THE INTERACTION OF CO_2 BETWEEN THE ATMOSPHERE AND SURFACE WATERS OF LAKE BAIKAL AND THE INFLUENCE OF WATER COMPOSITION

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Abstract: Investigations into the inventory of CO_2 in the hydrosphere are primarily aimed gas exchange between the atmosphere and oceans. However, lakes often are not considered as possible sources and sinks, even if they can be locally important for many geographical regions. Lake Baikal covers a tremendous area and has locally high biotic activity, and thus it can be expected to play an essential role in regional CO_2 dynamics. Measurements of atmospheric CO_2, dissolved gases and various aqueous chemical parameters were performed at the Limnological Institute SB RAS site near Bolshie Koty in 2003-2004

Key words: carbon dioxide, gas exchange, chemical composition of water, organic matter.

1. INTRODUCTION

The Kyoto Protocol on climate change occupies a particularly important place among international conventions and agreements. This Protocol, which will start in 2005, will for the first time apply economic market mechanisms to addressing intergovernmental and trans-boarder environmental problems. As such specialists involved in the investigation of CO_2 sources and sinks should now concentrate on regional scale processes.

Investigations of the hydrosphere CO_2 inventory are primarily focused on the study of gas exchange between the atmosphere and ocean. Lake systems, in contrast, are often not considered as possible sources and sinks even if

S. Lombardi et al. (eds.),
Advances in the Geological Storage of Carbon Dioxide, 35–45.

they can be important for many geographical regions. In this aspect, Baikal is a unique natural study site. Taking into account its tremendous area and biotic activity, one can expect that Baikal plays an essential regional role in the processes of CO_2 generation and consumption. Prior to the present study no other research group had monitored CO_2 (one of the most problematic greenhouse gases) in the atmosphere of the Baikal region. Measurements were performed at the Limnological Institute SB RAS site near Bolshie Koty in August–September 2003 and September 2004.

2. DIURNAL VARIABILITY IN THE WATER-TO-ATMOSPHERE GAS EXCHANGE PROCESS DURING DIFFERENT SEASONS

The main purpose of this chapter is to study the relationship between changes in the chemical composition of Lake Baikal surface water and the content of carbon dioxide in the near-water atmospheric layer. For this work the concentration of CO_2 in air and the pH values of the surface water were directly monitored in situ.

In order to decrease the effect of advective processes on the measurement results and subsequent estimation of the CO_2 fluxes from the water surface, a semi-immersed transparent chamber (Fig. 1) was used. Carbon dioxide concentration, temperature, relative humidity and wind velocity were recorded at 1 and 4 m above the water surface at a meteorological mast situated near the chamber. In situ observations were performed around the clock, while at the same time water samples were collected every 3 hours at a distance of 100 m from the coast for subsequent laboratory chemical analysis. The concentrations of dissolved O_2, bicarbonate, nitrate, phosphate and pH were measured in the upper water layer. The dissolved CO_2 concentration was then calculated from the pH and bicarbonate data. Results obtained during four measurement cycles are shown in Figures 2–5.

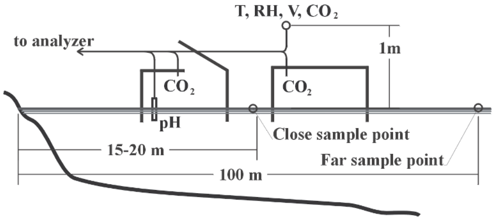

Figure 1. Diagram of the experiment.

As can be seen in all measurement series, the gas exchange process has a well-defined diurnal behaviour, which is correlated with the change of near-surface aqueous chemistry (pH). It can be seen that the rapid increase of water pH and simultaneous decrease of CO_2 concentration in the near-water layer of the atmosphere begins at sunrise. This is an illustration of the fact that the transfer of CO_2 from the atmosphere to the water surface begins practically simultaneously with the decrease of CO_2 content in the water. This process reverses direction shortly before sunset, and CO_2 begins to be transferred to the near-water layer of the atmosphere. The ratio between the durations of "positive" and "negative" stages of the process is different in different seasons, as well as the amplitude of the diurnal CO_2 fluctuations both in the atmosphere and in the measurement chamber, because these parameters are related to the duration of insolation.

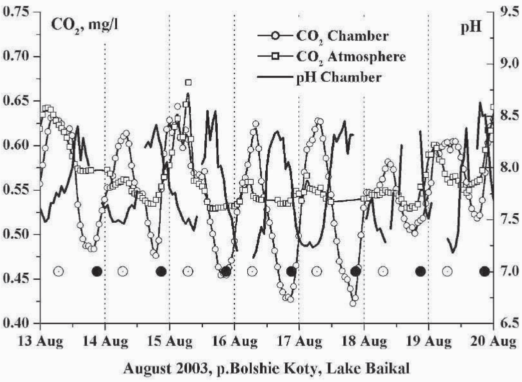

Figure 2. The results of measurements of CO_2 and pH of water in August 2003.

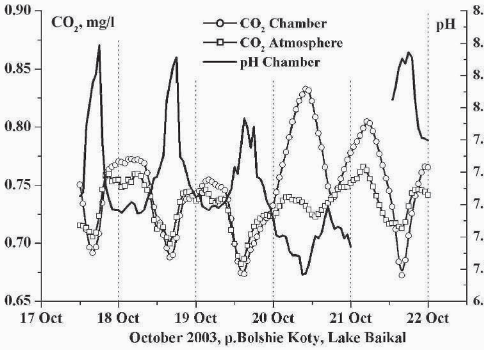

Figure 3. The results of measurements of CO_2 and pH of water in October 2003.

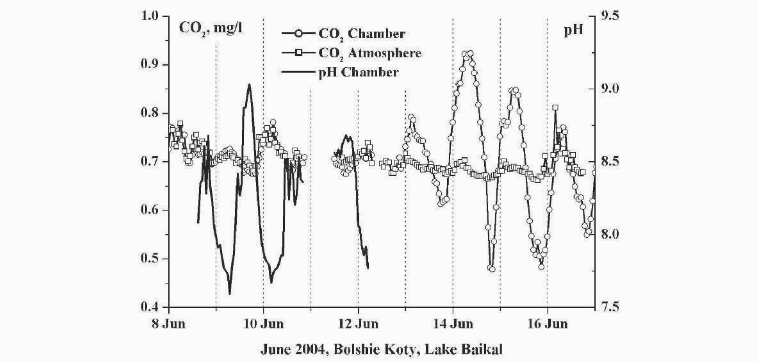

Figure 4. The results of measurements of CO_2 and pH of water in June 2004.

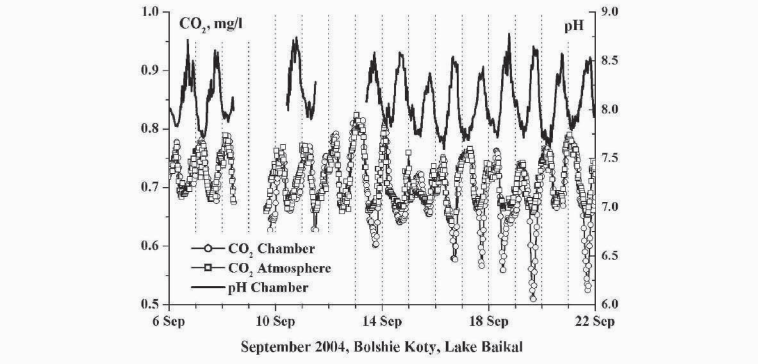

Figure 5. The results of measurements of CO_2 and pH of water in September 2004.

The most interesting result of both the October (Fig. 3) and June (Fig. 4) measurement cycles is the significant flux of carbon dioxide to the atmosphere from the water surface observed during acidic precipitation events (pH ~ 5). This is well seen in Figure 3 from October 20 to 221 and in Figure 4 from June 14 to 15. Although in this case the process can be clearly understood and explained, it should be noted that the role of acid precipitation in the atmospheric carbon dioxide budget has not yet been taken into account, at least not for the region under consideration.

Another chamber was applied in September of 2004 for a more accurate estimation of the CO_2 flux, as this chamber can be ventilated hourly. An example of the data obtained with this system is shown in Figure 6, while the mean diurnal behaviour of pH in the surface water in the chamber is shown in Figure 7. The diurnal behaviour of both the intensity and the direction of gas flux and corresponding variations of CO_2 content in water are clear from a comparison of the figures.

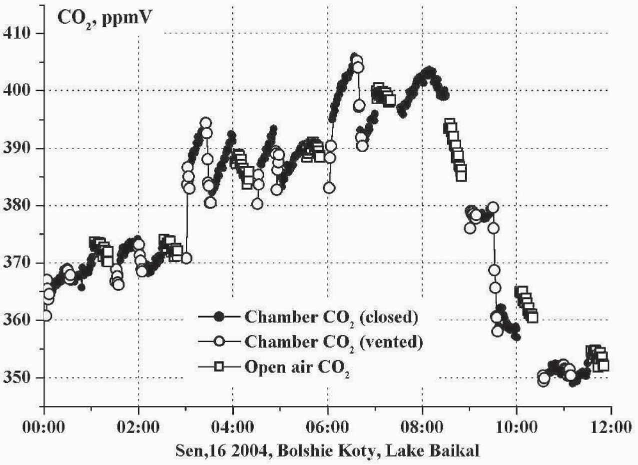

Figure 6. A portion of the signal record in the ventilated chamber (solid circles – closed chamber, open circles – open chamber, squares – the atmospheric concentration at 1 m above the water surface).

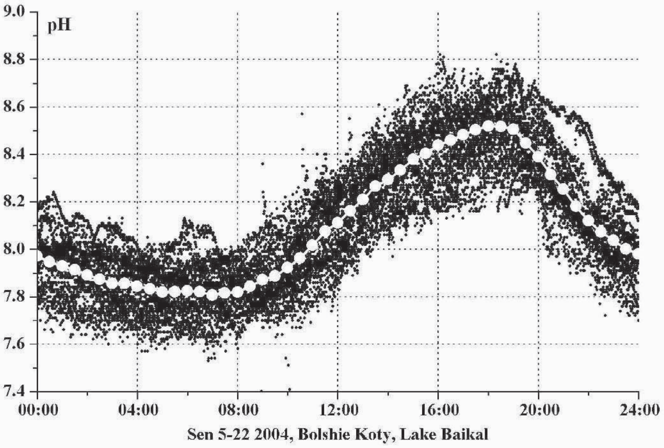

Figure 7. Mean diurnal behavior of pH in water.

3. ESTIMATION OF THE CO_2 FLUX ACROSS THE WATER SURFACE BY THE SEMI-IMMERSED VENTILATED-CHAMBER METHOD

The flux (in this case) is the change of the mass of gas (m[μg]) in an isolated air volume (v[l]) above an area (s[m^2]) of the water surface due to emission/absorption. Pure CO_2 at a pressure of one atm weights 44 g/mol. The mass of carbon dioxide in 1 litre (denoted as C_{CO2}) at pressure P and volume fraction c is:

$$C_{CO_2}[\mu g/l] = \frac{1.96[g/l]\cdot P[mmHg]}{760[mmHg]}\cdot c[ppmV] \tag{1}$$

The mass of gas M_{CO_2} in the chamber of the volume V is:

$$M_{CO_2}[\mu g] = C_{CO_2}[\mu g/l]\cdot V[l] \tag{2}$$

Thus, 238.2 mg of CO_2 are contained in a chamber having a volume V=320 l at the atmospheric content of carbon dioxide, where c = 400ppmV and atmospheric pressure P = 720 mmHg.

The use of the “ventilated” chamber provides the possibility of more accurate flux estimations, with an example shown in Figure 8.

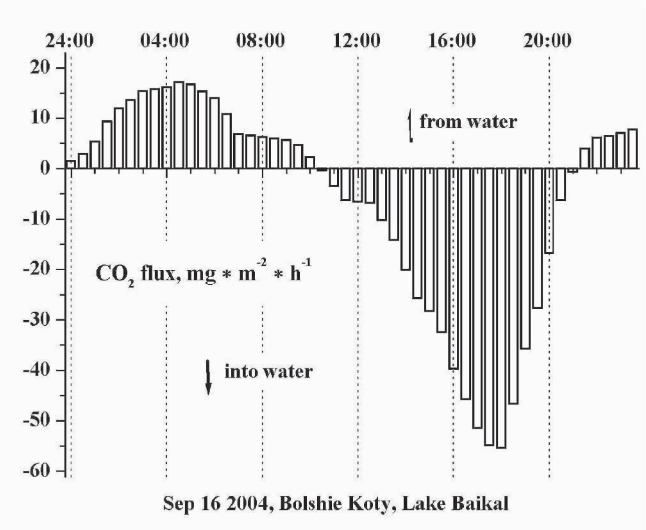

Figure 8. An example of diurnal CO2 flux across the water surface.

4. THE CHEMICAL COMPOSITION OF NEAR-SURFACE WATER IN GAS EXCHANGE EXPERIMENTS

A series of round-the-clock observations of some hydro-meteorological and hydro-chemical parameters were carried out simultaneously with CO_2 measurements. Measurements were performed every 3 hours at 2 stations situated in the littoral zone of the lake at a water depth of 2 and 5 m. Temperature, pH and the concentrations of dissolved oxygen, carbon dioxide and bicarbonate ion were measured in the near-surface water layer (5cm). Measurements of pH were carried out with an "Econics-Expert-001" ph-meter (accuracy of ±0.02 pH units), the oxygen concentration was measured with the Winkler technique with a relative error of 0.3% (the sensitivity of the method is 0.05 mg O_2/l), and the bicarbonate ion concentration was measured with the potentiometric method with an accuracy of ~ ± 2%. The carbon dioxide concentration was determined with the titrimetric method (the accuracy was ±10%) and the concentration of free CO_2 was calculated using the HCO_3^- concentration, water temperature and pH reduced to in situ temperature. The biogenic elements were determined using colorimetric methods: silicone as silicic-molybdenum heteropolyacid, phosphates with the formation of complex phosphorous-molybdenum acid, and nitrates by liquid chromatography (with an accuracy of ±5%).

Water samples were collected in September not only at the far site (marked as "far" in graphs) but also between the chambers ("close"). Water temperature differences (up to 9°C) and, possibly, the occurrence of water plants cause the observed difference in gas geochemistry (Fig. 9).

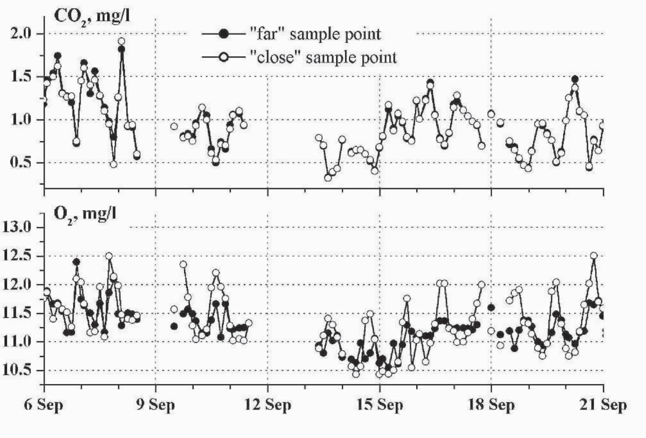

Figure 9. Chemical composition of near-surface water at "close" and "far" sites.

The main factors determining the diurnal dynamics of dissolved gases are the processes of photosynthesis and the destruction of organic substance. Emission of oxygen and absorption of not only carbon dioxide but also biogenic elements occur as a result of the synthesis of organic substances by water plants. Breakdown of the organic substances via heterotrophic organisms leads to the emission of carbon dioxide and biogenic elements as well as the consumption of oxygen. Diurnal variations of these processes depend on the duration and level of illumination, which results in the timing of diurnal maximums and minimums of the chemical concentrations (Fig. 10). Absorption and emission of gases across the water surface to maintain phase equilibrium is not rapid enough to smooth the kinetically faster O_2 and CO_2 exchanges caused by biological reactions. The diurnal dynamics of dissolved gases and biogenic elements is favored by slow vertical water exchange under the ice during the winter and in the period of thermal stratification (epilimnion) during the summer. Convective and dynamic mixing and turbulent diffusion during both spring and fall homothermy lead to a decrease in the amplitude of diurnal concentration variations of dissolved gases and biogenic elements. In addition, water temperature and lake roughness also affect the amplitude of diurnal chemical variations.

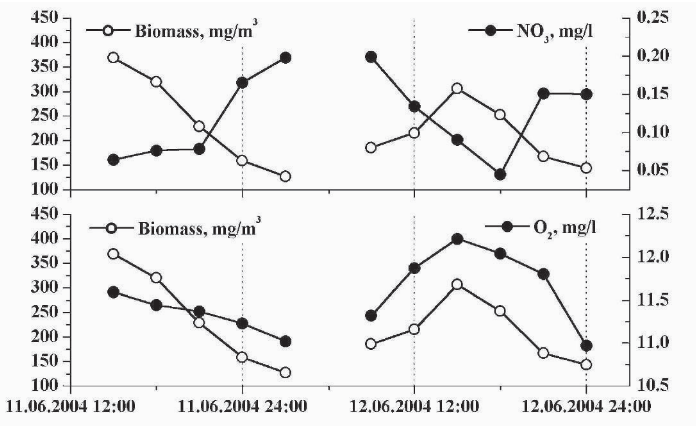

Figure 10. Diurnal dynamics of total biomass (phytoplankton and picoplankton) and the concentrations of nitrates (a) and oxygen (b) (data on biomass of phyto- and picoplankton were kindly presented by Prof. G.I. Popovskaya and Dr. O.I. Belykh).

Thus the diurnal behaviour of chemical components results from the superposition of variations in the external hydro-meteorological conditions and the biological rhythms of production and consumption of organic matter and (for dissolved gases) with the physical-chemical processes of gas absorption and emission across the water surface.

In general the diurnal O_2 variations are inverse to that of the biogenic elements and CO_2. The absolute content of O_2decreases during the night and in the morning, while the contents of free carbonic acid, nitrates and phosphates increase. Minimum concentrations of CO_2, NO_3^- and PO_4^{3-} correspond to daytime O_2 maximums. The timing of extreme O_2 and CO_2 values during the diurnal cycle depends on the relative intensities of photosynthesis and organic matter destruction. The amplitude of the diurnal concentration variations of the studied components increases with increasing photosynthesis intensity and decreases with increasing organic matter consumption. Temperature variations, maxim of water masses and gas exchange with the atmosphere do not affect the timing of diurnal concentration maximums and minimums.

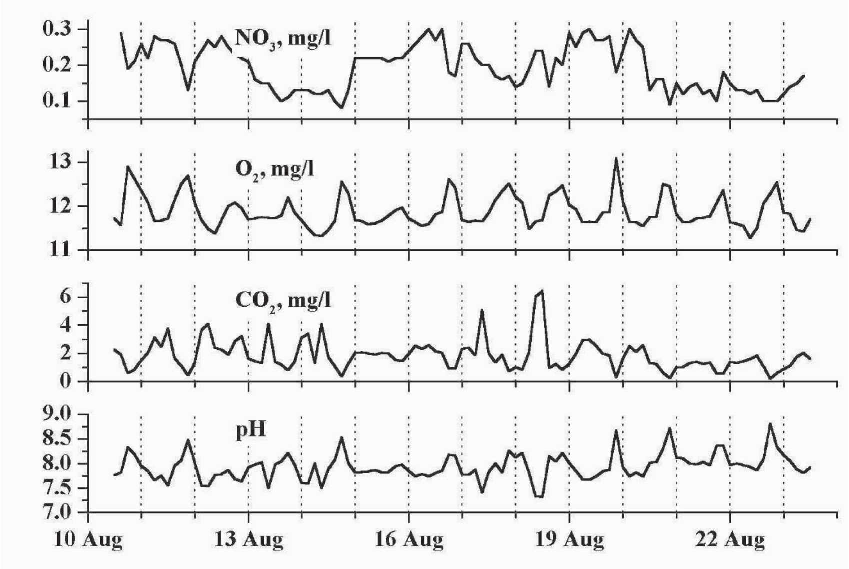

Figure 11. Diurnal aqueous chemistry behaviour in the littoral of southern Baikal in August 2003.

Data analysis has shown that the temperature maximum of the water surface is observed between 3–6 p.m. in the summer. The greatest pH value, O_2 concentration, and minimum CO_2 and biogenic element concentrations are recorded at the same time (Fig. 11). Enrichment of biogenic elements and CO_2 and the decrease in pH and O_2 concentrations are observed during the night and in the morning (6–9 a.m.). The concentration maximums and minimums in the winter are observed at 6 a.m. and 3 p.m., respectively (Fig. 12). The maximum amplitude of the diurnal variations was observed in June

2004 (ΔO_2=1,7 mg/l, ΔCO_2=2,1 mg/l), and the minimum was observed in the winter (ΔpH=0,1 unit, ΔO_2=0,47 mg/l, ΔCO_2=0,55 mg/l).

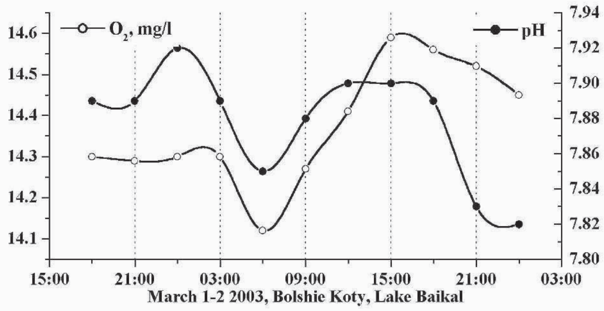

Figure 12. Diurnal behavior of oxygen and pH in March 2004.

The relative estimate of the CO_2 flux is calculated using the difference between the measured and equilibrium concentrations of CO_2 (Fig. 13).

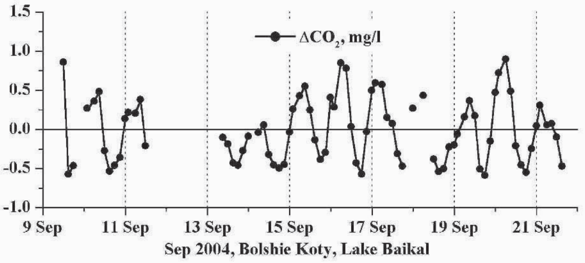

Figure 13. Difference between the measured and equilibrium concentrations of CO_2.

5. CONCLUSIONS

Thus complicated diurnal and day-to-day periodic oscillations of pH, CO_2, O_2 and biogenic elements occur in the near-surface water of Lake Baikal. They are caused by hydro-meteorological and hydro-biological factors. Deviations of the dissolved gas concentrations from their values in equilibrium with the atmosphere should cause the observed short-period variations in gas exchange intensity with the atmosphere, and the variations of the state of the carbonate system of the trophogenic zone of the lake.

ACKNOWLEDGEMENTS

The work was supported in part by program No. 3 of the Department of Earth Sciences RAS “Water resources, dynamics and preservations of underground water and glaciers”, project “ The study of pollution of the atmosphere and near-surface water of Lake Baikal” as well as SB RAS expedition grant “Baikal”.