CARBON DIOXIDE EXCHANGE IN THE COASTAL OCEAN–SEA ICE–ATMOSPHERE SYSTEM

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1. INTRODUCTION

The mean annual concentration of atmospheric carbon dioxide has its absolute maximum in the Arctic. Measurements made along the coast of the Arctic Ocean, especially at Barrow, Alaska, show that the concentration of carbon dioxide has increased substantially over the past several decades (e.g., Conway et al. 1994). Together with this increase in the annual mean of CO_2 concentration, its seasonal variation has dramatically increased also. Keeling et al. (1996) explain this large seasonal variation as increasing assimilation of CO_2 by land plants in response to the increase in air surface temperature and the duration of the growing season.

A related and unstudied issue, though, is the presence of perennial or seasonal sea ice cover on the Arctic Ocean, in particular, directly adjoining Barrow, which is the site of the longest data set usually used for investigating the longterm variability of CO₂ in the Arctic. But, as mentioned by Tison et al. (2002), continuous sea-ice cover is considered to impede gaseous exchange with the atmosphere so efficiently that no global coupled models include CO₂ exchange over sea ice. Even leads, which cover 2-5% of the total icecovered area in winter, are sometimes ignored. These seem to be serious omissions in light of the pioneering measurements of Gosink et al. (1976) in the 1960-70s, which showed that sea ice is highly permeable to CO₂ at temperatures above -15°C. Nevertheless, the role of CO₂ transport through sea ice in the regional carbon budget has not been evaluated because there are only scanty experimental data.

In this paper, we will discuss small-scale and large-scale processes that relate to the influence of the sea ice cover on CO_2 exchange between the Arctic Ocean and the atmosphere.

2. SMALL-SCALE GAS EXCHANGE PROCESSES

We obtained data about small-scale CO_2 exchange processes in the presence of sea ice during a joint IARC/UAF and CRREL pilot project in June 2002. Using eddy-correlation techniques, we measured the carbon dioxide flux and the turbulent heat and momentum fluxes on fast ice near Point Barrow, Alaska, with a LI-COR 7500 open-path CO_2/H_2O analyzer and a three-axis sonic anemometer/thermometer installed on a tower at a height of 3.8 m. To our knowledge, these are the first eddy-correlation measurements of CO_2 flux ever made over sea ice.

Additionally, to evaluate the CO_2 concentration and to obtain rough estimates of CO_2 fluxes through different parts of the sea ice cover (melt ponds, dry snow, bare ice), we used a chamber technique. For these latter measurements, we used small (1–2 gallon) and large (25 gallon) chambers and a closed cell LI-COR 820 gas analyzer. We used the static headspace technique for measuring CO_2 partial pressure (p CO_2) in ice brine and sub-ice water samples taken just beneath the ice and at depths below the sharp halocline that is closely related to the bottom of the sea ice. Figure 1 shows the preliminary results of our measurements.

In Fig. 1, panels a and b show that the magnitude of the CO_2 flux is typically 0.01– 0.02 mg m⁻² s and close to values measured by Oechel et al. (1998) in the northern part of their transects above Alaskan tundra (their Fig. 5). Our values are also close to preliminary estimates of CO_2 fluxes between air and soil measured by Y. Harazono (2002, personal communication) near the NOAA Base Observatory in Barrow during our measurements.

Oechel et al. (1998) discuss how representative turbulent and chamber measurements are over a tundra region that had strong spatial inhomogeneity and experienced various stratification regimes in the atmospheric surface layer. Despite the scatter in our results, we infer that the turbulent flux of carbon dioxide (F_{CO2}) during onshore

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a. CO_2 turbulent flux during onshore winds (negative values mean the flux is toward the surface).



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.



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).

Figure 1 (cont.). 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.

winds (Fig. 1a) tends to become more negative with time, indicating increasing surface gas absorption from air masses coming from the Arctic Ocean. For offshore winds, we see the same absolute values but an opposite trend in F_{CO2} with time (Fig. 1b). The positive trend of F_{CO2} in Fig. 1b may be explained by decreasing CO₂ concentration as a result of absorption by photosynthesis in the tundra as air masses crossed Alaska in late June.

These results agree well with our pCO_2 measurements in brine and in the water under the ice (Fig. 1c). These latter show significant undersaturation, down to 130–150 ppm. Our chamber data also show a drastic decrease of the equilibrium CO_2 concentration in the headspace above the growing melt ponds, especially during the last four days of our measurements, when the daily mean temperature rose above 0°C and the melt pond depth increased dramatically to 20 cm (Fig. 1d).

These results agree well with the increase of incoming solar radiation absorbed in the melt ponds and beneath the sea ice. We suggest that increased photosynthetically active radiation (PAR) caused enhanced photosynthesis in the water in the melt ponds and in sea ice brines; consequently, pCO₂ decreased in and beneath the sea ice (Fig. 1c). Probably the transfer of CO₂ across the sea ice increased also because the sea ice becomes more permeable for any gas when ice temperature increases (Gosink et al. 1976). Some evidence of such processes can be seen by comparing CO₂ concentrations in the near-surface layer and in the chamber situated on dry ice (curves 1 and 2, Fig. 1d). However, the role of biological and physical factors in the CO₂ flux in and from the sea ice needs additional studies.

3. THE IMPORTANCE OF ACCOUNTING FOR SEA ICE COVER IN LARGE-SCALE CO₂ EXCHANGE PROCESSES

The seasonal variation of CO_2 concentration has its maximum value in the Arctic (e.g., Keeling et al. 1996). Figure 2a, constructed from data obtained during 1974–2001 at Barrow, Mauna Loa, and the South Pole (http://www.cmdl. noaa.gov), confirms this conclusion. Notice that, in summer, the CO_2 concentration at Barrow is much lower than the concentrations measured at Mauna Loa and the South Pole. This observation is interesting because the yearly averaged Barrow CO_2 concentration has the absolute maximum among these observation sites.

Equally interesting is the suggestion that the

amplitude of the seasonal cycle at Barrow, calculated following Fig. 2a as the difference between the monthly mean values of CO_2 concentration in May and August, tends to increase during the observation period (Fig. 2b). As mentioned earlier, Keeling et al. (1996) explain this increase as a consequence of a longer growing season resulting, in turn, from an increase in surface air temperature in the Arctic. Below we will discuss the possible importance of a changing sea ice cover in the regional CO_2 budget.

We compare the temporal variations of the seasonal cycle of CO_2 amplitude and sea ice area for 1974–2001 in the Arctic Ocean, including the Central Arctic and the Laptev, East Siberian, Chukchi, and Beaufort Seas. Our definitions of these areas follow Parkinson et al. (1999) (http://polynya.gsfc.nasa.gov/seaice_datasets.html). We calculate the amplitude of the variability of sea ice area as the difference between the May and September mean values for each year. Figure 3a presents our comparisons.

The similar behaviors of both CO₂ and sea ice seasonal amplitudes (Fig. 3) and the inverse behavior of the annual mean of CO₂ concentration and sea ice area (Fig. 4) in the Arctic Ocean are evident. The calculated correlation coefficients, however, are rather small, especially if we calculate them after removing linear trends in the series. The maximum correlation coefficient, 0.61, is for the annual mean values of CO₂ and sea ice area in the Arctic Ocean in September. This low correlation is not surprising in view of the complicated behavior of gas exchange processes, partly described in Section 2, and the difficulties of comparing data obtained at one point with data averaged over thousands of square kilometers. But the relation between changes in sea ice area, determined by opening or closing leads and, especially, by seasonal variations of ice cover in the marginal seas, is evident.

We offer the following possible explanation for these observations. In summer, biological uptake of atmospheric CO₂ in the ice-free parts of the Arctic Ocean dominates because of intense algae production in the stably stratified near-surface ocean. In contrast, in the fall, upwelling to the surface (or to the bottom of the sea ice) of bottom water enriched in CO₂ because of the decomposition of organic material reverses the direction, with more CO₂ moving from the ocean to the atmosphere. Under this scenario, the increase in the seasonal amplitude of CO₂ over the Arctic can be related to the summer decrease of sea ice extent in the Arctic Ocean and to the lengthening





Figure 2. Climatic characteristics of carbon dioxide in the atmospheric surface layer measured at Barrow, Mauna Loa, and the South Pole.



Figure 3. Interannual variability in the amplitude of the seasonal cycle of atmospheric CO_2 at Barrow (1) and in sea ice area in the Arctic Ocean (2).



Figure 4. Comparisons between atmospheric CO_2 concentration at Barrow and ice area in the Arctic Ocean in September.

of the ice-free period in the marginal seas. Both trends enhance the summer uptake of atmospheric CO_2 by the ocean.

The possible summer increase of melt ponds and lead concentration also could increase the absorption of atmospheric CO_2 by ice algae and sub-ice water through open brine channels. Likewise, the general shrinking of sea ice extent and convective mixing in the ocean allow enhanced flux of CO_2 into the atmosphere from sub-ice waters enriched by CO_2 in autumn before and during freeze-up (Pipko et al. 2002). Additional gas transfer to the atmosphere through leads and the relatively "warm" ice cover is also possible.

Data from investigations in the Laptev and Chukchi Seas tend to support our assumption concerning the importance of accounting for sea ice in CO_2 exchange in the Arctic. Our measurements in the Buor–Khaya Gulf of the Laptev Sea show a dramatic change in pCO₂ in the bottom and upper layers of the ocean between periods with an ice-free sea surface (Fig. 5a, September) and an ice-covered surface (Fig. 5b, August). During winter and spring (when decomposition of organic materials dominates), pCO₂ exceeds 4000 ppm near the bottom and 1500 ppm in the near-surface water. In contrast, in the summer and early autumn (when photosynthetic processes above a strong pycnocline dominate), pCO₂ in the water does not exceed 250 ppm in the surface layer. Values of pCO₂ measured in September 1996 along transects in the Chukchi Sea also show that, in general, the direction of the CO₂ flux changed from atmosphere to sea in early September to opposite that in late September in response to the deepening of the mixed layer and to partial upwelling of bottom water enriched by CO₂ (Semiletov 1999a, 1999b; Pipko et al. 2002).



Figure 5. Spatial distribution of pCO₂ in the Buor–Khaya Gulf.

4. CONCLUSIONS

These first eddy-correlation and chamber measurements obtained on fast ice near Barrow provide some insights into the influence of sea ice on carbon dioxide exchange between the ocean and the atmosphere. We infer that, in early summer, despite the presence of sea ice, the ocean's absorption of atmospheric CO_2 dominates. We also suggest the important role of melt ponds in gas exchange.

Based on climatic data consisting of routine measurements of carbon dioxide concentration at Barrow and on satellite data about sea ice area in the Arctic Ocean, we hypothesize that ice conditions in the Arctic Basin influence the long-term and seasonal variability of atmospheric carbon dioxide concentration. Scanty data from ship observations in the Chukchi and Laptev Seas give some support to this hypothesis.

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