points.

It is seen that good correlation is observed between different characteristics of the surface water at two distant points. Such correspondence between rhythms of variations of water characteristics at two sampling points is observed in all measurement seasons. Therefore, the measurements quite reliably represent the character of temporal variability of the chemical composition of water in the littoral of Lake Baikal and, hence, it is possible to correctly parameterize the gas exchange process in the system “water surface – atmosphere” at variations of the water composition.

Main results

Taking into account the review manner of the paper, let us briefly describe the most interesting results obtained to date.

Diurnal rhythms of gas exchange for different hydrological seasons

First of all, note that the diurnal rhythm of the amplitude and the sign changes for carbon dioxide fluxes are well observed in practically all series of measurements (see Fig. 2).[13,14] To compare the diurnal rhythms in different hydrological seasons, the following data processing was preliminary carried out. To decrease the effect of inter-day variability, we used the following technique. First, the mean value of the considered parameter for a day was calculated. Then, each diurnally measured value was normalized to the corresponding mean. Such procedure enabled us

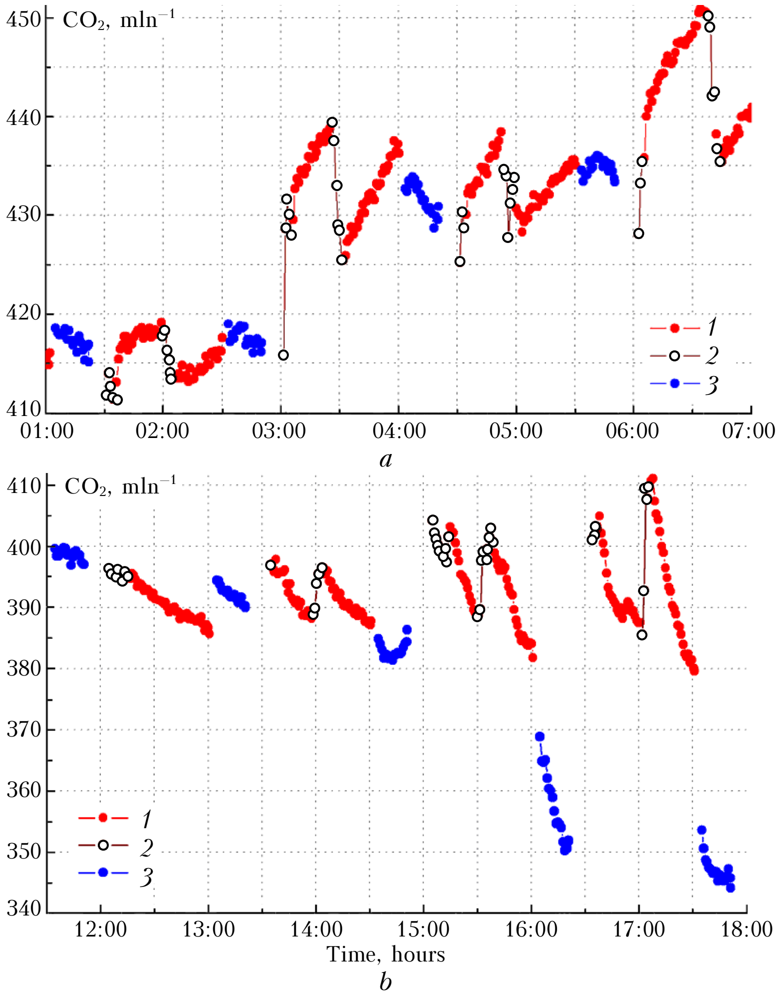

Fig. 3. A fragment of record of the measured signals: the flux of CO_2 from water (*a*); the sink of CO_2 on the water surface (*b*) (*1* is record of the signal after closing the chamber; *2* is the signal during ventilating the chamber; *3* is record of the signal in the permanently closed chamber).

to decrease variations of the analyzed parameters under the effect of external factors, which were not related to the diurnal rhythm (for example, the change of air mass or water piling up from pelagic zone of the Lake Baikal, etc.).

Consider the results of comparison of the diurnal behaviors of carbon dioxide in different hydrological seasons in the near-water atmosphere (Fig. 6). Figures 6*a* and *b* show the data obtained at the level of 1 m above the water surface in the open atmosphere. The well pronounced diurnal rhythm of variability of the analyzed parameters is characteristic of each analyzed season.

First, pay attention to the fact that the amplitude of diurnal oscillations in the chamber reaches ±13% of the daily mean, while its amplitude in the near-water atmosphere does not exceed ±5%. May be, some portion of diurnal variation of CO_2 in the near-water atmosphere is not related directly with the gas exchange process between water surface and the atmosphere, but is caused by the effect of, for example, coastal vegetation.

Even if to relate completely the carbon dioxide variations in the near-water atmosphere with some other processes, then even this rough approximation shows that more than 70% of the diurnal amplitude of variations of the gas concentration in the semi-immersed chamber is determined by the gas exchange with water surface (emphasize that the atmosphere in the chamber is practically isolated from direct arrival of the external air).

When changing the winter season to summer one, the insolation becomes longer and the Lake warmer, then the increase of the amplitude of diurnal oscillations of the parameters under study is observed both in the surface water and in the near-water layer of the atmosphere.

Maximal amplitudes are observed in the period of hydrological summer from June to September inclusively. The inverse process is observed in autumn.[15]

Such diurnal behavior of the parameters under study and the changes of their amplitudes in different hydrological seasons make it possible to conclude that biological processes in the Lake Baikal play a leading role.

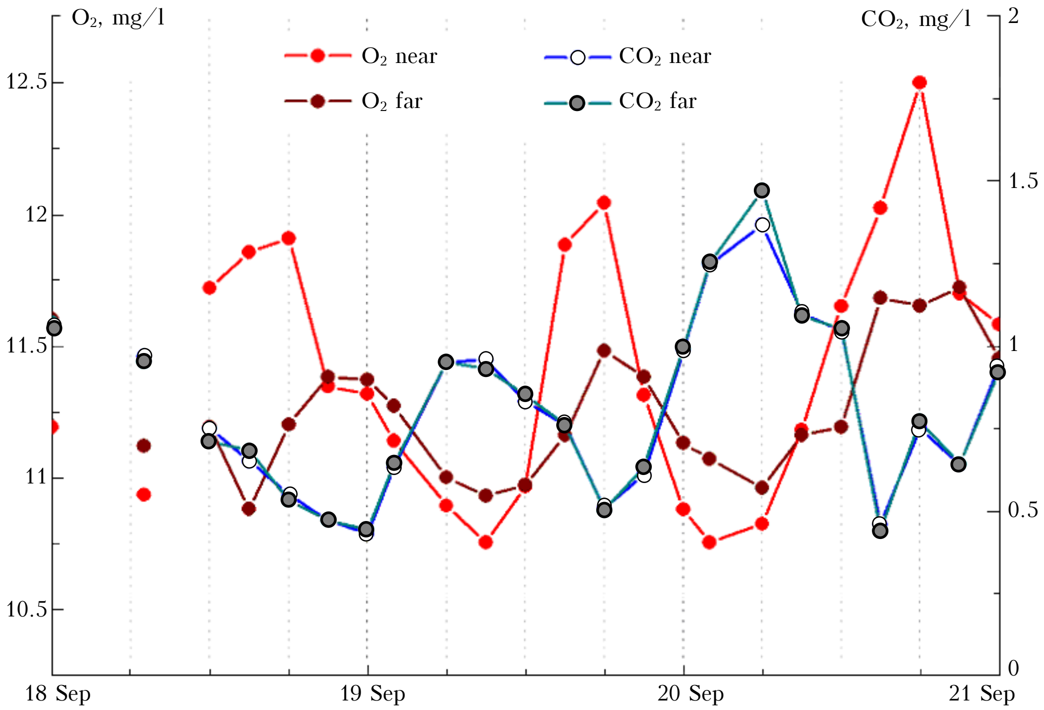

Fig. 4. Comparison of the concentrations of carbon dioxide and oxygen at near and far points of sampling.

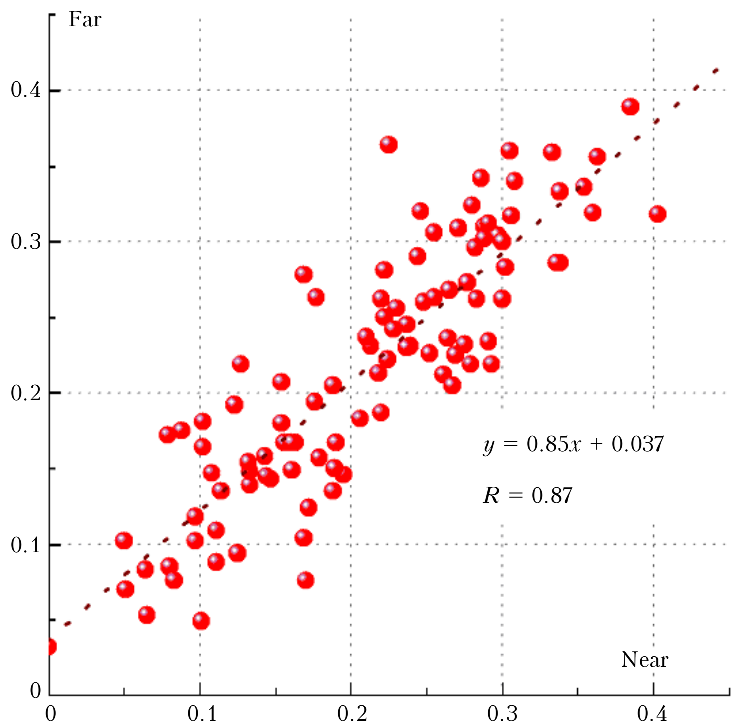

Fig. 5. Correlation between the values of the coefficient of photosynthetic activity at near and far points of sampling.

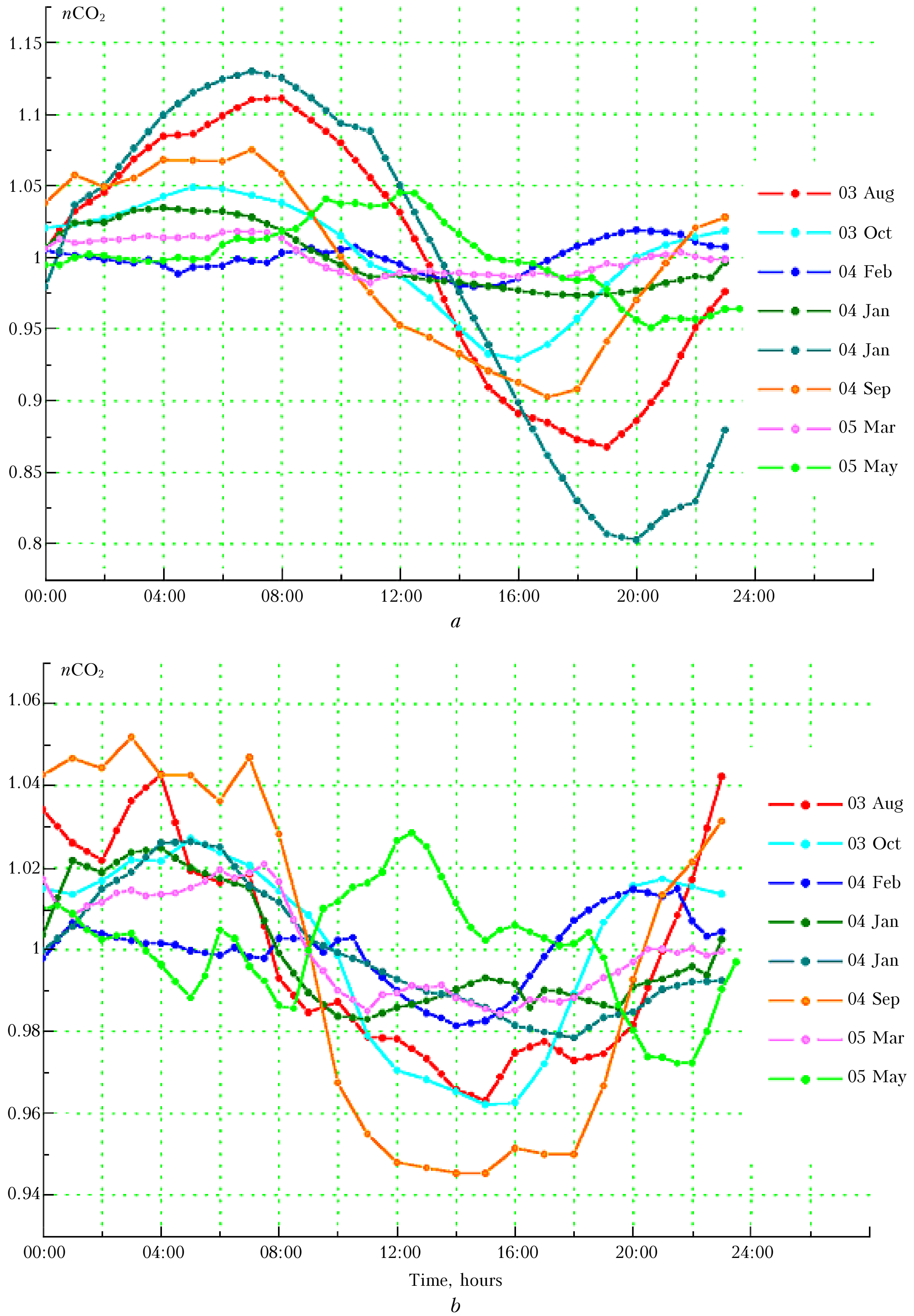

Fig. 6. Mean normalized diurnal behavior of the concentration of carbon dioxide in different measurement seasons: in the measurement chamber (*a*), in the near-water atmosphere at the height of 1 m (*b*).

Diurnal behavior of the gas exchange and its connection with photosynthesis

Let us select two stages in kinetics of low induction of fluorescence of chlorophyll.[12] The fluorescent signal reaches the stationary level F_s within 3–10 min after switching on the exciting radiation. The magnitude of the signal at the stationary level is connected with the physiological state of the phytoplankton. Then, introduce into the sample under study a disconnector of the electron-transport chain, for example, duron and the intensity of fluorescence increases up to the maximum level F_d, which lower depends on the activity of the photosynthetic apparatus. The intensity of photosynthesis is usually estimated by CPA, which is calculated by the formula[12]:

$$\text{CPA} = (F_d - F_s)/F_d. \qquad (2)$$

Zero value of CPA is an evidence of terminating the photosynthesis process, and values of 0.7–0.8 are characteristic of the laboratory cultures of water plants growing under optimal conditions.

Figure 7 shows the diurnal behavior of the flux of carbon dioxide, and Figure 8 shows the diurnal behavior of the coefficient of photosynthetic activity, the concentration of carbon dioxide and the biomass in the surface water.

Note that maximum of the coefficient of photosynthetic activity is observed near 9 a.m., and minimum at 3–6 p.m. The same behavior is characteristic of the concentration of carbon dioxide in water. Hence, the flux of carbon dioxide in the system "atmosphere – water surface" is opposite. The content of biomass is practically doubled as compared to nighttime and reaches its maximum by noon.

Therefore, maximum activity of photosynthesis is observed in the morning, when the maximum content of carbon dioxide has been accumulated in the surface layer of water, that is caused by biochemical processes (respiration) and destruction of organic matter.

Then, as insolation increases, the upper water film is heated, and values of CPA are still high, the increase of biomass is observed in this layer. Active absorption of carbon dioxide by photosynthetics leads to soon CO_2 decrease. The flux of CO_2 from the atmosphere has not time to compensate the expense of CO_2 consumed by photosynthesizing organisms, and its concentration in water reaches its minimum by 3 p.m. Further heating and the decrease of carbon dioxide in the surface water layer at the afternoon cause motion of photosynthesizing organisms to the deeper water layers, which are more reach with CO_2 [Ref. 16].

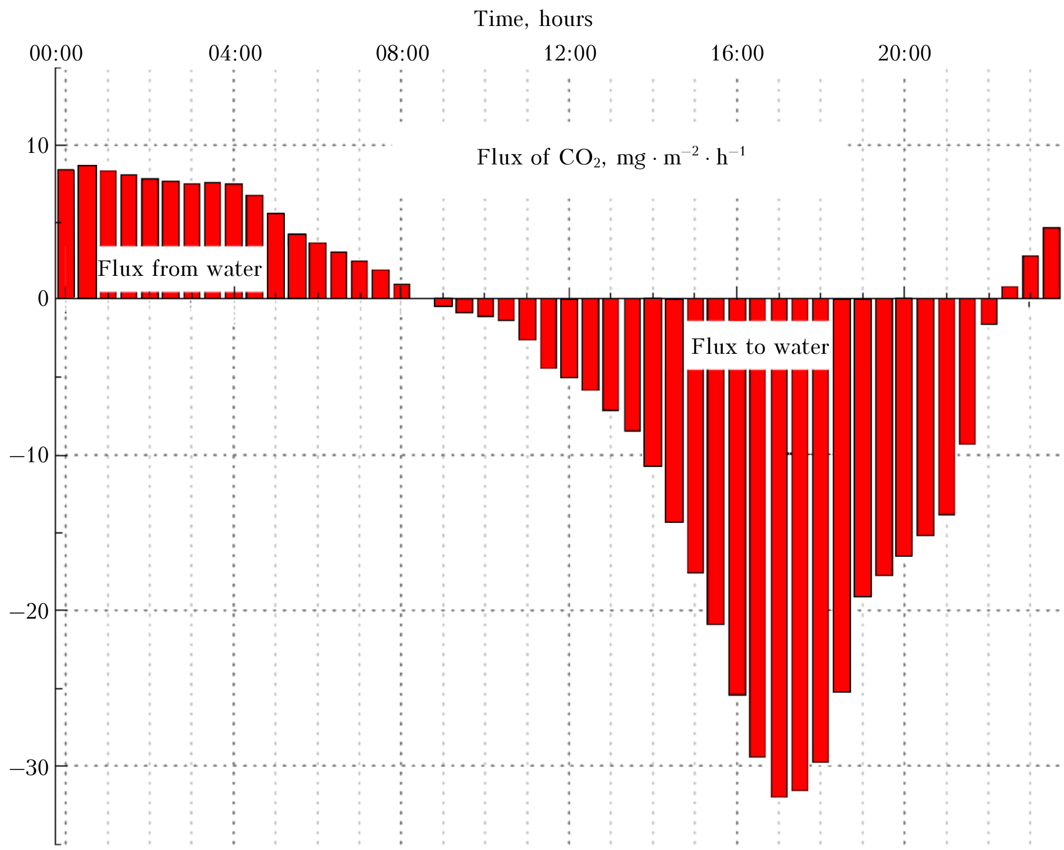

Fig. 7. Diurnal behavior of the flux of carbon dioxide.

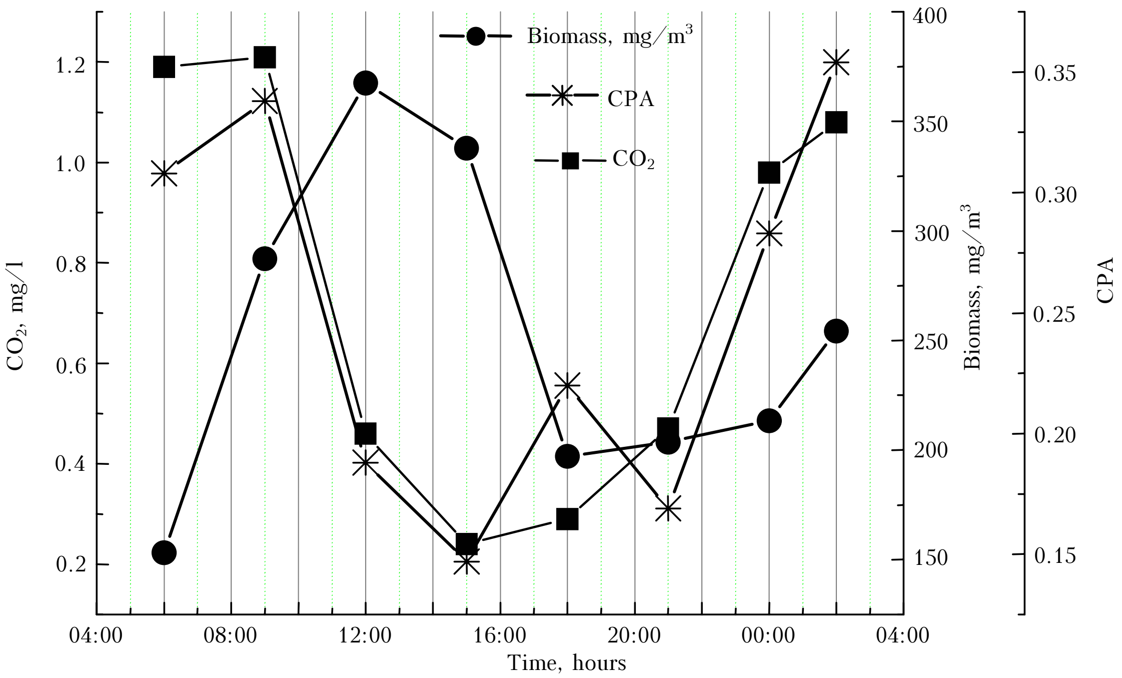

Fig. 8. Diurnal behaviors of the concentration of CO_2, CPA, and biomass of phytoplankton.

Conclusions

Summarizing the results of synchronous measurements of the carbon dioxide content in the near-water atmosphere and in the surface layer of water in different hydrological seasons at Lake Baikal, one can draw the following conclusions.

The well-pronounced diurnal rhythm of variability of the analyzed parameters is characteristic of each season. The greatest amplitudes are observed in hydrological summer.

The results of comprehensive analysis of the diurnal behavior of the CO_2 exchange in the system "atmosphere – water surface" of Lake Baikal demonstrate that the rates of metabolic reactions of phytoplankton exceed the rates of physical processes. The data obtained also evidence the fact that physical mechanisms of the gas exchange process, in its turn, restrict the photosynthetic activity of plankton organisms.

Note for conclusion that the started investigations, on the one hand, raise a lot of new multi-disciplinary problems, which are not solved yet, on the other hand, the first results make sure that the true natural laboratory Lake Baikal will enable us to answer many questions about gas exchange between the atmosphere and fresh water.

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