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OPTICAL INSTRUMENTATION

Diurnal Behavior of the Flux and Partial Pressure of Carbon Dioxide in the Surface Water in Solar Time Coordinates (the Period of Open Water in the South Baikal Littoral in 2004–2015)

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Abstract—A long-term series of regular measurements of the carbon dioxide concentration in the surface water and CO_2 fluxes in the Baikal littoral zone demonstrated a diurnal rhythm related to processes of photosynthesis activity of plankton during the entire period of open water (from May to December). To isolate the role of only the photoperiodicity process on the background of many various factors having an effect on the change in the concentration of carbon dioxide in the surface water and CO_2 fluxes in the atmosphere–water system, the scheme of the diurnal behavior of CO_2 during the open water period in 2007–2015 in the littoral zone of South Baikal is considered in coordinates of sunshine duration which was calculated proceeding from the theoretically possible sunshine duration (from sunrise to sunset in the case of clear sky and open horizon). The proposed scheme of parameterization and reconstruction of these characteristics for any time instant can find application in estimating calculations in carbon cycle models and be useful in planning the optimum regime for studying biological and chemical processes in Lake Baikal.

Keywords: carbon dioxide, partial pressure, flux, solar radiation, diurnal variation, photosynthesis, destruction, plankton, Lake Baikal

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INTRODUCTION

Determination of causes of the steady increase in carbon dioxide in the atmosphere requires setting a broad array of measurements on different spatiotemporal scales [1]. The vast territory and variety of natural complexes in Siberia are factors which are considered as most important regulators of the carbon cycle in the Northern Hemisphere in all scenarios [2–4]. Different model estimates of the carbon budget [4] make little use of facts about the contribution of Russian boreal lakes, although foreign specialists pay much attention to this aspect [5–10].

In Siberia, Lake Baikal is undoubtedly one of natural objects of universal importance [11]. It is evident that choosing Baikal for our investigations [12] of the CO_2 gas exchange process is caused primarily by the necessity to consider its effect on the change in greenhouse gases in the atmosphere, at least on a regional scale. It should be noted that Lake Baikal is also a unique natural laboratory for studying carbon gas cycles in the atmosphere–water surface system. Due to the exclusive purity of Baikal water [13], the set of different components of the complex aggregate of factors influencing the gas exchange process in the atmosphere–water surface system is considerably less as compared to the World Ocean.

To isolate the role of only the photoperiodicity process in the vital activity of plankton on the background of many various factors influencing the change in the concentration of carbon dioxide in the surface water and CO_2 fluxes in the atmosphere–water system, the scheme of the diurnal behavior of CO_2 during the open water period in 2004–2015 in the littoral zone of South Baikal is considered in coordinates of sunshine duration.

MATERIALS AND METHODS

Regular observations were carried out in the littoral of the lake at the western coast of South Baikal

(51°54′ N, 105°04′ E) inside the territory of the Scientific Research Station of the Limnological Institute by measurement cycles with a duration of 2–3 weeks in different hydrological seasons. Among different methods of measuring gas fluxes, the chamber method [12] was chosen proceeding from the posed problem of a complex investigation of physical, chemical, and biological components of the atmosphere–water gas exchange process in the littoral of the lake. Concentration of dissolved carbon dioxide was determined both by the chemical composition of the surface water and using an equlibrator [12]. The remote measuring point is located at the pierhead at a distance of 30 m from the shore.

DIURNAL BEHAVIOR OF THE GAS EXCHANGE IN THE ATMOSPHERE–WATER SYSTEM AND PHOTOSYNTHESIS

To determine the hierarchy of physical, chemical, and biological components in the gas exchange process, we carried out the analysis based on the diurnal behavior of the measured characteristics. The diurnal behavior of CO_2 in the near-water atmosphere and in water is formed as a result of the joint action of external interannual, seasonal, and hydrometeorological conditions on biological rhythms of production and destruction of organic matter [14] and, for gases dissolved in water, on the intensity of physicochemical processes of the gas transition through the water surface [15, 16]. No doubt that reciprocal processes—on the one hand, photosynthesis with absorption of CO_2; on the other hand, breathing of hydrobionts and destruction of the organic matter (CO_2 release)—is an important factor influencing seasonal variations and the diurnal behavior of the content of gases dissolved in Baikal water [17–21]. A long-term series of regular direct measurements of the carbon dioxide concentration in the surface water and CO_2 fluxes in the Baikal littoral zone clearly showed a diurnal rhythm throughout the open water period (from May to December) on the background of interannual and seasonal variability [22–28]. The rhythm is obviously related to processes of plankton vital activity.

It is well known that, according to [29], each point on the Earth's surface has its own light rhythm which is reflected in the biology of plants, animals, and microorganisms. The response of organisms to the diurnal rhythm of the solar energy intake, i.e., to the relation between light and dark periods, was called photoperiodism. Photoperiodism is expressed in the fact that organisms from different geographical latitudes adapted to a definite cycle of solar illumination during many years and the length of daylight is here both the condition for the growth and development and a signal for the beginning of other processes in their vital activity [29]. In an aqueous environment, after the sunrise with an increase in the intensity of insolation, the photosynthesis process is initiated (CO_2 consumption); however, after reaching a certain (specific for different plankton species) level, the so-called inhibiting illumination, the photosynthesis activity begins to decrease [30–33].

The counter process of carbon dioxide release as a result of the respiration of aquatic organisms and destruction of organic material continues runs simultaneously. The duration and intensity of the incoming solar radiation, hydrometeorological conditions, as well as the species composition and quantitative composition of plankton [14] vary during the year; correspondingly, the interrelation of contributions of these counter processes to the formation of the diurnal behavior of dissolved gases varies significantly [33].

The analysis of the data array of our measurements from 2004 to 2015 [34] shows the following stable pattern of the diurnal behavior throughout the open water period: the concentration of carbon dioxide in water decreases after the sunrise (i.e., CO_2 consumption in the process of photosynthesis prevails over CO_2 delivery into water) and this decrease stops in the afternoon. From this time to the next sunrise, due to the respiration of the biota and decomposition of the organic material, the CO_2 content increases. The diurnal cycle manifests itself quite reliably (Fig. 1a) even in the period before the freeze-up (December) which is characterized by the highest values of carbon dioxide partial pressure P_{CO_2} in surface water and when these values considerably exceed those in the atmosphere.

Taking into account the fact that the diurnal cycle of P_{CO_2} in the near-water atmosphere in all seasons is weakly expressed even in summer months (the variations amount to about 5% of the daily average value [24]), it is evident that the increase and decrease in P_{CO_2} in the surface water manifest themselves also in the diurnal behavior of carbon dioxide fluxes. For the period from May to the beginning of November, the typical phenomena are the nocturnal carbon dioxide emission into the atmosphere and diurnal sink; in December, on the background of permanent CO_2 emission from the water surface, a decrease in the flux magnitude in the daytime is clearly seen (Fig. 1b).

DIURNAL BEHAVIOR OF THE CO_2 FLUX AND PARTIAL PRESSURE IN THE SURFACE WATER IN SOLAR TIME COORDINATES

Average values of CO_2 fluxes and partial pressure, as well as the amplitude and time interval between their maxima and minima in the diurnal cycle vary regularly in the period of open water in the littoral of Lake Baikal in different months (see Fig. 1).

It is evident that the *amplitude* and *time interval* of the analyzed characteristics in the diurnal behavior depend mainly on the solar flux (of the direct and scattered radiation) which is incident on the lake sur-

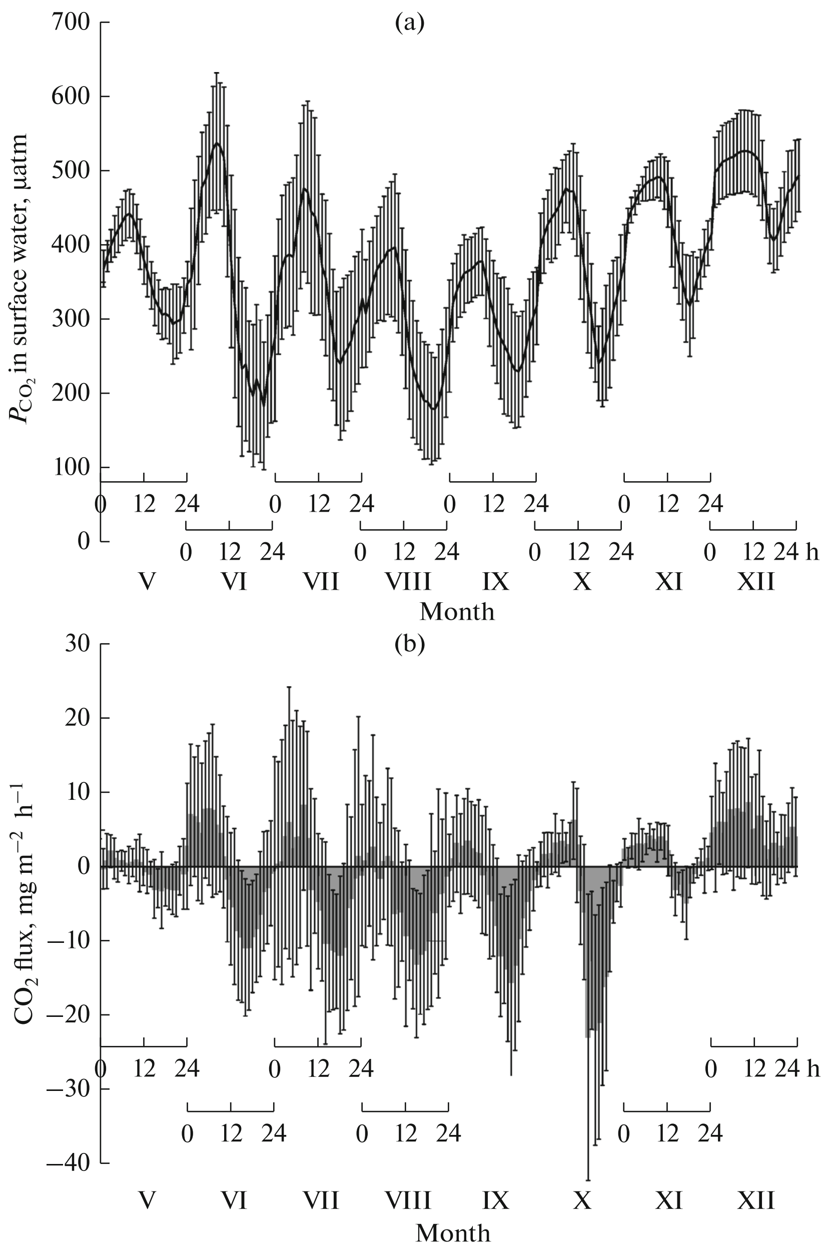


Fig. 1. Average diurnal behavior and RMSD during the open water season (averaging over all measurement cycles since 2004–2015): (a) partial pressure of carbon dioxide in the surface water and (b) carbon dioxide flux (here and below, negative values of the flux correspond to the direction of the CO_2 flux from the atmosphere to the water surface).

face and necessary to start and to complete the process of photosynthesis [32, 33].

To clearly demonstrate the part of photoperiodicity of vital activity of water biota in variations in the carbon dioxide concentration in the surface water and fluxes in the atmosphere–water system on the background of the action of various factors of different nature, a procedure for describing the diurnal behavior of these characteristics throughout the open water period on a common scale was proposed.

First, the daily average behavior of P_{CO_2} and CO_2 flux were calculated in zonal time coordinates in absolute units for *every* month in the open water period (see Fig. 1). Then, the difference between the maximum and minimum in the average diurnal cycle (the amplitude) and average value of the analyzed characteristics over 24 h were calculated. The results for each month are presented in Table 1.

Conversion of the Calendar Time into Solar Coordinates

To present the diurnal behavior for different seasons on a common time scale, the calendar time was converted to solar time which was calculated proceed-

Table 1. Average values and amplitude of the diurnal behavior of partial pressure and CO_2 fluxes

Month	Partial pressure in water, μatm		CO_2 flux, mg m^{-2} h^{-1}	
	average value	amplitude	average value	amplitude
May	371	144	−0.7	4.3
June	365	328	−0.9	18.7
July	362	202	−2.3	20.2
August	289	216	−4.5	15.8
September	308	162	−3.9	19.1
October	376	217	−4.5	29.2
November	420	167	0.9	9.0
December	482	121	4.9	7.7

Negative values mean that the flux is directed from the atmosphere to the water surface.

ing from the theoretically possible duration of sunshine (from sunrise to sunset under the condition of clear sky and open horizon, see www.esrl.noaa.gov/gmd/grad/solcalc/).

First, the times of sunrise and sunset below the horizon were calculated for the given coordinates (51.90° N, 105.06° E) for every day of the year [35]. The calendar day was divided into 24 solar hours. The sunrise time was taken as 06:00 of the solar time; the sunset time, as 18:00. The obtained time intervals of the daytime and nighttime periods were divided into 12 equal parts. It is evident that the duration of the solar hour in the light and dark time of the day is different and varies during the year.

Figure 2 shows the distribution of solar hours for every day of the year. For the standard local time, here and below, we take the universal coordinated time set ahead by 7 h (UTC+7). In this case, the midday sun at the measurement point reaches the maximum altitude at 12:00.

Then, the daily average diurnal behavior determined earlier in coordinates of standard time in absolute units was converted to solar time coordinates. An example of the averaged diurnal behavior of the CO_2 partial pressure in water in June and December before and after the passage to the solar time scale for the observation cycles of 2007–2015 is presented in Fig. 3.

Normalization of the Diurnal Behavior in Solar Coordinates

After the data conversion into the solar time, the CO_2 partial pressure and fluxes were normalized in the following way: for every month of the daily average

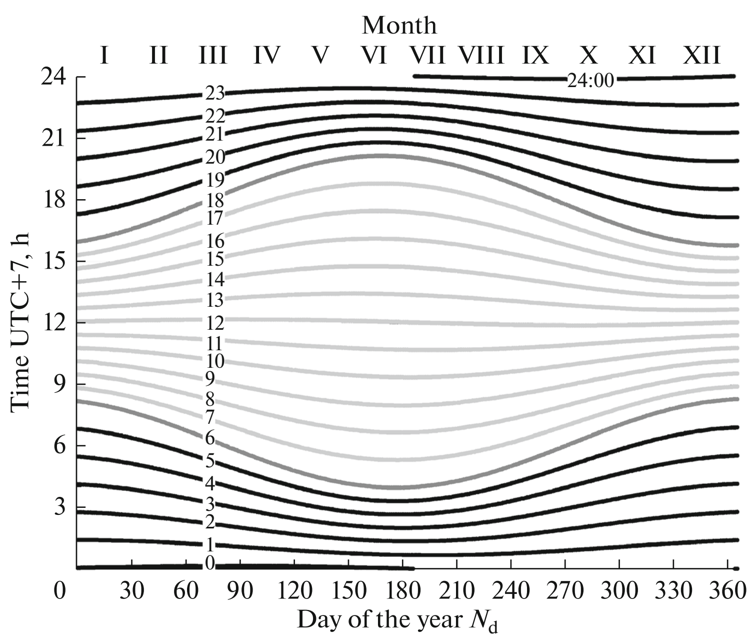


Fig. 2. Plot of the transfer from the standard time to solar time for every day of the year N_d at the measurement point (51.90° N, 105.06° E).

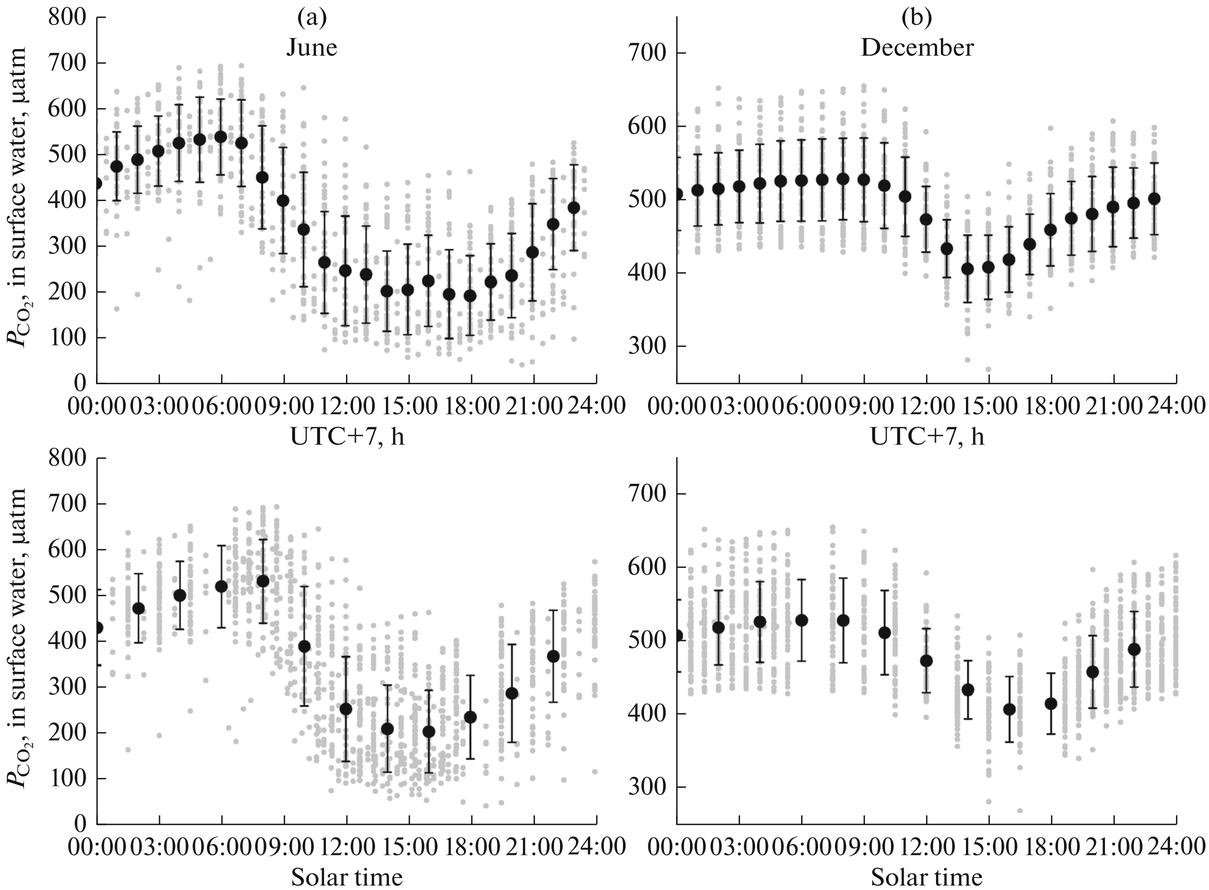


Fig. 3. Daily average variations in the partial pressure of CO_2 in surface water according to data of measurements in 2007–2015 for (a) June and (b) December for the standard time UTC+7 (top) and in solar coordinates (bottom).

behavior (now, in solar coordinates), the corresponding value of its daily average value (see Table 1) was subtracted and the difference was divided by the amplitude of the diurnal behavior.

The implementation of the transfer of the calendar time to solar coordinates and the described normalization procedure provided the possibility to represent the diurnal behavior of the CO_2 partial pressure and fluxes for all months of the open water period (Fig. 4, Table 2) on a common scale.

As seen from Fig. 4, just the diurnal cycle in the photosynthesis process is clearly seen in this repppresentation in all months of the open water period. Its action begins with the surise (at 06:00 solar time). Note that the normalized diurnal behavior of the CO_2 partial pressure in water is described in solar coordinates with a lesser error than the carbon dioxide flux in the atmosphere–water system. This is a quite expected result because, in comparison with the procedure of determining the partial pressure of gas in water, the error in measuring the flux with the use of the chamber method is higher and the gas exchange process in the atmosphere–water system depends on a greater number of factors (for the application of the chamber method, see [36]).

The proposed parameterization scheme can be used with a certain accuracy for estimating the value of these characteristics at any time. Table 2 presents the normalized daily average behavior calculated in solar time coordinates for the entire open water period according to the data presented in Fig. 4.

The partial pressure in water and flux of CO_2 for given date and time are reconstructed in the following order:

(i) First, proceeding from the given time and date, the solar time is calculated. For this purpose, one can use a plot (see Fig. 1);

(ii) According to Table 2, the normalized diurnal behavior value corresponding to this time is calculated;

(iii) The value obtained in (ii) is multiplied by the amplitude in the corresponding month (see Table 1) and the product is summed with the average value.

An example of the reconstructed diurnal behavior of carbon dioxide fluxes in the atmosphere–water system throughout the open water period is presented in Fig. 5.

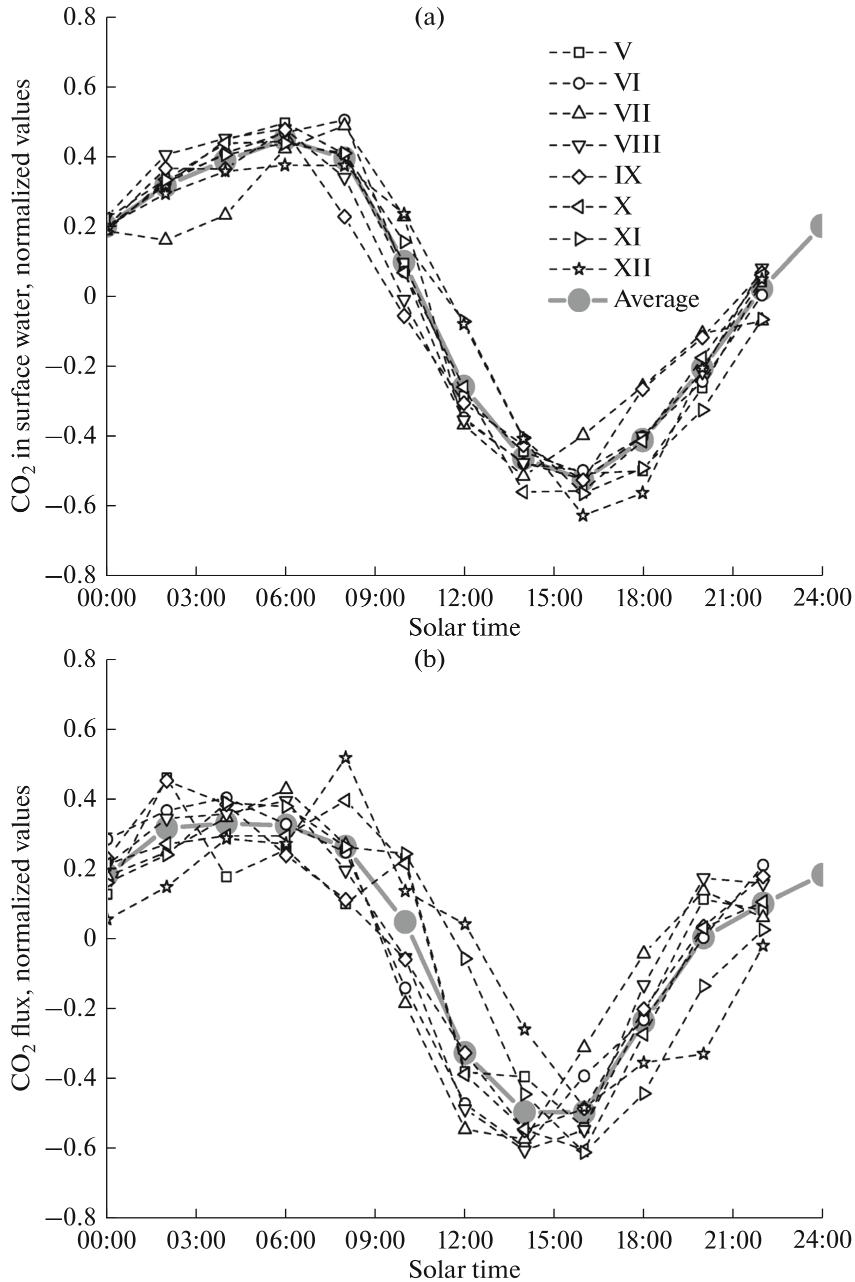


Fig. 4. Normalized diurnal behavior of the (a) CO_2 partial pfessure in the surface water and (b) CO_2 flux in the water–atmosphere system in solar time for all months during the period of open water.

DISCUSSION

As mentioned above, the diurnal behavior of photosynthesis depends on the total direct and scattered radiation flux incident on the lake surface [32, 33]. The magnitude of the flux is caused by the seasonal behavior, variability of the optical state of the atmosphere [35, 37–40], and—for a specific observation point—also by the degree of how the horizon is obstructed by the landscape. Our observation point is

Table 2. Average normalized diurnal behavior in solar time coordinates throughout the open water period

Solar time	00:00	02:00	04:00	06:00	08:00	10:00	12:00	14:00	16:00	18:00	20:00	22:00
P_{CO_2} in water	0.200	0.316	0.387	0.448	0.393	0.098	−0.259	−0.463	−0.524	−0.411	−0.206	0.021
CO_2 flux	0.182	0.315	0.329	0.323	0.261	0.047	−0.328	−0.496	−0.498	−0.238	0.003	0.099

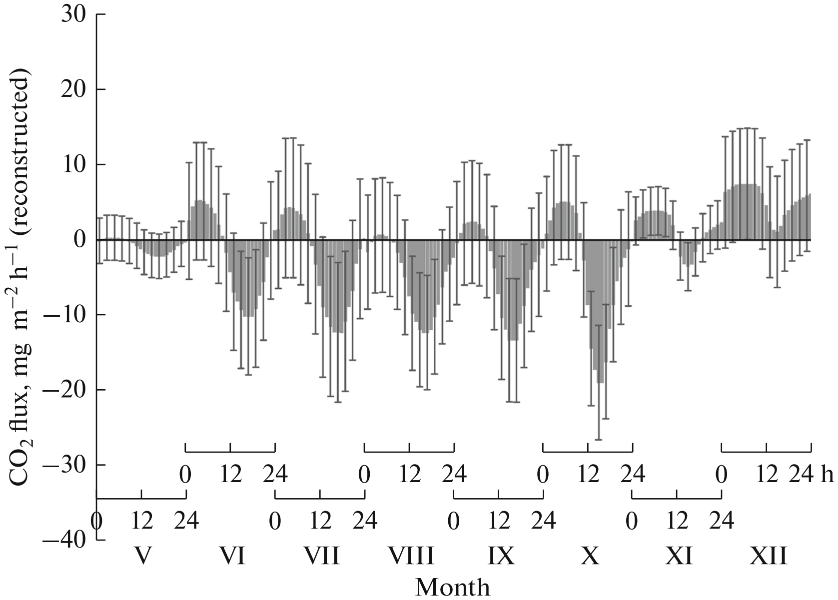


Fig. 5. Reconstructed diurnal behavior and RMSD of carbon dioxide flux for the 15th day of every month during the open water period. Time UTC+7.

surrounded by a mountain range from the northeast and west (Fig. 6a). It is seen that the surrounding landscape impedes the income of the direct solar flux to the measurement point from June to September at the time of sunrise and sunset. Only in December (before the end of the open water period) the direct flux falls on the water surface during the whole day. At the same time, the comparison of direct readings of a pyranometer with the calculated data on the incoming solar radiation (Fig. 6b) (we emphasize that the calculation was carried out for the open horizon) shows that the landscape has little effect on the magnitude of the incoming radiation flux at the instant of sunrise throughout the period under study. As for the sunset, the hiding of the Sun behind the mountain range in June and September (see Fig. 6b) clearly manifests itself on pyranometer readings.

To show to which degree the landscape has an effect on the diurnal behavior of the analyzed characteristics, we turn to data on P_{CO_2} in water. They are presented in (see Fig. 4a). It is seen that, in the period from May to October from 06:00 solar time (the calculated time of the sunrise), a decrease in the CO_2 content in water is observed, which is caused by the photosynthetic activity of plankton. Therefore, in these months, even immediately after the sunrise, the incident scattered radiation flux (the direct flux is obscured by the mountain range) is quite sufficient for the beginning of an intense photosynthesis; it means that the landscape has little effect on this process. At the same time, in November and December in the period when the landscape shadow is absent, the start of the change in the partial pressure of carbon dioxide in water is observed 1.5–2 h later after the sunrise (see Fig. 4a). This probably indicates the fact that the solar radiation flux at first morning hours at a low position of the Sun above the horizon (see Fig. 6b) is still insufficient for the necessary power of the photosynthetic process during which the CO_2 consumption could noticeably exceed the income of carbon dioxide into water due to destruction and respiration. We emphasize that the partial pressure of carbon dioxide in water considerably exceeds the atmospheric pressure and its flux is directed to the atmosphere just in these last months of the open water season (see Table 1).

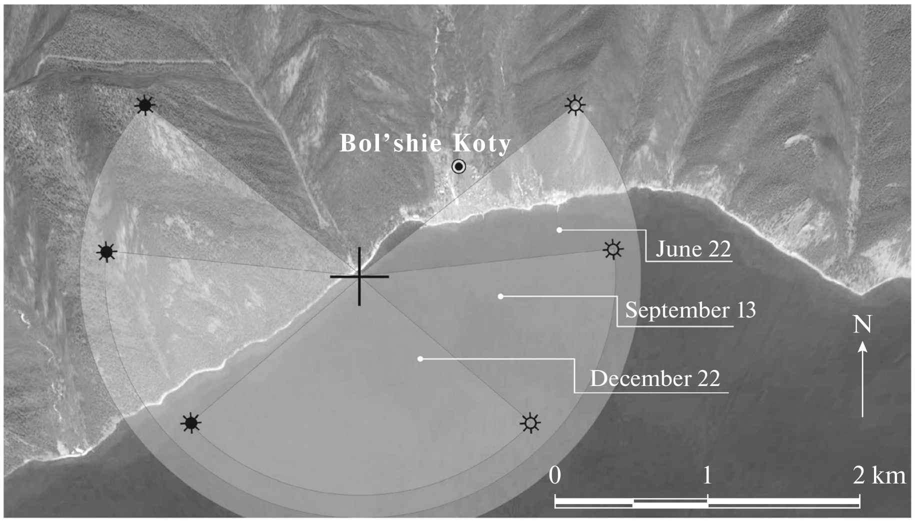
It also follows from data in Fig. 4a that the decrease in the carbon dioxide content in water during the daylight time in all the months is observed till 15:00–16:00 h in solar coordinates and then there begins its growth, i.e., the intense CO_2 consumption by the water plankton stops. Therefore, one can conclude that the restriction of the incident flux by the mountain range surrounding the measurement point during sunset already has no effect on the diurnal behavior.

Considering the description of average characteristics in solar hours calculated from the theoretically possible duration of sunshine (under conditions of clear sky and open horizon), one should note that the proposed scheme reflects only the most stable (regularly reproducible) diurnal behavior features which are controlled mostly by photosynthesis.

In the Baikal littoral zone and in each specific implementation, the diurnal behavior of the analyzed characteristics is affected by biological rhythms and, in addition, by some other processes depending on the duration and intensity of solar insolation.

For example, in a solar day and under almost still-air conditions, the surface water is heated by the post-

(a)



(b)

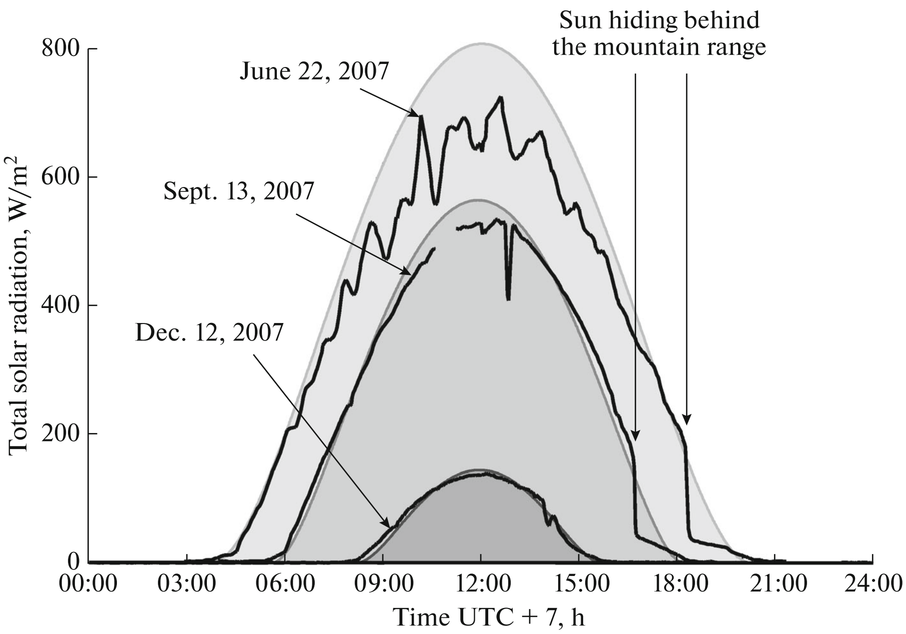


Fig. 6. (a) Angular position of the sunrise and sunset on June 22, September 13, and December 22 at the measurement point denoted by the black + sign. (b) Readings of the pyranometer on June 22, September 13, and December 22, 2007, and calculated value of the total radiation flux without regard to the landscape for those days (gray background).

meridian time by 1°–3°, which leads (if the concentration of CO_2 is constant) to an increase in the CO_2 partial pressure of 3–5% on the average. As a result, the magnitude of the carbon dioxide flux from the atmosphere decreases. In the absence or under a weak wind with one or another preferable direction in near-coastal conditions at 10:00–11:00 h, the action of the breeze circulation (wind from the lake) begins. Then, after the evening pause at 17:00–18:00 h, the direction of wind reverses. With an increase in the wind velocity, the swelling which ensures good intermixing of water in the inshore also increases. The intermixing, in turn, noticeably decreases the effect of the diurnal increase in the surface layer temperature on the CO_2 content in water, reduces the possible contribution of the vertical migration of the biota, and incorporates into the gas exchange mechanism all participants of photosynthesis in the water thickness, from phytoplankton to phytobenthos. We see that the breeze regime which has a clearly pronounced diurnal cycle also affects the process of the gas exchange in the atmosphere–water system in the Baikal littoral zone.

It is clear that the contribution of these and, probably, some other processes have an effect to some extent on quantitative values of the duration and amplitudes of the diurnal behavior of CO_2 partial pressure and fluxes when averaging a large array of our data.

CONCLUSIONS

This description of the diurnal behavior of CO_2 fluxes and partial pressure in surface water in solar coordinates, in our opinion, clearly demonstrates the role of the photosynthetic activity of *phytoplankton* in the process of gas exchange in the atmosphere–water system in the littoral zone of South Baikal in the open water season.

We believe that the proposed parameterization scheme, which can be used for reconstructing these characteristics with definite accuracy at any time, can find applications in estimating calculations in models of the carbon cycle. These results will be also useful in planning the optimum regime of investigating biological and chemical processes in Lake Baikal.

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