

---

---

G E O P H Y S I C S

---

---

## Sinks and Sources of Carbon Dioxide in the Arctic Ocean: Results of Direct Instrumental Measurements

I. P. Semiletov<sup>a</sup> and I. I. Pipko<sup>b</sup>

Presented by Academician G.S. Golitsyn August 2, 2006

Received August 8, 2006

DOI: 10.1134/S1028334X07040332

The growing interest in the investigation of the carbon cycle in the Arctic region is caused, first of all, by the climatic changes that are best manifested in the northern latitudes as an increase in the annual mean air temperature, intensity of the atmospheric circulation, melting of permafrost and mountain glaciers, and scale of coastal erosion and river discharge, which finally lead to an increase in the greenhouse gases emission (carbon dioxide CO<sub>2</sub> and methane CH<sub>4</sub>) from the northern ecosystems and intensification of global warming [1]. Up to the present time, the eastern sector of the Russian Arctic seas (EAS), which includes the Laptev Sea, East Siberia Sea (ESS), and Chukchi Sea, was considered the least studied geographical region. Previous studies and data were characterized by the following major drawbacks: poor investigation of gas components in the carbon cycle (CO<sub>2</sub> and CH<sub>4</sub>) in the water surface–atmosphere and ice–water surface systems, mismatches and contradictions in the calculated data on the structure and quantitative relation between the main components of the carbon cycle, and an insufficient amount of data needed to generalize the total pattern of the fluxes and mass budget of carbon in the Arctic Ocean (AO) [2].

Analysis of the literature data shows that the role of the AO is not even considered in the atmospheric CO<sub>2</sub> budget in modern studies [3]. Until now, the enormous amounts of organic matter (OM) buried in the land and underwater permafrost surrounding the AO have not been taken into account [4]. Climate warming and the consequent degradation of land and underwater permafrost can lead to the additional involvement of an enormous amount of OM (CO<sub>2</sub> and methane) into the modern biogeochemical cycle and intensification of lateral

transport of dissolved and suspended OM due to enhanced coastal erosion and increase in the river runoff. Moreover, if we assume that approximately 89% of the organic carbon accumulated in the EAS is mineralized at the bottom [2], it becomes clear that the dynamics of the carbonate system plays an important role in the regional carbon cycle. The available historical data on the dynamics of the carbonate system in the Arctic seas are very limited and nonuniform. Unfortunately, Soviet polar researchers at the drifting stations *Severnyi Polyus* measured only pH and total alkalinity (Alk). The methods and errors of pH and Alk analyses were different in different expeditions. Hence, we cannot estimate correctly errors of the calculation of the partial pressure (pCO<sub>2</sub>) in water not only in individual years but even in individual expeditions. Therefore, the known estimates of annual absorption of the atmospheric CO<sub>2</sub> by the Arctic waters are based on episodic measurements by hardly comparable methods. They differ by almost an order of magnitude from 24 Tg C-CO<sub>2</sub> (1 Tg = 10<sup>12</sup> g) [5] to 176 Tg C-CO<sub>2</sub> [6].

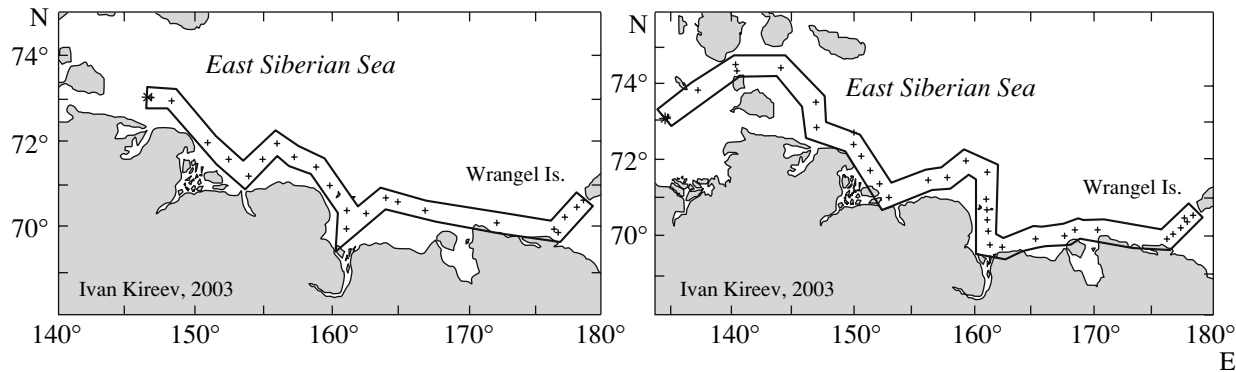
In this paper, we present the results of the first direct precise measurement of pCO<sub>2</sub> in water in the ice-free basin in summer and under ice in winter ( $n = 7000$ ) and concentrations of CO<sub>2</sub> in the air carried out in 2002–2005 in the EAS within the framework of the agreement about the cooperation between the Pacific Institute of Oceanology (Far East Division of the Russian Academy of Sciences) and the International Arctic Research Center (University of Alaska, Fairbanks). The new data demonstrate the high variability and mosaic character in the pCO<sub>2</sub> distribution and give grounds for revising the role of the AO in the atmospheric CO<sub>2</sub> budget.

*Summer measurements in ice-free water.* Direct measurements of pCO<sub>2</sub> in the surface water layer were carried out with a time interval equal to 30 min using a high-precision autonomous instrument (SAMI-CO<sub>2</sub> sensor, error <1% of the measured value [www.sunburst-sensors.com, 7]) on the alongshore route of the ship (Fig. 1). The water was taken by a powerful pump

---

<sup>a</sup> Pacific Institute of Oceanology, Far East Division, Russian Academy of Sciences, ul. Baltiiskaya 43, Vladivostok, 690041 Russia; e-mail: irina@poi.dvo.ru

<sup>b</sup> International Arctic Research Center, University of Alaska Fairbanks, P.O. Box 757 335, Fairbanks, Alaska, USA



**Fig. 1.** Alongshore transect in the East Siberia Sea made by hydrographic vessel *Ivan Kireev* in September 2003 and 2004. Dots indicate the locations of multidisciplinary oceanographic stations.

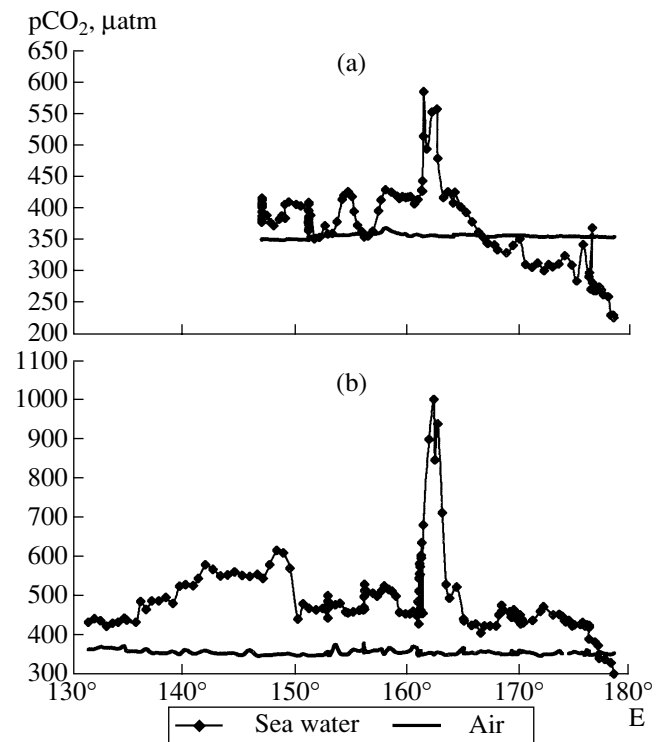
( $100 \text{ l min}^{-1}$ ) from a depth of 4 m. The concentration of  $\text{CO}_2$  in the air was measured continuously using a Li-Cor 820 nondispersive infrared spectrometer [www.licor.com] with an error within  $\pm 2\%$ . The air was taken at a height of 10 m above the sea level using an overboard reinforced hose attached to a 3-m rod ahead of the ship. The results were automatically reduced to the standard conditions using the software package of the instrument. Continuous measurements of wind direction and speed were carried out using a Li-Cor 1440 meteorological station. Data filtration to exclude possible air pollution by the ship was based on the meteorological station data. Figure 2 shows distributions of the atmospheric  $\text{CO}_2$  content and  $\text{pCO}_2$  values in the alongshore transect in 2003 and 2004. One can see that the average  $\text{pCO}_2$  value in 2004 exceeded the corresponding value in 2003 by 70–100  $\mu\text{atm}$  with a maximum up to 1000  $\mu\text{atm}$  at the Kolyma beam.

Change in the direction of the flow between  $167^\circ$  and  $170^\circ$  E in 2003 coincides with the location of the hydrological frontal zone between low-productive turbid shelf waters and high-productive transparent waters of the Pacific origin [8, 9]. In 2004, the entire studied water area practically represented a source of  $\text{CO}_2$ . This fact agrees with the pH–Alk data on samples collected at a depth of 1 m with a Niskin bottle [10]. The location of the frontal zone can be shifted from its climatic position by  $10^\circ$  (in 2003) or more (in 2004) over longitude depending on the predominance of the type of atmospheric circulation [8, 11]. This is manifested in the scale of its influence on the  $\text{CO}_2$  budget at the shallow-water shelf [10].

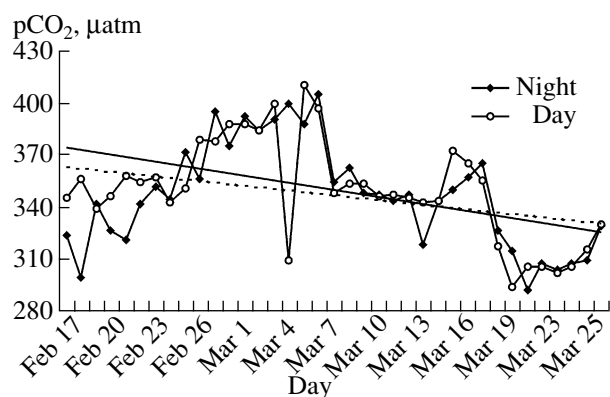
Let us consider possible causes of the increase in  $\text{pCO}_2$  in 2004 compared to 2003. Increase in river discharge is among them. For example, the discharge of the Lena River in August 2004 was 29% greater and the discharge of the Kolyma river was 34% greater than the corresponding values during the same period in 2003 [http://www.arctic.noaa.gov/detect/]. This situation was responsible for a significant decrease in salinity, warming, and concentration of  $\text{CO}_2$  in the coastal water

of the Laptev Sea and the EAS. The “erosion signal,” which was more prominent during warm year 2004, is another possible cause. The erosion signal designates an increase in the mean and integral values of the distribution of dissolved organic carbon, suspended matter, and dissolved  $\text{CO}_2$  as a product of erosional OM decay [12].

In 2004, the interannual water temperature difference could have increased the  $\text{pCO}_2$  by not more than 10  $\mu\text{atm}$ . In 2004, growth of the concentration of suspended matter in the surface layer of the EAS increased its integral content by approximately 20% compared to



**Fig. 2.** Profile of  $\text{pCO}_2$  (depth 4 m) and synchronously measured  $\text{CO}_2$  concentration in the air (height 10 m) over the alongshore section in (A) 2003 and (B) 2004.



**Fig. 3.** Distribution of  $p\text{CO}_2$  values under fast ice at a depth of 2.5 m over the shelf of the Chukchi Sea near Cape Barrow ( $72^\circ\text{N}$ ). Solid line shows the trend for daytime measurements, and dashed line indicates nighttime trend.

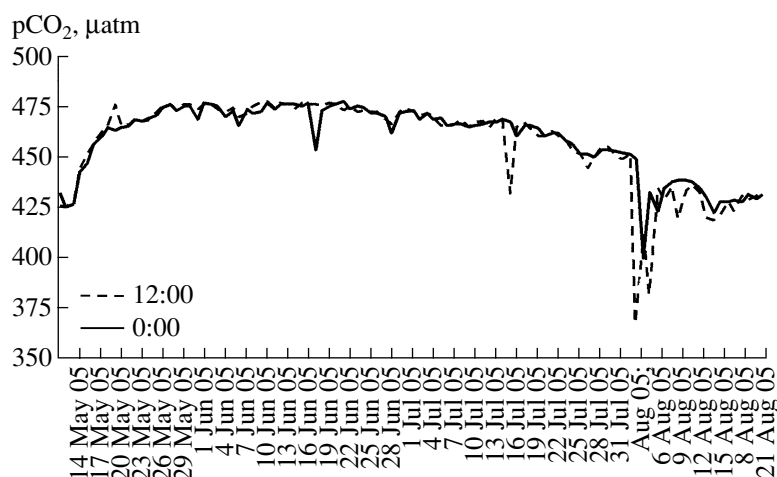
2003 [12], which caused a decrease in transparency in the surface water layer in September 2004. We can suppose that variation in the transparency of waters owing to intensification of erosion is one of the important causes responsible for the decrease of primary productivity in 2004 and, correspondingly, the increase of  $p\text{CO}_2$  compared to 2003.

The results allowed us to distinguish the typical distribution patterns of the parameters of EAS carbonate system in the summer–autumn season. Decrease of  $p\text{CO}_2$  in the surface waters from west to east is the main feature. In 2004, the mean values of  $\text{CO}_2$  flux based on  $p\text{CO}_2$  calculated from the measured pH and Alk values ( $10.9 \text{ mmol m}^{-2}$  per day) were one order of magnitude higher than in 2003 ( $1.0 \text{ mmol m}^{-2}$  per day). This is explained by greater differences in  $p\text{CO}_2$  (between water and air) and wind velocity in 2004 [10]. If we suppose that the shallow shelf of the EAS and the Laptev and Kara seas (total area  $\sim 3 \text{ mln km}^2$ ) with significant coastal erosion and river discharge served as a source of  $\text{CO}_2$  emission into the atmosphere (minimal evasion of  $\text{CO}_2$  is  $1 \text{ mmol m}^{-2}$  per day) during the ice-free period of 50 days, then the minimal estimate of summer emission of  $\text{CO}_2$  into the atmosphere would be  $4.2 \text{ Tg C-CO}_2$ . If we assume the minimum evasion of  $\text{CO}_2$  during observations in different years (1999, 2003, and 2004) in the EAS and Laptev Sea approximately equal to  $5 \text{ mmol m}^{-2}$  per day, a moderate estimate of summer emission of  $\text{CO}_2$  into the atmosphere would be  $21 \text{ Tg C-CO}_2$ , which is more than two times greater than the amount of carbon annually accumulated as organic compounds in the bottom sediments of the EAS [2]. At the same time, according to the estimates in [13], the highly productive Chukchi Sea absorbs  $2 \text{ Tg C-CO}_2$  in September and approximately  $10 \text{ Tg C-CO}_2$  during the entire vegetation period. If warming continues in the Arctic region, emission of  $\text{CO}_2$  into the atmosphere from the AO waters can increase. They would be

enriched in  $\text{CO}_2$  as a product of the decay of OM stored in the land and underwater permafrost. The distinguished mosaic pattern of the distribution of sinks and sources of  $\text{CO}_2$  into the atmosphere in the summer period give grounds to revise the role of the AO in the  $\text{CO}_2$  budget.

*Winter measurements under ice.* In the polar night period of February 2003, we deployed a SAMI- $\text{CO}_2$  sensor at a level of 2.5 m under the ice over the shallow shelf of the Chukchi Sea ( $72^\circ\text{N}$ , Alaska, United States) near Cape Barrow to study the dynamics of the AO carbonate system during the winter period. The measurements were carried out with a time interval of 30 min from February 17 to March 23 (air temperature over the ice varied from  $-32$  to  $-43^\circ\text{C}$  and the wind speed was as high as  $10$ – $12 \text{ m/s}$ ). Water temperature under ice corresponded to the temperature of ice formation and did not change during the observation period [14]. The analysis of the results of measurement (approximately 2 million measurements in situ) shows that the  $p\text{CO}_2$  value increased in the second half of February up to  $400$ – $410 \text{ µatm}$  (Fig. 3), indicating significant respiration under ice not compensated by photosynthesis during the polar night. On the contrary, after the beginning of the polar dawn in March, the values decreased to  $288 \text{ µatm}$ , which can suggest a significantly earlier beginning of photosynthesis under ice than was considered earlier. This supposition is indirectly confirmed by a sharp increase in the concentration of dissolved oxygen in the beginning of March under 2-m-thick fast ice in the other shelf region of the AO located in Buor-Khay Inlet, Laptev Sea (unpublished data of the Tiksi Hydrometeorological service).

In May 2005, our SAMI- $\text{CO}_2$  sensor equipped with a spherical sensor (Li-Cor Li-193-SA PAR sensor, www.licor.com) for recording photosynthetically active solar radiation (PAR) was deployed under ice in the central basin of the AO at the Russian drifting station *Severnnyi Polyus 33* with the logistic support of the Arctic and Antarctic Research Institute. The obtained results based on approximately 4000 measurements show that the under-ice water in the spring–summer period (May–August) is characterized by high  $p\text{CO}_2$  values ranging from  $425$  to  $475 \text{ µatm}$  (Fig. 4). This is much greater than the equilibrium values with the atmosphere (based on the data from the monitoring station located at Cape Barrow, the  $p\text{CO}_2$  value in the air during this period of the year usually varies from  $345$  to  $365 \text{ µatm}$ ). These preliminary results indicate that the Central Basin of the AO can serve as a source of  $\text{CO}_2$  emission into the atmosphere but not as a sink as was commonly accepted before [15]. We note that no significant correlation was found between the  $p\text{CO}_2$  and PAR values. Hence, increase in the PAR value during melting of perennial ice is not crucial for the budget of carbonate system in this region of the AO. High  $p\text{CO}_2$  values in the under-ice layer can be caused by the influence of the following factors (or their combination): high



**Fig. 4.** Direct measurements of  $p\text{CO}_2$  under ice in the central basin of the Arctic Ocean at the Russian drifting station *Severnyi Polyus 33*.

rates of bacterial respiration (exceeding the rate of photosynthesis) and import of waters of the upper halocline or waters of the Lena River entrained in the Transarctic drift and enriched with  $\text{CO}_2$  [9, 11, 12]. Multidisciplinary works previously carried out on the fast ice of the Chukchi Sea [14] should be revived to scrutinize the role of sea ice in the regional budget of  $\text{CO}_2$ .

#### ACKNOWLEDGMENTS

The authors thank Academicians V.I. Sergienko, G.S. Golitsyn, and V.A. Akulichev; Prof. S. Akasof; and Prof. J. Calder for supporting the Russian–US research in the Arctic region. We acknowledge the support of the International Arctic Research Center/University Alaska Fairbanks and Cooperative Institute for Arctic Research through NOAA Cooperative Agreement NA17RJ1224.

This work was also supported by the Presidium of the Far East Division of the Russian Academy of Sciences and the Russian Foundation for Basic Research (project nos. 04-05-64819, 05-05-64213, and 06-05-79080).

#### REFERENCES

1. *Climate Change 2001: The Scientific Basis. Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change* (Cambridge Univ. Press, Cambridge, 2001).
2. E. A. Romankevich and A. A. Vetrov, *Carbon Cycle in the Arctic Seas of Russia* (Nauka, Moscow, 2001) [in Russian].
3. *Global Carbon Project, Science Framework and Implementation. Earth System Science Partnership (IGBP,*

*IHDP, WCRP, DIVERSITAS)*, Global Carbon Project Rept. no. 1 (Canberra, 2003).

4. I. Semiletov, N. Shakhova, V. Romanovsky, and I. I. Pipko, *World Resource Rev.* **16** (4), 503 (2004).
5. L. G. Anderson, K. Olsson, and M. Chierici, *Global Geochem. Cycles* **12**, 455 (1998).
6. Yu. I. Lyakhin and V. P. Rusanov, *Dokl. Akad. Nauk* **271**, 198 (1983)].
7. M. D. De Grandpre, M. M. Baehr, and T. R. Hammar, *Anal. Chem.* **71**, 1152 (1999).
8. I. Semiletov, O. Dudarev, V. Luchin, et al., *Geophys. Res. Lett.* **32**, L10614 (2005).
9. I. I. Pipko, I. P. Semiletov, S. P. Pugach, *Dokl. Earth Sci.* **402**, 624 (2005) [*Dokl. Akad. Nauk* **402**, 398 (2005)].
10. I. I. Pipko, I. P. Semiletov, and S. P. Pugach, in *Report of V Arctic Coastal Dynamics Int. Workshop* (Montreal, 2005), pp. 89–93.
11. I. P. Semiletov, N. I. Savelieva, G. E. Weller, et al., in *The Freshwater Budget of the Arctic Ocean, NATO Meeting/NATO ASI Series* (Kluwer Acad. Publ., Dordrecht, 2000), pp. 323–366.
12. I. P. Semiletov, *Carbon Cycle in the Atmosphere–Land–Shelf System in the Eastern Arctic Region (Fluxes, Forms of Existence, Spatiotemporal Variability of Components)*, Doctoral (Geogr.) Dissertation (Vladivostok, 2005).
13. I. I. Pipko, I. P. Semiletov, P. Ya. Tishchenko, et al., *Progress Oceanogr.* **55**, 77 (2002).
14. I. P. Semiletov, A. P. Makshtas, S. Akasofu, and E. Andreas, *Geophys. Res. Lett.* **31**, L05121 (2004).
15. T. Takahashi, S. C. Sutherland, C. Sweeney, et al., *Deep-Sea Res. II* **49**, 1601 (2002).