SOURCES AND SINKS OF CARBON DIOXIDE
IN THE ARCTIC REGIONS

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The data base required to adequately ascertain seasonal source and sink strengths in the arctic regions is difficult to obtain. However, there are now a reasonable quantity of data for this polar region to estimate sources and sinks within the Arctic which may contribute significantly to the annual tropospheric CO₂ concentration fluctuation. The sea-ice-air and the sea-air interfaces account for most of the contribution to the sources and sinks for carbon dioxide. Although the arctic and subarctic region is small in extent, it certainly is not impervious and ice sealed. Our estimate, based on historical data and current research, indicates that the Arctic, which is about 4% of the earth's surface, is an annual net sink for $\sim 10^{15}$ g CO₂ accounting for an equivalent of approximately 3% of the annual anthropogenic contribution of CO₂ to the troposphere.

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INTRODUCTION

The issue of a world-wide rising atmospheric carbon dioxide concentration is international in scope and interest because of its potential role in atmospheric heating. The Arctic can be significantly affected by this heating (Manabe and Stouffer, 1979) and in turn trigger other climate modifications (e.g. Fletcher and Kelley, 1978; Broecker, 1975; Keeling and Bockstow, 1977).

The Arctic regions (Figure 1) at first consideration appear to be almost insignificant with respect to the air-sea-ice and air-land exchange of carbon dioxide. The entire area of the Arctic is only 4% of the earth's surface; its ocean-sea area is 3.8% of the world oceans surfaces. In addition it is greatly influenced by both glacier and sea ice. Winter to summer average variations in arctic and subarctic tropospheric carbon dioxide levels are the largest recorded at all of the remote world-wide monitoring sites. The annual rate of increase of carbon dioxide concentration on the other hand is the same as those recorded in the tropics and at the South Pole (e.g. Bolin and Keeling, 1963 and Keeling *et al.*, 1976a, b). These annual arctic tropospheric CO₂ fluctuations are generally ascribed to transport of polluted lower latitude continental air into the region during the winter, and reduced in the spring-summer due to hemispheric resurgence of photosynthetic activity. Our observations in the Arctic, however, indicate that the arctic hydrosphere, and possibly to a lesser extent land, significantly affect tropospheric carbon dioxide, and that these effects operate throughout the year. Direct observation of seasonal sources and sinks is difficult in this polar region. The data base, however, is now reasonable enough to allow us to estimate the effect of natural sources and sinks of carbon dioxide within the arctic which contribute significantly to the annual tropospheric CO₂ concentration fluctuation.

Further direct evidence (Gosink and Kelley, 1981a) based on samples of air collected from low-altitude (50 and 3000 m) aircraft transects also reflect source-sink effects for CO₂ over the Arctic Ocean and tundra throughout the year, particularly during the period of freeze and thaw. The most important observation is that the peripheral arctic seas appear to act as a source of CO₂ to the atmosphere during the winter and a sink in summer.

Recent estimates of annual tropospheric anthropogenic carbon dioxide input are about 2.6×10^{16} g of CO₂ when considering recent recognition of tropical forest clearing (Rotty, 1977; Bolin, 1977; Wong, 1978; Woodwell *et al.*, 1978). Anthropogenic factors within the Arctic and the adjacent subarctic regions are virtually inconsequential ($< 10^{13}$ g CO₂) with respect to carbon dioxide. They are likely to remain so even with increased oil exploration and production activities.

Physical-chemical rather than biological processes dominate the entire annual cycle with respect to CO₂ exchange. Arctic phenomena are so intense, for example, that we estimate that an equivalent of nearly 4 percent of the entire burden of carbon dioxide introduced annually by all anthropogenic activity is absorbed by north polar seas just during the short summer period. On the other hand, we have also shown that porous annual sea ice is permeable enough so that about a third of the carbon dioxide absorbed by the seas over the summer months is transferred back to the troposphere during the remainder of the year.

EXPERIMENTAL METHODS

All gas analyses were accomplished on a Carle 311 M gas chromatograph. Carbon dioxide reference gas standards prepared at the Scripps Institute

of Oceanography (S.I.O.; C. D. Keeling Laboratory) were used. In addition, air samples were periodically taken in the vicinity of the Point Barrow NOAA/ERL-GMCC site for comparison. Values for CO_2 in air agreed with the NOAA measurements within 1 ppm by volume. The NOAA analyses were made by means of a nondispersive infrared analyzer using S.I.O. standards.

Air samples were either collected and held briefly under slight positive pressure in teflon coated steel and glass (10 ml) gas tight syringes or in 250 ml gas sample bottles. It was necessary to employ oversize O-rings under the plunger in order to achieve a gas tight fit at low temperatures. Analyses were completed within 24 hours; usually within 1 to 6 hours. Standards held in these syringes were stable for 24-72 hours, depending on the particular syringe in question. Standards stored in slightly pressurized commercial glass gas sample bottles were stable for several weeks.

Samples of air from under a snow cover were taken by holding the gas tight syringe upwind of the operator, and inserting the needle or extended cannula beneath the snow and frost to withdraw 5 to 10 ml of air.

In some experiments over sea ice or tundra, the increase of carbon dioxide over the original air trapped in a chamber was followed. In other experiments, the sealed chamber was flushed with helium. The recovery rate of CO_2 versus oxygen was determined as a function of time, temperature and salinity of the ice. The sealed chambers on the sea ice were prepared by packing snow around the chambers, wetting it with fresh-water and allowing it to freeze to provide a gas tight ice seal.

Experiments with atmospheric sampling from aircraft are published elsewhere (Gosink and Kelley, 1981a) as are the procedures for research from on board research vessels (Gosink and Kelley, 1978).

The CO_2 concentration is expressed as a volume fraction (mixing ratio) in parts per million by volume (ppm) when the total pressure is 1 atmosphere. To an approximation sufficiently accurate for this discussion, the barometric pressure is assumed to be 1 atmosphere and the concentration of CO_2 in air is taken to be approximately equal numerically to the partial pressure of CO_2 in air, i.e., 1 ppm or 1 microatmosphere.

The terms supersaturated or undersaturated are used in discussions of the equilibrium partial pressure of CO_2 with respect to air in sea or freshwater. If the observed partial pressure in water is higher or lower than the atmospheric value, then it is termed either supersaturated or undersaturated. Another term used is million metric ton (MT) where one million metric tons = 10^{12} g of CO_2 .

DISCUSSION

In order to calculate seasonal quantities of carbon dioxide exchanged across various surfaces it is first of all necessary to define and describe the areas of these interfaces which may interact with the troposphere.

The surface area of the Arctic above the Arctic Circle, based on simple spherical geometric calculations, is $2.1 \times 10^7 \text{ km}^2$. The arctic troposphere is evaluated to be $2.1 \times 10^8 \text{ km}^3$ in volume and to contain 6.9×10^{16} g of CO_2 at an average concentration of 335 ppm by volume. The estimated areal extent of oceanic and terrestrial regions in the Arctic are described briefly below and shown in Table 1.

The central pack ice, including about a third of the Canadian Archipelago, is the largest of all subcategories. It is mostly composed of multiyear ice and is considered to be almost closed to ocean-air interaction. Two exceptions for the central pack region are the estimated

year round 5-10% open water in cracks, leads and polynyas (Whitman and Schulle, 1966) and the approximately 50% annual sea ice which has been shown to be permeable (Gosink *et al.*, 1976) and will be discussed further in this article.

It is convenient to divide the seas surrounding the the arctic pack ice (Central Basin) into four regions. The reason is that they appear to display different partial pressures of carbon dioxide, particularly during the summer period. A second reason has to do with the amount and duration of the ice cover. The four areas are denoted in Tables 1 and 4. The extent and duration of the sea ice used in our calculations are shown in Table 4. The Greenland Sea-Baffin Bay category for our consideration contains the the Canadian Archipelago water area.

All of the arctic seas surrounding the central basin may be referred to as the seasonal sea ice zone (SSIZ) which Barry (1979) defines as annually varying between 8.4 and $15 \times 10^6 \text{ km}^2$. His definition, however, includes subarctic sea ice, e.g. the Bering Sea and Sea of Okhotsk, etc. Sverdrup *et al.* (1942) tabulate the Arctic Ocean and surrounding seas as covering $14.1 \times 10^6 \text{ km}^2$, but they include areas south of the arctic circle such as the Norwegian and North seas which we consider to be perpetually open water. Our estimate of the total Arctic Ocean and surrounding seas area is therefore $13.8 \times 10^6 \text{ km}^2$ as shown in Table 1.

We estimate the land area within the Arctic to be predominantly glaciated or mountainous, e.g. Greenland. We know of no significant ($> 1 \times 10^{12} \text{ g CO}_2$) sources or sinks for carbon dioxide in these glaciated areas, and thus will not consider them in the source-sink calculations. The remaining land area within the arctic circle is conservatively estimated to encompass $1.6 \times 10^6 \text{ km}^2$. It is composed primarily of wet tundra and taiga and the respective areas are shown in Table 1.

Exchange Rates - In addition to the areas involved, two more pieces of information are required in order to compute the source and sink strengths of a region. One is reliable seasonal data for partial pressure differences (ΔPCO_2) between the air and surface of the sea, and the other is knowledge of the rate of exchange of CO_2 across the sea surface and across the surface of the tundra. We have reasonable ΔPCO_2 information for the various regions of the Arctic as will be discussed in following sections. However, a reliable rate measurement is difficult to make and depends on a number of factors. Direct observations from one oceanic region may not be applicable to another. Table 2, for example, shows the range of CO_2 fluxes observed at sea by several investigators and for a variety of environmental conditions and CO_2 partial pressure differences. Much more is known about the CO_2 flux in the Bering and Chukchi seas than in the Barents, Norwegian, and Kara seas.

If the residence time for carbon dioxide is 7 years, the flux should be $21.1 \text{ moles m}^{-2} \text{ y}^{-1}$ (Sugiura *et al.*, 1963); slightly less if the residence time is eight years. It can be seen from Table 2 that actual fluxes vary from 0.08 to $35.2 \text{ moles m}^{-2} \text{ y}^{-1}$. Items 1 and 5 are rates determined by the same investigators, using the same equipment, both from the Bering Sea and both with essentially the same ΔPCO_2 . The only environmental difference was that the high rate (item 1) was determined in newly upwelled waters before productivity had commenced. The low rates (item 5) were obtained when the experiments were performed in productive waters. Similarly, rates 2, 6, 8 and 10 were obtained by the same investigators, using the same equipment, etc. Again, the only significant difference was with the productivity of the water with the most productive waters exhibiting the lowest air-sea exchange rates. In the last case, item 10, there was no visible sheen on the water from films, nor in fact was there in

any other case when we made the observations. Compare for example items 6 and 8. We were essentially in the same water mass, yet apparently an imperceptible film, presumably derived from the ship, lowered the rates by nearly a factor of 3.

Two observations appear to be pertinent to CO_2 air-sea interactions in the Arctic. The first point is that for a given water mass and exchange rate, the larger the ΔPCO_2 , the larger the quantity of carbon dioxide that will be exchanged in a given period of time (see Sugiura *et al.*, 1963). Fluxes or exchange rates are commonly reported as a quantity per unit area and time as shown in Table 1. Unless the ΔPCO_2 information is available as well (also shown in Table 2), the fluxes are of little value. This is particularly true in the Arctic where ΔPCO_2 is an order of magnitude larger than those commonly encountered at lower latitudes. This point is discussed more below. The second observation is that sea surfaces in the Arctic are less productive than those at lower latitudes and Antarctica. Antarctic seas, all at lower latitudes, have more sunlight and better vertical mixing of nutrients. The rates of exchange in the lower productivity waters of the Arctic in general appear to be larger than those from lower latitudes. The ΔPCO_2 between air and the sea surface observed to date appear to be always large (80-160 ppm) and show large reversals between winter and summer.

Great care must be exercised in using or reporting fluxes. There is a tendency to simplify the labels on the numerical values so that they appear like those in Table 2 or in the fourth column of Table 3. That is, the pressure difference term is eliminated. This can lead to serious misinterpretations of the data. Column 5 of Table 3 is the rate for *in situ* observations with the pressure difference term (ppm) left in.

It is the proper form in which the data was originally collected. Columns 6 and 7 are the ranking and rates relative to the fastest rate of column 5. If the pressure term is eliminated by multiplying the rate (column 5) by the pressure difference at which it was determined (see Table 1 and references), the result is the rate shown in Table 3 column 4. Column 1 is the item number from Table 2 for cross reference purposes. Note the serious reordering of both the ranking of the latter rates and relative rates as shown in columns 2 and 3. What had been fourth with the pressure term is now sixth. Only the item ranked third remained the same in this arbitrary choice of examples. Note the 45% difference between the first and second item in column 7 versus the 7% difference in column 2.

In fact, it is possible to generate any flux rate if the pressure term is missing. For example, item 3 in Table 2 suggests that Sugiura *et al.* (1963) reported observed fluxes of CO_2 at sea that were in the range of 10.9 to 26.7 moles $\text{m}^{-2} \text{y}^{-1}$. Sugiura *et al.* actually reported rate constants of 1.09 to 2.32×10^5 moles $\text{m}^{-2} \text{y}^{-1} \text{atm}^{-1}$. (The units have been modified to fit the format of this paper.) They artificially induced an initial air-sea ΔPCO_2 of 100-130 ppm and followed the changes in CO_2 between the air and sea down to as little as 3 ppm ΔPCO_2 . If you eliminate the pressure difference term by multiplying the above rates by the pressure difference ($115 \times 10^{-6} \text{ atm}$) one obtains a number within the range shown in Table 2. A ΔPCO_2 of 100-130 ppm fits within normal pressure differences routinely observed in many areas of the Arctic for long periods of time (Kelley, 1970; Kelley and Gosink, 1979; Gosink and Kelley, 1981). If we had chosen an average ΔPCO_2 of say 8 ppm as suggested by Broecker *et al.* (1979), the values for item 3 in Table 2 would have been 0.87-1.86 rather than 10.9-26.7 moles $\text{m}^{-2} \text{y}^{-1}$.

All of our calculations in the following section are based on a rate one half of the rate we observed in the Barents Sea (item 2 of Table 1) namely $0.74 \times 10^{12} \text{ g CO}_2 \text{ km}^{-2} \text{ mo}^{-1} \text{ atm}^{-1}$. This is 20% of the global average flux suggested by Broecker *et al.* (1979) when the pressure terms are included, but between the Broecker *et al.* (1979) rate and the 7-year rate of Sugiura *et al.* (1963) when the pressure term is eliminated. The rate we employed in this paper is a reasonable median for all of the rates we have observed in the Arctic and subarctic.

ARCTIC CO₂ SOURCE-SINK INVENTORY

In the following sections available field evidence is used to estimate the source and sink strengths for various regional or environmental categories and are separated for a summer or winter period. The results are compiled in Table 4. It is emphasized that the data base was established from direct observations made over more than two decades from various ice platforms, ships of opportunity, or terrestrial field stations.

Central Pack Ice - The central pack ice of the Arctic apparently shields the troposphere from a large area of high to very high partial pressures of carbon dioxide, particularly during the winter period. Kelley (1968) reported an average ΔPCO_2 between the water and air (water-air) of +42 ppm for a 3 week station during the month of January near 78°N and 175°W. The range of ΔPCO_2 was +14 to +87 ppm. Personal communications with chemical oceanographers on the Canadian LOREX 79 Experiment near the North Pole permits us to estimate (Gosink and Kelley, 1981c) the partial pressure of carbon dioxide (PCO_2) in the winter period at 475 ppm or a ΔPCO_2 of about 120 ppm considering typical winter arctic tropospheric burden of CO_2 at 345 ppm.

Lyakhin and Rusanov (1980) provide historical pH data for the surface waters of the arctic basin for 1948 to 1978. Estimation (Gosink and Kelley, 1981b,c) of CO_2 partial pressures from their data show that surface water PCO_2 values are in the range of 301 to 383 ppm or a ΔPCO_2 of -40 to +40 ppm. The exact time of "winter" and locations for the historical data are unknown.

Summer data for the Central Arctic is even more sparse. Recent data (Gosink and Kelley, 1981c, YMER-80 cruise) indicate that surface waters along the periphery of the arctic ocean basin are slightly undersaturated with respect to air (~ -10 to -30 ppm) during the summer period. Lyakhin and Rusanov's (1980) pH data afford an estimation of summer PCO_2 values to be in the range of 223 to 359 ppm for the arctic basin; $\Delta\text{PCO}_2 = \text{ca.}$ -100 to +36 ppm, or approximately averaging -30 ppm. This is in reasonable agreement with our YMER-80 observations along the periphery of the basin, but slightly low compared to surface waters we observed flowing out of the Arctic east of Greenland (Gosink and Kelley, 1981). If the arbitrarily assigned range of -30 to +10 ppm for the ΔPCO_2 of the summer central Arctic is reasonable, then the central Arctic provides for a summer source and sink range of 37 MT and 112 MT of CO_2 respectively as shown in Table 4. Some smaller subsections of surface waters of the central basin are probably supersaturated in CO_2 with respect to air as the compilation of Lyakhin and Rusanov (1980) data suggest.

Melt ponds on the surface of the sea ice were observed from the YMER-80 (late summer to early fall) cruise (80-82°) to have very high PCO_2 values in August (420-490 ppm), but this may have been due to the decay of plankton. Those ponds in August were covered with ice and had a salinity of about 6‰, and as far as can be estimated at this time,

this potential source effectively cancels their presumed sink condition of earlier in the summer based on our observations north of Alaska (71°N). They are shown as 20 MT sources and sinks in Table 4.

The low winter source figure of 28 MT CO₂ for the central arctic open water, is based on the assumptions that 5% of the total area is open water with a ΔPCO₂ of 10 ppm, and that the length of time under such conditions is 9 months. If the open water is 10% as has been suggested by Whitman and Schulle (1966), and if the ΔPCO₂ = 100 ppm, then the output of CO₂ to the air in the central arctic during winter increases to 560 MT CO₂ as is shown in Table 4 for the high figure.

Barents Sea - The Barents Sea region has been confirmed to have exceedingly low (180-250 ppm) summer partial pressures of CO₂ at the surface (Kelley, 1970; Gosink and Kelley, 1981, 1981d). The average ΔPCO₂ for that region is on the order of -110 ppm). Considering the general easterly circumpolar flow of surface waters in that region, the phenomenon is assumed to extend into the Laptev Sea. If this intensity is maintained for a 4 month summer period over the entire area of $2.5 \times 10^6 \text{ km}^2$, then an average value of 851 MT of CO₂ will be absorbed. As can be seen from inspection of Table 4, this region's summer value alone overwhelms all of the other sources or sinks within the Arctic suggesting that the Barents Sea region is a predominant cause for Arctic to be a net CO₂ sink. The influence of the tundra is still controversial. It too may be a dominating factor but for the present we are using more conservative figures as will be discussed later.

The partial pressure of CO₂ in the Barents Sea in the winter is unknown. If the explanation for the principal cause of those low partial pressures is the cooling of surface waters as they are transported north,

then it would be expected that those waters would remain undersaturated in CO_2 with respect to air for a long time if not throughout the remainder of the year, but perhaps only at a ΔPCO_2 of only -20 to -40 ppm due to organic decomposition and the lack of photosynthesis. The winter open water factor (Table 4) is reduced to 25% due to the presence of annual sea ice, and thus the winter transfer from the atmosphere would be about 113 MT CO_2 for the Barents Sea area and time period. If the water under the annual sea ice in the Barents region is undersaturated, we hypothesize at this time that an additional sink of 225 MT may occur in that region and would be the only sink for CO_2 in the arctic during winter. This latter conjectural figure is not reflected in Table 4.

Chukchi and Beaufort Seas - Summer ΔPCO_2 values in the Chukchi and Beaufort Seas are significantly less than that in the Eurasian basin, being on the order of -60 ppm (Kelley and Gosink, 1979). Winter data for the Beaufort Sea suggests supersaturation of 20 to 40 ppm. Therefore the East Siberian, Chukchi, Beaufort subcategory is estimated to be a summer sink for CO_2 of 120 MT and a winter source in the range of 8-16 MT CO_2 based on the following observations.

Our experiments (Gosink and Kelley, 1978, and Kelley and Gosink, 1979) indicate that winter partial pressures of CO_2 measured under sea ice are variable from undersaturated to the supersaturated. For example, PCO_2 returns rapidly to the supersaturated (to 360+ppm) condition in the fall or during the month of November. Furthermore, indications are that partial pressures on the order of 400 ppm occur close (10-20 m) to the surface at that time (Kelley and Gosink, 1979).

In the northern Bering Sea we consistently measured PCO_2 values of 400-440 ppm at and just below the thermocline which was located at 20-40 m

(Gosink and Kelley, 1978; Hakuho Maru cruise; Gosink and Kelley, 1981c). At lower latitudes, where photosynthesis extends below the thermocline, the depth at which the high PCO_2 water is encountered is as much as several hundred meters (e.g., Li *et al.*, 1969). In the Beaufort Sea within 200 km of the coast, the thermocline is only 10-20 m below the surface. In the Barents Sea area, equilibrium PCO_2 was observed to be between 40 to 120 m depth (Gosink and Kelley, 1981). On 11 November 1978, for example, the PCO_2 of newly ice-covered surface waters 30 km offshore had already risen to 341 ppm, about 10-12 ppm greater than the ambient air. The PCO_2 just 6-7 m below the surface was 420 ppm. Two months earlier the PCO_2 was around 250-300 ppm. Light levels were low at that time with the sun being above the horizon for only one hour per day, thus photosynthesis effectively had ceased or was greatly diminished, and the high PCO_2 water from shallow depth was approaching the surface again.

It would appear from three sets of winter experiments (1-30 day observations each) (Kelley, 1968; Kelley and Hood, 1971) in addition to several spot samples, that the surface sea water PCO_2 in the winter within 2-300 km of the coast is about 340-360 ppm, but with an occasional high observations of ca. 400 ppm. However, on one occasion, two separate samples of sea water from under the ice ~ 200 km north of Alaska during early April 1978 (floating ice station ARLIS-VII) displayed PCO_2 values of 295 and 300 ppm. The light level at that time of year was low to moderate, but nearly constant for ca. 15 hours/day. Those isolated low PCO_2 observations suggest that slight but significant offshore biological activity had commenced under the sea ice by April. This departs from other winter and spring observations when the PCO_2 values for surface Beaufort

Sea waters were generally 340-350 ppm and higher (Kelley, 1968; Gosink and Kelley, 1978). Coastal and near-coastal waters maintained 10-60 ppm above ambient atmospheric CO_2 values at Barrow in April to early May 1979.

Migratory filter-feeding whales move into the general offshore area of Barrow, Alaska during April. It may be assumed that plankton are abundant enough at that time to sustain them as well as to modify the carbon dioxide in the water column.

Another seemingly anomalous situation was observed in June of 1979 over two days. Partially trapped coastal waters inside an offshore bar and grounded ice displayed the expected low PCO_2 (280-300 ppm) due to photosynthesis. On the other hand, waters just 1-2 km further offshore consistently showed PCO_2 values of about 400 ppm. Zooplankton were noted to be abundant, and their respiration may have overcome the prior influence of the phytoplankton.

Greenland Sea-Baffin Bay - The Greenland Sea and Baffin Bay region is dominated by sea ice throughout the year. We estimate for our calculations that it is 10% open in the winter and 50% open in the summer. The only PCO_2 data we have are for the summer period in the Lena Trough area (Gosink and Kelley, 1981). The surface sea water coming out of the Arctic in that region was slightly undersaturated with a ΔPCO_2 of about 0 to -10 ppm. Surface waters farther south, probably modified by lower PCO_2 waters from the Spitsbergen and North Atlantic current, were undersaturated by -10 to -45 ppm. We can only assume that winter waters are similar to the central pack ice, and have supersaturation ΔPCO_2 values on the order of 10 to 100 ppm. On the basis of the data and our assumptions, the winter source strength range for the E. Greenland Sea and perhaps the Baffin Bay region is estimated to be 14-144 MT CO_2 and the summer sink strength 15-58 MT CO_2 .

Norwegian Sea - The Norwegian Sea and southern edge of the Barents Seas are ice free all year and have summer partial pressures ranging from 50 to 100 ppm below that of the atmosphere (Gosink and Kelley, 1981; Kelley, 1970) and is considered to be a year long phenomenon. The winter partial pressure difference is unknown but is assumed at this time to be -25 ppm. Thus this small area is listed as a sink for the entire year with winter and summer season sink strengths of 56 and 111-222 MT CO₂ respectively.

The remaining months, not included in the above or following estimations, are considered to be transition periods during which the Δ PCO₂ is relatively small and self compensating as the process changes from source to sink or vice versa.

Gases at the Sea Ice-Air-Snow Interfaces - Annual sea ice, because of its porosity due to brine channels and the carbonate nature of the brine, is permeable to carbon dioxide (Gosink *et al.*, 1976; Gosink and Kelley, 1977, 1978, 1982). Carbon dioxide, carbon monoxide, methane and nitrous oxide have all been observed to emanate from the sea ice surface. All of these gases can usually be found over the surface of annual sea ice in concentrations significantly greater than that of the ambient air (Gosink and Kelley, 1977, 1978). We report at this time, however, only on the concentration and exchange of carbon dioxide. Air samples withdrawn by syringe from beneath the snow cover over sea ice were enriched in carbon dioxide if the wind velocity was low or if the sample came from a wind protected area. This difference between the subnivean concentration and air at 2 m ranged from 0 to 80 ppm.

A full description of sea ice and the probable causes of its porosity and permeability to gases is presented elsewhere (Gosink and Kelley, 1982; Heminsen, 1959).

A summary of results for the recovery of gases in helium-flushed chambers sealed to annual sea ice are shown in Figure 2. The fact that the oxygen concentration in the ice sealed, helium-flushed chambers did not recover nearly as rapidly as the CO_2 , proves that the gases are being evolved from the sea ice surface, and are not leaking around the edges. Full (100%) recovery to ambient conditions for CO_2 corresponds to 340 ppm and for O_2 (+Ar), 22%. In all cases (Figures 2: a, b, c) oxygen recovery lagged behind CO_2 recovery. The CO_2 partial pressures in the brine in the sea ice matrix have been observed to be in excess of 440 ppm and as high as 1000 ppm (Gosink and Kelley, 1978). The brines are probably depleted in O_2 because of the high salt concentration, and because of the suspected low-level biological and chemical oxygen consumption within the relatively warm sea ice matrix.

Curve pairs (Figure 2a) denote experiments performed on relatively warm (-10 to -15°C) saline ($3-4\text{‰}$) coastal annual sea ice. In that case, the CO_2 concentration exceeded ambient atmospheric concentration levels (then about 340 ppm) and reached a plateau of about 360 ppm within a few hours, while the O_2 level continued its slow rise over the following 12 hours to only 60% recovery when the experiment was terminated. Curve pairs b and c resulted from experiments performed over less saline ($1-2\text{‰}$), colder (-20 to -25°C) offshore ice at floating ice station ARLIS VII (about 220 miles NNE of Point Barrow, Alaska) during 7-11 April 1978. The temperatures in all cases were the ambient air temperatures. The effect of the salinity difference is clearly demonstrated by curve pairs b and c. The ice for cases b and c were, respectively, annual sea ice probably formed late in the previous spring, and 1-2 year ice. It is uncertain if the difference between curve pair (a) and pairs (b) and (c) is caused more by

the temperature rather than the salinity differences. More information is available about the effects of temperature and salinity of ice on its permeability (Gosink and Kelley, 1982; Gosink, 1982).

Based on experiments at -10 to -15°C , the rate at which carbon dioxide was being released to the atmosphere from annual ice surfaces was $2-4 \times 10^{-3} \text{ ml cm}^{-2} \text{ hr}^{-1}$. At -20 to 25°C , it apparently dropped to about $10^{-4} \text{ ml cm}^{-2} \text{ hr}^{-1}$. It was calculated that the veins in sea ice should close by two orders of magnitude at -20°C , which is in agreement with the 20-40 fold decrease in gas fluxes observed for annual sea ice, assuming the much larger brine channels opened and closed at about the same levels as did the much smaller multi-grain boundary veins (Gosink and Kelley, 1982).

Chambers containing ambient air rather than helium sealed to the ice at ARLIS VII, showed carbon dioxide levels of 351-362 ppm when sampled a few hours later (4 and 24 hours). They suggest a transfer rate compatible with the $10^{-4} \text{ ml cm}^{-2} \text{ hr}^{-1}$ discussed above. The ambient air CO_2 concentration was stable between 339-341 ppm. Samples of the subnivean air at ARLIS VII generally were about 350 ppm. The range was 337-374 ppm, with the samples taken over multi-season ice being the lowest.

There are brief periods in early May when sea ice begins to thaw when 2 liter ice-sealed chambers covering 200 cm^2 of sea ice were enriched (10-20 ppm) in CO_2 in a few minutes. The PCO_2 of winter sea ice brine was on the order of 400-1000 ppm. We suggest that this is one of several possible causes for the small repeatable atmospheric surge of carbon dioxide before the rapid summer decline. That is, the brine and multi-grain boundary veins were opening up with the onset of warmer weather, thus allowing for a final burst of carbon dioxide to the atmosphere from the brines before photosynthesis at the surface reversed the process.

Contact of high PCO_2 sea water under the ice during the winter with porous annual sea ice should lead to a net flow of CO_2 to the atmosphere. Resistance to exchange in this case is affected by the sea ice as compared to the thin film exchange on open water. A definite value for this ice-resistor effect is unknown at this time, but must be related to the 10^{-3} to 10^{-4} $\text{ml cm}^{-2} \text{ hr}^{-1}$ flux rate stated earlier. It is this high PCO_2 water rather than the brines in the sea ice that is the probable cause of the continued outgassing of CO_2 from the annual sea ice to the atmosphere. There is insufficient CO_2 in the small amount of brine trapped in annual sea ice to maintain the observed winter-long output of the CO_2 .

Our only data for carbon dioxide being evolved from annual sea ice comes from the Beaufort Sea area. If the ΔPCO_2 in the Barents Sea area remains negative as discussed earlier, there is the probability that annual sea ice in that region of the arctic does not evolve CO_2 to the atmosphere over the winter, but might also operate as a small sink for tropospheric CO_2 . The Barents Sea region is perhaps one of the most critical regions for further research particularly in the winter.

Given a total area of annual sea ice on the order of $6.7 \times 10^6 \text{ km}^2$ (Barry, 1979) then 50-520 MT of CO_2 is probably being evolved to the atmosphere over the winter from annual sea depending on the salinity and temperature of the annual sea ice.

Bolin and Keeling's (1963) high altitude samples and our (Kelley and Gosink, 1979) recent intermediate altitude sampling also indicate a source of CO_2 at the surface during winter. Low altitude winter atmospheric CO_2 values are usually always larger than those at higher altitude.

These considerations of sea-ice-air interfaces alone account for most of the source-sink strengths as we know it at this time as shown in Table 4.

The net result indicates that the oceanic sectors of the Arctic are an annual net sink for CO_2 of nearly 700 MT and is equivalent to almost 3% of the annual anthropogenic contribution of CO_2 to the troposphere. The sink strength for this portion of the Arctic CO_2 budget would be twice as large if we had employed the larger rate we observed in either the Barents or the Bering Seas (Table 2). It also may be half as large, but still a sink, if we had employed the lower rates from the Bering and Chukchi Seas (Table 2).

The relatively small but fairly numerous sources and sinks associated with the land portion of the Arctic as shown in Table 4 are explained in the following section.

Gases from Tundra, Lakes and Ponds - A large net source of carbon dioxide in the arctic is the tundra with its bogs, ponds and lakes. Extremely high levels of methane and carbon monoxide as well as carbon dioxide were found at the surface of the tundra and in the lakes and ponds of the Arctic in the vicinity of Point Barrow. Kelley *et al.* (1968) and Coyne and Kelley (1974a), reported on the existence of elevated levels of carbon dioxide under the snow, particularly in the spring. The level of carbon dioxide was inversely proportional to the wind speed (high wind velocity aspirates and replaces the carbon dioxide enriched subnivean air) and the highest levels (over 2000 ppm at the ground surface for a few hours over a few days) occurred in May. Gas chromatographic procedures required only 5 cc samples of air. Thus the natural microenvironment was not disturbed. In this manner, small (0-30 ppm) but nearly continuous enrichments of carbon dioxide under the snow were noted throughout the winter. Similar subnivean enrichment of CO_2 has been observed for samples taken in the subarctic environment of Fairbanks, Alaska, area (65°N). Insufficient data are available to calculate the evasion rate of CO_2 from frozen tundra

surfaces, but it is estimated to be on the order of 10^{-4} ml cm⁻² hr⁻¹, or an almost insignificant 7 MT of CO₂ evolved to the atmosphere over winter.

Anthropogenic Sources - Anthropogenic sources of CO₂ in the Arctic are negligible (est. < 10¹² g). However, recent petroleum development may make this a source comparable to the natural outgassing of the winter tundra, particularly if CO₂ stripped from the petroleum gases is released to the atmosphere rather than being reinjected into the well.

During the months of June and September, the period of thaw and freeze, the concentration of land surface-evolved gases are large and variable, at least in the vicinity of Point Barrow. The region is dominated by ponds and lakes with organic rich sediment (Brown and Johnson, 1965; Douglas and Tedrow, 1960). Partial pressures of carbon dioxide in the lakes average about 115 ppm higher than that of the ambient atmosphere. The ponds, with warmer bottom sediment and smaller volume dilution, had an average PCO₂ of 357 ppm greater than the ambient air (Coyne and Kelley, 1974b). These lakes and ponds constitute 50-80% of the tundra in the vicinity of Barrow (Miller *et al.*, 1976). Coyne and Kelley (1974b) calculate an evasion rate of CO₂ of 0.34 mg cm⁻² atm⁻¹ min⁻¹ (16.1 moles m⁻² y⁻¹ with an average ΔPCO₂ of 397 ppm). Using this evasion rate for tundra lakes and ponds, with an estimated average gradient between lakes and ponds of 300 ppm greater than that of the atmosphere, and that 60% of the 0.6 x 10⁶ km² of tundra is involved, then 48 MT of CO₂ is estimated to evolve to the atmosphere over the summer from that interface.

Miller *et al.* (1976) and Coyne and Kelley (1975), calculate that the vascular plants on the wet tundra fix about 400-770 g CO₂ m⁻² season⁻¹, with about 43% of the CO₂ being drawn from the atmosphere. During periods of low photosynthesis, the hours around midnight, the soil is a source of

about $0.2 \text{ g CO}_2 \text{ m}^{-2} \text{ hr}^{-1}$. Therefore, given the facts and estimates that wet tundra emits more CO_2 than the plants can fix during a portion of this time, i.e. Miller *et al.*'s (1976) source rate for an estimated 8 hours a day over 90 days, Coyne and Kelley's (1974b) vegetation CO_2 depletion values, and that 40% of the tundra and 100% taiga or boreal vegetation are involved then 179 MT of CO_2 are added to the atmosphere from the soil while the vascular and other plants remove 213-411 MT from the air. This figure is also in general agreement with that estimated for tundra and alpine ecosystems tabulated by Revelle and Munk (1977).

Based on a recent (1982) personal communication from Miller, the effect of the tundra may be substantially larger, i.e. it may be a sink of up to 992 g CO_2 in the Arctic as we have defined it. If this is so the tundra's influence on the arctic tropospheric carbon dioxide content is as significant and possible more so than the Barents region discussed earlier.

Finally there is the phenomena that the tundra is known to outgas carbon dioxide during freezing and thaw at the rate of 500-90,000 l/hectare (Coyne and Kelley, 1971). The effect of this is to add yet another 0.4 to 56 MT of CO_2 , depending on soil type, to the arctic troposphere over short periods of time both at the beginning and end of the arctic winter. This small quantity alone could influence near ground level monitored concentrations of atmospheric CO_2 by a few tenths of a ppm as suggested in a recent articles by Peterson *et al.* (1980), and Halter and Peterson (1981). This phenomena may contribute in part to and surge in CO_2 concentrations monitored in the near-surface atmosphere during late spring.

CONCLUSIONS

The Arctic emerges from this conservative source-sink analysis to be a source of 508 MT of CO_2 during the winter period, a sink for 1241 MT of atmospheric CO_2 during the summer to yield a net annual sink of 729 MT. The annual sink is equivalent to 2.8% of the global anthropogenic input of CO_2 to the troposphere. We believe that this budget is reliable to within a factor of two. Questionable categories as we see them at this time tend to be toward a larger net sink. The seasonal effect of the sources and sinks affecting the lower troposphere of the Arctic is even larger if one considers that the Arctic is a relatively closed septum and that source and sink effects tend to remain in the lower portion of the troposphere for several weeks (Bischof, 1973).

The seasonal data base in the Arctic is still inadequate or absent in some cases primarily because of the very difficult logistics problems in working in these peripheral polar seas. This is especially true during the winter and during the time of freeze and thaw. In the Arctic, we do not know how much, if any, CO_2 is removed, e.g. into the Eurasian basin by way of the dense waters flowing from the norther Barents Sea or into the deep waters of the North Atlantic Ocean. Until a more substantial seasonal data base for both polar regions is obtained, the Arctic, which is mostly an oceanic region appears to be a small but potentially significant sink for atmospheric CO_2 .

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Table 1. Estimated Surface Areas of Various Regimes of the Arctic.

	<u>Region</u>	<u>(Area x 10⁶ km²)</u>
Ocean/Sea	Central Pack Ice	8.4
	Barents, Kara, Laptev Seas	2.5
	East Siberian, Chukchi,	
	Beaufort Seas	0.9
	Greenland Sea and Baffin Bay	1.3
	Norwegian Sea	<u>0.5</u>
	TOTAL OCEAN-SEA AREA:	13.8
Land	Tundra	0.6
	Taiga	1.0
	Mountainous and/or Glaciated	<u>6.0</u>
	TOTAL LAND AREA:	7.6
	TOTAL AREA:	21.2 x 10 ⁶ km ²

Table 2. Observed Fluxes Across the Sea-Air Interface.

	<u>Flux (moles m⁻² y⁻¹)</u>	<u>ΔPCO_2 (μ atm)</u>	<u>Comments and Reference</u>
1.	35.2	155	Bering Sea - low productivity upwelling area; Hood and Kelley, 1976
2.	32.8	80	YMER-80 - 80°N; 30°E, 1980, -1°C water, low patchy productivity, Gosink and Kelley, 1981
3.	10.9-26.7	(100-130)	Gulf of Mexico - Sugiura <i>et al.</i> , 1963
4.	25.2	-	Sable Island, Nova Scotia - eddy diffusion experiment; Jones and Smith, 1977
5.	2.7-14.9	160	S. Bering Sea - high productivity; Hood, 1981
6.	11.9-13.2	120	71°N; 165°W, 1981, moderately productive water at ice edge; Kelley and Gosink, 1982
7.	6.3-9.6	-	Broecker and Peng, 1974
8.	4.2-4.6	120	69°N, 165°W, 1981, in lee of ship-productive waters; Kelley and Gosink, 1982
9.	4.5	25	30°N-30°S; Keeling, 1965
10.	0.08	110	highly productive experimental sea water ponds, 61°N, 1981, Gosink and Kelley, 1982

Table 3. Changes in Numerical Order Caused by Ignoring the Pressure Gradient (ppm^{-1}) Term in the Flux of CO_2 Across the Air-Water Interface

(1) Items From Table 2	(2) Rate Rel. to 35.2	(3) Rank 2	(4) (moles $\text{m}^{-2}\text{y}^{-1}$)	(5) (moles $\text{m}^{-2}\text{y}^{-1}\text{ppm}^{-1}$)	(6) Rank 1	(7) Rate Rel. to 0.410
2	0.93	2	32.8	0.410	1	1.00
1	1.00	1	35.2	0.226	2	0.55
3	0.60	3	21.1	0.068	3	0.45
9	0.13	6	4.5	0.179	4	0.44
6	0.38	4	13.2	0.110	5	0.27
8	0.12	5	4.4	0.037	6	0.09

Table 4. Seasonal Source-Sink Strength of the Various Regions in the Arctic

Season	Region	Area (10^6 km ²)	% Area Active	Exchange Rate	Δ PCO ₂ (ppm)	Duration (Months)	Source ($\times 10^{12}$ g CO ₂)	Sink ($\times 10^{12}$ g CO ₂)
<u>Winter</u>	1. Central Basin	8.4	5-10	0.74×10^{12}	10 to 100	9	28 - 560	-
	2. Barents, Laptev, and Kara Seas	2.5	25	(g km ⁻² mo ⁻¹ atm ⁻¹)*	-20 to -40?	8	-	75 - 150
	3. East Siberian, Chukchi and Beaufort Seas	0.9	10	"	20 to 40	6	8 - 16	-
	4. Greenland Sea and Baffin Bay	1.3	25	"	10 to 100?	6	14 - 144	-
	5. Norwegian Sea	0.5	100	"	-25?	6	-	56
	6. Annual Sea Ice	6-7	100	$2.8-28.3 \times 10^6$ (g km ⁻² mo ⁻¹)	-	6	50 - 520	?
	7. Tundra and Taiga	1.6	100	See text	-	6	7	-
Winter Totals							107-1247 (avg 677)	131 - 206 (avg 169)
Net Winter							508	
<u>Summer</u>	1. Central Basin	8.4	10	0.74×10^{12} (g km ⁻² mo ⁻¹ atm ⁻¹)*	-30 to + 10	3	18	56
	2. Barents, Laptev and Kara Seas	2.5	100	"	-90 to -140	4	-	666 - 1036
	3. East Siberian, Chukchi and Beaufort Seas	0.9	100	"	-40 to -80	3	-	80 - 160
	4. Greenland Sea and Baffin Bay	1.3	50	"	-10 to -40?	3	-	15 - 58
	5. Norwegian Sea	0.5	100	"	-50 to -100	6	-	111 - 222
	6. Sea Ice Melt Ponds	1?	?	See text	-	2	20?	20
	7. Tundra-Taiga	1.6	78	See text	-	3	179	-
	Freeze-Thaw	1.6	100	"	-	0.5	0.4 - 56	-
	Plants	1.24	100	"	-	3	-	213 - 411*
	Ponds and Lakes	0.36	100	1.47×10^{11} (g km ⁻² mo ⁻¹ atm ⁻¹)*	300	3	48	-
Summer Totals							265 - 321 (avg 293)	1161 - 1907 (Avg 1534)
Net Summer								1241
Annual	1. Anthropogenic			See text			1 - 7	
Annual Totals							373 - 1575 (avg 974)	
Annual Net Sink							729×10^{12} g CO ₂	

*May be as large as 992 - see text

*This is the same as $16.4 \text{ mole m}^{-2} (\text{atm}^{-1}) \text{ y}^{-1}$

CAPTIONS

Figure 1. The Arctic Ocean and surroundings (from Polar Regions Atlas, C.I.A., May 1978).

Figure 2. Recovery of CO_2 and oxygen in helium flushed chambers over sea ice as a function of time, salinity and temperature. (a) -10 to -15°C ; 3-4‰ S, (b) -15 to -20°C ; 2‰ S, (c) -15 to -20°C ; 1‰ S.