# Atmospheric $CO_2$ balance: The role of Arctic sea ice

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[1] Climatic changes in the Northern Hemisphere have led to remarkable environmental changes in the Arctic Ocean, including significant shrinking of sea-ice cover in summer, increased time between sea-ice break-up and freeze-up, and Arctic surface water freshening and warming associated with melting sea-ice, thawing permafrost, and increased runoff [*Carmack*, 2000; *Morison et al.*, 2000; *Semiletov et al.*, 2000; *Serreze et al.*, 2000]. These changes are commonly attributed to the greenhouse effect resulting from increased carbon dioxide ($CO_2$) concentration. The greenhouse effect should be most pronounced in the Arctic where the largest air $CO_2$ concentrations and winter-summer variations in the world for a clean background environment were detected [*Conway et al.*, 1994; Climate Monitoring and Diagnostics Laboratory Data Archive, http://www.cmdl.noaa.gov/info/ftpdata.html]. Some increased seasonal variation may be a consequence of increasing summer $CO_2$ assimilation by plants in response to higher temperature and longer growing season [*Keeling et al.*, 1996]. Here we show that sea-ice melt ponds and open brine channels form an important spring/summer air $CO_2$ sink that also must be included in any Arctic regional $CO_2$ budget; both the direction and amount of $CO_2$ transfer between air and sea during the open water season may be different from transfer during freezing and thawing, or during winter when $CO_2$ accumulates beneath Arctic sea-ice. *INDEX TERMS:* 0312 Atmospheric Composition and Structure: Air/sea constituent fluxes (3339, 4504); 0330 Atmospheric Composition and Structure: Geochemical cycles; 1610 Global Change: Atmosphere (0315, 0325); 4806 Oceanography: Biological and Chemical: Carbon cycling. **Citation:** Semiletov, I., A. Makshtas, S.-I. Akasofu, and E. L Andreas (2004), Atmospheric $CO_2$ balance: The role of Arctic sea ice, *Geophys. Res. Lett.*, *31*, L05121, doi:10.1029/2003GL017996.

[2] Understanding $CO_2$ exchange between atmosphere, ocean, and land is important, because marine and terrestrial environments are currently absorbing about half of the $CO_2$ emitted by fossil-fuel combustion. Where and how land and ocean vary in their uptake of $CO_2$ from year to year has been the subject of much scientific research and debate [*Ciais et al.*, 1995; *Everett et al.*, 1998; *Feely et al.*, 2001; *Prentice et al.*, 2001].

[3] The Arctic Ocean's role in determining regional $CO_2$ balance has been ignored because continuous sea-ice cover is considered to impede gaseous exchange with the atmosphere so efficiently that no global climate models include $CO_2$ exchange over sea-ice [*Tison et al.*, 2002]. However, pioneering measurements by Gosink and Kelley in the 1960–70s [*Gosink et al.*, 1976; *Kelley and Gosink*, 1979] showed one year sea-ice was highly permeable to $CO_2$ at temperatures above $-15°C$ through numerous tiny channels. Mechanism involved in this process has been roughly discussed. In this paper we present new data concerning the carbon flux across the sea ice and dynamics of the carbonate system in the Amerasian Arctic seas.

[4] The leads, polynyas, and melt ponds of the Arctic Ocean can be significant sinks of air $CO_2$ in summer and sources in winter. Flight data [*Bolin and Keeling*, 1963; *Kelley and Gosink*, 1979] support this conclusion. Shipboard data show that low summer $CO_2$ partial pressure ($pCO_2$) in surface waters is rapidly replaced with high $pCO_2$ in fall and winter [*Kelley*, 1970; *Pipko et al.*, 2002; *Semiletov*, 1999a], concurrent with rising atmospheric $CO_2$ levels at Barrow, Alaska. In synchrony with variations in atmospheric $CO_2$, phytoplankton blooms in perennial pack ice and ice algae density over the Arctic Basin and continental shelves [*Gosselin et al.*, 1997; *Melnikov*, 1997] also show large variation in primary and secondary production.

[5] To determine the impact of $CO_2$ transport through sea-ice of the North American-Siberian Arctic Ocean shelf zones, we conducted observations in two representative areas: 1) fast ice near Barrow, influenced strongly by marine input of organic material, and 2) the eastern Laptev Sea and western East-Siberian Sea, an area with high coastal erosion and fluvial input rates.

[6] Initial field investigations of $CO_2$ exchange through melting sea-ice were conducted for the first time on fast ice near Point Barrow, June 6–24, 2002 using previously described eddy correlation [*Oechel et al.*, 1998] and chamber techniques [*Zimov et al.*, 1993] which were applied early only for land-based studies. Figures 1a and 1b show data from tower-based turbulent $CO_2$ flux measurements. Flux magnitude was typically 0.01–0.02 mg $m^{-2}$ $s^{-1}$, close to values previously measured in transects above Alaskan North Slope tundra [*Oechel et al.*, 1998]. The turbulent flux of $CO_2$ ($F_{CO2}$) measured above fast ice during onshore winds (Figure 1a) becomes more negative with time, indicating increasing $CO_2$ absorption by the sea-ice surface from air masses originating over the Arctic Ocean, which contain higher $CO_2$ concentrations than "terrestrial" air masses. Absolute values are similar for offshore winds, but the $F_{CO2}$ trend is reversed (Figure 1b). The positive trend of $F_{CO2}$ in Figure 1b may result from a decreasing $CO_2$ concentration in air masses coming across Alaska to

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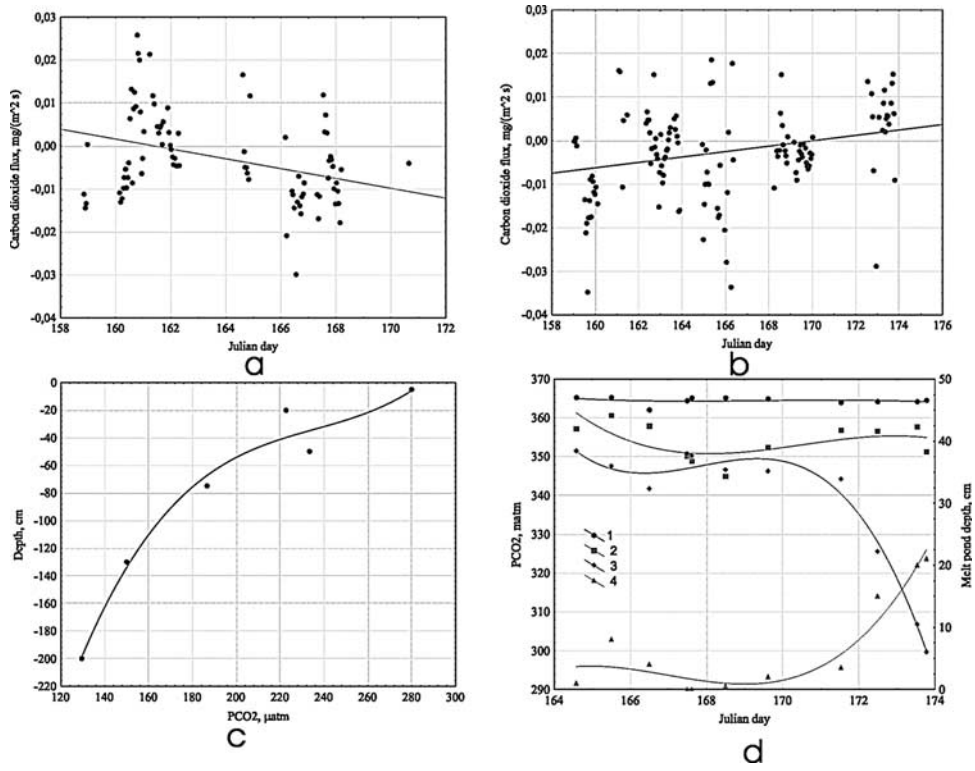


**Figure 1.** The main results of our observations of $CO_2$ exchange in a system comprising the atmospheric surface layer, the sea ice, and the upper ocean near Barrow in June 2002: **a**. $CO_2$ turbulent flux during onshore winds (negative values mean the flux is toward the surface); **b**. the same as for a. but for offshore winds; **c**. $pCO_2$ in brines and under fast ice; **d**. $CO_2$ concentration in the air (1) and $pCO_2$ measured by chambers near (2) and in the center (3) of a growing melt pond whose depth is shown by line (4).

the sea-ice surface, as burgeoning photosynthesis depletes tundra air $CO_2$ in the second half of June (Y. Harazono, personal communication, 2002). In general, flux observations show significant absorption of air $CO_2$ by the melting sea-ice surface. Note, that in fall the situation can be reversed and ''terrestrial'' air masses may contain higher $CO_2$ concentrations than ''marine'' air masses because soil respiration becomes dominate over the land.

[7] Measurements of $pCO_2$ in sea-ice brines and in under-ice water (Figure 1c) demonstrated significant $CO_2$ undersaturation of 220–280 µatm and 130–150 µatm, respectively, compared to air concentrations of 365–375 µatm. The chamber data show a drastic decrease of equilibrium $CO_2$ concentration (down to 300 µatm) in the headspace above growing melt ponds, especially during the last four measurement days, when daily mean temperature rose above 0°C and melt pond depth increased dramatically from a few cm to 20 cm (Figure 1d). Almost all chamber $CO_2$ flux measurements show atmospheric $CO_2$ uptake by the sea-ice surface. Chamber $CO_2$ influx ranged between 0.002 and 0.003 mg $CO_2$ mg $m^{-2}$ $s^{-1}$ at sites with water depth = 0–2 cm, and between 0.003 and 0.026 mg $m^{-2}$ $s^{-1}$ at sites with water depth = 2–5 cm.

[8] These results confirm the turbulent flux measurements and reflect increased incoming solar radiation absorption by melt ponds and beneath sea-ice. We suggest that increased photosynthetically active radiation (PAR) may cause decreased $pCO_2$ in and beneath sea-ice (Figure 1c) by enhancing photosynthesis. $CO_2$ transport rates across sea-ice likely also increase because sea-ice becomes thinner and more gas-permeable when ice temperature increases [*Gosink et al.*, 1976]. Some evidence of such processes can be seen by comparing drastically decreased air head-space $CO_2$ concentrations in the chamber situated on dry ice near and also directly above a melt pond (curves 2 and 3, Figure 1d).

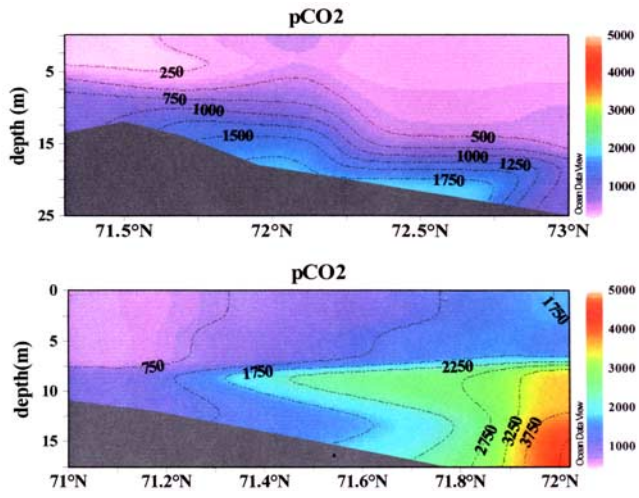


**Figure 2.** Vertical distribution of $pCO_2$ (µatm) across the Buor-Khaya Gulf in the Laptev Sea in September 2000 (top) and April 2002 (bottom).

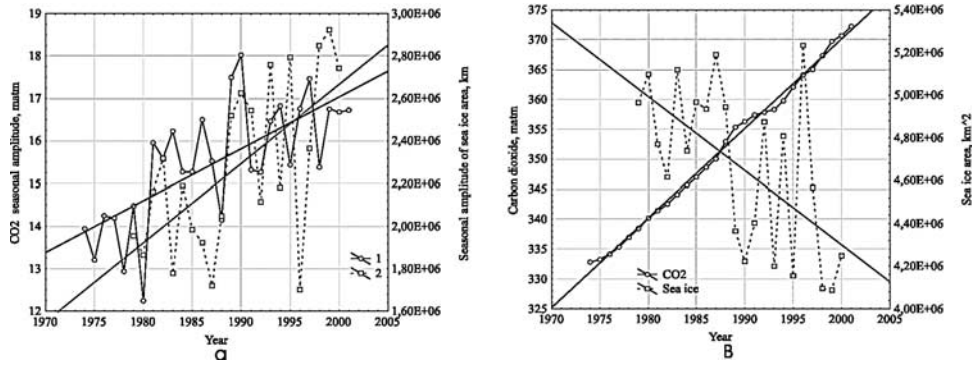


**Figure 3.** **a**. Interannual variability of atmospheric $CO_2$ seasonal cycle amplitude at Barrow (1) and sea ice extent in the Arctic Ocean (2). **b**. Comparisons between atmospheric $CO_2$ concentration at Barrow and sea ice extent in the Arctic Ocean in September.

[9] The effects of summer temperature and PAR increase on the sea-ice/sub-ice water ecosystem is expected to enhance Arctic Ocean-scale sinks. We evaluated the significance of this Arctic sea-ice air $CO_2$ sink, assuming that mean downward turbulent flux ($-0.005$ mg $CO_2$ $m^{-2}$ $s^{-1}$) obtained over fast ice in June is representative of the entire Arctic Ocean ice during melting (>50 days). It is very a rough estimate though wide distribution of deep melt ponds and increased brine drainage over multi-year ice and flight data give us a clue that summertime multi-year ice can become gas permeable. Estimated total air $CO_2$ absorption by sea-ice would be $\approx$150 Mt $CO_2$ (40 Mt C) per summer. Updated global carbon budgets in the IPCC assessment [*Prentice et al.*, 2001] show that the net terrestrial biosphere sink of atmospheric $CO_2$ was $\approx$200 Mt C/yr in the 1980s, only five times more than mean uptake by sea-ice. We suggest that sea-ice plays a significant but hitherto unappreciated role in the spring/summer invasion of atmospheric $CO_2$.

[10] Data obtained in the Buor-Khaya Gulf of the Laptev Sea, an area with high rates of coastal erosion and fluvial input [*Semiletov*, 1999b], show dramatic $pCO_2$ changes in bottom and upper sea layers from summer, when the sea surface was ice-free (Figure 2a), to winter (Figure 2b), when fast ice thickness exceeded 2.0 m. In winter and early spring, when organic materials decomposition dominates, $pCO_2$ exceeded 4,000 $\mu$atm near the bottom and 1,500 $\mu$atm near the surface. Both present and literature data [*Kelley and Gosink*, 1979; *Semiletov*, 1999a] show that $CO_2$ supersaturation beneath sea-ice is a principal feature of carbon cycling in Arctic Siberian seas. Assuming an evolution of $CO_2$ from porous one year sea-ice in the range 0.01–0.1g C $m^{-2}$ $day^{-1}$ (recalculated from *Gosink et al.* [1976] and *Kelley and Gosink* [1979]) and $\approx 2 \times 10^6$ $km^2$ of Arctic Siberian sea-ice coverage, we estimate possible winter (November–May, $\approx$200 days) efflux from sea-ice over Siberian shelves to the atmosphere of $\approx$4–40 Mt C.

[11] In contrast, in summer and early autumn, due to dominant photosynthetic processes above a strong pycnocline, surface water over the Laptev sea study area was undersaturated by $CO_2$ ($\cong$250 $\mu$atm) compared to the atmosphere. Similar data were obtained over other Siberian and Alaskan shelves [*Kelley*, 1970; *Pipko et al.*, 2002; *Semiletov*, 1999a]. Note that bottom waters were significantly oversaturated (up to $\sim$10 times) by $CO_2$ year-round due to high influx of old eroded terrestrial carbon, available for fast biodegradation [*Semiletov*, 1999b]. The highest $pCO_2$ values in the marine environment may exist over the East Siberian shallow shelf (I. Semiletov et al., Air-sea $CO_2$ exchange in the Arctic, manuscript in preparation, 2004) where biogeochemical consequences of coastal erosion are most pronounced.

[12] New information on $pCO_2$ dynamics beneath fast ice was obtained February 17–March 23, 2003, when mooring-based $pCO_2$ observations were executed with the autonomous device SAMI-$CO_2$ designed by *De Grandpre et al.* [1999]. The device was installed 2.5 m below the sea-ice surface and measured $pCO_2$ at half-hour intervals in stable water temperature. In late February, $pCO_2$ values increased to 400–410 $\mu$atm (that may be an effect of biological respiration), while in March a drastic $pCO_2$ decrease from 410 $\mu$atm to 288 $\mu$atm was recorded. The decrease in $pCO_2$ may reflect increased photosynthetic activity beneath sea-ice shortly after polar sunrise.

[13] We compared temporal variations in amplitude of $CO_2$ seasonal cycles and summarized amplitudes of sea-ice extent in the central Arctic and the Laptev, East Siberian, Chukchi, and Beaufort seas for 1974–2001. The region for comparison was chosen after *Parkinson et al.* [1999]. Using available sea-ice data from http://polynya.gsfc.nasa.gov/seaice_datasets.html, we calculated the amplitude of Arctic sea-ice extent as the yearly difference between May and September areas. We found similar behavior of $CO_2$ and sea-ice seasonal amplitudes (Figure 3a) and inverse behavior of annual mean $CO_2$ concentration and sea-ice extent (Figure 3b). The calculated correlation coefficients, however, are rather small, especially if we calculate them after removing linear trends in the time series. The maximum correlation coefficient (0.61) was found between air $CO_2$ concentration and sea-ice extent in September. Such low correlation is not surprising in view of the complicated behavior of gas exchange processes, partly described above, and the difficulties of comparing the data obtained at a point with data averaged over thousands of square kilometers. But the relation between changes in sea ice area, determined by opening or closing leads, especially, by seasonal variations of ice cover in the marginal seas, is evident.

[14] Decreased sea-ice extent and lengthening ice-free periods, longer photosynthetic activity, and absorption of air $CO_2$ through leads and melt ponds in late spring and

summer could be a significant unappreciated determinant of Arctic $CO_2$ balance. Our results show that the spring/summer $CO_2$ sink formed by sea-ice melt ponds and open brine channels must be included in any complete Arctic regional $CO_2$ budget. Large, rapid changes in seawater $pCO_2$ and vertical $CO_2$ fluxes above/through sea-ice were found in two representative areas of the Arctic Ocean, indicating that $pCO_2$ beneath sea-ice can be highly variable in near-shore environments. Extremely high marine $pCO_2$ values indicating wintertime accumulation of $CO_2$ beneath sea-ice exist over the shallow East Siberian shelf, where biogeochemical consequences of coastal erosion are most pronounced. In winter the shelf waters may be a source of $CO_2$ through leads and open brine channels. The Arctic Ocean's contribution to the formation of the largest seasonal variations of air $CO_2$ on Earth cannot be ignored.

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