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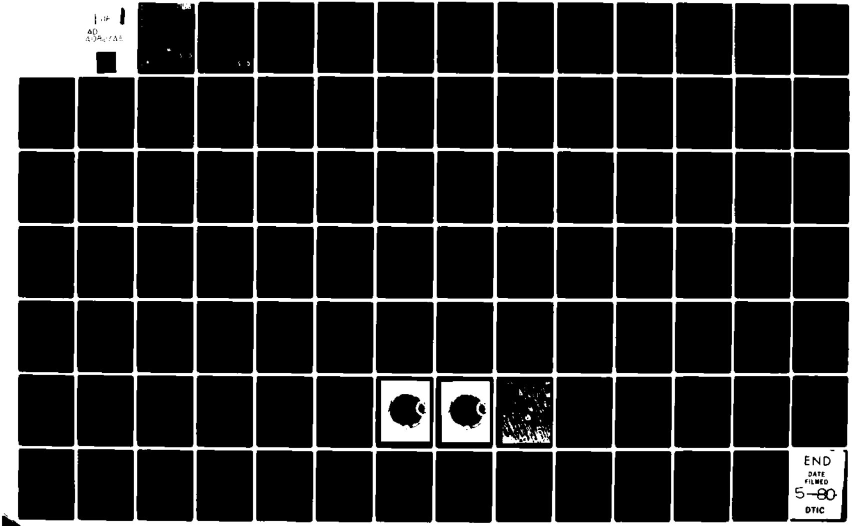

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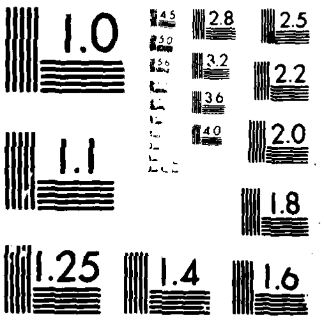

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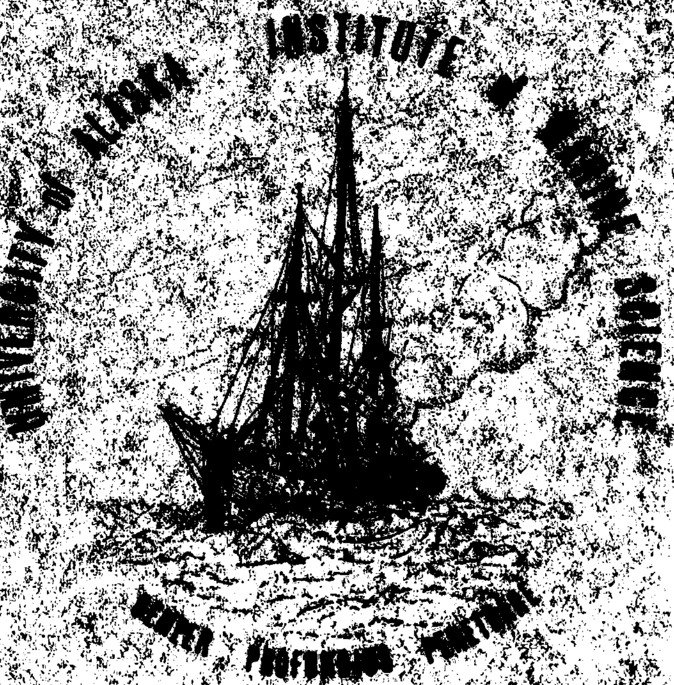
Fairbanks, Alaska 99701

John J. Kelley and Thomas A. Gosink

Gases in Sea Ice
1975 - 1979



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FINAL REPORT

to

Department of the Navy
Arctic Branch, Code 461
Office of Naval Research
Arlington, Virginia 22217

from the

Institute of Marine Science
University of Alaska
Fairbanks, Alaska 99701

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John J. Kelley [redacted] Thomas A. Gosink

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Gases in Sea Ice

1975 - 1979

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ABSTRACT

In this report we cover the research accomplished during 1979. A review of our research from 1975-1978 based on previous reports and journal contributions is also given.

Although this research was concerned with several trace gases, carbon dioxide was of primary concern. The arctic and subarctic regions represent nearly 10% of the northern hemispheric surface, half of which is Arctic Ocean and tundra. Global atmospheric diffusion models for CO_2 are not entirely satisfactory for the arctic where winter-summer differences in CO_2 concentration are the largest in the world. There is a substantial amount of data on measured atmospheric CO_2 levels of the arctic environment, but there is a significant lack of information for sources and sinks, particularly with respect to seasonal and geographic rates of exchange. Annual sea ice and frozen tundra are not sealed media, but evolve significant quantities of carbon dioxide throughout the winter. The high latitude arctic region is found to be a significant net annual source of carbon dioxide to the atmosphere.

During the past 2-3 years we have also directed some of our effort to understanding the magnitude and rate of exchange of CO, CH_4, and N_2O in the arctic. These trace gases are crucial to many important tropospheric and stratospheric phenomenon, such as ozone and .OH formation and destruction, and aerosol and haze production.

Annual sea ice is permeable to gases because of its brine content, that it is enriched in some of these trace gases, that it outgasses throughout the winter, and that for periods of time it controls tropospheric concentrations for some of these gases. We have also observed and reported similar effects for the tundra for both summer and winter conditions.

Copies of recent technical papers submitted for publication are appended.

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6. Appendicies

1. INTRODUCTION

The ONR has supported research on carbon dioxide in the atomsphere and sea for almost two decades. A summary of those studies is given in Appendix D. Since 1975, we have concentrated our efforts on carbon dioxide and other trace gases in association with sea ice. This final report covers our progress during FY 1979 and summarizes our research of the previous four years.

2. FISCAL YEAR 1979 PROGRESS REPORT

A. Carbon Dioxide

Discrepancies with pH values have been resolved, and the alkalinity values from the *Hakuho Maru* cruise (1978 ONR report) are now being processed for comparison with our direct observations of PCO_2 in the Bering Sea. Agreement is about ± 6% and is presented in rough form in Appendix B5.

Studies of CO_2 partial pressures under the sea ice in April show consistently high values over a 24 hour period ($\sim$ 360 ppm), with an occasional high and low deviation from these values. This is in general agreement with previous (Kelley, 1968B) observations, and shows the presence of high PCO_2 water under the ice. Similar values were observed in February. Spot checks of sea water from about 25 miles north of Point Barrow showed the presence of both lower and higher PCO_2 waters offshore in February and April, i.e., on the order of 330 ppm in February and 400-420 ppm in April. Subnivean PCO_2 values in April were on the order of 420 ppm and 340 ppm in February, thus tending to substantiate the claim that CO_2 is evolved from annual sea ice, and is ultimately derived from the sea water PCO_2. Curvettes left in place on the new ice since November 1978 on Elson Lagoon near Barrow showed concentrations of 420 ppm in Feburary of 1979.

Surface sea water in the vicinity of Point Barrow was still undersaturated (∿ 280 ppm) in September. By mid-November about 50 miles north of Oliklok (71° 17.7'N, 150° 38' W) ice covered surface water had a PCO_2 slightly in excess (341 ppm) of the atmosphere (∿ 330 ppm) and at a depth of 6 m below the ice, the PCO_2 was 420 ppm thus indicating a rapid return to winter high PCO_2 conditions at the surface.

In June of 1979, during the active melt of sea ice, large variations in PCO_2 were observed within 1 mile lateral distance. The differences were due to both difference in circulation and the presence of zooplankter as opposed to phytoplankter. Waters under the ice near the NARL had poor circulation due to the presence of an unusually large offshore bar caused by a severe storm late in the previous autumn. Inshore, in the restricted circulation area in late June, the PCO_2 in the water under the ice actually rose again to supersaturation after having previously declined in April-May due to a spring plankton bloom. Large zooplankter were evident. Surface ice melt water was undersaturated in June. Offshore, in a 1/2 to 1 acre open area in the ice, the water graded from 2 to 22°/₀₀ salinity in the top 2 meters of water. Few plankter were visible. The surface water had a PCO_2 of 290 ± 10 ppm and it was 210-260 ppm at 2 m.

Water samples from under the Soviet ice station NP 22 in November of 1978, which had drifted to within 120 nautical miles of Point Barrow, suggested that surface waters were being subducted under the pack ice. The station was about 20 miles inside the pack and was 30 meters thick. At 32 m, or 2 m just below the ice island, the PCO_2 was 360 ppm, which was similar to surface water near Barrow. At 55 m, or 25 m below the island, the PCO_2 was 410 ppm.

Surface waters 10-20 miles northwest and northeast of Point Barrow in August of 1979, in the vicinity of drifting ice patches, were fairly consistent in the 230-290 ppm range from the surface to 30 m.

Appendices 2, 3 and 4 contain research papers based on our research on CO_2 in ice covered arctic regions.

B. Carbon Monoxide

In early August, 10-20 miles north of Point Barrow, the concentration of CO in surface waters were on the order of 4-8 x 10^{-5} ml/l. At 10 to 30 m depth it was nondetectable in some cases or < 0.8 to ∿ 2 x 10^{-5} ml/l. This is comparable to the work of Swinnerton and Lamontagne (1974). The vacuum expansion method for stripping gases from water as described by Herr and Berger (1978 and personal conversations) was the analytical method used.

Results of research on this trace gas are presented in a recent publication (See Appendix B1).

C. Methane

In August 1979, north of Point Barrow, the concentration of methane in sea water from the surface to 30 meters was fairly uniform at ∿ 2 x 10^{-4} ml/l. This is about twice the average reported by Lamontagne *et al.*, 1974. A large shallow water coastal lagoon (Elson Lagoon) showed about half the concentration reported for the open sea. See also Appendix B1 for some additional comments about methane in the atmosphere during the melt period.

Surface waters in melting sea ice zones were unusually rich in methane. Using the McAuliffe (1971) equilibrium extraction method, the concentration was ∿ 1 to 2.4 x 10^{-3} ml/l.

D. Nitrous Oxide

Some of this work was accomplished by means of the gas stripper described by Cohen (1977). The majority of it was accomplished by the McAuliffe (1971) method with 73% extraction efficiency. Kaplan *et al.*, (1978) also used the latter method for initial surveys.

Sea ice was not uniform with respect to the quantity of N_2O present, thus suggesting *in situ* biological production. Carbon dioxide, which elutes immediately before N_2O on porapak Q, interfered in several cases. A modification to the McAuliffe sampling method will be required for future measurements.

During June, surface low salinity melt waters were below the detection limit for N_2O. At 2 meters depth, the concentration was 0.5-1 x 10^{-5} ml/l, which is more than an order of magnitude below that reported by Cohen and Gordon (1979) for northern ocean waters.

Later in the summer (July, August), the concentration from surface to 30 m was fairly uniform at $\leq 5 \times 10^{-4}$ ml/l or similar to that reported by Cohen and Gordon (1971).

E. Hydrogen

Our newly adapted method of mercury generation and detection (Herr and Barger, 1978) was not working at the time we were sampling in the Beaufort and Chukchi Seas. Using gas chromatographic technique with argon carrier, the concentration appeared to be very low, with only an occasional high value of about 3 x 10^{-5} ml/l. The detection limit was slightly better than 10^{-5} ml/l. This is in general agreement with Herr and Barger (personal conversation 1979).

F. Methyl Chloride

Nothing quantitative can be stated at this time. All that is known that at least methyl chloride (CH_3Cl) a naturally produced halocarbon, is present and variable in sea ice as observed by electron capture detector gas chromatography while studying nitrous oxide.

No particularly noticeable concentrations at this time have been noted in the subnivean environment over sea ice.

3. SUMMARY OF OUR RESEARCH ON CO_2 IN THE ARCTIC

Atmospheric CO_2. The Barrow data for most of the year show little daily variation with the exception of July and August. There is, however, a ca. 2 ppm variation over 5-15 days due to the shifting of isobaric windflow to and from lower latitudes. The data for September through May resemble the daily trend observed in the Antarctic (Brown and Keeling, 1965). During the autumn, the water and land surfaces freeze and become snow-covered in early September on the tundra and late September on the numerous lakes which cover over 50 percent of the tundra surface. Snow-melt does not usually occur until late May or early June. Thawing of the lakes begins 2-3 weeks later. There is no vegetation to deplete the atmosphere of CO_2 near the ground. Since tundra surface temperatures are below -10°C (Kelley and Weaver, 1969) for most of this period, soil respiration is negligible. However, slow leakage of CO_2 through the cracks in the permafrost is apparent. (See section on Subnivean CO_2). By June, when the tundra snow-cover is thawing, the surface temperatures are near the freezing point. A slight daily variation in CO_2 is superimposed upon smoothed monthly data. The amplitude of the variation depends upon fluctuations of the windspeed and air temperature. At this time, the early stages of photosynthesis and soil respiration occur. July and August are the warmest periods of the year and a time of maximum plant productivity. Open water affords exchange of CO_2 across the air-water boundary. Average daily variations of CO_2 are greatest during this period, over 1 ppm, with maximum concentrations occurring in the early morning and minima by mid-afternoon

(Kelley, 1968a, Kelley and Weaver, 1966). This period resembles, in general, the daily variations of CO_2 observed at the Mauna Loa Observator, Hawaii, (Pales and Keeling, 1965).

The daily variation in CO_2 diminishes greatly by September, however. the daily variation for individual days fluctuates much more for the month of September due to the alternating freeze-thaw conditions on the tundra. Air intake ports placed close to the tundra surface showed that the soil was still a source of CO_2 (Kelley, *et al.*, 1968). A positive surface flux is also indicated by aircraft sampling (See Appendix 3).

A seasonal oscillation is clearly evident, probably produced principally by land plants and the Arctic Ocean and ice. A detailed study of the amplitudes and phases at different latitudes (Bolin and Keeling, 1963) suggest the hypothesis that the summer decrease in CO_2 is due to regional and local weather patterns and vertical mixing. Although there is strong evidence in support of ozone fluctuation and downward mixing since ozone is produced at high altitudes, the evidence is not strong for such an explanation for carbon dioxide in the absence of supporting data well above the surface during winter. What evidence does exist tends to support a polar surface source for CO_2 rather than transport by winds aloft (Bolin and Keeling, 1963, and Appendix B3).

Carbon dioxide concentrations rise steadily to a maximum in May and then rapidly decrease to a minimum in August, just after the maximum in plant productivity is attained (Johnson and Kelley, 1970). In contrast, minimum values in CO_2 concentrations at Mauna Loa, Hawaii, are reached in late September and early October (Pales and Keeling, 1965; Keeling *et al*, 1976a). The lateness of the maximum at Barrow cannot be explained by photosynthesis and spaceheating arguments. Maximum space-heating occurs several months earlier, and photosynthesis resumes in most of the northern hemisphere before late May. Furthermore, the increase in atmospheric CO_2 at Barrow commences in late August, months before space-heating occurs and the cessation of photosynthesis at lower latitudes.

From August to December, CO_2 in the air increases steadily but with wide fluctuations. Variable conditions of freezing and thawing and variable snow cover tend to diminish the magnitude of CO_2 sources from the soil and land plants. By late May, more radiation is gained by the tundra and surface layers than is given out (Kelley and Weaver, 1969). Thawing occurs and carbon dioxide builds up under the snowpack reaching high concentrations by June (Kelley *et al.*, 1968). The CO_2 enters the atmosphere by diffusion and convection to add to the late spring rise of CO_2 in the atmosphere.

Air was also sampled by means of flasks twice a month on Ice Stations ARLIS-II from 1962 to 1964. This drifting station moved about the central Arctic Basin at distances of 300 to more than 800 miles from the Barrow coast. Comparison between the analyses of air sampled by the flasks and by infrared analysis is very good. The concentration of CO_2 at Barrow closely follows the values for CO_2 at ARLIS II but show a definite lag period. Persistent high levels of CO_2 in the Arctic Basin are also reflected in our recent aircraft samplings (See Appendix B3).

During 1962, it was possible to sample air at several areas in northern Alaska (near Anaktuvuk Pass, 68°11'N, 153°15'W; Umiat, 69°20'N, 152°W; Bettles, 66°55'N, 153°15'W). Umiat is located on the treeless north slope of Alaska near the foothills of the Brooks Mountain range. Anaktuvuk Pass is located within the Brooks Mountain range, and Bettles is located near the foothills south of the Brooks Mountain range. During April, all of the CO_2 values are nearly the same, with the concentration at Bettles being a little over 1 ppm higher than at Barrow. During early July, the inland stations, with the exception of Umiak, are significantly lower than Barrow. At this time, the snow has long cleared the region of Bettles and Anaktuvuk Pass while this does not happen at Barrow until late June. These low inland CO_2 values may reflect greater uptake of CO_2 by plants at this time. The high CO_2 concentration at Umiat may have reflected outgassing caused by local tundra thaw. Similar results were seen in more recent aircraft flights (See Appendix B3). By August, minimum CO_2 concentrations are experienced at Barrow with carbon dioxide even lower at the inland stations.

Bolin and Bischof (1970) conclude that 35 percent of the CO_2 output stays in the atmosphere. The decline in the rate of CO_2 increase in the 1960's during a period of rising industrial CO_2 production, if real, may be the result of increased uptake either by the oceans or land plants (Keeling *et al.*, 1976b). Bainbridge (1971) suggested cooling of the surface ocean water may lead to increased CO_2 uptake from the overlying air. Namias (1970) demonstrated that a cooling trend began in 1963. The water north of 35°N cooled remarkably and remained cold for a few years. The cooling trend was associated with major changes in the atmospheric pressure gradient north of 40°N. These low pressures were also associated with abnormal cyclonic activity, particularly in the eastern north Pacific Ocean resulting in considerable wind and cloudiness. These factors are of prime importance in producing low sea surface temperatures through water stirring, reduced isolation, and increased sensible and latent heat losses from the water. Carbon dioxide exchange between the sea and air may be enhanced during this period. Keeling, (1965), however, state that the period of cooler water is too short to account for the CO_2 trend.

Subnivean CO_2. Arctic tundra soils are, in general, characterized by a seasonal freeze-thaw or active zone which overlays perennially frozen ground (permafrost). During the summer thaw period, vascular plant roots and rhizomes, microbial decomposition, and animal respiration are continual sources of CO_2 to the soil environment. The CO_2, moving down its concentration gradient, escapes at the soil surface where it may be immediately refixed photosynthetically or mixed with the ambient atmosphere. Throughout the thaw season, tundra soils represent a significant source for CO_2.

There is an increase in subnivean CO_2 over ambient CO_2 concentrations beginning a few days after the first snowfall. This increase continues into December, at which time CO_2 declines to relatively stable concentrations approaching but still in excess of ambient air levels. Soil surface CO_2 increases from early May to late June when the snow melts.

CO_2 production during a portion of the fall and spring can be associated with biological activity when media temperatures are above the minimum physiological threshold of approximately -7°C. Litter decomposition in these soils also ceases at about -7.5°C.

Carbon dioxide concentration profiles across the snowpack, monitored during the spring of 1971, show that subnivean CO_2 was continually higher than ambient CO_2 throughout the period 1 May to 9 June. Twice during this period, subnivean concentrations at the ground surface under the snow increases rapidly, reaching values greater than 800 to 2500 ppm, respectively. These concentrations appeared to result from the release of gas pockets contained during fall freeze-up of the active soil layer. Maximum concentration differentials of atmosphere CO_2 across the snowpack approached 2000 ppm with an average for the 40-day period greater than 150 ppm. Tundra soils of the arctic coastal plain of Alaska are apparently CO_2 sources throughout the year even when temperatures are too low for significant biological activity. CO_2 from biological sources, expressed from the soil solution during freezing, evidently leaks to the subnivean environment throughout the winter months. In spring thermally induced physical processes may suddenly release the contained gases. Mycological blooms, which are likely to occur under the above conditions, have also been implicated as an additional contributing factor.

CO_2 in tundra surface waters. Seasonal changes in the CO_2 partial pressure (PCO_2) regime were measured for an arctic tundra fresh-water pond and lake. PCO_2 was measured through infrared gas analysis by determining the CO_2 concentration of air in equilibrium with the water. These arctic waters were generally supersaturated in CO_2 with respect to air throughout the period of open water and indicate a CO_2 source to the arctic atmosphere. Melt-water standing on the bottom-fast ice of the lake in spring and water beneath the newly formed ice in fall also had CO_2 partial pressure greater than ambient air (recently observed to be in the 1000-3000 ppm range, Gosink and Kelley, 1977). The seasonal mean CO_2 partial pressure differential between the water and the ambient air was 397 + 185 ppm for the pond and 115 + 83 ppm for the lake. PCO_2 was inversely related to windspeed and water temperature but directly related to sediment temperature. Evasion rate coefficients calculated for the lake, based on *in situ* rate experiments, indicated an average transfer of 0.34 ± 0.17 mg CO_2/cm^2-atm-min to the atmosphere.

CO_2 in sea surface waters. Prior to this study (Kelley, 1970), little was known about the distribution of the CO_2 in Arctic Ocean surface waters. Measurements of PCO_2 with respect to air in the Kara, Barents, Norwegian, Bering, Chukchi, and Beaufort Seas during the late summer show general undersaturation, with a PCO_2 anomaly (PCO_2 - pCO_2) as low as -160 ppm north of Novaya Zemlya, USSR and, more recently, in parts of the Bering Sea. Positive PCO_2 anomalies (supersaturation) occur in the Kara Sea near the mouth of the Ob and Yenisey Rivers. The North Atlantic Ocean, during late summer, is slightly undersaturated except for limited areas such as the North Sea, an area south of Nova Scotia, and within the Gulf Stream where conditions of supersaturation are found. These observations (Kelley, 1970) across the North Atlantic Ocean from the North Sea to Massachusetts Bay agree closely with the results of K. Buch (1939) from a similar track in 1935.

Principal features of the PCO_2 anomalies in the Bering Sea are: an intense undersaturation of -100 ppm in the north central part, a general undersaturation of -60 ppm in the western part; and supersaturation in the eastern part. The principal features of the subarctic Pacific are: a general undersaturation of as much as -45 ppm in the western North Pacific Ocean, near equilibrium in the Gulf of Alaska, and a belt of near saturation water in the west ranging to supersaturation in the east, between the Pacific Ocean and Bering Sea, along the Aleutian Komondorskie Arc.

CO_2 in and over sea ice. The concentration in CO_2 under the snow on sea ice was also found to be enriched in CO_2 as in the tundra work. We also discovered that gases can penetrate annual sea ice in trace quantities (Gosink, *et al.*, 1976), a fact that is of significance to air-sea interactions. Subsequent experimentation disclosed that the evolution of CO_2 from sea ice to the atmosphere was in the range of 10^{-4} to 10^{-3} ml cm^{-2} hr^{-1} (Gosink and Kelley, 1976). The rate depends on the temperature and, to a certain extent on the salinity of the ice. Multiyear ice (50% of the arctic sea ice) is not porous because of the fresh ice layer on the top. The 10^{-3} ml cm^{-2} hr^{-1} figure is similar in magnitude to Keeling's (1965) estimate of the CO_2 flux across open sea water and is effective when the air temperature is about -10°C. The arctic oceans are 90-95 percent ice-covered in the winter so that even if the rate of CO_2 outgassing from sea ice were 1/10 that of the high PCO_2 winter waters, CO_2 outflow through ice would still at least equal outflow through the open water.

CO_2 in the seawater under ice. The surface of the Bering Sea and Arctic Ocean show that these waters are supersaturated in CO_2 with respect to air. Open water during the winter in the form of leads and polyni may amount to as much as 11 percent in area and are important in the air-sea transfer of CO_2 in the arctic. These observations of the surface PCO_2 are too limited in number and geographic location to make definitive statements about the whole Arctic Basin in the winter.

Upwelling. Smalga and Amukta Passes in the eastern Aleutian Islands showed conditions of high positive PCO_2 anomalies indicative of upwelling. Supporting evidence in the areas of upwelling show high nutrient content, high salinities and low sea surface temperatures, and low dissolved oxygen. Based on maximum recorded CO_2 concentrations in excess of 600 ppm, the source of the upwelled water was estimated to be from 200 m depth. Thus by measuring the quantity of escaped CO_2, the transfer of water from depth can be computed (Hood and Kelley, 1976).

Estimated Arctic Annual CO_2 Budget. Our present arctic CO_2 summer and winter source and sink strengths are summarized in the following table and are covered in more detail in the appendices, particularly Appendix B2.

ARCTIC SOURCES AND SINKS OF CARBON DIOXIDE

	SOURCES		SINKS	
OCT-MAY	ANNUAL SEA ICE	849	NONE[2]	
	LEADS AND POLYNI	49[3]		
	TUNDRA	7		
	WINTER NET SOURCE	903		
	ANTROPOGENIC	Negligible[4]		
JUNE-SEPT	TUNDRA SOIL	86	VASCULAR PLANTS	145
	TUNDRA PONDS/ LAKES	111	OCEAN SURFACES	778[5]
	TOTAL SUMMER SOURCE	197	TOTAL SUMMER SINK	923
				-197
			SUMMER NET SINK	726
	ANNUAL SOURCE	11 oz.		
	ANNUAL NET SOURCE	179		

1. Quantities in teragrams (10^{12}g).
2. Transport to lower altitudes.
3. Assuming 5% open water supersaturated with CO_2 in Nov.-Feb. (20 ppm)
4. New flaring practices may make this a significant minor contribution.
5. Assuming 50% open water of low PCO_2 (40 ppm).

It must be emphasized that the data in the table are our first estimates and, in many cases are only extrapolations of limited data.

4. CONCLUDING REMARKS

This research is by no means finished. Solutions to some of the problems yields new questions. Some general statements of the problems to be addressed in future research are presented.

Very little is known about the exchange of trace gases in the arctic regions. Ice-dominated environments are neither passive nor impervious to the exchange of trace gases. Annual sea ice, for example, is a very porous substance (Gosink *et al.*, 1976) which acts as a substantial storage reservoir for gases and permits significant exchange (Gosink and Kelley, 1979a). The freeze and thaw periods, both at sea and on the land, figure prominently in the transfer of trace gases in the arctic environment. Even though observations have been made in the past of several trace gases (Gosink and Kelley, 1977, 1978), the data are insufficient to draw any significant conclusions. One reason for this is that seasonal aspects are important, if not critical, to an adequate interpretation.

There are many phenomena which appear to be related to trace gas interactions, particularly in the atmosphere, such as formation of aerosols and haze, stratospheric destruction of ozone, and the dynamics of critically important species such as .OH (Crutzen, 1970 and Penner *et al.*, 1977). Furthermore, some of these trace gases have been observed in high concentration over tundra and sea ice during the winter and at the time of the thaw (Gosink and Kelley, 1979b). It is not clear how extensive and important these phenomena are to regional or global budgets and its possible influence on climate modification (Fletcher and Kelley, 1977).

Although the Arctic Ocean and surrounding seas are very small in relation to surface area, according to a recent World Meteorological Organization report

(Tech. Note NO. 486 in 1977): "Of all the subsystems of the climate system, the one that is likely to play the most significant part in a warming of the earth is the Arctic Ocean ice pack." "Referring to the Arctic Ocean specifically, the major question is how much of a warming would be required to remove the pack ice completely, and whether such a complete removal will mean that it will remain open and not freeze over again in winter. There are a number of reasons for arguing that it probably would tend to remain open once the ice pack had been melted, barring a major change in sea level . . ." "An open Arctic Ocean would, of course, allow a great deal more evaporation (and CO_2 exchange) than the frozen Arctic Ocean, and this would presumably result in more rain in summer and snow in winter around its shores . . ." Additional comments about the importance of polar regions and global climate are to be found in one of our publications (Fletcher and Kelley, 1977).

The dynamics of atmospheric carbon dioxide interaction with the ocean and land masses is manifested in subtle fluctuations and long-term trends. Measurements over the past 100 years indicate that there has been an increase in atmospheric carbon dioxide as a result of the industrial revolution. Theories have been formulated on how an increase in carbon dioxide might effect climatic change, but the validity of historical data collection remains uncertain.

Carbon dioxide is increasing at a rate of approximately one part per million or more by volume per year in the arctic atmosphere as well as in the tropics and the Antarctic. The rate of increase of CO_2 in the atmosphere, based on anthropogenic input studies, indicates that about half of the CO_2 is removed. The oceans in general are a net sink for a major portion of that CO_2 but with uncertainty factors of about 35% (Broecker 1975). The uncertainty factor for polar oceans is even larger.

The seasonal variation for CO_2 in the air, greatest in the arctic and very small in the antarctic, is primarily a response to photosynthetic utilization of carbon dioxide by terrestrial and marine plants and the winter use of fossil fuels for space heating. Furthermore, our recent work on arctic sources shows that the high atmospheric concentrations of CO_2 during the arctic winter are further enhanced by high CO_2 partial pressures in surface waters in the Arctic Ocean and due to the porosity of sea ice to CO_2. The reason why sea ice, particularly annual sea ice, is very different from fresh water ice with respect to its permeability to gases is the presence of brine which allows for significant air-sea exchange of CO_2 throughout the winter. Other gases were also noted to be enriched in and over sea ice, but less is known about their importance to air sea interactions at this time. Physical (temp. salinity and high PCO_2 water) and biological factors are suspect of causing and modifying the nature of the gases evolved from the surface of sea ice.

A long-term study in 1961 (Kelley, 1973) was initiated to accurately document the concentration and variation of carbon dioxide in the arctic atmosphere near Barrow, Alaska. Carbon dioxide in air was measured continuously by infrared analysis and calibrated with reference gases in a cooperative program of CO_2 observations in Hawaii and the antarctic. Our more recent observations of sources and sinks have made use of modern gas chromatographic techniques which are not as prone to contaminant errors in the standards and require much smaller sample volumes.

Differences in CO_2 partial pressures between the atmosphere and sea surface generally are about 5% or 10-20 ppm. Regions of upwelling and the intertropical convergence zone on the one hand have partial pressures of CO_2 in the surface water as much as 30% or 100 ppm above the ambient air. On the other hand, we have shown that high latitude summer oceans' surface waters display exceptionally low (-60% or 150-200 ppm) CO_2 partial pressures (Kelley, 1970). We have further shown that the exceptionally low summer carbon dioxide concentration in the surface waters is, at least in the Alaskan region, rapidly replaced with the high to very high CO_2 partial pressures in the fall-winter (Gosink and Kelley 1978 and Kelley 1968b). It would be a mistake to model arctic waters based on summer water PCO_2 values only. The same is true for the surrounding tundra and the taiga which are normal to very active sources and sinks year-round and not just in a brief summer period.

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APPENDICIES

A. List of Reports, Presentations and Publications

Reports

1. Dynamics of the exchange of carbon dioxide in arctic and subarctic regions. J. J. Kelley 1973.
   Copy enclosed as Appendix D under separate cover
2. Gas in Sea Ice - Annual report to the Office of Naval Research Code 461, Arlington, VA from the Institute of Marine Science, University of Alaska, Fairbanks. 1976. J. J. Kelley, T. A. Gosink and J. G. Pearson
3. Gases in Sea Ice - Annual report to the Office of Naval Research, Code 461, Arlington, VA from the Institute of Marine Science, University of Alaska, Fairbanks. 1977. T. A. Gosink and J. J. Kelley.
4. Gases in Sea Ice - Annual report to the Office of Naval Research, Code 461, Arlington, VA from the Institute of Marine Science, University of Alaska, Fairbanks. 1978. T. A. Gosink and J. J. Kelley.

Presentations

1. Exchange CO_2 across sea-ice-land interface seminar for NOAA. Surface Springs, MD. October 1978.
2. Background levels and biogeochemical cycle of CO_2 in the Arctic: Multimedia monitoring requirements. Proceedings of the International Symposium on the Multimedium Monitoring of Environmental Pollution. Riga, USSR. May 1979.
3. The Arctic - A significant source and sink of CO_2. American Geophysical Union Annual Meeting, Miami. April, 1978.
4. Trace Gases in the Arctic Atmosphere. Air-sea-ice-land exchange. 11th International Polar Meeting, Berlin. October 1978.
5. Seminar on Trace Gas CO_2. Dept. Meteorology Ahrennius Laboratory, University of Stockholm. October 1978.
6. Trace Gas Source-Sinks on the Arctic. American Chemical Society Annual Meeting. Honolulu. April 1979.
   Copy of extended extract in Appendix C.
7. Partial Pressures of Carbon Dioxide in Surface Waters of the Bering Sea and other Arctic Seas. XIV Pacific Science Congress, Khabarovsk, Russia. August 1979.

8. The Nature of Sea Ice and its Affect on Atmospheric Trace Gases. XIV Pacific Science Congress, Khabarovsk, Russia. August 1979.

9. Measurements of Partial Pressure of CO_2 in Arctic Ocean and the Affect of Annual Sea Ice. Universities of Stockholm and Goetenborg. September 1979.

10. Trace Gas Studies in the Arctic. Poster Session Presentation to the Joint Meetings of the Alaskan AAAS and ACS. Fairbanks, Alaska. September 1979.

Publications

1. Gas Movement through Sea Ice. *Nature* 263:41-2. 1976. T. A. Gosink, J. G. Pearson and J. J. Kelley.

2. Automatic Gas Sample Pressure Controller. *Intern. J. Environ. Anal. Chem.* 6:263-266. 1979. T. A. Gosink and R. L. Seitz.

3. Carbon Dioxide Exchange over the Alaskan Arctic Tundra: Meteorological Assessment by an Aerodynamic Method. *J. Appl. Ecol.* 12:587-611. 1975. P. I. Coyne and J. J. Kelley.

4. Evaluation of mean vertical transports in an upwelling by CO_2 measurements. *Mar. Sci. Comm.* 2:387-411. 1976. D. W. Hood and J. J. Kelley.

5. The Role of the Polar Regions in Global Climate Change. *In* Polar Research to the Present and Future. M.A. McGhinnie, editor. A.A.A.S. pp. 97-116. 1977. J. O. Fletcher and J. J. Kelley.

B. Current Papers in press (1), submitted (3) and in preparation (1).

Appendix B1. Carbon Monoxide Evolution from Arctic Surfaces during Spring Thaw.

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Carbon Monoxide Evolution from Arctic Surfaces During Spring Thaw

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Thawing tundra soils and newly rotting sea ice bubbles are rich in carbon monoxide (5–100 ppm) for a few weeks in May–June. Recent air samples in the vicinity of Barrow, Alaska, showed dramatic increase near the coast and overland. Several hundred kilometers out over winter sea ice the atmosphere concentration of CO was 0.02–0.06 ppm. Near the coast over rotting sea ice the concentration was 0.09 ppm. Inland, atmospheric carbon monoxide rose to a 0.2 ppm. Short term enrichments of carbon monoxide at the tundra and sea ice surfaces have been observed in the past.

Arctic tundra soils may be a significant source of CO during the initial period of thaw. Atmospheric CO in the Alaskan arctic normally is present in concentrations of 0.05 ppm or less, as routinely observed by methanization and flame ionization detector gas chromatography. This is considerably lower than the 0.1–0.2 ppm concentrations reported over the Norwegian and Greenland seas, though the latter most probably reflects European anthropogenic influences [*Wilkness et al.,* 1975]. Carbon monoxide concentrations in the bubbles escaping from thawing tundra lake ice are on the order of 100 ppm. Newly rotting coastal sea ice (June at Barrow, Alaska, 71°N) surface bubbles contain 5–20 ppm CO, but not later in July [*Gosink and Kelley,* 1977]. During the later part of the thaw of the tundra, CO in the air at the base of tundra plants, as sampled by gas-tight syringes, was on the order of 20–40 ppm, whereas turbulent mixing dilutes it to <0.1 ppm near the top of the low plants (about 10–15 cm). Later in the summer no such enrichment was observed. Two-liter canopies, subtending 200 cm^2 of soil surface, have been observed to build CO concentrations of 20–80 ppm in 24–48 hours in the later part of the active thaw period, but no more than about 1 ppm later in the summer.

On recent (June 4–6, 1979) air sampling flights from 850 km out over the sea ice to 210 km inland over the tundra in the Barrow, Alaska, region, the CO in the glass sample flasks (analyzed within 2–18 hours after collection) showed a marked increase (400%) for the nearshore and overland samples. The methane concentration was essentially constant at ~0.8 ppm with only a 10% increase overland. Over the sea ice the CO levels varied between 0.02 and 0.06 ppm at low (30 m) and high altitude (3000 m). A few CO analyses by this method were not detectable to traces of about 0.01 ppm. The sample taken from within 10 km of the coast contained 0.09 ppm CO. Low altitude samples taken 10, 100, and 150 km inland contained 0.18, 0.14, and 0.38 ppm CO. At 210 km inland, over rolling hills, the CO concentration from 30 to 3000 m was 0.16–0.25 ppm.

Surface sea ice initial melt apparently was not taking place more than 50–100 km out to sea, as visually determined from the low-altitude aircraft. The sea ice cover was still ~95%. The first 50–100 km inland was 50–10% snow covered, ponds thawed, and lakes about 50% thawed. Beyond that, the tundra and rolling hills graded to completely thawed. The temperature at 30 m over the sea ice was essentially constant at −4°C and rose to 17°C 210 km inland over the dry low hills. Over wet tundra, 150 km inland, the temperature was 8°C. The surface wind was either from the north or from the offshore ice. The wind at 3000 m was from the southeast.

The suspected cause of the CO around the sea ice is biological. By June the underside of the coastal sea ice and much of the water just under the ice is heavily loaded with plankter. Past winter analyses of sea ice for carbon monoxide (3×10^{-4} ml kg^{-1}) have shown ordinary sea water concentrations ($1\text{–}30 \times 10^{-5}$ ml l^{-1}) [*Gosink and Kelley,* 1977; *Swinnerton et al.,* 1970]. Sea water is, however, usually slightly supersaturated with CO, and the winter surface of annual sea ice usually displays small but definite enrichment of CO as compared to the ambient air. In June 1979 the CO concentrations in the coastal sea water near Barrow was in the range of $1\text{–}4 \times 10^{-4}$ ml l^{-1} as determined by the *McAuliffe* [1971] equilibrium extraction method. Lake melt water contained 2.4×10^{-3} ml l^{-1} CO. Oxygen, nitrous oxide, and methane levels were also enhanced.

Biological factors are also suspected for tundra surface enrichment of CO, but, in addition, there is evidence that physical processes are involved as well. For example, cuvettes placed over tundra that had had a sheet of aluminum foil placed about 10 cm below its surface did not show as large an increase in its trace gas content as did the cuvettes over undisturbed tundra.

We suspect that the evasion of CO from the tundra, sea, and lake ice surfaces is related to the seasonal thaw cycle as it progresses northward during the spring. The duration of the thaw at any one location depends on a number of climatic and geographic variables and may persist from a few days to weeks. The high CO evolution from the newly thawed tundra continues until normal summer biological processes again reduce the CO levels in the active layers of the tundra soils.

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Appendix B2. The Arctic. A significant source-sink of carbon dioxide.

Submitted to *Arctic*

ABSTRACT

The winter to summer variations in the tropospheric loading of CO_2 in the arctic is the largest in the world for a clean remote environment. About half of the annual variation in atmosphere CO_2 is due to natural causes. Brine channels, as well as leads and polyni in annual sea ice, and the numerous fractures in the frozen tundra perimeter of the arctic permit a significant evolution of CO_2 to the atmosphere during the winter. Thawing and freezing cause short term noticeable injections of CO_2 to the relatively closed arctic lower atmospheric circulation. Tundra soil, lakes and ponds are moderate sources during summer, while the arctic ocean and vegetation are the only major sinks. We estimate that the amount of CO_2 added to the arctic atmosphere in the winter is 0.91×10^{15}g and that 0.73×10^{15}g is removed in the summer.

INTRODUCTION

Observations of CO_2 in various arctic environments show that large quantities of CO_2 are evolved at arctic surfaces (sea, ice, tundra) to the atmosphere during the winter. Both sources and sinks exist in the summer after the onset of melting and before refreezing takes place. These phenomena are masked in long-term atmospheric monitoring by lower latitude anthropogenic factors in the winter and to a degree by natural events in the spring and summer.

The annual variation of surface level (10 m) atmospheric carbon dioxide concentrations (Kelley, 1973) at Barrow, Alaska, is largest when compared to other remote atmosphere measurements. At Barrow (71.3°N), the winter to summer atmospheric CO_2 difference is about 12 ppm by volume. At Ocean Station Papa (50°N, 145°W), the difference is 10 ppm (Keeling, personal communication). The variation at Mauna Loa, Hawaii (20°N) is 6 ppm (Keeling *et al.*, 1976a). At 20°S, the annual variation is about 3 ppm (Boling and Keeling, 1963), and at the South Pole, 1 ppm (Keeling *et al.*, 1976b).

In general terms, the northern hemisphere contains most of the land mass, human population, and industrial activity. The high concentration of CO_2 in the atmosphere during the winter is the result of increased use of fossil fuels and diminished uptake of this gas by the biosphere. The southern hemisphere, largely an oceanic environment, should be a net sink for CO_2. There is a significantly smaller anthropogenic CO_2 contribution to the atmosphere in the southern hemisphere, even when considering the recent citations in the literature concerning tropical forest clearing (Bolin, 1977; Wong, 1978; Woodwell *et al.*, 1978).

Our specific interest is with the large atmospheric CO_2 variations in the arctic where negligible anthropogenic factors still are not directly involved, and the biospheric activity is diminished for most of the year. Northern hemisphere CO_2 data suggest a high latitude winter source of carbon dioxide to the atmosphere and that the arctic regions are not ice-sealed and passive, simply accumulating CO_2 transported in from lower latitudes. The atmospheric carbon dioxide maximum near Barrow occurs in late May, which is several months after the maximum fossil fuel consumption from December to February and a month or two after significant spring biological activity is in progress at latitudes below 65°N. Closer examination of the Barrow data shows a small, but clear and repeatable increase in the atmospheric content of carbon dioxide in late May (Kelley *et al.*, 1968; Coyne and Kelley, 1973). Furthermore, the atmospheric CO_2 concentration at Barrow increases again in August, months before any significant northern hemisphere space-heating occurs and the biosphere is still active to ~70°N. The annual increase in atmospheric CO_2 at Mauna Loa, Hawaii, does not commence until late October.

The arctic, particularly in the winter, is a comparatively closed cyclonic center below the tropopause (Vowinckel and Orvig, 1970). Relatively small masses of air are injected into or escape from the winter arctic troposphere so that it remains a well-mixed closed system. The CO_2 added from arctic sources tends to stay there for longer periods of time, as compared to mixing at lower latitudes. Thus, it appears that arctic derived CO_2 sources are a significant part of the cause of the large variations in the atmospheric loading of CO_2 as recorded at Barrow, Alaska. Bolin and Bischof (1970) indicate that a significant portion of surface source CO_2 tends to remain in the lower part of the troposphere and would thus enhance these proposed atmospheric CO_2 concentration factors. Aircraft data (Gosink and Kelley, 1979a), show the repeated presence of a CO_2 enhanced layer below 1 km altitude in the arctic.

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 Oceanogrpahy (S.I.O.) (C. D. Keeling Laboratory) were used. In addition, air samples were periodically taken in the vicinity of the 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 and glass (10 ml) gas tight syringes, or in 250 ml gas sample bottles. It was necessary to employ oversize O-rings under the teflon 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 springs were stable for 24-72 hours, depending on the particular syringe in question. Standards stored in slightly pressurized routine 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 and wetting it with freshwater to provide a gas tight ice seal.

Experiments with atmospheric sampling from aircraft are published elsewhere (Gosink and Kelley, 1979a).

ARCTIC OCEAN SURFACE WATERS

Like most other ocean surfaces, the arctic ocean, at least at latitudes below 80°N, are net sinks for CO_2 during the summer months (Gordon *et al.*, 1973; Kelley, 1970; Keeling, 1965; and this work). Partial pressures of CO_2 in the Bering, Barents, and Kara Seas surface waters can go as low as 80 ppm but are usually in the range of 160-260 ppm. We have observed Beaufort and Chukchi Sea surface waters to show similar summer P_{CO_2} values. On the other hand, during the winter, the partial pressures of CO_2 in Bering and Beaufort seas surface waters appear to be equal to or significantly greater than ambient atmospheric CO_2 levels because of the prolonged period of low or no photosynthesis, and the probable mixing of high P_{CO_2} waters from below the surface (Kelley, 1968; Park *et al.*, 1974; and this work).

In the northern Bering Sea we measured P_{CO_2} values of 400-440 ppm at and just below the thermocline located at 20-40 m (Gosink and Kelley, 1978 *Hakuho Maru* cruise). At lower latitudes, where photosynthesis extends below the surface thermocline, the depth at which the high P_{CO_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. On 11 November 1978, the P_{CO_2} of newly ice-covered surface waters 30 km off shore had already risen to 341 ppm, about 10-12 ppm greater than the ambient air, and it was 420 ppm 6-7 m below the surface. Light levels were low at that time with the sun being above the horizon for only about one hour per day. Therefore, photosynthesis could be expected to have effectively ceased.

The uniformity of the partial pressures of CO_2 in surface waters in the Arctic is uncertain. It would appear from three experiments (1-30 day observations) (Kelley, 1968; Kelley and Hood, 1971 and this report) in addition to several spot samples, that the surface P_{CO_2} in the winter is about 340-360 ppm, but with an occasional high observations of *ca.* 400 ppm in the winter. 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) analyzed for P_{CO_2} yielded 295 and 300 ppm. The light level at that time of year was low to moderate, but nearly constant for *ca.* 15 hours/day. These isolated low P_{CO_2} observations suggest that slight but significant offshore biological activity had commenced under the sea ice in April. This departs from other winter and spring month observations when the P_{CO_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 the offshore bar and grounded ice displayed the expected low P_{CO_2} (280-300 ppm) due to photosynthesis. On the other hand, waters just 1-2 km further offshore consistently analyzed for a P_{CO_2} of *ca.* 400 ppm. Zooplankton were obviously abundant, and their respiration may have overcome the prior influence of the phytoplankter.

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 carbon dioxide, methane, and carbon monoxide were found at the surface of the tundra and in the lakes and ponds of the arctic in the vicinity of Point Barrow. We report at this time only on the carbon dioxide. Kelley *et al.* (1968), and Coyne and Kelley (1974a), reported on the existence of elevated levels of carbon dioxide under the snow across the tundra, 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 (as much as several thousand ppm for a few hours over a few days) occurred in May during the annual final rise in atmospheric carbon dioxide mentioned earlier. 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 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}.

During the months of June and September, the period of thaw and freeze, the concentration of 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 P_{CO_2} 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 CO_2 of 0.34 mg cm^{-2} atm^{-1} min^{-1}. Miller *et al.* (1976), and Coyne and Kelley (1975), calculate that the vascular plants on the wet tundra fix about 400-770 g CO_2 m^{-2} $season^{-1}$, with about 43% of the CO_2 being drawn from the atmosphere. During periods of low photosynthesis, the hours around midnight, the soil is a source of about 0.2 g CO_2 m^{-2} hr^{-1}.

GASES AT THE SEA ICE-AIR-SNOW INTERFACE

Carbon dioxide, carbon monoxide, methane and sometimes nitrous oxide have all been observed to emanate from the sea ice surface, and all 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 only on the concentration and exchange of carbon dioxide. A description of sea ice and the probable causes of its porosity to gases is presented elsewhere (Gosink and Kelley, 1979b). 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 summary of results for the recovery of gases in helium flushed chambers sealed to sea ice are shown in Figure 1. The fact that the oxygen concentration in the fresh ice sealed, helium flushed chambers (Fig. 1) 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 in around the edges. Full (100%) recovery to ambient conditions for CO_2 was as 0.034% (340 ppm) and for O_2, 21%. In all cases (Fig. 1: a, b, c) oxygen recovery lags behind CO_2 recovery. In Figure 1a, it is noted that CO_2 recovery exceeded ambient conditions. The CO_2 partial pressures in the brine in the sea ice matrix have been observed to be in excess of 400 ppm (Gosink and Kelley, 1978). Probably, the brines are depleted in O_2 because of the high salt concentration, and because of the suspected biological oxygen consumption within the relatively warm sea ice matrix. Curve pairs (Fig. 1a) denote experiments performed on relatively warm (-10 to -15°C) saline (3-4°/₀₀) 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 were for experiments performed over less saline (1-2°/₀₀), colder (-20 to -25°C) offshore ice at ARLIS VII 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 multi-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.

Based on experiments at -10 to -15°C, the rate at which carbon dioxide is being released to the atmosphere from annual ice surfaces is 2-4 x 10^{-3} ml cm^{-2} hr^{-1}. At -20 to -25°C it apparently drops to about 10^{-4} ml cm^{-2} hr^{-1}. The veins in sea ice theoretically should close by two orders of magnitude at -20°C, which is in agreement with the approximate factor of 20-40 decrease in gas fluxes observed for annual sea ice, assuming the much larger brine channels open and close at about the same levels of magnitude as do the much smaller multi-grain boundary veins (Gosink and Kelley, 1979b).

Keeling (1965) computes an evasion rate of 1.5 mg CO_2 cm^{-2} min^{-1} atm^{-1} for CO_2 from the Pacific sea surface to the atmosphere. A P_{CO_2} of 20 ppm provides almost the same evasion rate for sea water as the former sea ice figures.

Chambers containing ambient air 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) and suggest a transfer rate compatible with the 10^{-4} ml cm^{-2} hr^{-1} values shown above. The ambient air was stable between 339-341 ppm. Samples of the subnivean air at ARLIS VII generally ran around 350 ppm. The range was 337-374 ppm, with the samples taken over multi-year ice being the lowest.

There was a brief period in early May when the sea ice was just beginning to rot, when 2 ℓ chambers covering 200 cm^2 of sea ice were enriched

(10-20 ppm) in CO_2 in a few minutes. The P_{CO_2} of winter sea ice brine was on the order of 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, as mentioned in the introduction. 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 from the brines before photosynthesis reversed the process.

Contact of high P_{CO_2} waters 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 effect 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} ml cm^{-2} hr^{-1} figures stated earlier. It is this high P_{CO_2} water rather than the brines in the sea ice that is the probable cause of the continual 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.

CO_2 SOURCES AND SINKS

We estimate that there are 1.4 x 10^6 km^2 of tundra surrounding 1.5 x 10^7 km^2 of Arctic Ocean 90-95% covered with sea ice and half of which is annual or seasonal sea ice (e.g. Vowinckel and Orvig, 1970). We assume that 60% of the tundra surface is ponds and lakes. We define the summer period in the arctic as the period between and including thaw and freezup, or June-September, and winter the balance of the year.

All of the quantities computed in this section are shown in Table 1 in terragrams (10^{12}g).

During the winter, we know of no sinks for CO_2 in the arctic except diffusion and wind transport to lower latitudes where the atmospheric concentrations are lower due to the sink effect of the oceans.

Anthropogenic sources of CO_2 in the arctic are negligible (est. $< 10^{12}$g). However, recent petroleum developments may make this a source comparable to the natural outgassing of the winter tundra, particularly if CO_2 stripped from the petroleum gases is released to the atmosphere rather than being reinjected into the well.

The largest winter source of CO_2 in the arctic is the annual sea ice. Open leads and polyni waters and frozen tundra surface provide significantly smaller quantities of CO_2 in the arctic. If half of the sea ice is warm and saline enough to provide 10^{-3} ml CO_2 cm^{-2} hr^{-1}, then 849 x 10^{12}g of CO_2 will evolve to the arctic troposphere. The leads and polyni, conservatively estimating an average 20 ppm supersaturation of CO_2 in their surface waters as compared to the local atmospheric concentration, should emit 49 x 10^{12}g of CO_2 between November and March, based on Keeling's (1965) evasion rate. The true value may be two or three times larger since we have frequently observed substantially larger partial pressure differences.

The slow outgassing of the frozen tundra soil is estimated to contribute 7 x 10^{12}g CO_2 over the winter.

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 10^{12} to 10^{13} g of CO_2 to the arctic troposphere over short periods of time at the beginning and end of the arctic winter. If half of the estimated naturally evolved 905 x 10^{12}g of CO_2 remained in the arctic troposphere (above 65°N), because of its relatively closed cyclonic circulation system, it would cause a change of about 3 ppm in the tropospheric CO_2 concentration there, or half of the observed winter-summer amplitude at Barrow. The other half that was advected to lower latitude might possibly change the tropospheric concentrations at Mauna Loa by nearly 0.1 ppm.

During the summer period in the arctic, both sources and sinks occur as shown in Table 1. The wet tundra emits more CO_2 than the plants can fix during a portion of this time. Given Miller *et al.*'s (1976) source rate of 0.2 g CO_2 m^{-2} hr^{-1} for an estimated 8 hours a day over 90 days, and that 40% of the tundra is involved, 86 x 10^{12}g of CO_2 are added to the atmosphere while the vascular plants remove 145 x 10^{12}g (see Gases from Tundra, Lakes, and Ponds section). Similarly, using Coyne and Kelley's (1974b) evasion rate of 0.34 mg CO_2 cm^{-2} atm^{-1} min^{-1} from 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 tundra is involved, then the 111 x 10^{12}g of CO_2 value is derived.

The summer Arctic Ocean and surrounding seas sink strength of 778 x 10^{12}g CO_2 was derived from CO_2 evasion rate given by Keeling (1965). We assumed a partial pressure difference of 40 ppm, and that 50% of the summer arctic oceans are free of ice. This value may be 2 to 4 times larger if partial pressures of CO_2 in arctic waters are uniformly low (80-280 ppm) as measured elsewhere (Kelley, 1970; Gosink and Kelley, 1978). We know nothing of the P_{CO_2} in the central arctic basin in either summer or winter, but suspect that they are not greatly undersaturated with P_{CO_2} in the summer.

The net effect during the arctic summer is a sink of 725 x 10^{12}g of CO_2. Again, in this relatively closed cyclonic system, half of this net sink effect could lower the arctic tropospheric CO_2 load by nearly 3 ppm or half of the amplitude. (The arctic tropospheric circulation in the summer is, however, not as isolated as in the winter.) The natural arctic factors can account for 6 ppm of the 12 ppm winter-summer variations in the arctic. The other half being due to net CO_2 transport to the arctic in the winter, and out of it in the summer.

Global atmospheric carbon dioxide budgets are on the order of 10^{18}g of CO_2, with annual anthropogenic contributions of nearly 10^{17}g CO_2 (e.g. Broecker, 1975). Our suggested arctic natural source and sink strengths of 10^{15}g CO_2, appear to be insignificant, but their effects are magnified because dilution is not as rapid as at lower latitudes.

These figures are only first estimates. Very little winter arctic and subarctic surface water P_{CO_2} data are available. No P_{CO_2} observations in the central arctic basin have been made. Frozen tundra outgassing rates are tentative, and the summer tundra ponds, lakes, soil and plant data need more extensive geographic coverage.

Global dispersion models (e.g. Machta, 1974) work well for predicting the fate of anthropogenic gases e.g., SF_6, CCl_4, and do fairly well for CO_2 at low latitudes and the southern hemisphere. Difficulties appear however for CO_2 at high northern latitude because it was incorrectly assumed that there were no significant sources above 70'N in the winter, and that the summer sinks were intense, but modest in size. It is hoped that the data and reasons presented in this article will help to correct the models.

ACKNOWLEDGMENTS

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TABLE 1

ARCTIC SOURCES AND SINKS OF CARBON DIOXIDE[1]

	SOURCES		SINKS	
October-May	Annual sea ice	849	None[2]	
	Leads and polyni	49[3]		
	Tundra	7		
		905		
	Anthropogenic	negligible[4]		
June-September	Tundra soil	86	Vascular plants	145
	Tundra ponds/lakes	111	Ocean surfaces	778[5]
		197		923
				- 197
			Summer net sink	725

Net annual source of (905-725) 180 x 10^{12} g CO_2

[1] Quantities in teragrams (10^{12} g) within a factor of about 2.

[2] Transport to lower latitudes.

[3] Assuming 5% open water supersaturated (20 ppm) with CO_2 November-March.

[4] New flaring practices may make this a significant minor contribution of an estimated 7 x 10^{12} g of CO_2/year in the future.

[5] Assuming 50% open water of low P_{CO_2} (40 ppm below atmospheric).

FIGURE CAPTION

Figure 1. 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 °/oo S (b) -15 to -20°C; 2 °/oo S (c) -15 to -20°C; 1 °/oo S.

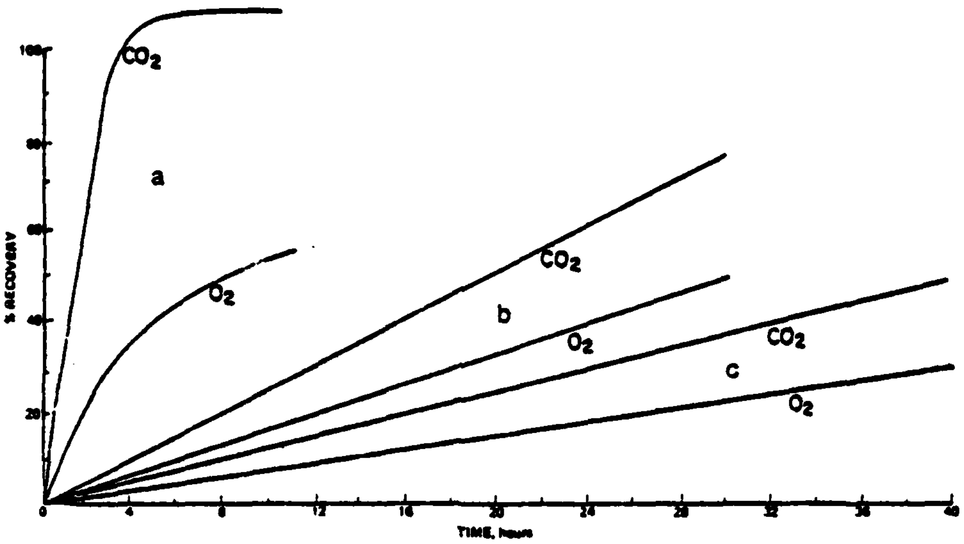
100
80
60
40
20
% RECOVERY
CO_2
a
O_2
CO_2
b
O_2
CO_2
c
O_2
0
4
8
12
16
20
24
28
32
36
40
TIME, hours

Figure 1

Appendix B3. Arctic Tropospheric Carbon Dioxide Low Altitude Aircraft Sampling.

Submitted to *Arctic*

ARCTIC TROPOSPHERIC CARBON DIOXIDE. LOW ALTITUDE AIRCRAFT SAMPLING

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ABSTRACT

Atmospheric carbon dioxide levels monitored at Barrow, Alaska show the largest winter-summer variations in the world for a clean background environment. Past high altitude aircraft data suggest a low altitude CO_2 source in the winter, and a sink in the summer. Our data, based on samples collected (3000 and 50 m), clearly show the source-sink effects of the Arctic Ocean and tundra throughout the year, particularly during the periods of freeze and thaw.

INTRODUCTION

Regular analyses of CO_2 in the atmosphere at Barrow, Alaska, and farther north, began in the early 1960's (Bolin and Keeling, 1963; Kelley, 1969 and 1973). Bolin and Keeling (1963) have shown extreme differences between the two poles with respect to atmospheric CO_2 concentrations. The South Pole shows minimal annual fluctuations ($\sim$1 ppm), the intertropical convergence zone shows a fairly persistant intermediate high, and the arctic atmospheric CO_2 varies ($\sim$12 ppm) from a worldwide high in winter to a worldwide low in the summer. Both poles, however, reflect similar long term trends in the gradual annual increase of CO_2 in the atmosphere of $\sim$1 ppm (Keeling *et al.*, 1976). Our low altitude (<4000 m) aircraft data refine some of the implications to be found in the earlier high altitude (>5500 m) arctic data of Bolin and Keeling (1963).

The atmospheric CO_2 level begins to rise at Barrow, Alaska in late August, months before it does at mid-latitudes (late October) and reaches a worldwide high (for clean backgrounds) of *ca.* 340 ppm in late May, months after northern hemispheric anthropogenic space heating has ceased, and lower latitude photosynthesis has recommenced. Furthermore, the late spring high is a resurgence rather than a continuous climb to that level, and the high levels persist a few hundred km offshore for 1-2 weeks as compared to Barrow (Kelley, 1973 and this work). Our estimates of the arctic source-sink strengths for CO_2, and for the role that annual sea ice plays in the winter-summer mixing ratio of atmospheric CO_2 have been published elsewhere (Gosink and Kelley, 1979a, b). This article deals with the results of our low altitude aircraft atmospheric CO_2 program, and shows the intensity of regional sources and sinks for CO_2 on the lower troposphere.

EXPERIMENTAL METHODS

The gas chromatographic procedure, standards and accuracy have been published elsewhere (Gosink and Kelley, 1979a). The sample collection procedures are described below.

A Naval Arctic Research Laboratory Twin Otter aircraft was usually used to collect air samples. Air was conducted to a 250 ml sampling flask *via* a small viton diapham air pump in the non-pressurized cabin at a rate of about 4-5 ℓ/min. The air intake tubing (Teflon) was located on a strut well ahead of the engines. A C117 aircraft was also occasionally used. The tubing was placed in one of the clean air scoops mounted above the fuselage forward of the engines. Sampling flight plans were established to fly 150 to 1000 km north of Barrow, Alaska. Samples were periodically collected at approximately 100 m altitude outbound. At the farthest point, a vertical profile was made from 40 m to 4500 m altitude. Samples taken inbound were made at 3200 m to a point usually about 80 km inland. Another set of samples was taken to establish a vertical profile over land.

Care was taken to flush the short section of glass tubing leading to the stopcock before the stopcock to the highly evacuated sample bulb was opened. After 1.5-2 minutes of flushing, the bulb was slightly pressurized before the stopcock was closed.

Some air samples were collected and held briefly under slight positive pressure in Teflon and glass (10 ml) gas light syringes. It was necessary to employ oversize O-rings under the teflon 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. Slightly pressurized gas sample bottle samples were stable for several weeks.

AIRCRAFT OVERFLIGHTS OF THE ARCTIC ICE AND TUNDRA

For the sake of brevity we have selected Figures 1 a-d and Figures 1 e,f from 7 of our 17 flights, to show horizontal and vertical profiles respectively of atmospheric carbon dioxide overland, seasonal ice from late spring to late summer when the changes are most pronounced. Other data show little horizontal and vertical change. A strict minority of our data point to opposite trends. The area sampled was always within a few hundred km from Point Barrow, Alaska. There was a strong enrichment of CO_2 over the sea ice, and a noticeable depletion only 80 km inland on 26 June 1977 (Fig. 1a). The sea ice was nearly continuous and had only begun to melt about 150 km north of Point Barrow at that time. Thus, offshore CO_2 evolution would have been high due to optimal opening of brine channels. The tundra at that time was free of snow and ice, and was biologically active i.e., soil respiration was going on. A few weeks later, 7 July 1977, there was only a suggested trend in enrichment over the ocean portion of the north-south transect. The sea ice around Point Barrow was breaking up and melting out to 300 km by that time, thus low P_{CO_2} surface waters may have influenced the local lower atmosphere at that time. The data for 20 July 1977 shows essentially constant oceanic atmosphere concentrations of CO_2 out to nearly 1000 km north of Point Barrow. It is important to note that the 20 July 1977 flight was at 2 km altitude, whereas the previous two were conducted at 30 m over the ice. There was, however, evidence for significant (10 ppm) enrichment at low altitudes on 18 July for a flight

300 km east of Point Barrow. That flight had nearshore altitudes over melting sea ice of *ca.* 150 m dropping to 15 m 100 km offshore over continuous ice which was beginning to melt.

The data shown in Figure 16 is for the same time period as Figure la, but a year later when the ice had already broken up several weeks earlier. The data from these flights show essentially constant low level atmospheric concentration of CO_2 from inland 90 km south of Point Barrow to 300 km offshore to the north. The only exception was the far inland early data of 27 June 1978. There was a sharp depression in atmospheric CO_2 130 km inland, presumably due to the uptake of CO_2 by the vegetation. The higher values 90 km inland may represent a seasonal latitude change when the surface was still thawing, and soil respiration was dominant. Similar data of slightly depressed CO_2 values near the mountains and of higher level of CO_2 further north over the tundra, have been observed in the past at surface monitoring sites (Kelley, 1973).

In early June of 1979, the sea ice and tundra were only beginning to thaw within 100 km of Point Barrow. The CO_2 partial pressure was essentially constant at 340-341 ppm to 850 km north of Point Barrow, and only dropped 2-3 ppm, 200 km inland. Carbon monoxide at that time showed a more dramatic change and has been reported elsewhere (Gosink and Kelley, 1979c).

Figure lc shows the data from flight transect during late summer (8-9 September 1978). Freezing had set in so that the intense biological activity in the tundra had greatly diminished, yet the ground had not frozen hard and could outgas without biological fixation of the CO_2 (Coyne and Kelley, 1971). The oceans were nearly clear of all ice out to about 200 km, and skim ice was showing in the many leads in the pack ice. Low P_{CO_2} water was still at the surface. This is in contrast to the 27 June data (Fig. 1b) when biological activity was uniformly high. The far inland atmospheric concentrations of CO_2 in this case were high and variable, and decreased northward to the coast where the 150-200 km of open low P_{CO_2} water appeared to influence the lower troposphere. Our aircraft sample data near Point Barrow are in general agreement with the NOAA-GMCC recorded values at Barrow for the 2 days prior to and during the flight as shown by the small bar in the figure. The surface winds were from a clean air northern (oceanic) sector. Winds aloft near Point Barrow usually have a westerly origin when the surface winds are from the north, and thus would have been influenced by the low P_{CO_2} open waters of the Chukchi and northern Bering Seas. The air from the pack ice region is clearly enriched in CO_2 near the surface as shown in Figures 1d and 1e.

Figure 1d presents data for a flight transect a few weeks later after the tundra had frozen (30 September 1978). There had been almost continuous high winds and wave activity from the northeast and northwest. The surface sea water P_{CO_2} level remained surprisingly low at about 270 ppm 20 km offshore. The lower atmosphere appears to be well mixed lower. There was however, a definite but small (2-3 ppm) trend for enrichment 300 km offshore for the air at 3200 m which suggest possible enrichment by either new sea ice or high P_{CO_2} surface waters very deep in the pack. Annual sea ice was forming in the leads in the pack ice, which was still 150 km offshore of the vicinity of Point Barrow. The offshore vertical gradient for the same flight is shown in Figure 1f.

On five ocassions, both north and south of Point Barrow, vertical profiles showed the layered presence of higher (6-10 ppm) CO_2 near 1 km altitude. Occasionally, enrichment at 3 km was evident too. Our tentative interpretation is that they are real since they are well within the limit of our analytical error. A complementary study on aerosols (G. Shaw, University of Alaska, personal communication), on one such flight showed that there were increases in aerosols at those same levels. These data suggest boundary layer entrapment. Ozone, incidently, displayed a minimum in those CO_2 maximum layers. On 16 January 1978, a low CO_2 concentration rather than a CO_2 maximum was evident at 600 meters. The ozone concentration in that CO_2 minimum layer was reversed in that it displayed a maximum.

The winter profiles were variable for the month of January 1978. There was generally a small trend for enrichment of CO_2 near the surface, and the air at altitude over the sea ice was more highly enriched compared to the over land profile.

Figures 1e and 1f are vertical profiles of CO_2 and temperature *ca.* 300 km offshore over pack and newly forming sea ice, 8 and 30 September 1978. Horizontal profiles for these same sites were discussed in connection with Figures 1c and 1d. The high offshore surface values for 8 September 1978 (Fig. 1e) are believed due to the relatively calm freezing weather, the formation of new sea ice, or possibly by high PCO_2 surface waters deeper in the pack. The low surface values and slightly elevated concentration offshore at altitude on 30 September 1978 (Fig. 1c) on the other hand, are interpreted to reflect the presistent turbulent mixing of the previous 3 weeks, and the influence of the low surface PCO_2 ocean water south of there.

By 8 November 1978, the annual sea ice had reformed. There was high PCO_2 water (341 ppm) under the ice and there was a definite enrichment of CO_2 in the air above the sea ice 180 km north of Barrow at that time. The air near (30 m) the surface 180 km north of Barrow had *ca.* 340 ppm CO_2, 80 km north it was 332 ppm at Barrow it was 327 ppm (∿328 ppm according to the NOAA data).

SUMMARY AND CONCLUSIONS

Low altitude aircraft sampling for atmospheric CO_2 shows how intense ground level sources and sinks can, on occasion, modify the observations made on a fixed ground level station (e.g. Fig. 1c). Layering effects are also seen on occasion as opposed to continuous gradients. The most important fact is that the Arctic Ocean shows itself to be a significant source of CO_2 in the winter and sink in the summer, which is furhter substantiated both by high altitude flights (Bolin and Keeling, 1963) and the low altitude data presented here. Therefore, future atmospheric models will have to account for the natural sources and sink of CO_2 in the Arctic (Gosink and Kelley, 1979a) and not to consider them as essentially inert regions.

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FIGURE CAPTIONS

Figure 1a. Horizontal profiles of atmospheric CO_2 at low and high altitudes north and south of Point Barrow, Alaska, June-July 1977.

Figure 1b. Horizontal profile of atmospheric CO_2 at low altitude north and south of Point Barrow, Alaska, June-July 1978.

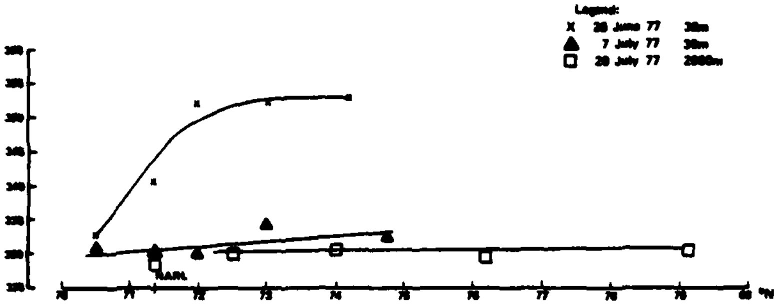
Figure 1c. High and low altitude horizontal profiles at atmospheric CO_2 north and south of Point Barrow, Alaska, 8-9 September 1978.

Figure 1d. High and low altitude horizontal profiles of atmospheric CO_2 north of Point Barrow, Alaska 30 September 1978.

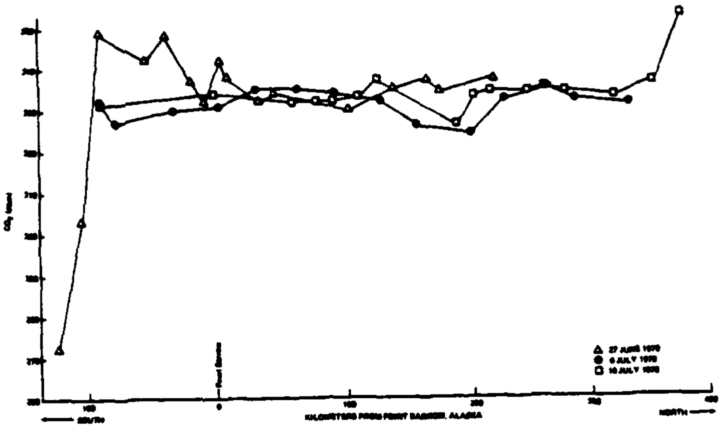
Figure 1e. Vertical profile of CO_2 and temperature 320 km north of Point Barrow, Alaska, 8 September 1978.

Figure 1f. Vertical profile of CO_2 and temperature 260 km north of Point Barrow, Alaska, 30 September 1978.

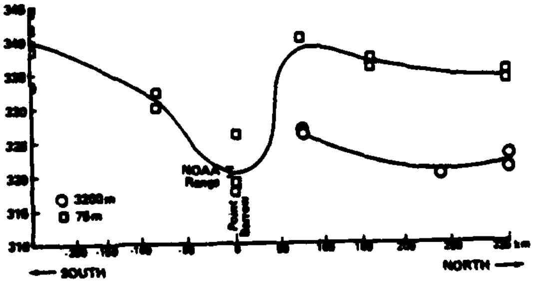
a



b



c



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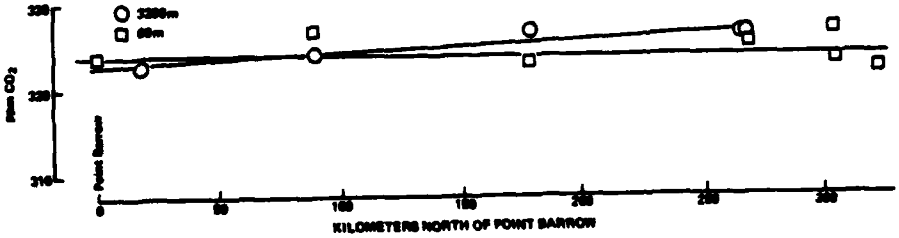

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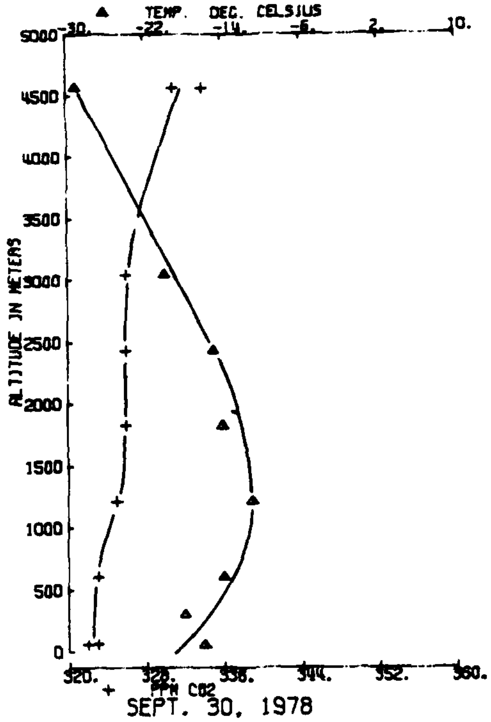

SEPT. 30, 1978

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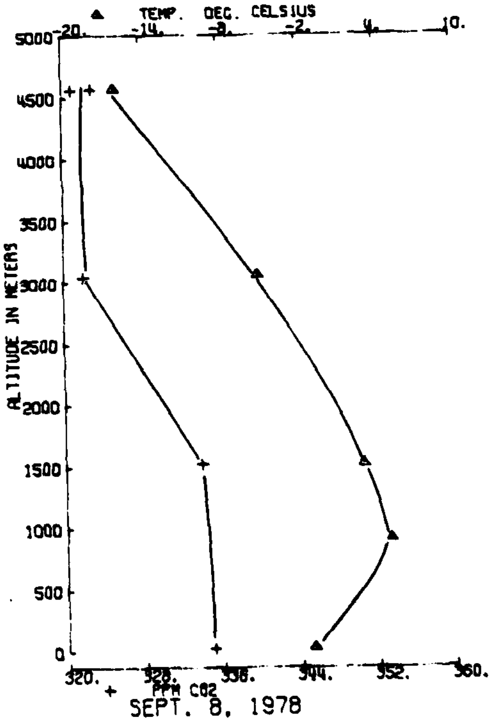

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Appendix B4. Annual Sea Ice. An Air-sea Gas Exchange Moderator.

Submitted to *Arctic*

ANNUAL SEA ICE. AN AIR-SEA GAS EXCHANGE MODERATOR

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ABSTRACT

Sea ice, particularly annual sea ice, is very different from freshwater ice with respect to its permeability to gases. The presence of brine allows for significant air-sea-ice exchange of CO_2 throughout the winter. Other trace gases are also noted to be enriched in sea ice, but less is known about their importance to air-sea-interactions at this time. Both physical and biological factors cause and modify evolution of gases from the surface of sea ice. Quantitative and qualitative descriptions of the nature and physical behavior of sea ice with respect to brine and gases are discussed.

INTRODUCTION

Freshwater ice (river, lake, glacier) is quite different, perhaps radically so, from annual sea ice with respect to its gas permeability. At the surface, multi-year sea ice, because of the melt water filling and refreezing in the intersticies, is for all practical purposes sealed against gas exchange. Hemminsen (1959) correctly reported that freshwater ice is nearly impermeable to gases. Gosink *et al.* (1976) reported that sea ice on the other hand was nearly a million fold more permeable to gases, and that the direction of penetration (platelet orientation of the sea ice) affects the penetration of gases by a factor of about 2. Our current estimate is that nearly 10^{15}g CO_2 enter the arctic troposphere from the annual sea ice surface (Gosink and Kelley, 1979a).

Sea ice maintains a high fluid content even at low temperatures. At -10, -20 and -30°C it is respectively 20, 12 and 3% liquid (Richardson, 1976). The virtually inexhaustible heat source of the ocean under it, and the insulating property of the snow and or hoar frost cover over it maintains high internal temperatures relative to the atmosphere. For example, 140 cm thick sea ice under *ca.* 50 cm of snow was observed to have an ice surface temperature of -6°C when the air was -28°C. That was, however, unusually thick snow for arctic ice; it normally runs between 2 and 20 cm of cover. At the other extreme, *ca.* 1.2 m thick sea ice deliberately swept clean of snow cover will be about 6°C warmer than the atmosphere 30 cm below the surface as compared to the air-ice interface, and the ice surface will maintain temperatures about 1-2°C warmer than the air measured *ca.* 10 cm above the ice (Shapiro, Geophysical Institute; personal communication).

GRAIN BOUNDARIES AND BRINE CHANNELS

In freshwater ice, the relatively light salt load tends to be concentrated at multi-grain boundaries. Figure 1 shows a three grain boundary of melting freshwater ice. The width of the melt zone between the grains in this case is on the order of 0.1 mm. However, when the temperature is lowered to just 0.037°C below the freezing point, the system closes dramatically so that the largest feature, the intersection, is on the order of 10^{-5} cm radius (Langhorn, 1974). A gas molecule is about 10^{-7} cm in diameter. At -0.2°C, the radius of the three grain boundary will have closed to about 10^{-6}cm. This explains why Hemminsen's (1959) data, collected between -0.5 and -10°C, shows pure ice to be virtually impenetrable to gases. Lake and river water ice did show an order of magnitude increase in permeability due to the low salt content.

In contrast, sea ice with its much larger inclusion of brines, has both larger platelet boundaries and brine channels. Figure 2 shows cold sea ice (*ca.* -20°C) with platelet separations on the order of 0.1 mm. The width of the platelets are about 1 mm. If one can extrapolate for sea ice brines channels and platelet separations with Raymond and Harrison's (1975) formula for multi-grain boundary sizes when impurities are present, sea ice multi-grain boundaries theorically should still be on the order of 10^{-7} cm at -10°C, and close by two orders of magnitude at -20°C. We did observe a 20-40 fold decrease in the flux of CO_2 across the sea ice-air interface in that temperature range (Gosink and Kelley, 1978, 1979a).

BUBBLES IN SEA ICE

Bubble occlusions in freshwater ices, particularly glacier ice, are essentially totally sealed off, and usually under moderate to high pressure (e.g. Gow and Williamson, 1975; Matsuo and Miyake, 1966). Because of this, they can be used to measure ancient atmospheres (e.g. Robbins *et al.*, 1973 and Berner *et al.*, 1978). Bubbles in tundra lake ices are also under pressure. Bubbles are common in sea ice (Fig. 2), but we have yet to find any under pressure. The quantity of entrained gas bubbles varies with season, age and depth of the ice sample. Elevated multi-year surface ice is highly vesicular and may contain 200 + ml of air kg^{-1} ice. Annual sea ice, above the hydrostatic level has a variable gas bubble loading of *ca.* 10 to >100 ml kg^{-1}. Below the hydrostatic level zone, the volume of the bubbles is <0.1 to ~5 ml kg^{-1} of sea ice, usually on the low end of the range (Kelley *et al.*, 1976; Gosink and Kelley, 1977). The volumes were determined in a manner similar to Langway (1963) by trapping the liberated bubbles of a weighed piece of ice allowed to melt under cold toluene.

There is also a period of 4-6 weeks during the initial period of melting of sea ice when bubbles photosynthetically form. The quantity escaping to the surface is unknown and variable. In early May, the bubbles from surface water on sea ice are still slightly enriched in CO_2 (340-350 ppm) as analyzed with a Carle 311M gas chromatograph (Gosink and Kelley, 1979a). However during June, after the CO_2 levels had dropped due to photosynthesis, high concentrations of CO (5-20 ppm) and methane noted in the bubbles (Gosink and Kelley, 1979b). Oxygen was also enriched because of the photosynthesis.

Later in July, no unusual CO was noted, and the CO_2 had been driven down by photosynthesis (<300 ppm).

Tsurikov (1975) has approached the question of sea ice porosity from the point of view that gases such as nitrogen and oxygen released from solution in sea water are mainly responsible for the porosity of sea ice. He lists seven mechanisms by which sea ice may gain its porosity.

DISSOLVED GASES AND BRINE IN SEA ICE

Most of our work with trace gases in sea ice has been with CO_2, which with exception of the influence of photosynthesis in the late spring, appears to be controlled by the physical-chemical transfer processes associated with high P_{CO_2} within and below the sea ice matrix. The winter transfer of other gases through annual sea ice is expected to be restricted relative to CO_2 because of their reduced solubility in brines, even though they (CO, CH_4) are enriched at the air-ice interface.

Whole annual sea ice, when melted, produces a liquid of 3-4°/₀₀ salinity. On the other hand, if a hole is drilled about half way through sea ice, the surface insulated and then inspected later, brine from the matrix will have pooled in the bottom of the hole. When air temperatures are cold (*ca.* -25°C) an overnight period is usually required to accumulate a few cm of brine. The salinity of this brine is about 120-150°/₀₀. If the air temperature is warmer (*ca.* -10°C) 10-20 cm of liquid will flow in a few hours and be of lower salinity (80-120°/₀₀). Under relatively warm air conditions (*ca.* -5°C) the hole will flood to the hydrostatic level with *ca.* 30-40°/₀₀ water in minutes. Eide and Martin (1975); Niedrauer and Martin (1979) have reported the active pumping of sea water and brines at the underside of sea ice, and that the brine channels extend upward at an angle of 30-60°. The brine channels, which are on the order of 1 mm in diameter, were reported earlier by Lake and Lewis (1970).

The chemistry of the cations and anions in sea ice has been covered elsewhere (e.g. Addison, 1977; Richardson, 1976; Cox and Weeks, 1974). We have noted that the pH of the concentrated brines is about 6.8-7.2 which is uncorrected for the sodium ion effect of the brine, and causes the reading to be 0.1-0.3 pH units high. This low pH helps to explain the high partial pressure of CO_2 associated with the brine (*ca.* 1000 ppm). The June standing water brine and surface water (0.5-3°/₀₀) still display a low pH (7.2) as compared to the sea water under (8.00 pH).

Several trace gases are found under the snow at the air-ice interface or in the ice matrix significantly enriched over the concentration found in the air 2 meters above the ice. This indicates that throughout the winter in the arctic, the sea ice is a source of these gases to the troposphere. Carbon dioxide is enriched in the subnivean by 0-80 ppm, and is inversely proportional to the wind speed (Gosink and Kelley, 1978, 1979a). Carbon monoxide is frequently enriched by *ca.* 0.1 ppm and CH_4 by 2-4 ppm in the subnivean. During the winter, we have not seen concentrations of these two trace gases within the ice matrix greater than those reported by Lamontagne *et al.* (1976); Swinnerton and Lamontagne (1976). As mentioned earlier, the CO and CH_4 concentrations rise substantially in the rotting sea ice in June, and are on the order of $\geq 10^{-4}$ ml 1^{-1} in the dissolved phase. Thawing sea ice and tundra appear to be of importance to temporary regional tropospheric loading of CO (Gosink and Kelley, 1979b).

If one bores a hole in the ice and samples the air in the hole before the drill is removed, nitrous oxide is irregularly found to be enriched over the atmospheric concentration by 10-1000%. Another gas, presumed to be methyl chloride, is also detected in concentrations greater than ambient air on occasion. Both of these gases are biologically produced.

MISCELLANEOUS OBSERVATIONS

A gas leak was heard during the course of flushing a surface-sealed hole in annual sea ice with a low pressure gas (< 2 psi). The pressure was increased to about 10 psi and some water was thrown onto the surface in an attempt to locate the leak. Active bubbling was observed in many places as much as a meter away from the hole.

There are the observations by several different persons at various locations who verbally reported active bubbling of scuba diver's air up through *ca.* 1.3 m of ice in the month of May 1977 and again in 1978.

Finally, a block of freshly quarried annual sea ice was laid on the surface when the air temperature was about -7°C. Some ink was mixed with brine and poured into a hole scraped on the top of the ice block. Within a half hour, the ink passed completely through the interior of the 30 cm block and made a stain on the snow under it (Gosink and Kelley, 1978).

CONCLUSIONS

The concept of the Arctic as an ice-sealed passive region in the winter with respect to trace atmospheric gas exchanges must be changed at least for CO_2. Saline or annual ice, particularly when it is relatively warm (> -15°C) permits significant gas exchange. Other trace gases such as CO, CH_4, N_2O and perhaps CH_3Cl also are observed to be evolved from the ice. Too little data are available, particularly on a seasonal basis, to adequately determine the dynamics of exchange.

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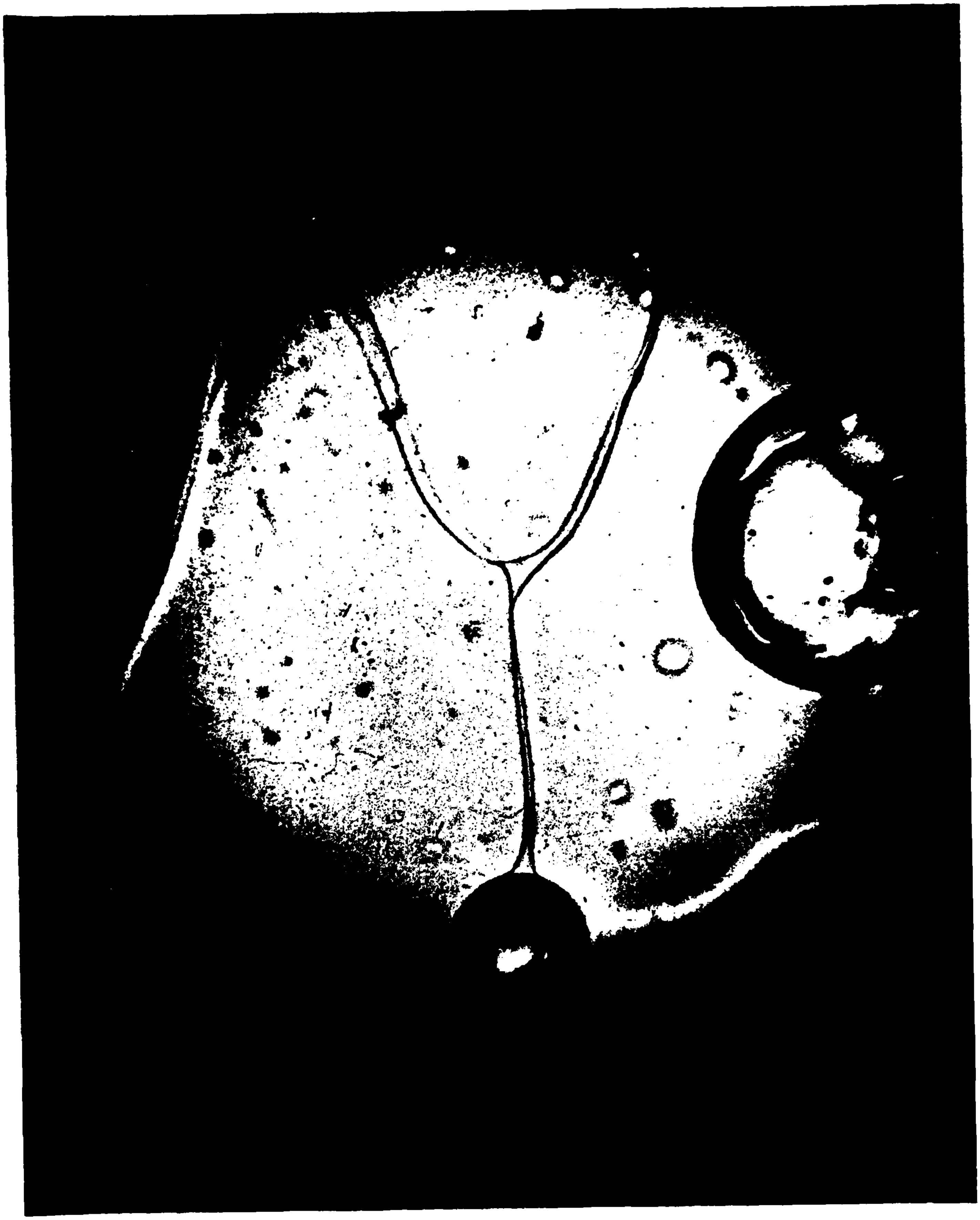
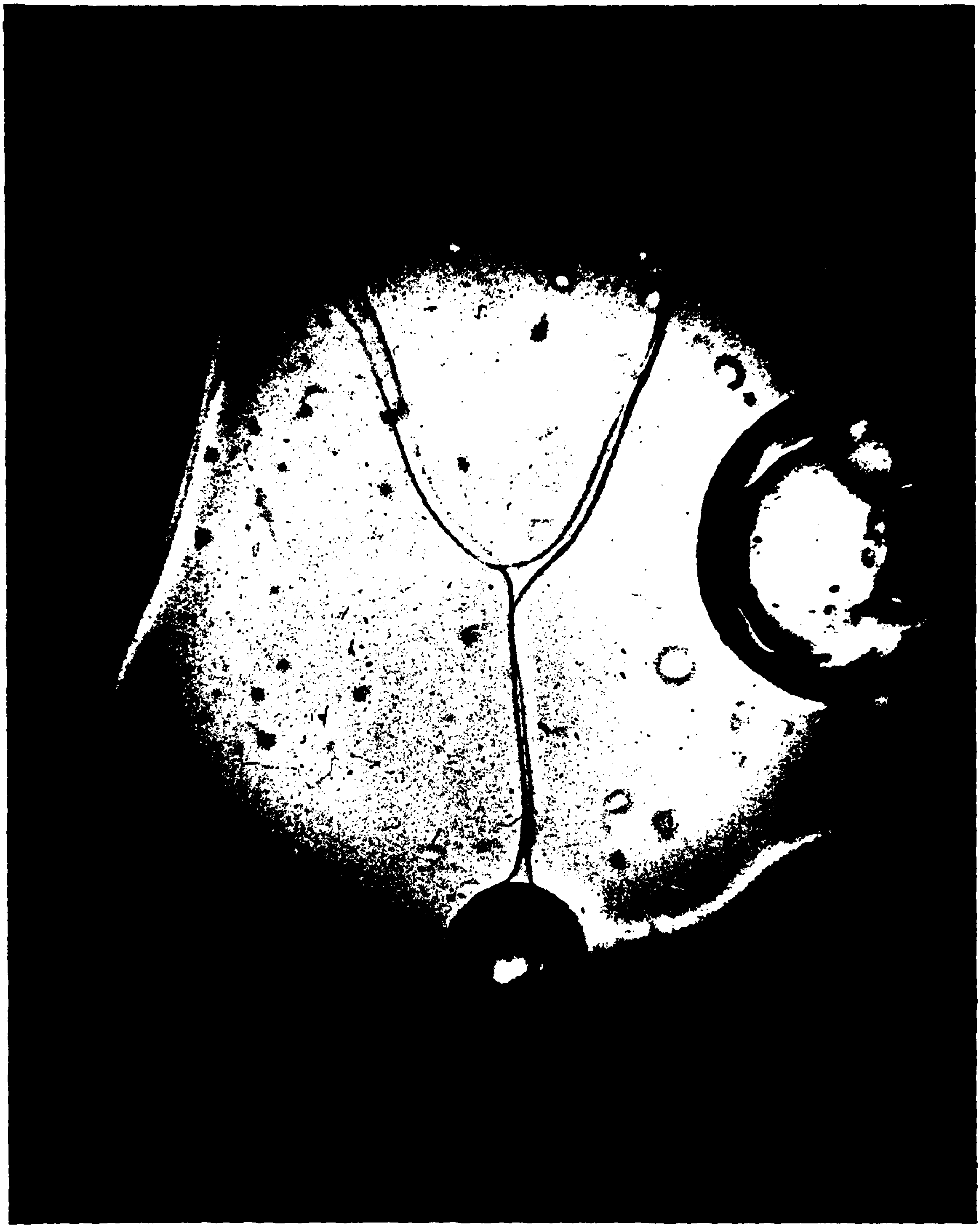
FIGURE CAPTIONS

Figure 1. Fresh ice at its melting point. Magnification 10x. Grain boundaries are on the order of 0.1 mm. (Photo courtesy of Tom Osterkamp).

Figure 2. Sea ice at about -20°C. Magnification 10x. Width of brine areas between ice platelets are on the order of 0.1 mm. (Photo courtesy of Tom Osterkamp). Note also the bubble and brine pockets and channels.





Appendix B5. Carbon Dioxide Partial Pressures in the Bering Sea Observed and Calculated

In preparation.

CARBON DIOXIDE PARTIAL PRESSURES IN THE BERING SEA OBSERVED AND CALCULATED

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ABSTRACT

Various algorithms are applied to several different formulas used for the calculation of PCO_2 from pH and alkalinity data, and are compared to observed PCO_2 data collected from Bering and Chukchi Seas surface waters. Hithertofore obscure algorithms for the calculation of K_1, K_2 and K_B are presented for cold waters, and based upon the trio buffer system are presented.

INTRODUCTION

In this paper, partial pressures of carbon dioxide, calculated by routine pH and alkalinity data, are compared with our observed PCO_2 measurements. We find, that given modern values for K_1, K_2, and K_3, the apparent dissociation constants for carbonic and boric acid, even the classical theoretically correct method of Harvey (1960), based on the earlier work of Buch, operates reasonably well for near surface waters. Other methods applied were those of Edmond and Gieskes (1970). Ivanenhov (1964) which is essentially the same algorithm as used by Alvarex-Borrego *et al* (1972) except that the latter authors corrected the parameters for pressure as well as temperature. We also have applied our relatively unknown algorithm to the problem (Kanamori, 1973 and Kanamori *et al* 1973a,b) and to the previously mentioned algorithms. The Karamori method appears in calculation detail in the appendix.

The apparent dissociation constants K_1 and K_2 for carbonic method as calculated by the Karamori method (   ) are similar but smaller than those of Lyman.

The portion of the cruise track of the Japanese Research Vessel *Hakuho Maru* in July and August of 1978 in the Bering and Chukchi Seas from which the data for this paper are based is shown in Figure 1.

METHODS

The partial pressures of carbon dioxide were determined every 11 minutes by continuous equilibration of air with sea water, and analysis of the equilibrated air on an automated Carle 311M chromatography by flame ionization detection of the methanized carbon dioxide.

Sea water from 6 m depth was provided directly to the laboratory at a high rate of flow. The temperature differences between *in situ* and the exit tube in the lab were usually no more than 0.1-0.2°C.

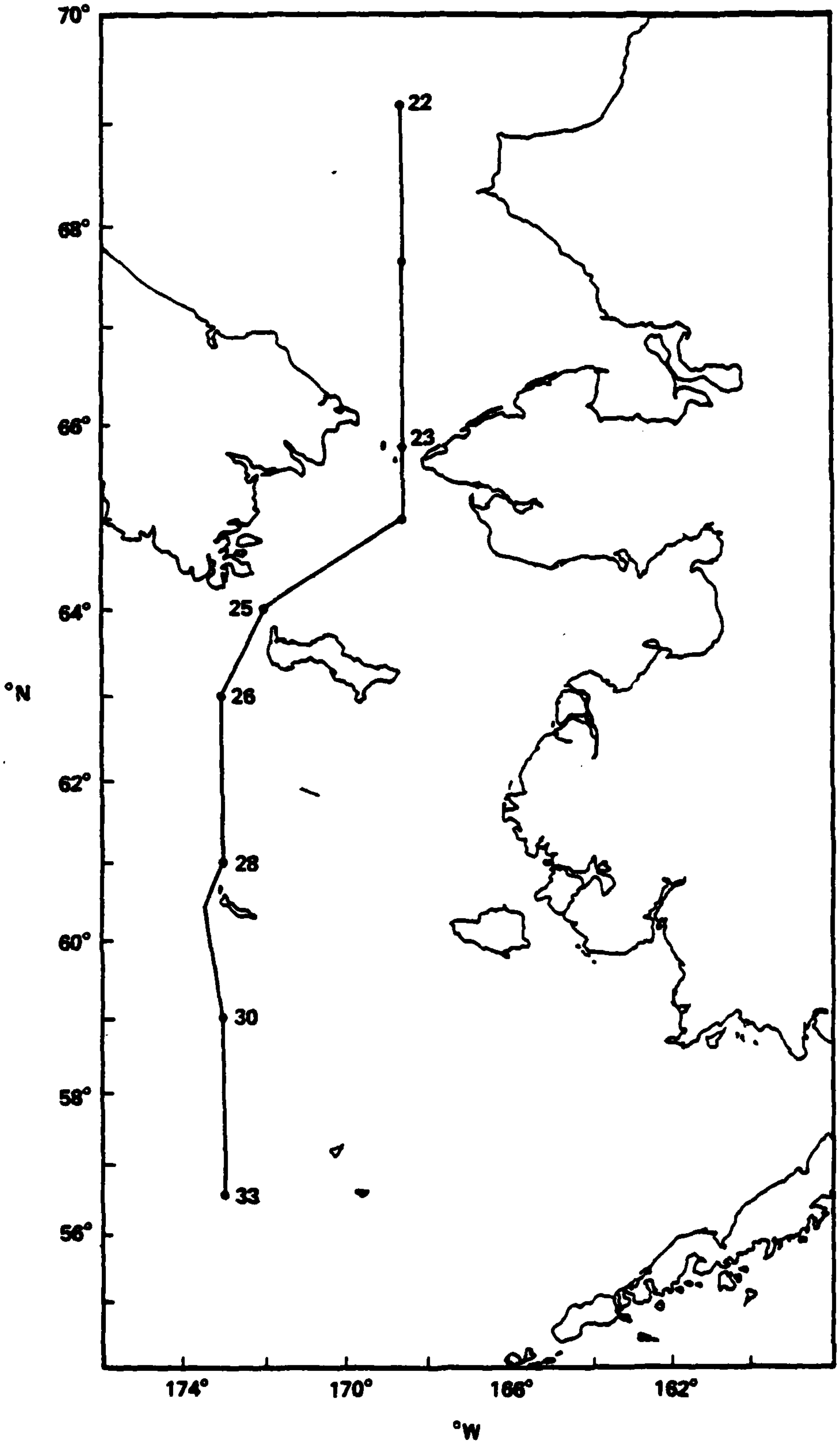
Clean air intakes were located amid ship on both sides at about 5 m above the sea surface. Air was taken from the windward and stack gas free side.

The air was equilibrated with the sea water with a glass counter current device described below and shown in Figure 2. The device provides for the facile equilibration of air-sea water carbon dioxide. The overall length as shown in the figure is about 90 cm. The active CO_2 transfer length is about 75 cm which consists of a 2.5 cm diameter glass column filled with short segments of smaller diameter glass tubing to provide a large amount of surface area. The system is thermally jacketed with a 5.0 cm diameter glass tube with auxilliary large flow of the water being equilibrated. The stopcock is adjusted to provide 600-800 ml/min of water to the top of the column. Clean air from a small pump is introduced through the side tube near the bottom at a rate to provide about 100 ml/min escape through the top. The pinch cock on the tubing on the bottom allows the water and excess air to escape. The device will function at atmospheric to slightly elevated pressures (800-1000 mm Hg). Equilibration is quantitative since slightly shorter columns show no difference when two are hooked in series with the air, and in parallel for the water to be equilibrated.

The gas chromatographic response was calibrated with CO_2 standards prepared at the Scripps Institute of Oceanography. Control of the pressure in the sample loop, which was held at constant temperatures in the analytical oven, was achieved by our electromechanical device as described elsewhere (Gosink and Seitz, 1979).

The data was read and reduced by hand so that the accuracy was only about ±0.5-1% or 1-3 ppm, which was more than adequate for this work. Automated analyses, not available at the time of this work, can improve the accuracy to better than ±0.2%.

Alkalinities and pH determinations were performed by routine methods at 25°C for samples taken from predetermined depths at the stations. Normal NBS phthalate buffers were used in the pH measurements.


70°
68°
66°
64°
62°
60°
58°
56°
°N
174°
170°
166°
162°
°W
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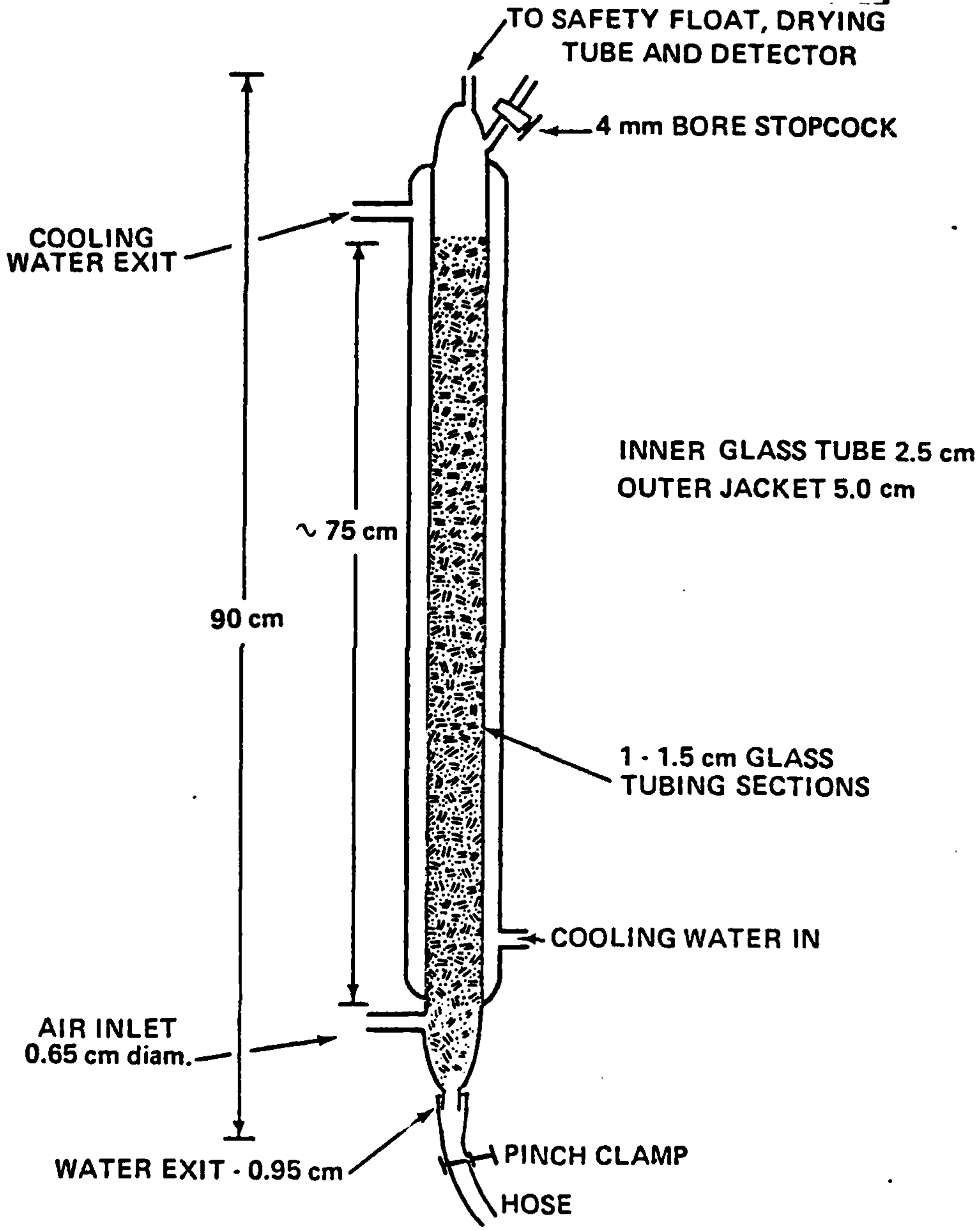
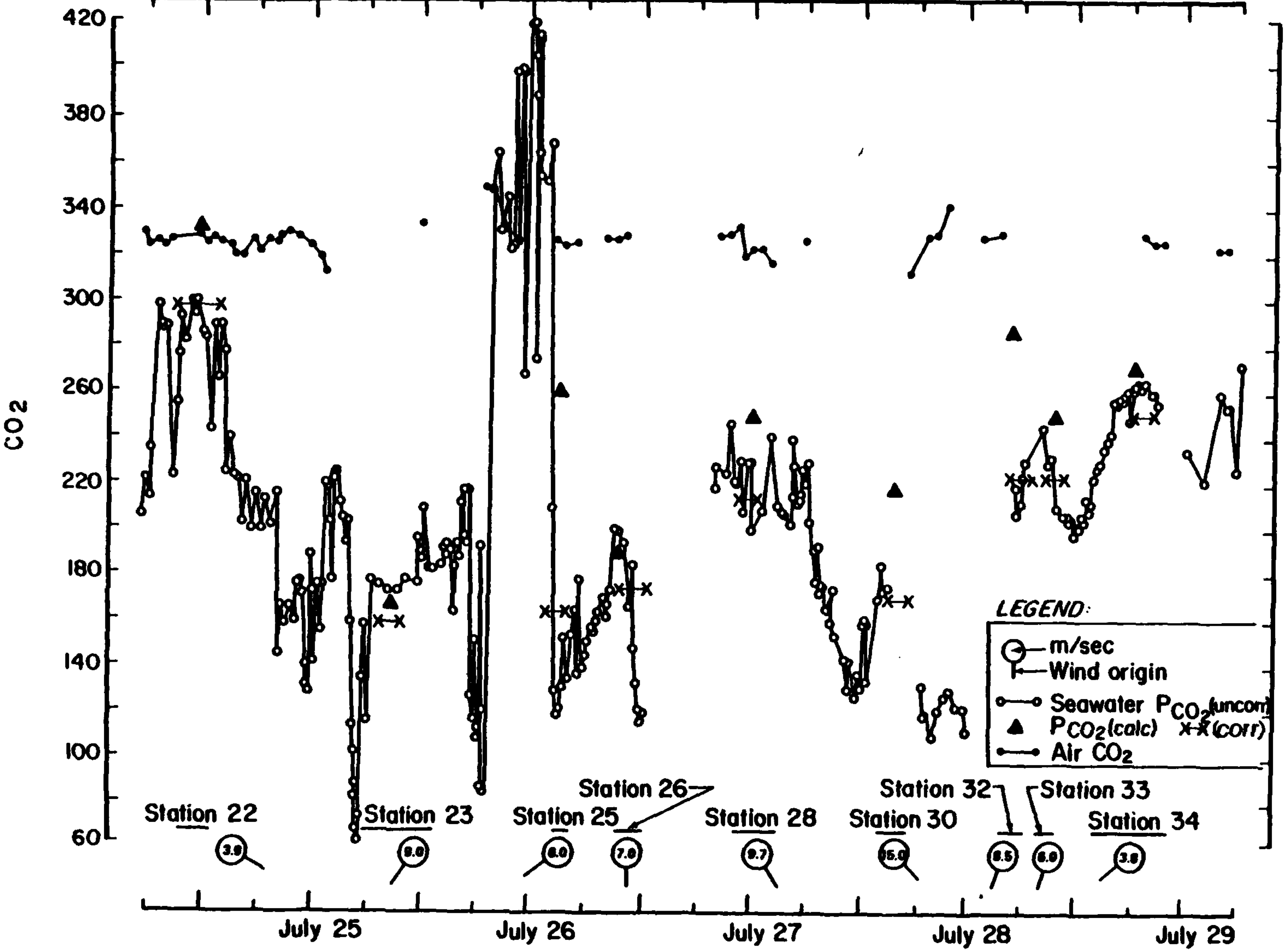
23
25
26
28
30
33


TO SAFETY FLOAT, DRYING TUBE AND DETECTOR
4 mm BORE STOPCOCK
COOLING WATER EXIT
~ 75 cm
90 cm
INNER GLASS TUBE 2.5 cm
OUTER JACKET 5.0 cm
1 - 1.5 cm GLASS TUBING SECTIONS
COOLING WATER IN
AIR INLET 0.65 cm diam.
WATER EXIT - 0.95 cm
PINCH CLAMP
HOSE

HOKUHO MARU – BERING SEA CRUISE, JULY 1978



PPM CO2

		OBSERVED	CALCULATED				
STA NO.	DEPTH(M)	AVG(6M)	METH-1	METH-2	METH-3	METH-4	AIR(5M)
22	0		346	341	205	342	327
	10	290	320	323	213	323	
	20		263	275	213	275	
	29		255	267	209	267	
	45		228	241	196	241	
23	0		170	174	124	174	334
	10	163	166	171	126	172	
	19		175	183	144	184	
	29		179	187	147	187	
	48		181	190	149	190	
25	0		150	148	92	148	325
	10	150	333	349	270	349	
	19		361	380	298	380	
	29		368	387	306	388	
	43		371	390	308	391	
26	0		191	191	123	191	327
	10	176	191	191	123	191	
	19		153	158	116	158	
	29		155	162	130	163	
	48		678	738	669	738	
28	0		253	253	165	254	321
	10	218	248	248	162	249	
	19		215	221	160	221	
	29		230	238	177	239	
	48		230	245	207	246	
30	0		216	215	136	215	328
	10	173	214	213	135	213	
	19		216	216	136	216	
	29		293	297	200	297	
	49		449	469	358	469	
32	0		272	273	176	273	328
	10	220	279	280	183	281	
	19		272	273	178	273	
	29		292	294	193	294	
	49		381	389	269	389	
33	0		254	253	161	254	328
	10	219	249	249	158	249	
	19		249	248	158	249	
	29		344	349	237	349	
	49		423	434	307	434	
34	0		280	279	176	279	325
	10	254	263	262	166	263	
	19		277	276	175	277	
	29		286	285	181	286	
	48		368	375	259	375	

*

PPM CO2

STA NO.	OBSERVED CORRECTED AVG/RANGE	NO.	CALCULATED-INTERPOLATED FOR 6M			
			METH-1	METH-2	METH-3	METH-4
22	290/281-297	3	331	330	284	330
23	163/110-203	23	168	172	146	172
25	150/129-171	4	260	268	227	269
26	176/146-197	5	191	191	163	191
28	218/206-239	3	250	250	213	251
30	173/168-182	4	215	214	181	214
32	220/205-237	5	276	277	235	278
33	219/208-235	6	251	251	212	251
34	254/234-259	20	270	269	228	269

*

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COMPARISON OF K1, K2, AND KB CONSTANTS CALCULATED
BY THE METHOD OF KANAMORI, EDMOND AND GIESKES,
AND OF MEHRBACH ET AL, S=34.32%
       TEMP   K1(10 )    K2(10 )    KB(10 )
K       0      6.971      3.763      1.278
EG             6.174      3.838      1.096
M              6.111      3.391
K       5      7.607      4.479      1.401
EG             7.118      4.545      1.270
M              6.945      3.851
K      10      8.235      5.125      1.555
EG             8.056      5.299      1.454
M              7.757      4.491
K      15      8.841      5.801      1.730
EG             8.960      6.086      1.646
M              8.521      5.305
K      20      9.410      6.610      1.916
EG             9.802      6.893      1.841
M              9.214      6.272
K      25      9.929      7.656      2.102
EG            10.555      7.702      2.039
M              9.815      7.335

*
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FIGURE AND TABLE CAPTIONS

Figure 1. Partial track of the Japanese Research Vessel *Hakuho Maru*, July-August 1978 in the Bering and Chukchi Seas.

Figure 2. Air-water CO_2 equilibration device.

Figure 3. Continuous record of PCO_2 data from the Bering and Chukchi Seas. *Hakuho Maru* cruise, July-August 1978.

Table 1. Comparison of observed and calculated near surface PCO_2 values in the Bering and Chukchi seas.

Table 2. Observed and calculated PCO_2 data in the Bering and Chukchi seas.

Table 3. Comparison of K_1, K_2 and K_B constants calculated by the method of Kanamori, Edmond and Gieskes, and of Mehrbach *et al.*, S=34.32°/₀₀.

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APPENDIX

COMPILATION OF METHODS AND ALGORITHMS

Harvey (Buch)

$$PCO_2 = CA \times \frac{a_H}{K_1 \, \alpha_o (1 + \frac{2K_2}{a_H}) a_{H_2O}}$$

where

$$CA = TA - \frac{K_B \times 2.2 \times Cl^\circ/_{\circ\circ} \times 10^{-5}}{C_H + K_B} - (C_{OH} - C_H)$$

TA = total alkalinity
α_o = the solubility of CO_2 in pure water

and $^{10}\log a_{H_2O} = -0.004211 \, \Delta t - 0.000022 \, \Delta t^2$

Δt = freezing point depression of the sea water below pure water

Edmond and Gieskes

$$PCO_2 = \frac{\Sigma CO_2}{K_o} \times \frac{a_H^{\,2}}{a_H + a_H K_1 + K_1 K_2}$$

where

$$TA = \frac{(a_H K_1 + 2K_1 K_2)}{(a_H^{\,2} + a_H K_1 + K_1 \, K_2)} \Sigma CO_2 + \frac{K_B \, \Sigma B}{(a_H + K_B)}$$

$$-\,^{10}\log K_1 = 3404.71/T + 0.03786T - 14.712 - 0.19178 \, Cl^{1/3}$$

$$-\,^{10}\log K_2 = 2902.39/T + 0.02379T - 6.471 - 0.4693 \, Cl^{1/3}$$

$$-\,^{10}\log K_3 = 2291.9/T + 0.01756T - 3.385 - 0.32051 \, Cl^{1/3}$$

$$-\,^{10}\log (K_o) = -2622.38/T + 15.5873 - 0.0178471 \, T + Cl(0.0117850 - 2.77676 \times 10^{-5} T)$$

$$\Sigma B = 0.0219 \, Cl^\circ/_{\circ\circ}$$

Ivanenkov (Alvarez-Borrego)

$$PCO_2 = \frac{a_H{}^2 \times CA}{\alpha_o K_1 \; (a_H + 2K_2)}$$

The above expression for PCO_2 by Ivanenkov (1964) (see Park *et al.*, 1974) is identical to the one used by Alvarez-Borrego *et al.* (1972) except that the latter authors corrected the parameters for both temperature and pressure (Culberson and Pytkowicz, 1968).

Kanamori

$$PCO_2 = \frac{a_H(TA - (\frac{\Sigma B \times K_B}{a_H + K_B}))}{\alpha \; (K_1 + 2 \frac{K_1 \times K_2}{a_H}}$$

where

$$TA(meq/KgH_2O) = TA(meq/Kg) \times \frac{1000}{1000 - (0.043 + 1.0044S)}$$

$$\Sigma B(meq/KgH_2O) = 0.0121 \times S\,^{\circ}/_{\circ\circ} \times \frac{1000}{1000 - (0.043 + 1.0044S)}$$

S = salinity; t = °C; T = °K = $t + 273.15$

$$K_1 = 1.864498 \times 10^{-5} - 1.66822 \times 10^{-7}T$$
$$- 1.57054 \times 10^{-8}S + 2.61641 \times 10^{-10}T^2$$
$$+ 1.08079 \times 10^{-12}T^3 - 2.556568 \times 10^{-15}T^4$$
$$+ 9.124781 \times 10^{-11}ST$$

$$K_2 - 1.7077053 \times 10^{-7} + 1.4195923 \times 10^{-9}T$$
$$- 1.9141124 \times 10^{-10}S - 2.0317424 \times 10^{-12}T^2$$
$$- 8.521135 \times 10^{-15}T^3 + 1.947788 \times 10^{-17}T^4$$
$$+ 7.2442747 \times 10^{-13}ST$$

$$\begin{aligned}
K_B &= 2.121302 \times 10^{-7} - 1.677761 \times 10^{-9} T \\
&\quad - 1.67712 \times 10^{-10} S + 2.206332 \times 10^{-12} T^2 \\
&\quad + 9.770430 \times 10^{-15} T^3 - 2.10475 \times 10^{-17} T^4 \\
&\quad + 6.8943376 \times 10^{-13} ST
\end{aligned}$$

$$\begin{aligned}
\alpha = {}^{10}\mathrm{arclog}\ [\ & -9.8490 + 2385.73/T \\
& + 0.0152642t - 0.002131S \\
& + 0.00002131\ St + {}^{10}\log 0.9869 \\
& + {}^{10}\log\ (1-S/1000)]
\end{aligned}$$

<u>Mehrbach *et al*.</u>

$$\begin{aligned}
pK_1 &= -13.7201 + 0.031334 \times T + 3235.76/T + 1.300 \times 10^{-5} \times \\
&\quad S \times T - 0.1032 \times S^{1/2}
\end{aligned}$$

$$\begin{aligned}
pK_2 &= 5371.9645 + 1.671221 \times T + 0.22913 \times S + 18.3802 \times \log\ (S) \\
&\quad - 128375.28/T - 2194.3055 \times \log\ (T) - 8.0944 \times 10^{-4} \times S \times T \\
&\quad - 5617.11 \times \log\ (S)/T + 2.136 \times S/T
\end{aligned}$$

Appendix D. Summary of work through 1973. Dynamics of the exchange of CO_2 in arctic and subarctic regions.

Under separate cover.

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