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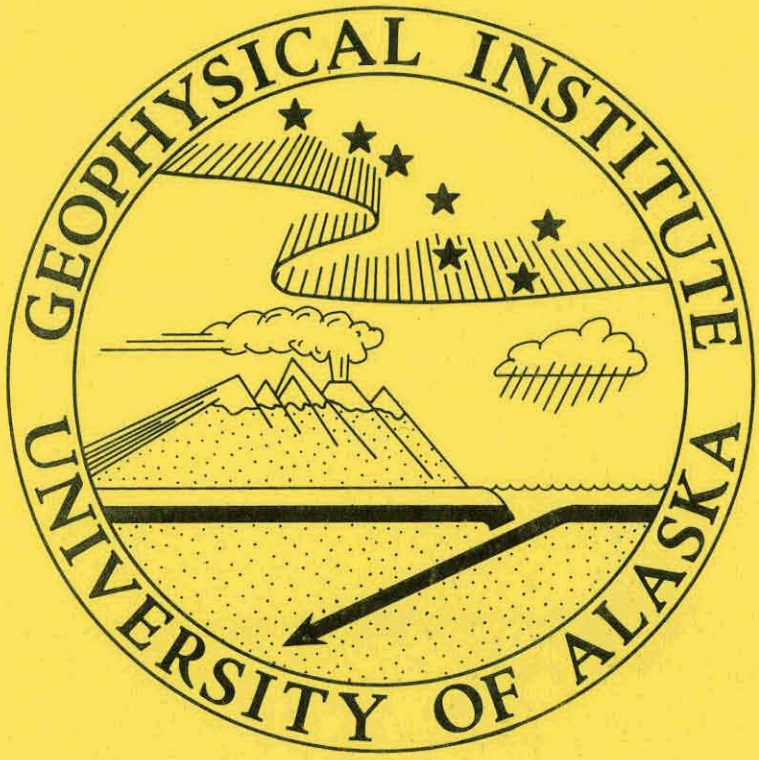

A RENEWAL PROPOSAL

to the

Department of Energy

The Second Year of a Three Year Proposal

(Contract No. AT06-80EV10429)

T. A. Gosink

and

J. J. Kelley

DISCLAIMER

GI80-15a

RESEARCH PROPOSAL SUBMITTED TO THE DEPARTMENT OF ENERGY

SECOND YEAR RENEWAL REQUEST

Carbon Dioxide in Arctic and Subarctic Regions
(Contract 80EV10429)

Geophysical Institute
University of Alaska
Fairbanks, Alaska 99701

March 1981

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TABLE OF CONTENTS

(Second Year Renewal Request)

RESEARCH PROPOSAL TO:	U.S. Department of Energy
INSTITUTION:	Geophysical Institute University of Alaska Fairbanks, Alaska 99701
TITLE:	Carbon Dioxide in Arctic and Subarctic Regions (Contract No. 80EV10429)
PRINCIPAL INVESTIGATOR:	Thomas A. Gosink Research Associate [redacted]
CO-PRINCIPAL INVESTIGATOR:	J. J. Kelley Associate Professor [redacted]
DURATION OF PROJECT:	36 months
INITIAL STARTING DATE:	July 1, 1980
SUM REQUESTED FOR SECOND YEAR:	$215,112

ABSTRACT

A three year research project was presented (first year) that would define the role of the arctic ocean, sea ice, tundra, taiga, high latitude ponds and lakes and polar anthropogenic activity on the carbon dioxide content of the atmosphere. Due to the large physical and geographical differences between the two polar regions, a comparison of CO_2 source and sink strengths of the two areas was proposed. Research opportunities during the first year, particularly those aboard the Swedish icebreaker, YMER, provided additional confirmatory data about the natural source and sink strengths for carbon dioxide in the arctic regions. As a result, the hypothesis that these natural sources and sinks are strong enough to significantly affect global atmospheric carbon dioxide levels is considerably strengthened. Based on the available data we calculate that the whole

arctic region is a net annual sink for about 1.1×10^{15} g of CO_2, or the equivalent of about 5% of the annual anthropogenic input into the atmosphere.

Three objectives are proposed for the second year of this three year proposed research effort. The first objective is to continue the research on the seasonal sources and sinks of CO_2 in the arctic. Particular attention will be paid to the seasonal sea ice zones during the freeze and thaw periods, and the tundra-taiga regions, also during the freeze and thaw periods.

A number of manuscripts have resulted from the work to date. The second objective is to complete the technical reports and manuscripts (9 at this time) which are in various stages of development.

The third objective is to prepare for the comparative Antarctic oceanographic studies which will be carried out in the third year.

INTRODUCTION

The increase in atmospheric carbon dioxide is generally expected to lead to increased global temperatures. It has been increasing at a rate of 0.7 - 1.0 ppm/yr or 1.5 - 3 x 10^9 mT (Keeling et al. 1976). Fossil fuel production has continued to increase also and it is estimated (Bocastaw and Keeling, 1981) that about half (0.505 - 0.548) of the carbon dioxide produced from anthropogenic sources remains in the atmosphere. While global temperatures may increase by 2°C, temperatures north of 60°N latitude may increase by 4°-11°C or higher (Manabe and Weatherald, 1975; Manabe, 1979). Carbon dioxide induced temperature changes will affect several environmental variables including decomposition, the production of organically bound carbon, the thickness and extent of sea ice as well as the transfer of gases across this interface.

Much of the recent discussion on global carbon balance has focused attention on temperate or tropical regions. Less attention has been given to the polar regions, and in particular the Arctic with its ice covered ocean, tundra and taiga ecosystems. The role of vegetation and soils in the world carbon budget is controversial. Furthermore, the effect of climatic change on net accumulation rates in northern ecosystems is poorly known. Fortunately, previous research efforts in the Arctic and subarctic regions, in particular the large research efforts of the AEC/DOE sponsored Cape Thompson Project and the NSF sponsored Tundra Biome project of the International Biological Program provided a substantial data base which is useful in gaining an understanding of the role of the arctic biosphere in the global carbon cycle (Tiezen, 1978; Coyne and Kelley, 1975).

It is unclear whether northern ecosystems will provide negative or positive feedback in the global carbon cycle with the predicted increase in atmospheric carbon dioxide, although most of the evidence indicates a negative

feedback role (Miller, 1980). Estimates of the current rates of carbon accumulation in northern ecosystems vary, but most estimates indicate net accumulation. If the carbon balance of terrestrial systems becomes negative with increased global temperature, increased carbon dioxide released into the atmosphere may have a positive feedback on global temperatures. The carbon dioxide release in northern ecosystems should be further accelerated where permafrost is thawed. Although it is desirable to estimate the current carbon balance of northern ecosystems as precisely as possible, it is equally important to understand the current fluxes of this gas across the land-atmosphere interface on a seasonal basis.

Information on the transfer of CO_2 across the air-sea-ice interface was known in previous years only from short-term observations from occasional oceanographic cruises or ice stations. The DOE carbon dioxide research and assessment program offered an increased opportunity to ascertain the role of the ice covered ocean in the exchange of CO_2. Although, there are still significant data gaps, the preliminary results of this research clearly indicate that the arctic region (taiga, tundra, and ocean) acts as a winter source (Gosink et al. 1976, Kelley, 1968, Gosink and Kelley, 1977) and a summer sink for atmospheric CO_2, resulting in a net annual average sink of 1188×10^{12} g CO_2. This amount is equivalent to 4.6 percent of the annual global anthropogenic input of CO_2 to the troposphere. Presumably, the very low sea water equilibrium partial pressures of CO_2 (with respect to air) in the arctic seas (Table 1; also Appendix 4) during the summer contribute significantly to the draw-down of atmospheric carbon dioxide (Gosink and Kelley, 1979).

In this proposal we describe current progress of our research (See also the interim report to DOE-Appendix 2), our proposed three tasks for the proposed contract renewal period, and a statement of future plans for prospective field research efforts in both polar regions.

Table 1. Seasonal Source-Sink Strengths of the Various Regions in the Arctic

Season	Region	Area (10^6 km^2)	% Area Active	Invasion Evasion Rate	ΔPCO_2 (ppm)	Duration (Months)	Source ($\times 10^{12}$ g CO_2)	Sink ($\times 10^{12}$ g CO_2)
Winter	1. Central Basin	8.4	5-10	1.48 x 10^{12}	10 to 100	9	56 - 1119	-
	2. Barents, Laptev, and Kara Seas	2.5	25	(g km^{-2} mo^{-1} atm^{-1})*	-20 to -40?	8	-	149 - 299
	3. East Siberian, Chukchi and Beaufort Seas	0.9	10	"	20 to 40	6	16 - 32	-
	4. Greenland Sea and Baffin Bay	1.3	25	"	10 to 100?	6	28 - 288	-
	5. Norwegian Sea	0.5	100	"	-25?	6	-	111
	6. Annual Sea Ice	6-7	100	2.8-28.3 x 10^6 (g km^{-2} mo^{-1})	-	6	101 - 1190	?
	7. Tundra and Taiga	1.6	100	See text	-	6	7	-
						Winter Totals	208 - 2636 (avg 1422)	260 - 410 (avg 335)
Summer	1. Central Basin	8.4	10	1.48 x 10^{12} (g km^{-2} mo^{-1} atm^{-1})*	-30 to + 10	3	-37	112
	2. Barents, Laptev and Kara Seas	2.5	100		-90 to -140	4	-	1332 - 2072
	3. East Siberian, Chukchi and Beaufort Seas	0.9	100	"	-40 to -80	3	-	160 - 320
	4. Greenland Sea and Baffin Bay	1.3	50	"	-10 to -40?	3	-	29 - 115
	5. Norwegian Sea	0.5	100	"	-50 to -100	6	-	222 - 444
	6. Sea Ice Melt Ponds	1?	?	See text	-	2	40?	40?
	7. Tundra-Taiga	1.6	78	See text	-	3	179	-
	Freeze-Thaw	1.6	100		-	0.5	0.4 - 56	-
	Plants	1.24	100		-	3	-	213 - 411
	Ponds and Lakes	0.36	100	1.47 x 10 (g km^{-2} mo^{-1} atm^{-1})*	300	3	48	-
						Summer Totals	304 - 360 (avg 332)	2108 - 3511 (avg 2811)
Annual	1. Anthropogenic			See text			1 - 7	
						Annual Totals	513 - 3403 (avg 1958)	2368 - 3924 (avg 3146)

*This is the same as 0.078 nmole cm^{-2} atm^{-1} min^{-1}

Annual Net Sink 1188 x 10^{12} g CO_2

ACCOMPLISHMENTS (FIRST YEAR)

YMER-80: Based on technical presentations in Sweden made by each of the principle investigators and a proposal submitted to the Swedish government YMER-80 organizing committee, we were invited to particiapte on both legs of the YMER-80 expedition to the eastern Arctic Ocean. A cruise report is given in Appendix 1. As a result of this cruise, earlier observations (Kelley, 1970) of the extensive low partial pressures of CO_2 (ca. 180-220 ppm) in surface sea waters were confirmed. It was also possible to show that these very low partial pressures had a much greater areal extent, thus affording a greater sea surface area for the exchange of atmospheric CO_2. It was also possible to estimate how deep these very low partial pressures penetrate (ca. 20 m) and the depth of which the PCO_2 equals the average partial pressure (ca. 130 m) in the late summer northern atmosphere. It was also possible to estimate the invasion rate of CO_2 across these cold surface waters (0.078 mmoles atm^{-1} cm^{-2} min^{-1}) which allowed us to determine that the Barents - Kara - Laptev - Norwegian Sea area acts as a strong summer sink absorbing about 2×10^{15} g CO_2.

Manuscripts: A backlog of publications resulted because we were waiting for confirming data (e.g. YMER-80 data). We now have articles in various stages of preparation to be submitted for publication (Appendices 3-7).

Techniques and Instrumentation: We have developed a new technique (Gosink and Kelley, 1981) tested on the YMER-80 expedition, whereby we can retrieve reasonably accurate data for CO_2 in sea water from accurate measurements of pH, salinity and temperature (Appendix 5 and 6). The preliminary results indicate that this method yields data that closely follow those obtained by gas chromatography. If this technique proves to be a reliable one, the data

base for CO_2 in oceanic surface waters and at depth could be considerably expended.

There have been long delays in acquiring urgently needed analytical instruments primarily as a result of late receipt of FY-1981 funds for this research from DOE. All of the instrumentation has only recently been acquired (due to long manufacturer lead times) but will be calibrated and ready for field testing in April, 1981.

Bering, Chukchi, East Siberian Seas: We expect to complete by the end of the first year of this study the first of four cruises to the area of the Bering, Chukchi, and East Siberian Seas. These cruises are scheduled aboard the R/V Alpha Helix (U of Alaska operated UNOLS vessel). These cruises will enable us to obtain information on the CO_2 partial pressure differences between the ocean and atmosphere during two critical periods of the year, namely around the time of the spring plankton bloom at the seasonal ice zone, and during freeze-up in the fall.

Tundra-Taiga Regions: Previous information on the evolution of CO_2 from frozen soils, especially during the period of change of phase (thaw or freeze-up) (Coyne and Kelley, 1971, Gosink and Kelley, 1977, and Gosink and Kelley, 1979) was obtained primarily by occasional in situ sampling at sites well above the Arctic Circle and laboratory experiments. Depending on the soil type, drainage conditions, depth of thaw, etc. the evasion of CO_2 to the atmosphere could be substantial. Laboratory experiments with different tundra and taiga soil types (Coyne and Kelley, 1971) indicates that release of CO_2 from soil during the period of change of phase may account for 0.4 -56 x 10^{12}g of CO_2 to the atmosphere. The objective of our springtime research is to complete a series of CO_2 observations in situ

on a transect from about 64°N to 70°N latitude which will traverse a north-south section of the northern tundra and taiga region including a wide variety of soil types. The first transect will occur during the period of phase change (thaw) which will allow us to test the validity of the data obtained from laboratory experiments as they relate to actual field measurements and to estimate the CO_2 flux from the soil to the atmosphere-associated with the northward march of the thaw line. This period of change of phase also is an important one to the various ecosystems encountered along this extensive north-south transect. The authors have also consulted with Dr. Philip C. Miller (San Diego State University, San Diego, CA) in order to bring about a mutually beneficial liaison for both DOE related projects. Dr. Miller will attempt to coordinate some of his field studies with ours whenever practical. The first transect is scheduled during a six day period at the end of April. During the period of phase as deduced from previous observations at 70°N latitude in Alaska, it is noted that subnivean CO_2 increases greatly (more than 8 times the atmospheric concentration) several times (Coyne and Kelley, 1973) during this period. This phenomena is not observed in the data from other temperate or tropical areas. It is suspected that this additional evolution of CO_2 may be due to fungal spore formation and mycelial growth which is enhanced during periods of high relative humidity under the snow and associated with the evolution of CO_2.

PROPOSED RESEARCH (SECOND YEAR)

Three objectives are proposed for the second year of this three year proposed research effort. The first objective is to continue the research on the seasonal sources and sinks of carbon dioxide in the arctic regions. Particular attention will be paid to the seasonal sea ice zone during the thaw and refreezing period, and the tundra-taiga regions, also during the freeze and thaw periods.

The University of Alaska Ship Committee has been apprised of our need for two cruises to the Bering/Chukchi Sea ice edge area. One is scheduled for the fall 1981; the other for the late spring 1982. In addition to obtaining sea surface water partial pressure data, as well as vertical PCO_2 profiles, attention will also be concentrated on the ice edge boundary particular during the spring.

The Bering Sea ice edge is an air-sea-ice frontal system that offers an opportunity to study the coupling of meteorological, physical and oceanographic processes in an area where events are concentrated in time and space and can be expected to occur each year within a more or less predictable time period (e.g. spring). After reaching its most southerly extent, this frontal ice edge system will move north eventually exposing the surface waters of the marginal seas of the Arctic Ocean (e.g. Chukchi, East Siberian). Whenever possible we will use cruise periods where other on-board projects will provide mutually beneficial data (hydrographic plankton, primary productivity data etc.).

The sea ice edge is a very heterogeneous region consisting of several types of sea ice of variable thickness and extent. Melt water may serve to stabilize the water column with the possibility of phytoplankton bloom production associated with an uptake of CO_2 from the water column. Any

upwelling phenomena associated with the ice edge will also serve to promote a phytoplankton bloom through nutrient enrichment of the photic zone. Storms will also modify the composition of the marginal ice zone and aid in the formation of plankton blooms and the possible release of alge from the ice with the net effect that CO_2 in the water and presumably in the near surface atmosphere will be affected. Data obtained from spring and fall cruises will allow us to more confidently assess the effect of these ice covered seas on the atmospheric CO_2 balance.

We anticipate some foreign participation on these cruises. Contact and letters of interest have been sent to Japanese and Swedish colleagues who have provided us with excellent logistic support in the Arctic for our research (Hakuho Maru 1978; YMER-1980) in the recent past.

A number of manuscripts have resulted from the work to date. The second objective, therefore, is to complete these technical reports and manuscripts which are in various stages of development. Draft manuscripts scheduled for submission to scientific journals are appended (Appendices 3-6). Manuscripts in preparation are listed by title in Appendix 7.

The third objective is to prepare for the comparative Antarctic oceanographic studies which will be carried out during the third year of this study. We anticipate an invitation to participate in the cruise of the Hakuho Maru (Japan) to Antarctica (ca. 5 months). We have already begun an analysis of previously collected pH, salinity and temperature data from past Japanese research vessels cruising in Antarctic waters. Although we cannot ascertain at this time the quality of these data, application of our pH method (Gosink and Kelley, 1981) does allow us to assess sea surface water CO_2 variability.

We have also been informed that a second cruise of the Swedish icebreaker YMER is under consideration by the Swedish government. It is expected that we will be invited to take part. Another YMER cruise would be especially attractive if it were scheduled to make a deep penetration into the summer pack ice as well as to revisit the Norwegian, Barents, and Kara Seas. Hoped for Russian participation on that cruise would assure that we could sample new areas to the east, namely the Kara and Laptev Seas.

Priority would be given to the Hakuho Maru cruise to Antarctica as much less is known about CO_2 in Antarctic waters, and ships of opportunity for this type of research are difficult to find. Since long lead-times are usually associated with preparations for these cruises it is necessary for us to prepare as early as possible. At this stage, preparations will entail primarily extensive liaison with our prospective hosts with regard to the overall scientific mission, interface of equipment, and potential scheduling problems so that no interference results with our second year research objectives.

Finally, there already exists a sufficient amount of information to warrant the convening of a small working group to synthesize existing information on the polar interactions among the atmosphere, land, sea, snow and ice in order to evaluate the hypothesis that with CO_2 induced climatic change the polar regions, particularly the Arctic, will become stronger carbon sinks than they are currently and that they will function significantly to damp out the global use in atmosphere CO_2 and temperature a prospectus for a workshop to be held in early 1982 was jointly drafted (Kelley, UA and Miller, SDSU) and submitted to the Department of Energy (See Appendix 8).

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PERSONAL DATA

NAME: Thomas A. Gosink

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EDUCATION:

B. A. Miami University, Oxford, Ohio, in Chemistry, 1959.
M. S. Massachusetts Institute of Technology, in Chemistry, 1962.
Ph.D. Oregon State University, in Chemistry, 1965.

POSITIONS HELD AND EXPERIENCE:

Research Associate, Geophysical Institute, University of Alaska, 1978-present.
Marine Chemist, Institute of Marine Science, University of Alaska, Fairbanks, 1975-Present.
Completed course in Air Chemistry, ODU-NASA, Spring 1973.
ASEE-NASA Summer Faculty Fellowship, Remote Sensing of the Environment, NASA, 1969.
Completed the Atomic Energy Commission short course in handling and measuring radioactive materials in 1968. (plus undergraduate course).
Visiting Associate Professor, University of Southampton, England, Fall 1974.
Associate Professor, temporary, Institute of Marine Science, University of Alaska, Fairbanks, 1973-1974.
Associate Professor, Old Dominion University, 1969-1974. (tenured)
NSF Summer Faculty Research Fellow, Ring Chain Tautomers, University of New Hampshire, 1971.
Taught courses in chemical oceanography and undergraduate and graduate-level organic chemistry, as well as introductory science.
Assistant Professor, Old Dominion University, 1965-1968.
Research Assistant, Oil Oxidation Inhibitors, Shell Oil Co., Summer of 1961.
Research Assistant, Organometallics, Dow Chemical Co., Summer of 1960.

PROFESSIONAL ORGANIZATIONS:

American Chemical Society, Past Section President
The Society of the Sigma Xi
American Association for the Advancement of Science
Limnology and Oceanography Society
American Geophysical Union

AWARDS AND/OR HONORS:

Two undergraduate awards
Stauffer Chemical Company Research Fellowship, 1964-1965

PUBLICATIONS:

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Gosink, T. A., Preparation of Triphenyllead Acetate (for use in antifoulant paints). Seaguard Finishes Company, Inc., 1969.

IN PREPARATION:

The globally significant sources and sinks of carbon dioxide in the Arctic.

Annual sea ice. An air-sea gas exchange moderator.

Observations and calculations of PCO_2 in sea waters. A new approach.

Arctic tropospheric carbon dioxide and low altitude aircraft sampling.

Calculations of the carbon dioxide-carbonate system from a single parameter-insitu pH.

An explanation for the extremely low partial pressure of carbon dioxide in surface waters of the Barentz, Kara and Greenland Seas.

Properties of sea ice and the natural sources and sinks of carbon dioxide in the Arctic.

Studies of trace gases in the Arctic and Subarctic.

February 1981

Biographical Sketch of

JOHN J. KELLEY

[redacted]

[redacted]

Education:
B.S. Pennsylvania State University, Geophysics Geochemistry, 1955-1958
University of Washington, Graduate Student and Scientist, Atmospheric Sciences, 1962-1968
University of Alaska, Fairbanks, Graduate Student, Ph.D. program, and professional staff member, 1968-1970
Ph.D. University of Nagoya, Nagoya, Japan, Chemical Oceanography, 1974

Member:
American Geophysical Union
Arctic Institute of North America (Fellow and Governor)
Explorers Club of New York

Professional Experience:
1959-1968, Principal Scientist, Chemical Micrometeorology Program, University of Washington
1969-1970, Invited participant in research design of Tundra Biome, International Biological Programme (USIBP)
1969-1975, Co-Principal Investigator, Tundra Biome, USIBP
1969-1973, Co-Principal Investigator, USN-ONR Contract, Carbon Dioxide in Polar Seas
1971-1972, Co-Principal Investigator, National Science Foundation Grant, Bering Sea Oceanography
1973-1974, Co-Principal Investigator, NSF-NCAR Experiment, Tropical Atmospheric Carbon Dioxide and Water Vapor
1973, Invited participant, International Bering Sea Oceanography Program, IDOE (NSF)
1974-1976, Principal Investigator, USN-ONR (Arctic Branch), AIDJEX (ALIX) Experiment
1974, Assistant Professor, Institute of Marine Science, University of Alaska, Fairbanks
1974-1976, Program Manager for Meteorology and Oceanography, Division of Polar Programs, NSF (Professional leave of absence, University of Alaska)
1976-1977, Liaison/Research Management Officer, Governor's Office, State of Alaska, at NOAA Outer Continental Shelf Environmental Assessment Program (OCSEAP), Boulder, Colorado (Sabbatical leave, University of Alaska)
1977-1980, Director, Naval Arctic Research Laboratory, Barrow, Alaska, and Associate Professor, University of Alaska, Fairbanks, Alaska
1980-Present, Associate Professor, Institute of Marine Science, University of Alaska, Fairbanks

Inventions: 1973, J. J. Kelley and G. Mimken. Logic Controlled solid-state manifold sampling system for liquids and gases. Invention Disclosure submitted to the U.S. Patent Office.

Publications:

Kelley, J. J., Jr. and E. LaChapelle. 1966. Atmospheric carbon dioxide variations on Mt. Olympus, Washington. J. Geophys. Res. 71(8):2173-2174.

Kelley, J. J., Jr. and D. F. Weaver. 1966. Carbon dioxide and ozone in the arctic atmosphere. Proc., 16th Alaska Science Conf. 151-167 pp.

Gudiksen, P. H., P. W. Hildebrandt and J. J. Kelley, Jr. 1966. Comparison of an electrochemical and a colorimetric determination of ozone. J. Geophys. Res. 71(2):5221-5223.

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Kelley, J. J., Jr., D. Weaver, and B. Smith. 1968. Variation of carbon dioxide under snow in the Arctic. Ecology 49(2):358-361.

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Johnson, P. L. and J. J. Kelley, Jr. 1970. Dynamics of carbon dioxide in the arctic biosphere. Ecology 51(1):73-80.

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Kelley, J. J. and D. W. Hood. 1971. Carbon dioxide in the surface water of the ice-covered Bering Sea. Nature 229(5279:37-39.

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Kelley, J. J. 1973. Surface ozone in the arctic atmosphere. In: Pure and Applied Geophysics, 106-108:1106-1115. Birkhauser Verlag, Basel (Switzerland).

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Gordon, L. I., P. K. Park, J. J. Kelley and D. W. Hood. 1973. Carbon dioxide partial pressure in North Pacific surface waters. 2. General late summer distribution. Marine chemistry 1:191-198.

Kelley, J. J. 1974. On the role of calibration integrity in atmospheric trace gas monitoring. Proc., lleme Colloque International sur les Atmospheres Polluees, IRCHA, Paris, France.

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Coyne, P. I. and J. J. Kelley. 1978. Meteorological Assessment of CO_2 exchange over an Alaskan Arctic Tundra (pp. 299-313, Chap. 12) in Vegetation and Production Ecology of an Alaskan Arctic Tundra. Ed. by L. L. Tiezen. Springer-Verlag, New York. 668 pp.

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T. A. Gosink and J. J. Kelley. 1979. Carbon Monoxide Evolution from Arctic surfaces during spring thaw. J. Geophys. Res. J. Geophys. Res. 84:C11, 7041.

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Technical Reports

Kelley, J. J., D. T. Bailey, and B. J. Lieske. 1964. Radiative energy exchange over arctic land and sea. Scientific Report No. 5, Dept. of Atmospheric Sciences, University of Washington. pp. 125.

Kelley, J. J., Jr. 1966. An analysis of carbon dioxide in the arctic atmosphere, Part 2. Scientific Report No. 7, Department of Atmospheric Sciences, University of Washington. pp. 133.

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Kelley, J. J., D. W. Hood and L. L. Longerich. 1973. Oceanography of the Bering Sea. Phase 2. Turbulent upwelling and water mass identification in the vicinity of Samalga Pass, eastern Aleutian Islands. Final Progress Report to the National Science Foundation, Inst. Marine Science, University of Alaska, Fairbanks, Vol. 2, Part 1. pp. 115.

Kelley, J. J., D. W. Hood, J. J. Georing, R. Barsdate, M. Nebert, L. Longerich, J. Groves, and C. Patton. 2973. Oceanography of the Bering Sea. Phase 2. Turbulent upwelling and water mass identification in the vicinity of Samalga Pass, eastern Aleutian Islands. Final Report to the National Science Foundation. Vol. 2, Part 2 (Methods and Data), Inst. Marine Science, University of Alaska, Fairbanks. pp. 263.

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Kelley, J. J. and G. A. Laursen. 1979. Investigation of the Occurrence and Behavior Patterns of Whales in the Vicinity of the Beaufort Sea Lease Area. Report to the Bureau of Land Management. 48 pp.

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Recent Publications:

Prentki, R. T., M. C. Miller, R. J. Barsdate, V. Alexander, J. Kelley, and P. Coyne. 1980. pp. 76-178. *In Limnology of Tundra Ponds*. Ed. by John E. Hobbie, Pub. by Dowden, Hutchinson and Ross, Inc., Pa. 514 pp.

Kelley, J. J. and G. A. Laursen. 1981. A Short History of the Naval Arctic Research Laboratory. *In Proceedings of the First International Symposium on Arctic Mycology*, Univ. of Washington Press (in press).

Recent Reports:

Kelley, J. J. 1981. Factors to be considered for the evaluation of a multipurpose arctic research laboratory on the north coast of Alaska. Report to the President, University of Alaska. Institute of Marine Science. 41 pp.

Gosink, T. A. and J. J. Kelley. 1981. Atmospheric Chemistry. A plan for a research-study program. Report to the Director of the Geophysical Institute. Geophysical Institute. 24 pp.

Kelley, J. J. 1981. Drift of Ice Island T-3 (Fletcher's Ice Island) in the Arctic Ocean. Report to NASA, Goddard Space Flight Center. 4 pp.

Kelley, J. J. 1981. Prospectus for the Science Advisory Committee of the Alaska Eskimo Whaling Commission. Institute of Marine Science. 18 pp.

ATTACHMENT A

Research Activities:

A. Gases in Sea Ice (Through Institute of Marine Science)
Agency - U.S. Navy - ONR Code 461
Amount: $85K FY-78
CO-P.I. Dr. T. A. Gosink

B. Gases in Sea Ice (Through Institute of Marine Science)
Agency - U.S. Navy - ONR Code 461 and
Department of Energy
Amount: $100K FY-79

C. Marginal Ice Zone Marine Experiment (MIZMEX) - (Through NARL)
Agency: U.S. Navy, ONR Code 461
Amount: $40.5K (concluded September 1978)
CO-P.I. Arnold Hanson

D. An Investigation of Whales in Beaufort Sea Lease Areas (Through NARL)
Agency: Bureau of Land Management
Amount: $150K FY-78

E. An Investigation of Whales in Beaufort Sea Lease Areas (Through NARL)
Agency: Bureau of Land Management
Amount: $650K FY-79

F. Training Program for Native Youths
Agency: Alaska Federation of Natives
Amount: $148K FY-79

G. An investigation of whales in Beaufort Sea Lease Areas (through the NARL)
Agency: Bureau of Land Management
Amount: $400,000 FY-80.

H. Trace Gases In The Arctic Environment: Air-Sea-Land Distribution And Exchange (thorough Institute of Marine Science).
Agency: National Science Foundation
Amount: $41,513 (first year FY-80).
Co-P.I. Dr. T. A. Gosink (Geophysical Institute).

I. Carbon Dioxide in Arctic and Subarctic Regions (through Geophysical Institute).
Agency: Department of Engergy
Amount: $196,912 (first year FY-80). Total requested for three years $557,000).
P.I. Dr. T. A. Gosink
Co-P.I. Dr. J. J. Kelley

ATTACHMENT A (cont'd)

J. Establishment of a Science Advisory Committee for the Alaska Eskimo Whaling Commission
Agency: AEWC, Barrow, Alaska
Amount: $22,000 (1980/81)
P.I.: Dr. J. J. Kelley

ATTACHMENT B

Informal or Unscheduled Instructional Activities:

In addition to the presentation of informal seminars at the NARL, the following activities have been pursued:

Editor - Newsletter - NARL NEWS.

Instructional television series on Environmental Sciences sponsored by North Slope Borough School District. The series is designed for the senior high school young adult level of education is taped and sent to nine Borough villages.

Cooperation with Alaskan Eskimo Whaling Commission and North Slope Borough School District to train students in various scientific and technical skills: Funding through AFN.

Consultation with the North Slope Borough School District on the development of a science curriculum for the Borough.

Conduct adult education short courses in various scientific subjects for Inupiat residents of the North Slope. Arrangements are made for in-house and outside experts to teach these courses.

Conduct appropriate technology seminars for the NARL staff, community teachers, and leaders in association with outside consultants.

Provide advice on various environmental science topics to North Slope Borough leaders.

Review proposals and scientific journal manuscripts for various funding agencies and professional journals.

Develope and Edit a quarterly publication: Institute of Marine Science Notes (1980/81).

Participate in the development of science training program for students living in remote villages (through WAMI Program). Courses will be taught on-campus (summer) with visits to the remote villages in the winter (1980/81).

ATTACHMENT C

External Service Activities:

In addition to actively participating in community planning and development activities (Alaska Eskimo Whaling Commission, N.S.B. planning conferences), I have been invited to participate in the following conferences during the period 1978-79:

1. Presented seminar on trace gases and exchange processes at the Annual NOAA/ERL-GMCC Conference at Hilo, Hawaii, January 1978.

2. Consultant on siting criteria for atmospheric physics and chemistry. UN/WMO, Geneva, Switzerland, April 1978.

3. Presented seminar on trace gases at the University of Mainz (Invited by Professor Christian Junge) May 1978.

4. Presented seminar on Carbon Dioxide Air-Sea-Land Transfer at the Institute of Meteorology, University of Stockholm October 1978.

5. Presented Seminar on trace gases and polar climate at the Meteorology Department, University of Uppsala, Sweden October 1978.

6. Invited to participate in Eastern Arctic Marine Sciences Conference (Chemistry Section) Technical University of Denmark, Copenhagen (Lyngby), January 1979.

7. Invited to participate in planning conference for Seasonal Ice Zone research. U.S. Postgraduate School, Monterey, California (February 1979).

8. Produced planning document for proposed Swedish (multidisciplinary) Icebreaker YMER-80 cruise to East Greenland and Svalbard in 1980.

9. Presented two papers at the 11th International Polar Meeting, Berlin, October 1978.

10. Presented invited paper at the International Symposium on Integrated Monitoring of Environmental Pollution, Riga, USSR, December 12-15, 1978.

11. Invited to participate at an expert meeting on producing an integrated multimedia monitoring/research plan at the UN/WMO, Geneva, September 1-5, 1980.

ATTACHMENT C (cont'd)

12. Panel Member: Interagency Committee on Ocean Pollution Research and Monitoring (provides review and future research recommendations for all U.S. Outer Continental research efforts) 7/26, 27, 28, 1980; 8/25, 26, 27, 1980; 9/22, 23, 24, 1980.

13. Serve on University of Alaska Telecommunications Committee (1980/81).

14. Serve as Chairman of the Alaska Eskimo Whaling Commission Science Advisory Committee (1980/81).

15. Serve as member of the President's UAF Arctic Research Laboratory Task Force (1980/81).

16. Invited to present two papers at the 10th Annual Arctic Workshop, INSTAAR, Boulder, Colorado, March 11-14, 1981.

17. Serve as IMS delegate to the 32nd Alaska Science Conference Committee.

In addition to the above, I review numerous proposals in marine sciences and meteorology for the National Science Foundation and Department of Energy.

I have also been appointed to serve on the Alaska State Review Panel for the Appropriate Technology Small Grants Program.

Budget

Salaries		
Co-Principal Investigator, T. Gosink, Research Assoc. in Geochemistry 6 mo. @ $4725	28,350	
Co-Principal Investigator, J. J. Kelley, Assoc. Prof. of Marine Science, 3 mo. @ $4326	12,978	
Laboratory/Field Technician, 12 mo. @ $2016	24,192	
Data Processing Asst., 3/4 mo. @ $1620	1,215	
Subtotal	66,735	
7.5% salary increment - FY 82	5,005	
Subtotal	71,740	
Reserve for annual leave 11%	7,891	
Holiday and sick leave 9.5%	6,815	
Total Salaries		86,446
Staff Benefits		
Hospitalization, Social Security, Retirement, 16% of total salaries		13,831
Travel		
(Domestic:)		
6 one-way trips, Fairbanks-Seward @$.35/mi.	1,260	
6 one-way trips, Fairbanks-Dutch Harbor including 20 days subsistence @$74/day	3,610	
2 round trips, Fairbanks to a National meeting, including 10 days @ $65/day	2,460	
8 round trips, Fairbanks-Barrow, including 24 days subsistence @$100/day	4,240	
2 round trips, Fairbanks-Denver-San Diego, including 10 days @ $65/day	2,504	
Subsistence for haul road travel, 30 days @$67	2,010	
(Foreign:)		
2 round trips, Fairbanks-Stockholm, including 6 days subsistence @ $100/day	3,872	
2 round trips, Fairbanks-Tokyo, including 6 days subsistence @ $100/day	3,020	
		22,976
Supplies		
Miscellaneous expendable materials & supplies		2,000
Services		
1200 miles vehicle use, haul road, $.50/mi.	600	
Shipping	3,000	
Report preparation and page charges	1,800	
Communications	700	
Computer costs	300	
		6,400
Logistics		
4 days cost share for 25 days at $6000 per day on R/V Alpha Helix		24,000
Total Direct Costs		155,653
Overhead - 38.2% of total direct costs		59,459
Total Budget		215,112

EXPLANATION OF THE BUDGET

A. Salaries and Wages: The Principal Investigator named in the proposal will be responsible for the overall management of this research. Salary for a total of nine man months is requested. Salary for a full-time technician is also requested. The investigators are the same as those supported under the DOE proposal for 1980-81.

It should be noted that due to the high cost of living in Alaska, salaries are considerably higher than the national average for any given position. For instance, the federal government recognizes this fact by paying a 25% taxfree cost of living allowance to its employees in Alaska; on similar grounds, NSF has agreed to raise the salary limitation for Alaskan investigators to $59,375 from the mandated $47,500 per annum.

B. Staff Benefits are provided at the current University of Alaska rate.

C. Travel requests are made for the transport of investigators to and from the field research sites, and to work with collaborators (Peterson, NOAA, Denver, and Miller, San Diego). Funds are requested at this time for one national meeting for each Principal Investigator.

Foreign travel is to transport the Principal Investigators to discuss and consult on data collected on the YMER-80 cruise, and to plan and join the Japanese Antarctic Research Expedition on the R/V Hakuho Maru.

D. Supplies refer to purchase of gases, glassware, mechanical and electronic parts not normally designated as permanent equipment. These are consumable items.

E. Other items (services) are divided into several categories. Report preparation includes costs involved with reproduction and journal page charges if applicable. Communication charges refer to telephone charges. Shop support is provided for electronic and mechanical repair and modifications.

Shipping charges for the transport of equipment are provided. This level of funding is conservatively estimated from charges normally inciurred during past years of operations.

F. Logistics are a direct charge item in line with past expenditures. The various categories are listed.

G. Indirect Costs: This item is listed in accordance with the current University of Alaska rate.

APPENDIX

The following appendices represent results of research carried out under DOE Contract 80EV10429 for fiscal year 1980. Except for internal reports, all manuscripts in this appendix are to be considered in preliminary or draft form. They are appended for the convenience of the DOE and its need for timely reporting of research products. Although, the manuscripts will undergo extensive editing, it is unlikely that the reporting of research results will change substantially. It is requested that the appended manuscripts be treated as internal documents and that republication or reproduction for public dissenumation not be done without the permission of the authors.

DRAFT

CRUISE REPORT, YMER-80 LEG I & II, July-September 1980

Nitrous oxide data are presented in tabular form
Reduced, corrected cruise data for PCO_2, temperature and salinity
are presented in graph form.

Activities

Nitrous oxide determination of surface waters at 15 stations on 3 transects were completed during Leg I. A few comparison measurements were also made during Leg II.

Partial pressures of carbon dioxide in the air and in surface waters were measured over the entire area covered by Leg II.

Partial pressures of CO_2 in surface waters for Leg I, were calculated from pH data from that period, and verified during Leg II.

Routine observations of the in situ pH temperature, and salinity of surface waters were recorded during both Leg I and Leg II.

Methods

pH and temperature measurements were made with a Corning Model 135 pH meter with a combination reference electrode. NBS standardized buffer solutions (4.01, 7.00, 9.12) were used for instrument calibration.

Salinity measurements were made with #4403 Electromark Digital Analyzer. Standardized sea water was used for calibration.

Nitrous oxide measurements were made on a Perkin Elmer Model 3920 gas chromatograph with electron capture device (ECD), using standardized ECD methods with a 2 m. Porapak Q column A 1 ppm Matheson calibrated gas standard was utilized. Samples were collected using the vacuum expansion methods of Herr and Barger (1978).

YMER-80 LEG I NITROUS OXIDE DATA

Date	Lat. (^{o}N)	Long. (^{o}E)	Depth (m)	nmoles N_2O/ℓ
3 August	79.5	40	10	22.4
			20	22.2
			40	17.5
			50	22.2
			100	18.0
			125	20.0
			150	20.9
			200	19.6
			275	21.2
3 August	79.7	44	10	21.3
			20	18.2
			30	19.4
			40	18.8
			50	16.7
			75	16
			100	16
			150	17
3 August	79.7	46	10	19.4
			20	19.3
			30	17.6
			40	17.1
			50	20
			75	15.6
			100	18.3
			125	18.5
			150	19.7
			200	17.5
			250	17.9
4 August	75.5	22	10	22.4
			20	22.1
			30	20.3
			40	22.9
			50	26.2
			65	23.6

Carbon dioxide measurements were made with a Perkin Elmer Model 3920 flame ionization detector (F 10) after methanization of the carbon dioxide. A 4' carbosieve B column with appropriate valving was used for restoring the CO_2. A Keeling international carbon dioxide standard (287 ppm) was used for calibration. Sample collection was achieved with a continuous countercurrent equilibrator as described by Gosink and Kelley (1978).

Results

The entire area covered by both legs I and II are markedly undersaturated with CO_2 in the water. Less so than any open waters of the Barents and Kara Seas, but still more than any open ocean areas at lower latitude. The undersaturation extends to a depth of about 75 meters, varies from 50 to 100 m and occasionally goes to a depth as great as 200 m. The only exception was the region in the vicinity of Nord, Greenland, 80'N 2.5'E.

Atmospheric carbon dioxide also decreased as one proceeded north, particularly in the vicinity of Greenland, and when the wind originated from maritime areas.

Late season carbon dioxide concentrations in the sea water seem to be essentially the same as the early season.

pH data are presented in only the broadest outlines. In general, the higher the pH the lower the PCO_2. The pH varied around $8.17 \pm .03$ for most of the cruise rising to $8.37 \pm .02$ during the deepest penetrations of the ice pack. There was a period between 27 and 31 July, during the trip from heavy ice NW of Franz Josefs Land to about 50% open water southwest of Franz Josefs Land when the pH steadily rose from 8.2 to 8.5.

Unfortunately there was some reference electrode problems at that time, but two replacement electrodes provided similar high values. This high pH would agree with the extremely low partial pressures of CO_2 reported by Kelley over a decade ago for the Barents and Kara Seas.

Surface (1-20 m) nitrous oxide measurements for 35 observations is 16.8 $\pm$ 4.2 nmoles N_2O/L. The range was from 7.4 to 22.4 nmoles N_2O/L. Average temperature and salinity were -1.5°C and 31‰. Intermediate depth waters ranged from 13-30 nmoles N2OL and deep waters between 12 an 16 n moles N_2O/L. Two stations near 79.3'N 36'E had unusually high values, up to ca. 50+nmoles N2O/L.

Discussion

The normal range of partial pressure differences between the atmosphere and ocean CO_2 is on the order of $\pm$30 ppm, usually on the negative side. Kelley has already reported exceptionally low (-90 to -190 ppm) for the entire Barents and Kara Seas surface. Confirmation of these values was successfully achieved during Leg II. The probable cause of the extremely low PCO_2 values is cooling of warmer N. Alantic waters rather than biological activity. A 10°C temperature drop in a body of water lowers its PCO_2 by about 140 ppm. If the water was already normally (biologically caused) low by 20-40 ppm, the net result would be to produce the extreme (-160 ppm) lows observed.

The arctic seas appear to be a major sink for atmospheric carbon dioxide during the brief summer period. As a preliminary estimate 0.3×10^{16} g of CO_2 may be absorbed in the region alone, and may represent the apparent missing sink for CO_2.

Nitrous oxide concentrations are about normal for surface and deeper waters. The principal difference is again due to temperature differences. These polar ocean surface waters are not highly saturated with N_2O as at lower latitude (110-180%) but almost exactly saturated ($\pm$ 30%) with respect to air at 330 ppb. Nitrous oxide is a ubiquitously produced trace gas which influences stratospheric chemistry.

References

YMER-80 LEG I NITROUS OXIDE DATA

Date	Lat. (^{o}N)	Long. (^{o}E)	Depth (m)	nmoles N_2O/ℓ	Sal.
13 July	81.0	23.0	0	7.4	
			15	20.3	
			22	21.1	
14 July	81.4	23.0	35	15.4	
			55	16.0	
			250	13.9	
			500	14.2	
			000	18.9	
			1500	14.4	
			2000	15.8	
			2500	15.8	
			3230	15.0	
17 July	82.2	25.0	all surface	16.3	
			samples	14.5	
			taken	13.3	
			from	14.3	
			around	15.2	
			melting	14.3	
			sea ice	13.4	
				15.2	
				13.8	
				14.8	
22 July	81.5	49.9	10	13.7	
			20	12.8	
			40	14	
			50	13.4	
			75	13.5	
			100	13.3	
29 July	80	38	all	20.7	29.4
			surface	21.4	30.2
			samples	17.9	32.4
			taken	18.4	31.4
			from	17.9	31.7
			around	21.8	31.4
			melting	19.9	27.9
			sea	17.9	26
			ice	17.7	28.5
				16.9	25.5

YMER-80 LEG I NITROUS OXIDE DATA

Date	Lat. (^{o}N)	Long. (^{o}E)	Depth (m)	nmoles N_2O/ℓ
4 August	75	20	10	16.1
			20	-
			30	19.7
			40	20.0
			50	19.3
			75	22.9
			100	24.0
			125	23.5
			150	21.0
			170	22.6
5 August	74	23	10	14.3
			20	16.7
			30	16.1
			40	17.8
			50	18.5
			75	17.8
			100	20.2
			150	19.9
			190	20.9
			250	19.3
			440	20.0
5 August	73	20	10	13.9
			20	18.0
			30	18.2
			40	14.2
			50	21.1
			150	15.9
			200	22.1
			300	21.7
			400	21.4

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KELLEY,J.J. 1970. "Carbon dioxide in the surface water of the north Atlantic and the Barents and Kara Sea." Limnology and Oceanography. 15:80-87.

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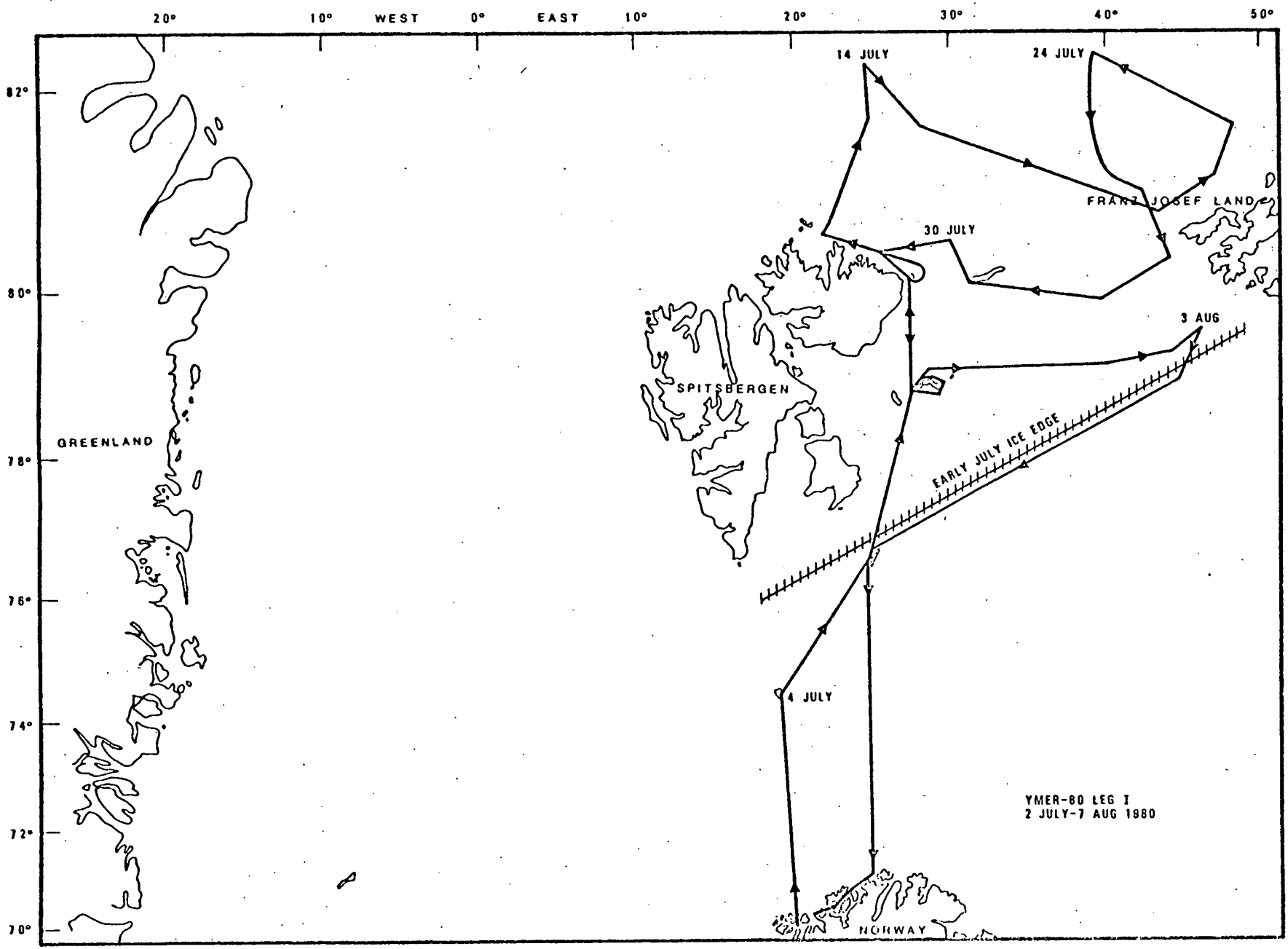
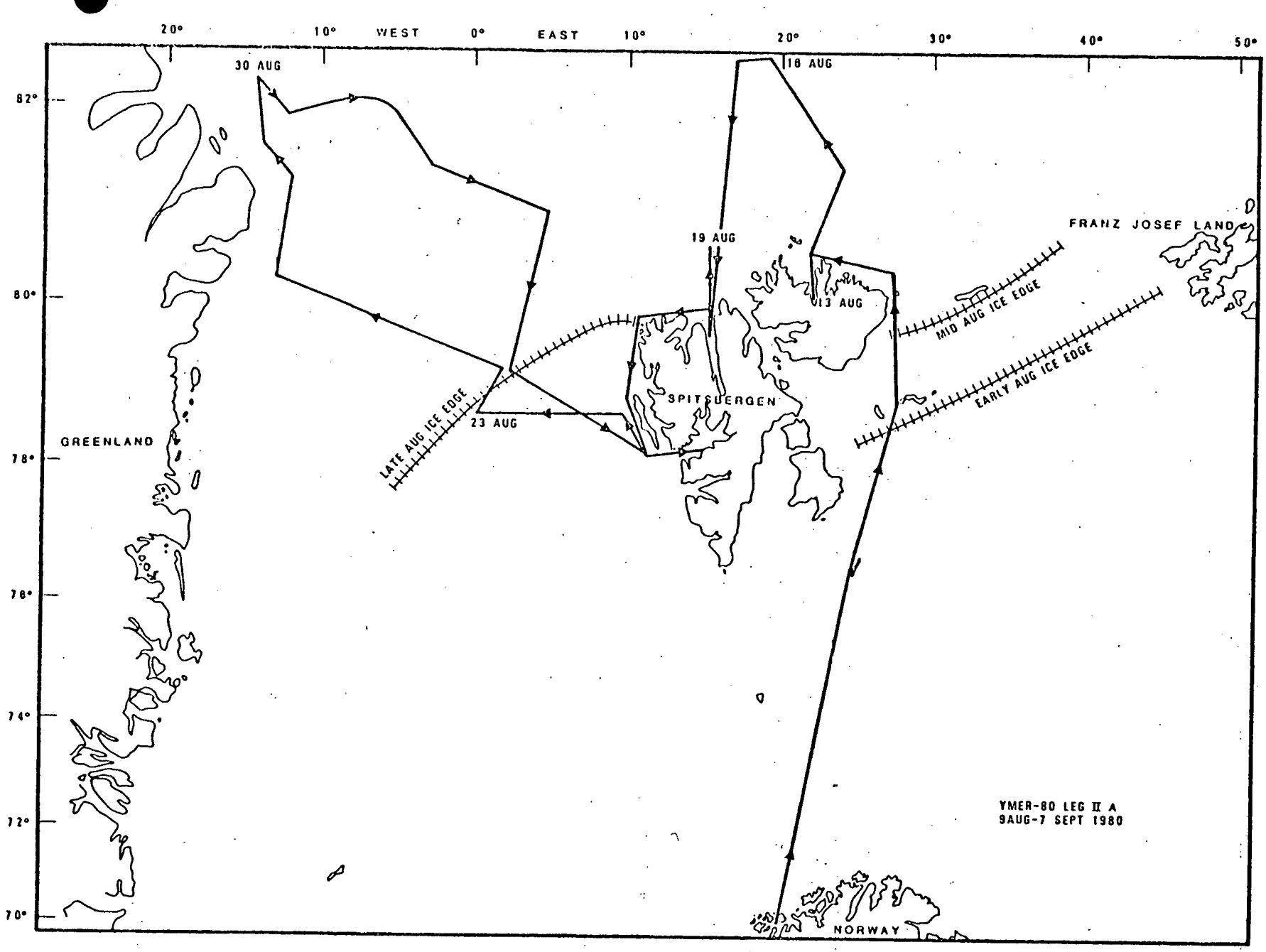
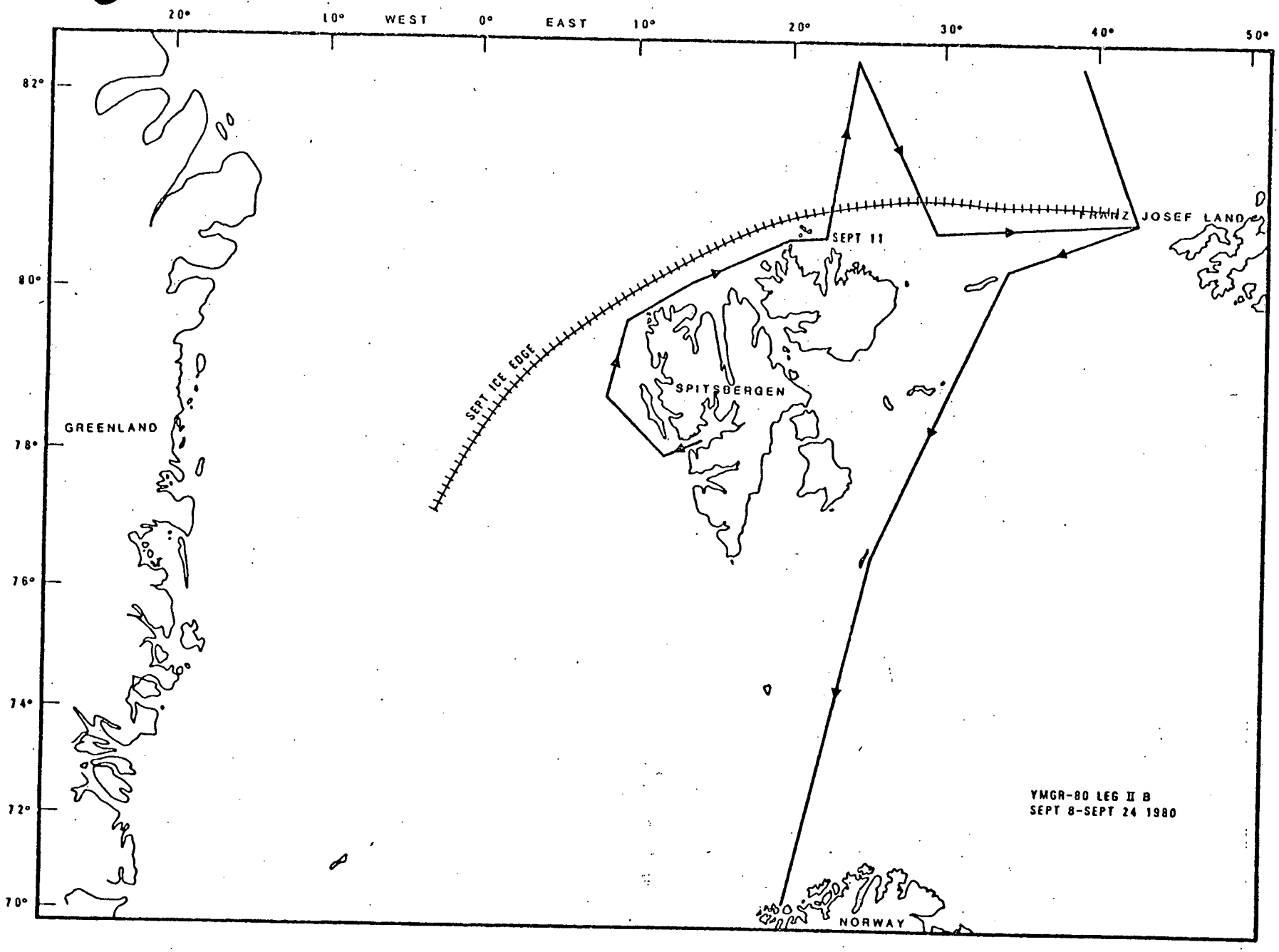

20°
10°
WEST
0°
EAST
10°
20°
30°
40°
50°
82°
80°
78°
76°
74°
72°
70°
14 JULY
24 JULY
FRANZ JOSEF LAND
30 JULY
3 AUG
SPITSBERGEN
GREENLAND
EARLY JULY ICE EDGE
4 JULY
NORWAY
YMER-80 LEG I
2 JULY-7 AUG 1980


20°
10° WEST
0° EAST
10°
20°
30°
40°
50°
82°
80°
78°
76°
74°
72°
70°
30 AUG
18 AUG
19 AUG
13 AUG
23 AUG
FRANZ JOSEF LAND
MID AUG ICE EDGE
EARLY AUG ICE EDGE
LATE AUG ICE EDGE
SPITSBERGEN
GREENLAND
NORWAY
YMER-80 LEG II A
9AUG-7 SEPT 1980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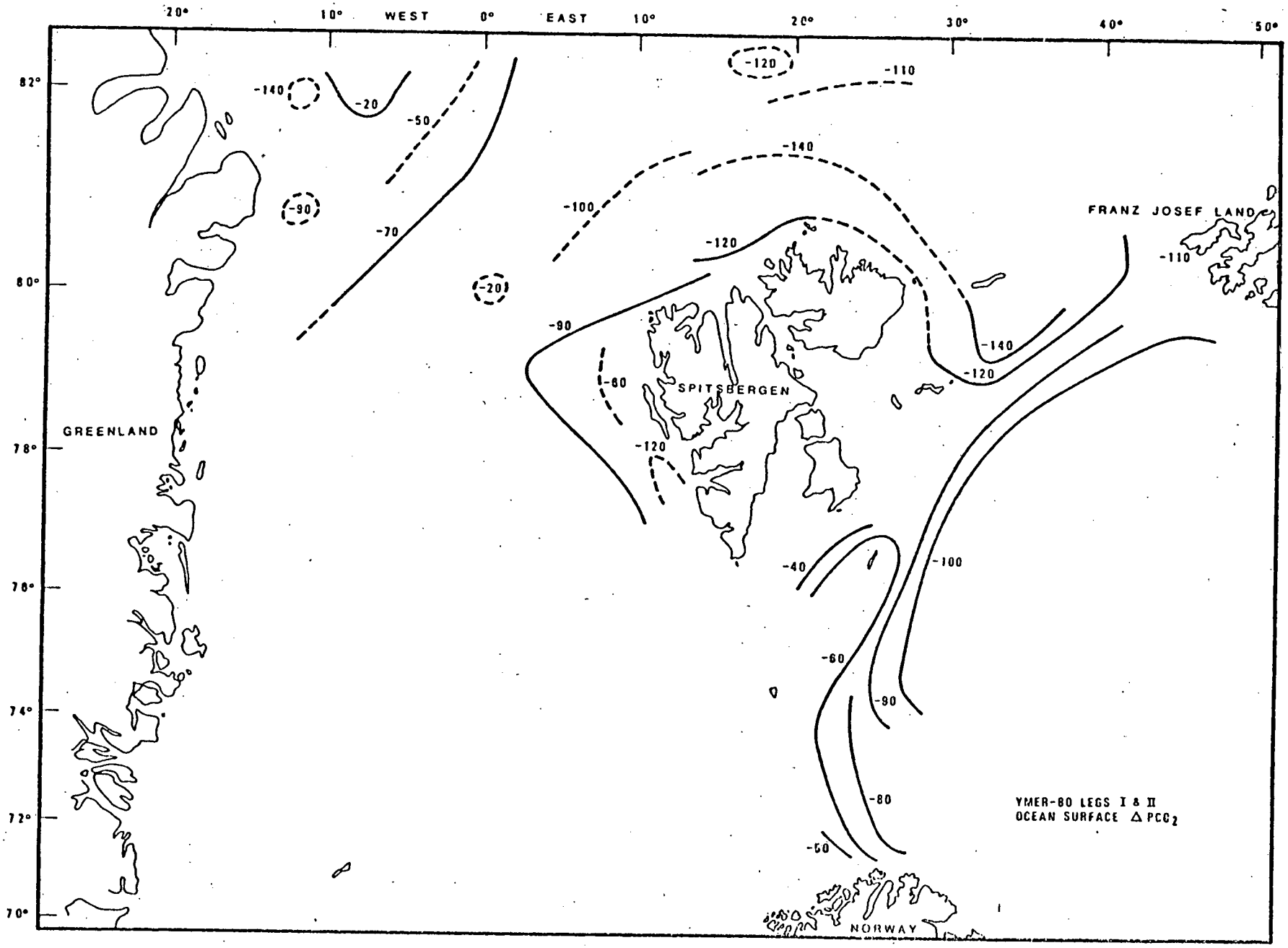
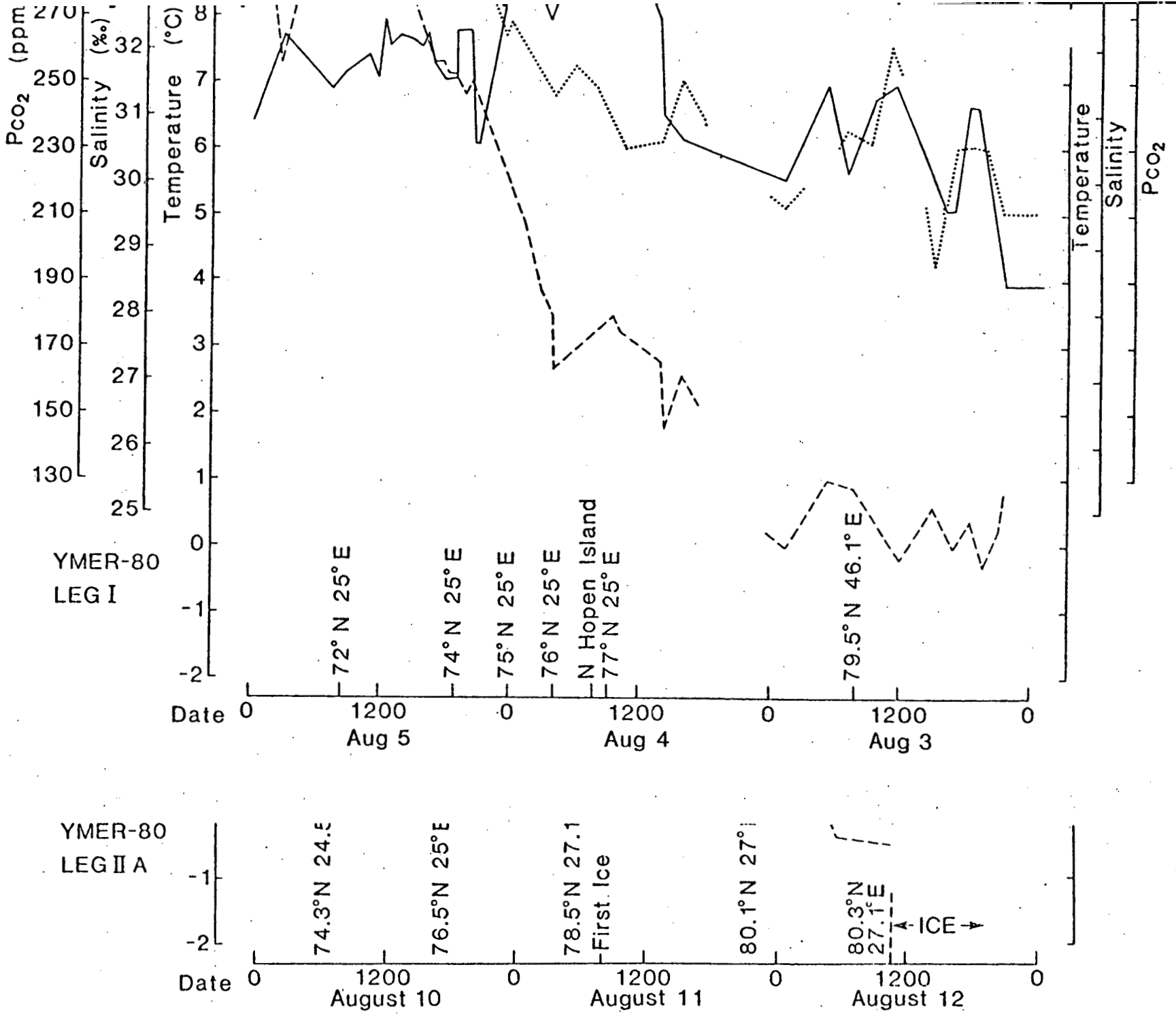
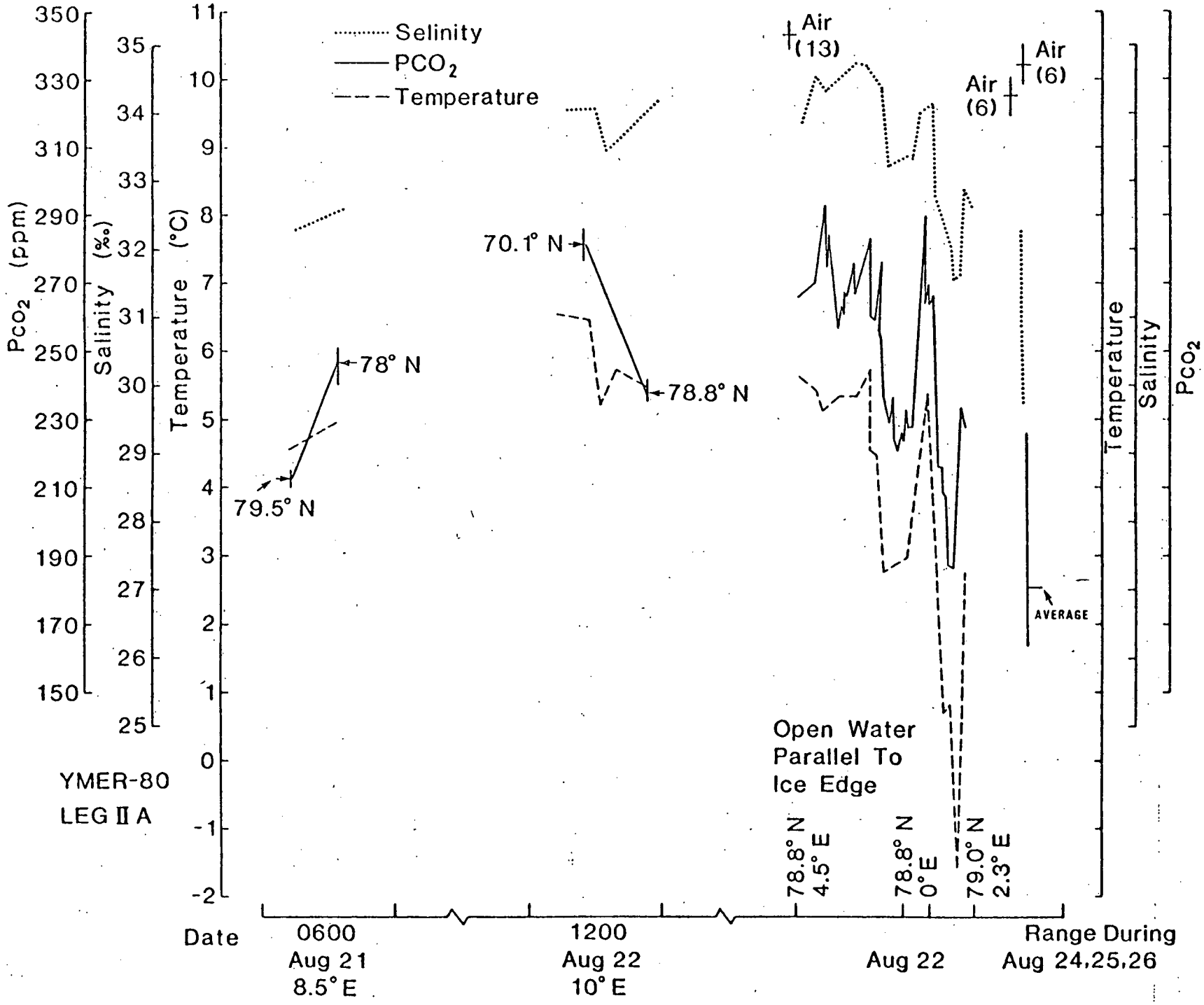
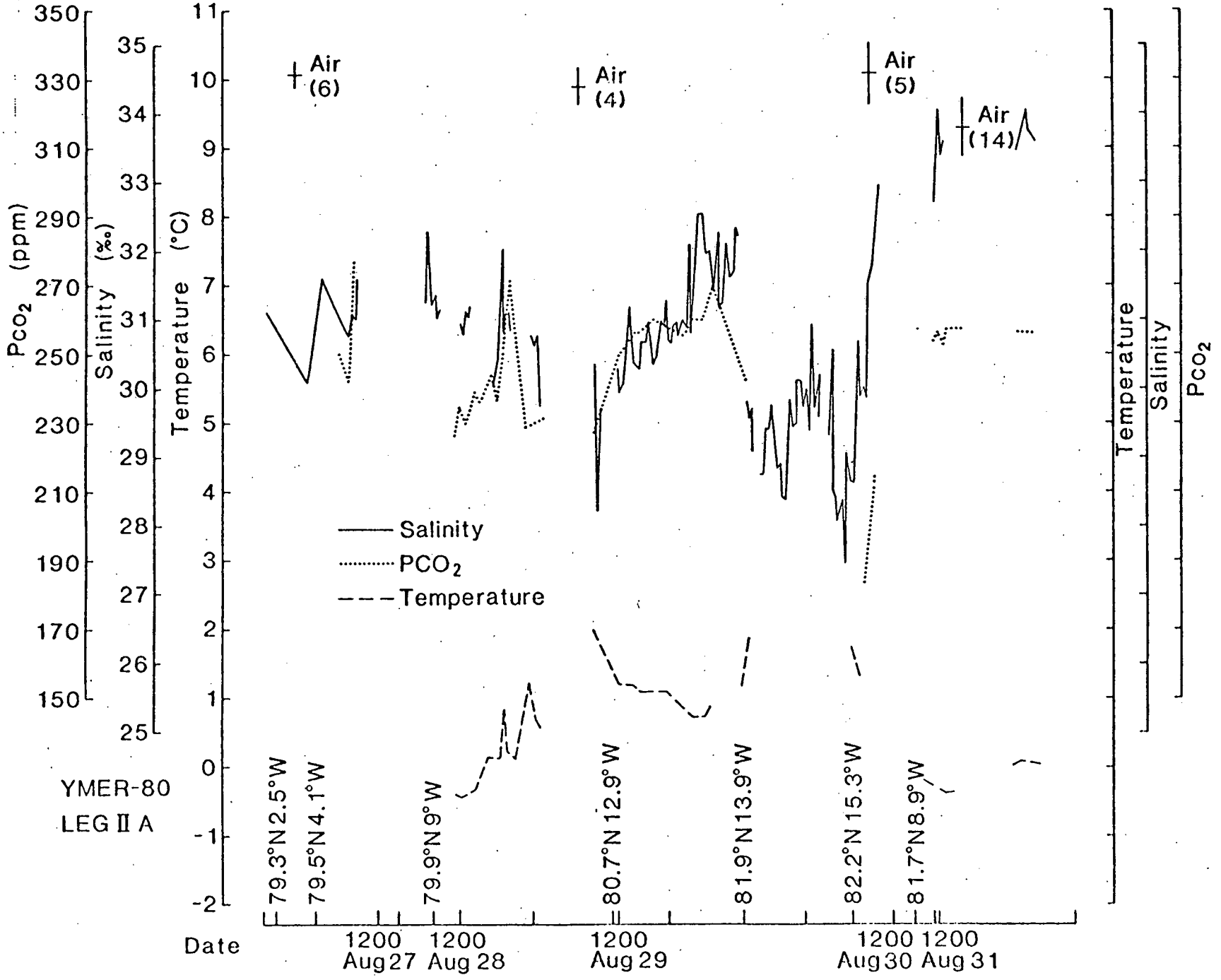
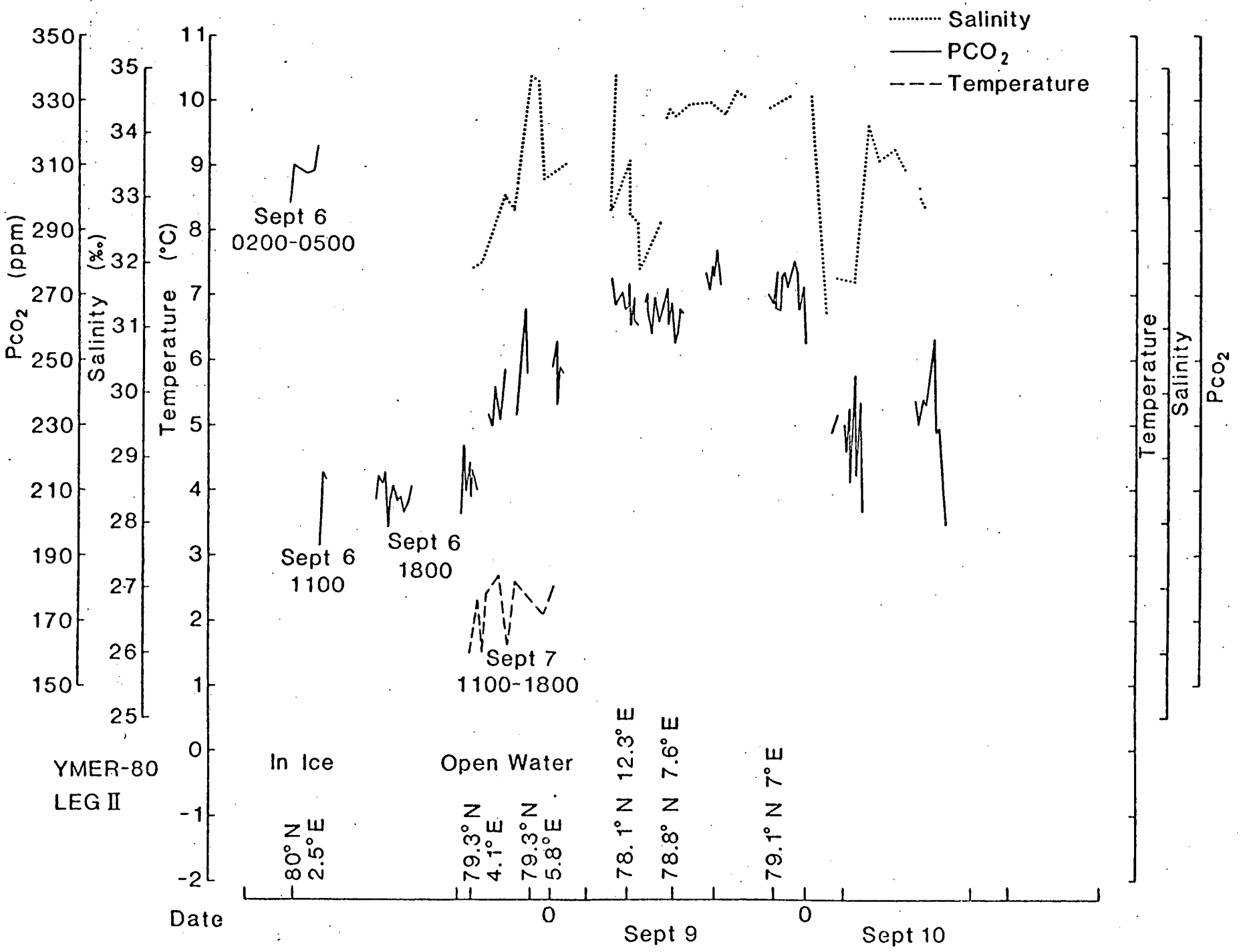
10° WEST
0°
EAST
10°
20°
30°
40°
50°
82°
80°
78°
76°
74°
72°
70°
GREENLAND
SEPT ICE EDGE
SEPT 11
SPITSBERGEN
FRANZ JOSEF LAND
NORWAY
YMGR-80 LEG II B
SEPT 8-SEPT 24 1980

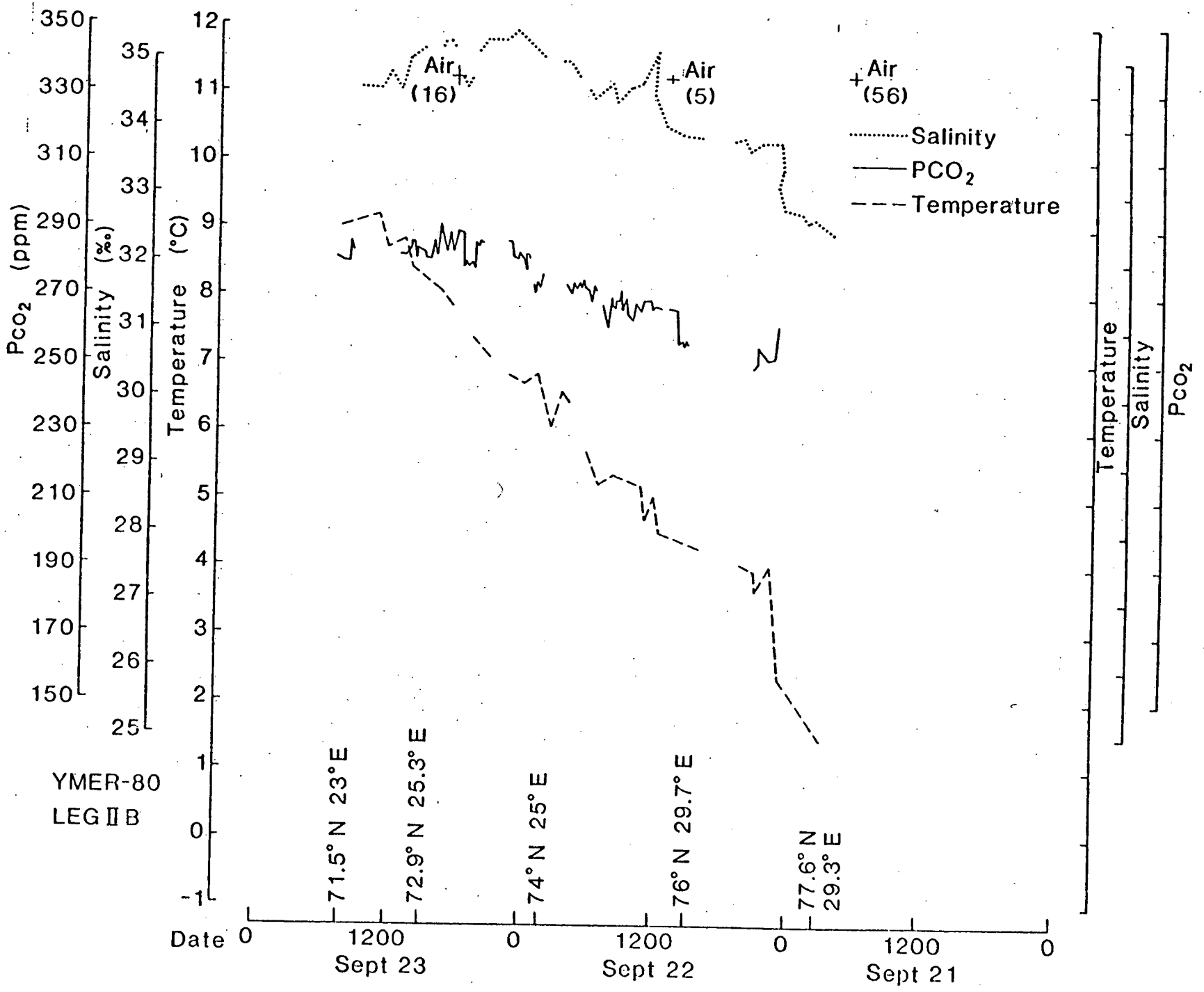

20°
10° WEST
0°
EAST
10°
20°
30°
40°
50°
82°
80°
78°
76°
74°
72°
70°
GREENLAND
SPITSBERGEN
FRANZ JOSEF LAND
NORWAY
-140
-20
-50
-70
-90
-120
-110
-100
-140
-120
-110
-90
-60
-120
-20
-140
-120
-40
-100
-60
-90
-80
-60
YMER-80 LEGS I & II
OCEAN SURFACE Δ PCO2


Pco_2 (ppm)
Salinity (‰)
Temperature (°C)
270
250
230
210
190
170
150
130
32
31
30
29
28
27
26
25
8
7
6
5
4
3
2
1
0
-1
-2
YMER-80
LEG I
72° N 25° E
74° N 25° E
75° N 25° E
76° N 25° E
N Hopen Island
77° N 25° E
79.5° N 46.1° E
Date
0
1200
Aug 5
Aug 4
Aug 3
Temperature
Salinity
Pco_2
YMER-80
LEG II A
74.3°N 24.5
76.5°N 25°E
78.5°N 27.1
First Ice
80.1°N 27°
80.3°N
27.1°E
ICE
August 10
August 11
August 12


Selinity
PCO2
Temperature
Air (13)
Air (6)
Air (6)
70.1° N
78° N
78.8° N
79.5° N
AVERAGE
Open Water Parallel To Ice Edge
78.8° N 4.5° E
78.8° N 0° E
79.0° N 2.3° E
Pco2 (ppm)
Salinity (‰)
Temperature (°C)
Temperature
Salinity
Pco2
YMER-80
LEG II A
Date
0600 Aug 21 8.5° E
1200 Aug 22 10° E
Aug 22
Range During Aug 24,25,26


Air (6)
Air (4)
Air (5)
Air (14)
Salinity
PCO2
Temperature
Pco2 (ppm)
Salinity (‰)
Temperature (°C)
350
330
310
290
270
250
230
210
190
170
150
35
34
33
32
31
30
29
28
27
26
25
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
YMER-80
LEG II A
79.3°N 2.5°W
79.5°N 4.1°W
79.9°N 9°W
80.7°N 12.9°W
81.9°N 13.9°W
82.2°N 15.3°W
81.7°N 8.9°W
Date
1200 Aug 27
1200 Aug 28
1200 Aug 29
1200 Aug 30
1200 Aug 31
Temperature
Salinity
Pco2

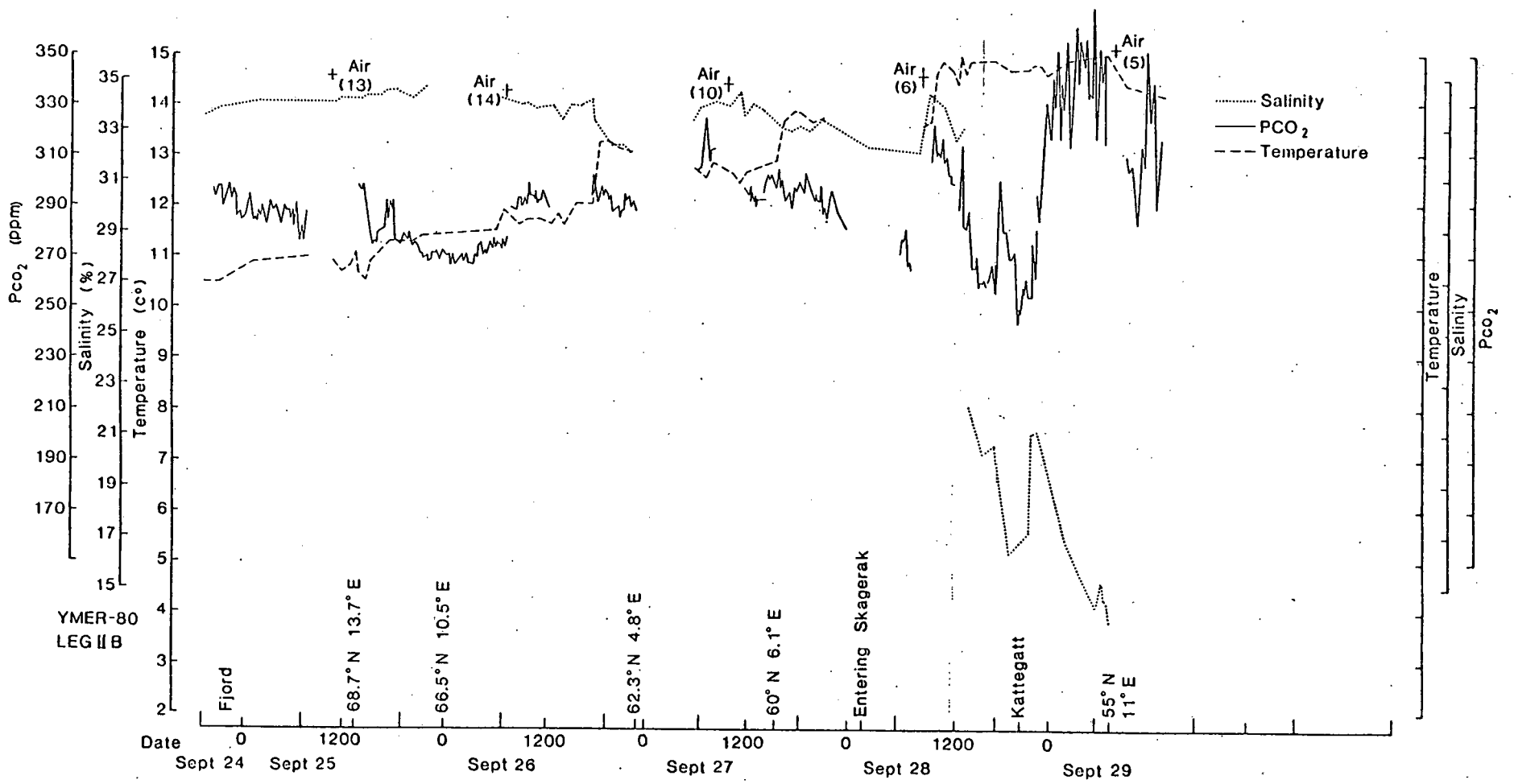

Salinity
PCO2
Temperature
Sept 6
0200-0500
Sept 6
1100
Sept 6
1800
Sept 7
1100-1800
Pco2 (ppm)
Salinity (‰)
Temperature (°C)
YMER-80
LEG II
In Ice
Open Water
80° N
2.5° E
79.3° N
4.1° E
79.3° N
5.8° E
78.1° N 12.3° E
78.8° N 7.6° E
79.1° N 7° E
Date
0
Sept 9
0
Sept 10
Temperature
Salinity
Pco2


Air (16)
Air (5)
Air (56)
Salinity
PCO2
Temperature
Pco2 (ppm)
Salinity (‰)
Temperature (°C)
Temperature
Salinity
Pco2
YMER-80
LEG II B
71.5° N 23° E
72.9° N 25.3° E
74° N 25° E
76° N 29.7° E
77.6° N 29.3° E
Date
0
1200
Sept 23
0
1200
Sept 22
0
1200
Sept 21
0

Depth	Date 7/27	8/4	8/5	8/5	8/13	8/14	8/14	8/16	8/17	8/17	8/19	8/23	8/27	9/2	9/5	9/6	9/7	9/11	9/13	9/15	9/18	9/22
													N. E. Greenland "Brown Water"						"Brown water"				
Surface Bucket					235			198	187		200			320	255				(195)	215		267
7 m Pump Sink		270	280	265	225	210	196	199	200	200		218	260	280	258	310	288	223	214	215	219	270
10 m						223											281					
15 m								229	233		208				271							272
20 m		280	280	280		239												262	224	229	237	
25 m								267		230			299	295	289							
30 m					220	249	212															271
40 m	(280)	280				282		311		270							290		258	278	271	
50 m			310	340	250		260		260		287	315	360	295	303	320		291				
75 m		310				277		321		285						334	310	320	289	297	301	333
100 m	(350)				(380)			353							319							
150 m							296		306		340					360	334	324	323		302	342
> -200 m			350			305			305									320 at 400 m				

— — — Equilibrium Depth – estimated ca. 130 m

.... Strong ΔPCO_2 depth (270 ppm) estimated ca. 20 m


Air (13)
Air (14)
Air (10)
Air (6)
Air (5)
Salinity
PCO2
Temperature
Pco2 (ppm)
Salinity (%)
Temperature (c°)
YMER-80
LEG II B
Fjord
68.7° N 13.7° E
66.5° N 10.5° E
62.3° N 4.8° E
60° N 6.1° E
Entering Skagerak
Kattegatt
55° N 11° E
Date
Sept 24
Sept 25
Sept 26
Sept 27
Sept 28
Sept 29

INTERIM REPORT

TO THE DEPARTMENT OF ENERGY

FROM THE GEOPHYSICAL INSTITUTE
UNIVERSITY OF ALASKA
FAIRBANKS, ALASKA 99701

CARBON DIOXIDE IN ARCTIC AND SUBARCTIC REGIONS

Drs. T. A. Gosink and J. J. Kelley

February 1981

(Contract No. 80EV10429)

This is our first interim report to the Department of Energy under this contract number (80EV10429). We reported last year through the Office of Naval Research (Code 461). We had had a long standing Arctic research contract program with ONR and through that agency last year we received phase-in funds from the Department of Energy.

We have completed our investigation of sea surface water PCO_2 between Greenland and Franz Joseph's Land. This was conducted in conjunction with the Swedish sponsored arctic expedition YMER-80 during the summer of 1980.

A copy of the cruise report is attached.

As a result of that cruise we:

(1) confirmed our earlier observations of extensive low partial pressures of CO_2 (ca. 180-220 ppm) in surface waters in that region (Kelley 1976).

(2) showed that the very low partial pressures extend farther north (ca. 82°N) and to the west (ca. 5°W) (see map in cruise report and cruise track data.

(3) obtained estimates as to how deep these very low partial pressures (ca. 20 m) and the equilibrium depth (ca. 130 m) penetrate (see cruise report).

(4) confirmed a new simple empirical method for the determination of PCO_2 in sea water (Technical paper in preparation).

(5) obtained an estimate for the invasion rate of CO_2 across cold Arctic surface waters (0.078 m moles atm^{-1} cm^{-2} min^{-1}).

(6) have estimated the Barents-Kara-Laptev Norwegian Seas area as enormously strong sinks, absorbing ca. 2×10^{15} g CO_2 during the summer months alone.

(7) can now estimate that the Arctic is an annual set sink of 1×10^{15} g CO_2 per year and that a large portion of its annual variations are naturally occurring. (Technical paper in preparation).

At the present time we are engaged in repairing our old equipment, obtaining and calibrating our new equipment, and preparing for two more field events before the end of our first fiscal year of support under this contract. One field trip is to observe tundra and taiga surface CO_2 emissions during spring breakup to confirm our earlier evidence of substantial release of gases from those soils during that period of time, e.g. Coyne and Kelley 1971 and 1973, Gosink and Kelley 1978 and Gosink and Kelley 1979. The second field trip is to be into the north Bering Sea edge during spring thaw.

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1. Coyne, P.I. and J. J. Kelley, 1971. Release of carbon dioxide from frozen soil to the arctic atmosphere. Nature, 234, 407-408.

2. Coyne, P. I. and J. J. Kelley, 1974. Variations of carbon dioxide across an arctic snowpack during spring. J. Geophys. Res., 79, 799-802.

3. Gosink, T. A. and J. J. Kelley, 1978. Annual report to the Office of Naval Research, Code 461. From the Inst. of Mar. Sci. Univ. of Alaska, Fairbanks.

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5. Kelley, J. J., 1973. Carbon dioxide in surface waters of the North Atlantic Ocean, the Barents and Kara Seas. Limnol. and Oceanog., 15 80-87.

Arctic Seas. Are they Overlooked Significant Sinks for Atmospheric Carbon Dioxide?

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Geophysical Institute and
Institute of Marine Science
University of Alaska
Fairbanks, Alaska 99701

ABSTRACT

Two arguments are presented to support the concept that the Arctic Ocean and its surrounding seas, 3.8 percent of world ocean and sea surface, can absorb during the summer between 5 and 10 percent, or more, of the annual anthropogenic production of carbon dioxide. The implication is that the arctic seas are important sinks for atmospheric carbon dioxide.

INTRODUCTION

During the recent Swedish Arctic Expedition, *YMER-80*, we measured the atmospheric and sea surface partial pressures of carbon dioxide. Observations aboard the *YMER* were made in the Norwegian and North Greenland Seas, and the oceanic areas north of Svalbard and Franz Josef Land including the associated seasonal ice zone. We present here two arguments which lead us to believe that the Arctic Ocean and surrounding seas are absorbing between 5 and 10 percent, and possibly as much as 40 percent, of the annual anthropogenic production of CO_2 during the 3 to 4 month summer period. We are aware of other seasonal and geographic arctic water mass sources and sinks of carbon dioxide (Gosink and Kelley, 1980a) but the apparent intensity of Barents Sea area warrents particular note and study.

Polar oceans and adjacent seas affected by sea ice constitute about 35×10^6 km^2, or essentially 10 percent of the world oceans and seas surface. In the northern hemisphere, sea ice extends over about 8.4×10^6 km^2 in the summer, and up to 15×10^6 km^2 in the winter including the seas of Japan and Okhotsk. The Arctic Ocean basin and surrounding seas comprise about 13.6×10^6 km^2 or 3.8 percent of world oceans and sea surfaces. (Sverdrup *et al*, 1942 and Barry, 1979). We have reported that carbon dioxide is transferred, through sea ice (Gosink, *et al*, 1976) and that it, based on Alaskan Arctic observations, can be a significant source of CO_2 to the Arctic atmosphere in the winter (Gosink and Kelley, 1980b). We are concerned here, however, only with the summer open ocean water which is moderately to extremely undersaturated with respect to carbon dioxide i.e., carbon dioxide partial pressures in sea water are less than atmospheric CO_2 partial pressures.

Most of the available data for carbon dioxide in seasonally ice covered sea water comes from the Bering Sea. Research results summarized by Park *et al*, (1974) shows the carbon dioxide in Bering Sea surface waters varies seasonally and spatially from strongly supersaturated to strongly undersaturated conditions. North Atlantic waters were reported nearly 50 years ago by Buch (1926) to have very low partial pressures of carbon dioxide (160 ppm) in the vicinity of sea ice, which was verified by Kelley (1970) when he extended those observations into the Barents and Kara Seas, and closely retraced Buch's transatlantic cruise track. Unlike Buch, however, Kelley did not observe extremely low atmospheric carbon dioxide concentrations, although it was significantly lower than continental air. On the recent *YMER-80* cruise, we further extended the sea surface and atmospheric observations to about 84°N between Greenland, Spitsbergen and Franz Josephs Land,

and south off the Norwegian coast. With the only exception of the region near Nord, Greenland, where arctic basin waters are flowing into the Greenland Sea, and a station at the Greenwich meridian at 80°N, the surface waters were all highly undersaturated with respect to CO_2 during the entire July through September period. The two Greenland sea stations were nevertheless undersaturated, but only to the extent of 5-25 ppm, respectively. We are publishing elsewhere the full report of the YMER-80 CO_2 observations, and our explanation for the principal cause for these exceptionally low surface water partial pressures of CO_2, which extend to 20-200 m depth (Gosink and Kelley, 1980c, d).

The First Argument

Near surface air flowing out of the Arctic was observed to have CO_2 concentrations on the order of 317 to 325 ppm (August and September 1980). Our analytical data for CO_2 are based on S.I.O. standards on the Jc Scale, and are accurate to ± 2 ppm). Under laboratory conditions, our gas chromatographic analytical method has an accuracy and precision of about ± 0.2 ppm. (Gosink and Kelley 1977). Air flowing into the arctic basin north of Norway (July, August and September) had concentrations in the range of 336 to 341 ppm. Lower tropospheric continental air at 55°N in the Skaggerak Strait region during September was observed to be 351 ppm. Thus tropospheric air passing through the summer arctic basin apparently loses 11 to 24 ppm of its carbon dioxide content. If the air in the arctic basin is exchanged every 2 weeks, there would be about 9 air mass changes during the summer open water period of June through September. Treating the arctic basin as a simple cylinder of 10×10^6 km^2 base area, and arbitarily

of 2 km in height, the CO_2 air mass volume is 20 x 10^6 km^3 per exchange. The rationale for the 2 km figure is based partly upon the work of Bolin and Bischof (1970) who point out that there is a 25 to 30 day delay in seasonal variation between the lower and upper troposphere (9 km). Thus, the entire arctic troposphere will not be uniformly relieved of part of its CO_2 burden, before it exits the Arctic. The other factor is that the density of the air column is not uniform, and 2 km seems a reasonable arbitrary first estimate to approximate the mass of air in the lower troposphere. An 11 ppm depletion of CO_2 in this simple scheme yields 220 km^3 or 4.3 x 10^{14} g of CO_2 per air mass change or 3.9 x 10^{15} g CO_2 in the summer period. If 24 ppm of CO_2 are removed, then 8.4 x 10^{15} g of atmospheric CO_2 are deposited in Arctic surface waters over the summer. The lowest figure is 12.4 percent of current annual fossil fuel and cement production figures, and the highest figure, 40 percent, based on a 2 percent/year updating of Rotty's compilations (1977). If a lower exchange rate (0.034 mmole cm^{-2} atm^{-1} m^{-1} min^{-1}) suggested by Keeling (1965) is employed, then the percentage range is reduced to 5.4 to 17.5 percent. The Hood and Kelley (1976) rate, as determined in cool (7-9°C) waters, affords a 6.9-22.0 percent range. The surface waters of the Eastern Arctic were in the -1 to +2°C range.

If during the winter freeze-up, the cooling and salt rejection from forming sea ice causes the otherwise stable surface waters to sink to great depths (below 2-500 m) with this added CO_2, then that CO_2 is effectively removed. If it remains near the surface and flows south again (as some portion of it certainly does) where it is warmed, then part of it will be released to the atmosphere again.

The difference between CO_2 in air and sea water based on *YMER* observations, (Eastern Arctic Ocean) indicated undersaturation in sea water of about -110 ppm. Kelley's (1970) observations in the Barents sea area (1970) suggests an average under saturation of about 130 ppm. If arbitrary geographic division of the arctic oceanic regions are used, then over a 100 day period, the Barents, Kara and Laptev seas (2.3×10^6 km^2 surface area) would absorb 1.3×10^{15} g of CO_2. The open water of western arctic ocean, also of about 2.3×10^6 km^2 area, with its apparent ΔPCO_2 of about - 60 ppm would absorb an additional 0.7×10^{15} g of CO_2 for a total of 2.0×10^{15} g of CO_2 (9.6 percent of anthropogenic production) which agrees with the results of our first argument. If, of course, some of the carbon dioxide above 500 m was also being absorbed, then the figures mentioned above would all be proportionally larger, and still in agreement with the results of the first argument.

Although the Arctic oceanic regions occupy a small area of the world oceans and seas surface (3.8 percent) it would appear that they may be a significant sink for CO_2 during the summer. Little can be said at this time about the possible role of Antarctic seas and the exchange of CO_2 across the sea surface. Data are difficult to obtain in both regions, both on an areal and temporal basis due to logistics problems. In order to further test these arguments it will be necessary to obtain data within the polar pack ice and marginal seas from spring to fall which may only be possible by taking advantage of future floating ice stations.

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THE GLOBALLY SIGNIFICANT SOURCES AND SINKS OF CARBON DIOXIDE IN THE ARCTIC

J. J. Kelley and T. A. Gosink

INTRODUCTION

This article is the first comprehensive consideration of the Arctic as a whole with respect to atmospheric carbon dioxide, its natural and anthropogenic origins and interaction with the various arctic surfaces. The paper is based on our own field research of more than two decades and other relevant scientific papers.

The issue of atmospheric carbon dioxide is international in scope and interest because of its potential disastrous effects on atmospheric heating. The Arctic can be markedly affected by this heating and in turn trigger other climate modifications (e.g. Fletcher and Kelley, 1978). In this paper we will develop the various factors and synthesize an annual cycle for the Arctic which clearly shows that this ice dominated region plays a surprisingly large role in moderating atmospheric dioxide.

The Arctic (above 67°N), at first glance, appears to be an almost insignificant region as far as atmospheric carbon dioxide is concerned. The whole surface area of the Arctic is only 4% of the earth, its ocean-sea area 3.8% of the world oceans surfaces, and is heavily influenced by both glacier and sea ice. The winter to summer average variations in tropospheric carbon dioxide are the largest (12-16 ppm) recorded at all of the remote monitoring sites in the world (eg. Bolin and Keeling, 1963 and Keeling et al, 1976a,b) and have a curious repeatable spring surge just before the summer minimum. On the other hand,

the annual rate of increase of the mean concentration is the same as recorded in Mauna Loa or the South Pole. These annual artic tropospheric CO_2 excursions are generally ascribed to transport of polluted lower latitude continental air into the region during the winter, and reduced in the spring-summer due to hemispheric resurgence of photosynthetic activity. Our own research in the Arctic, however, decidedly shows that the arctic hydrosphere, and to a lesser extent the geosphere, markedly affect tropospheric carbon dioxide, and that these effects operate throughout the entire year. These natural arctic phenomenon have indeed been obscurred by transport of anthropogenically polluted air from lower latitudes, but we have been reasonably successful in reading through that masking by means of seasonal source-sink experimentation. We estimate that the natural sources and sinks of carbon dioxide within the Arctic are causing about 20-40% of the annual apparent tropospheric CO_2 concentration excursion.

Current estimates of annual tropospheric anthropogenic carbon dioxide input are about 2.6×10^{16} of CO_2 when considering recent recognition of tropical forest clearing (Rotty, 1977; Bolin, 1977; Wong, 1978; Woodwell et al, 1978). Anthropogenic factors within the Artic and the adjacent subarctic are virtually inconsequential with respect to carbon dioxide. They are likely to remain so even with the increased oil exploration and production activities.

We will show that physical-chemical rather than biological processes dominate the entire annual cycle. Arctic phenomena are so intense, for example, that we estimate that an equivalent of nearly 10 percent of the entire burden of carbon dioxide introduced annually by all anthropogenic activity is absorbed by north polar seas just during the short summer period. On the other

hand, we have also shown that annual sea ice is permiable enough towards carbon dioxide so that about a third of the carbon dioxide absorbed by the seas over the summer months is transferred back to the troposphere during the remainder of the year. Tundra soil, plants, ponds and lakes are also treated in our discussions as well as preliminary estimates of latitudinal transport.

EXPERIMENTAL METHODS

All gas analyses were accomplished on a Carle 311 M gas chromatograph. Carbon dioxide reference gas standards prepared at the Scripps Institute of Oceanography (S.I.O; C. D. Keeling Laboratory) were used. In addition, air samples were periodically taken in the vicinity of the Point Barrow NOAA/ERL-GMCC site for comparison. Values for CO_2 in air agreed with the NOAA measurements within 1 ppm by volume. The NOAA analyses were made by means of a nondispersive infrared analyzer using S.I.O. standards.

Air samples were either collected and held briefly under slight positive pressure in teflon coated steel and glass (10 ml) gas tight syringes, or in 250 ml gas sample bottles. It was necessary to employ oversize O-rings under the plunger in order to achieve a gas tight fit at low temperatures. Analyses were completed within 24 hours; usually within 1 to 6 hours. Standards held in these syringes were stable for 24-72 hours, depending on the particular syringe in question. Standards stored in slightly pressurized routine commerical 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 verus 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, 1981a) as are the procedures for research from on board research vessels (Gosink and Kelley, 1978).

DISCUSSION

Description of the Arctic

Our physical description of Arctic is one of defining the areas of the various interfaces which may interact with the troposphere. These estimates are used through out this article to calculate seasonal quantities of carbon dioxide exchanged across those surfaces.

The surface of the Arctic, based on simple spherical geometric calculations, is taken to be 2.12×10^7 km^2. The troposphere of the Arctic is assumed to be 2.1×10^8 km^3 in volume and to contain 6.9×10^{16} g of CO_2 at an average concentration of 335 ppm (μ atmospheres). Table 1 shows our breakdown of the various land and sea areas that have different degrees of influence on tropospheric carbon dioxide.

The central pack ice, including about a third of the Canadian Archipeligo, is the largest of all subcategories, and is considered to be almost closed to ocean-air interaction. The two exceptions are the estimated year round 5-10% open water in cracks, leads and polynas. (Whitman, 1966) and the ca 50% annual sea ice which we have shown to be permiable (Gosink et al, 1976) and will dicuss further in this paper. The surrounding seas have been subdivided into four categories for two different reasons. The principle reason is that these regions appear to display different partial pressures of carbon dioxide, particularly during the summer period. The secondary reason has to do with the amount and duration of the ice cover. Three of these areas are considered to be 10% open water during the winter due to wind and current stress on the ice. Only two are considered to be 100% open for a 3 to 4 month period during the summer.

The Greenland Sea-Baffin Bay category is considered to contain the remainder of the Canadian archipeligo water area, and to be 50% open water during the summer period. All of these Arctic seas may be referred to as the seasonal sea ice zone (SSIZ) which Barry (1979) defines as annually varying between 8.4 and 15 x 10^6 km^2. His definition, however, includes subarctic sea ice, e.g. the Bering Sea and Sea of Othosk etc. Sverdrup et al, (1942) tabulate the Arctic Ocean and surrounding seas as covering 14.1 x 10^6 km^2, but they include areas south of the Arctic circle such as the Norwegian and North seas which we consider to be perpetually open water. Our total Arctic Ocean and seas area is therefore 13.8 x 10^6 km^2.

We estimate the land area within the Arctic to be predominantly glaciated and or mountainous, e.g. Greenland. We know of no significant (> 1 x 10^{12} g CO_2 sources or sinks for carbon dioxide in these glaciated areas, and thus will not consider them in our source-sink calculations. The remaining

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

	Region	(Area x 10^6 km^2)
Ocean Sea	Central Pack Ice	8.4
	Barents, Kara, Laptev Seas	2.5
	East Siberian, Chukchi, Beaufort Seas	0.9
	Greenland Sea and Baffin Bay	1.3
	Norwegian Sea	0.5
	Total Ocean-Sea Area	13.8
Land	Tundra	0.6
	Taiga	1.0
	Mountainous and/or Glaciated	6.0
	Total Land Area	7.6
	Total Area	21.4 x 10^6 km^2

land area within the Arctic circle is conservatively estimated to cover 1.6×10^6 km^2. It is composed of the wet tundra, for which there is some field data, and the more dominant higher taiga for which we will have to use estimates from other souces about its effect on atmospheric CO_2. We estimate the wet tundra as occupying 0.6×10^6 km^2 as shown in Table 1.

Aside from knowledge of the area and the partial pressure differences between the air-sea boundary, a reliable figure for the rate of invasion or evasion of carbon dioxide across the interface is required. Skirrow (1975) tabulates eleven laboratory and field study rates that vary between 0.00045 and 1.5 mmoles cm^{-2} $atm^{-1} min^{-1}$ (see Figure 1). We have recently observed within the Arctic an apparent invasion rate of 0.078 mmoles cm^{-2} atm^{-1} mm^{-1} which we use in all of our calculations for this article (Gosink and Kelley 1981b). We use this figure since there is an apparent trend in change in rate as a function of sea water temperature. The numerical value of Keeling's rate (0.034) was for mid-latitude waters (assumed to be ~25°C). Hood and Kelley's rate (0.043) was for colder Bering sea water (ca.9°C) and our recent value (0.078) was for surface water at -1 to 0°C.

Arctic CO_2 Source-Sink Inventory

In the following sections we will utilize our field evidence to calculate the source and sink strengths for the various categories listed above for a summer and winter period. The results are compiled in Table 2.

Figure 1. INVASION RATES - OPEN WATER - ΔPCO_2

mmoles cm^{-2} atm^{-1} min^{-1}

0.15

0.078 YMER *

0.043 (Hood & Kelley - Bering Sea)

0.034 (Keeling - 1965)

30 × Factor ← 11 Literature Values (Skirrow, 1975)

0.0125 - 7 year mean (Broecker)

0.0077 (Coyne & Kelley - Tundra and Lakes)

0.0045

* Stable Inversion ~ 500 m , calm - 5 knots (20 Sept

339 to 331 ppm over 48 hours

Sea water ~ 255 ppm; ΔPCO_2 80 ppm

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

Lyakin and Rusanov (1980) have recently published historical data for the surface waters of the Arctic Basin for 1948 to 1978. When we employ their pH data (8.05 to 8.15) in our empirical method (Gosink and Kelley, 1981c) the surface water partial pressures are thereby determined to be in the range of 301 to 383 ppm or Δ PCO_2 of -40 to +40 ppm. The exact time of "winter" and locations for the historical data are unknown.

Summer data for the Central Arctic is even more sparse. Our recent YMER data (Gosink and Kelley, 1980c) indicate that surface water along the periphery of the Arctic Ocean Basin are slightly under saturated (~-10 to -30) ppm) during the summer period. Lyakhin and Rusanov's pH data (1980) affords a calculation of summer PCO_2 by the empirical method (Gosink and Kelley 1981c) to be in the range of 223 to 359 ppm for the Arctic Basin. This is in reasonable agreement with our YMER-80 observations along the periphery of the basin; Δ PCO_2 = ca. -100 to +36 ppm, or approximately averaging -30 ppm. If the arbitrarily assigned range of -30 to +10 ppm for

the ΔPCO_2 of the summer central Arctic is correct, then the summer central Arctic operator provides for a source and sink range of 37 MT and 112 MT of CO_2 respectively as shown in Table 2. Some smaller subsections of the central basin are probably supersaturated with CO_2 at the surface as the compilation of Lyakhin and Rusanov suggest.

Melt ponds on the surface of sea ice were observed from the YMER cruise (80 - 82°) to have very high PCO_2 in August (420-490 PPM), but this may have been due to the decay of plankter. Those ponds in August were covered with ice and had a salinity of about 6°/oo, and as far as we can estimate at this time efectively cancels their presumed sink condition of earlier in the summer based on our observations north of Alaska (71°N). They are shown as 40 MT sources and sinks in Table 2.

The winter low figure for the Central Arctic open water, assuming that 5% of the total area is open water with a ΔPCO_2 of 10 ppm, that the length of time under such conditons is 9 months, is that 56×10^{12} g CO_2 (10^{12} g = million metric tons = MT) will be transferred from the ocean to the atmosphere. If the open water is 10% as has been suggested by Whitman (1966), and if the Δ PCO_2 = 100 ppm, then the output of CO_2 to the air in the Central Arctic during winter jumps to 1119 MT CO_2 for the high figure.

The Barents Sea Region has been confirmed to have exceedingly low (180-250 ppm) summer partial pressures of CO_2 at the surface (Kelley 1970 and Gosink and Kelley 1981b). The average ΔPCO_2 for that region is on the order of -110 ppm). Considering the general easterly circumpolar flow of surface waters on that region, the phenomenon is assumed to extend into the Laptev Sea. If this intensity is maintained for a 4 month summer period over the entire area of 2.5×10^6 km^2, then 1628 MT of CO_2 will be absorbed. As can be seen from inspection of Table 2, this figure alone overwhelms all of the other sources or sinks within the Arctic.

The Barents Sea region therefore is the predominant cause for the Arctic to be a net CO_2 sink. The partial pressure of CO_2 in those waters in the winter is unknown, but if our explanations for the principal cause of those low partial pressures is correct (Gosink and Kelley, 1981d) i.e. the cooling of surface waters as they are transported north, then we would expect those waters to remain undersaturated throughout the remainder of the year, but perhaps only at -20 to -40 ppm due to organic decomposition and the lack of photosynthesis. The winter open water factor would be reduced to ca 25%, and thus the transfer from the atmosphere would be ca. 225 MT CO_2 for that area and time period.

Chukchi and Beaufort Seas summer ΔPCO_2 values are significantly less than that in the Eurasian basin, being on the order of -60 ppm (Gosink and Kelley, 1979). Winter data in the Beaufort Sea suggests super-saturation of 20 to 40 ppm. Therefore the East Siberian, Chukchi, Beaufort subcategory is calculated to be a summer sink for CO_2 of 240 MT and a winter source in the range of 16-32 MT CO_2 based on the following observations.

Our experiments (Gosink and Kelley, 1978, 1979, 1981b) indicate that winter partial pressures of CO_2 under sea ice are patchy and mixed from under-saturated to the more common super-saturated. For example, PCO_2 returns rapidly to the supersaturated (to 360+ppm) in the fall or during the month of November. Furthermore, indications are that partial pressures on the order of 400 ppm are close (10-20 m) to the surface then (Gosink and Kelley 1979).

In the northern Bering Sea we measured PCO_2 values of 400-440 ppm at and just below the thermocline located at 20-40 m (Gosink and Kelley, 1978 Hakuho Maru cruise, 1978 and 1981c). At lower latitudes, where photosynthesis extends below the surface thermocline, the depth at which the high PCO_2 water is encountered is as much as several hundred meters (e.g. Li et al., 1969). In the Beaufort Sea within 200 km of the coast, the thermocline is only 10-20 m below the surface. On 11 November 1978, the PCO_2 of newly ice-covered surface waters 30 km offshore had already risen to 341 ppm, about 10-12 ppm greater than the ambient air. The PCO_2 just 6-7 m below the surface was 420 ppm. Light levels were low at that time with the sun being above the horizon for only one hour per day, thus photosynthesis effectively had ceased.

It would appear from three sets of winter experiments (1-30 day observations each) (Kelley, 1968; Kelley and Hood, 1971 and this report) in addition to several spot samples, that the surface sea water PCO_2 in the winter within 2-300 km of the coast is about 340-360 ppm, but with an occasional high observations of ca. 400 ppm. However, on one occasion, two separate samples of sea

water from under the ice ~ 200 km north of Alaska during early April 1978 (floating ice station ARLIS-VII) unequivocally displayed PCO_2 of 295 and 300 ppm. The light level at that time of year was low to moderate, but nearly constant for ca. 15 hours/day. Those isolated low PCO_2 observations suggest that slight but significant offshore biological activity had commenced immediately under the sea ice in April. This departs from other winter and spring month observations when the PCO_2 values for surface Beaufort Sea waters were generally 340-350 ppm and higher (Kelley, 1968; Gosink and Kelley, 1978). Coastal and near-coastal waters maintained 10-60 ppm above ambient atmospheric CO_2 values at Barrow in April to early May 1979.

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

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

The Greenland Sea-Baffin Bay region is dominated by sea ice throughout the year. We estimate for our calculations that it is 10% open in the winter and 50% open in the summer. The only PCO_2 data we have are for the summer period in the Lena Trough area (Gosink and Kelley 1981d). The surface sea water coming out of the Arctic in that region was slightly undersaturated with a ΔPCO_2 of about 0 to 10 ppm. Surface waters farther south, probably modified by the Spitsbergen Atlantic current, were undersaturated by 10 to 45 ppm. We can only assume that winter waters are similar to the central pack ice, and have supersaturation ΔPCO_2 on the order of 10 to 100 ppm. On the basis of these data and assumptions, the winter source strength range for the Greenland Sea-Baffin Bay region is estimated to be 28-288 MT CO_2 and the the summer sink strength 29-115 MT CO_2.

The perpetually open water of the Norwegian Sea and southern edge of the Barents Seas have summer partial pressures ranging from 50 to 100 ppm below that of the atmosphere (Gosink and Kelley 1981c) and is considered to be a year long phenomenon for reasons mentioned above. The winter partial pressure difference is unknown but is assumed at this time to be -25 ppm. Thus this small area is listed as sink for the entire year with winter and summer season strengths of 111 and 222-444 MT CO_2 respectively.

The remaining months, not included in the above or following calculations are considered to be transition periods during which the ΔPCO_2 is relatively small and self compensating as the process changes from source to sink or vice versa.

Gases at the Sea Ice-Air-Snow Interfaces. The only air-sea interface left for discussion at this point is the sea ice-air interface. We have reported that annual sea ice, not multi-year ice, because of its brine channels and the carbonate nature of the brine, is permiable to carbon dioxide (Gosink et al, 1976 and Gosink and Kelley 1977, 1978, 1979 and 1981e). Carbon dioxide, carbon monoxide, methane and sometimes nitrous oxide have all been observed to emanate from the sea ice surface. All of these gases can usually be found over the surface of annual sea ice in concentrations significantly greater than that of the ambient air (Gosink and Kelley, 1977, 1978). We are reporting at this time, however, 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, 1981e). 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 to sea ice are shown in Figure 2. The fact that the oxygen concentration in the fresh ice sealed, helium flushed chambers (Figure 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

Table 2. Seasonal Source-Sink Strengths of the Various Regions in the Arctic

Season	Region	Area (10^6 km^2)	% Area Active	Invasion Evasion Rate	ΔPCO_2 (ppm)	Duration (Months)	Source ($\times 10^{12}$ g CO_2)	Sink ($\times 10^{12}$ g CO_2)
Winter	1. Central Basin	8.4	5-10	1.48×10^{12}	10 to 100	9	56 - 1119	-
	2. Barents, Laptev, and Kara Seas	2.5	25	(g km^{-2} mo^{-1} atm^{-1})*	-20 to -40?	8	-	149 - 299
	3. East Siberian, Chukchi and Beaufort Seas	0.9	10	"	20 to 40	6	16 - 32	-
	4. Greenland Sea and Baffin Bay	1.3	25	"	10 to 100?	6	28 - 288	-
	5. Norwegian Sea	0.5	100	"	-25?	6	-	111
	6. Annual Sea Ice	6-7	100	$2.8\text{-}28.3 \times 10^6$ (g km^{-2} mo^{-1})	-	6	101 - 1190	?
	7. Tundra and Taiga	1.6	100	See text	-	6	7	-
						Winter Totals	208 - 2636 (avg 1422)	260 - 410 (avg 335)
Summer	1. Central Basin	8.4	10	1.48×10^{12} (g km^{-2} mo^{-1} atm^{-1})*	-30 to + 10	3	-37	112
	2. Barents, Laptev and Kara Seas	2.5	100	"	-90 to -140	4	-	1332 - 2072
	3. East Siberian, Chukchi and Beaufort Seas	0.9	100	"	-40 to -80	3	-	160 - 320
	4. Greenland Sea and Baffin Bay	1.3	50	"	-10 to -40?	3	-	29 - 115
	5. Norwegian Sea	0.5	100	"	-50 to -100	6	-	222 - 444
	6. Sea Ice Melt Ponds	1?	?	See text	-	2	40?	40?
	7. Tundra-Taiga	1.6	78	See text	-	3	179	-
	Freeze-Thaw	1.6	100		-	0.5	0.4 - 56	-
	Plants	1.24	100		-	3	-	213 - 411
	Ponds and Lakes	0.36	100	1.47×10 (g km^{-2} mo^{-1} atm^{-1})*	300	3	48	-
						Summer Totals	304 - 360 (avg 332)	2108 - 3511 (avg 2811)
Annual	1. Anthropogenic			See text			1 - 7	
						Annual Totals	513 - 3403 (avg 1958)	2368 - 3924 (avg 3146)

*This is the same as 0.078 mmole cm^{-2} atm^{-1} min^{-1}

Annual Net Sink 1188×10^{12} g CO_2

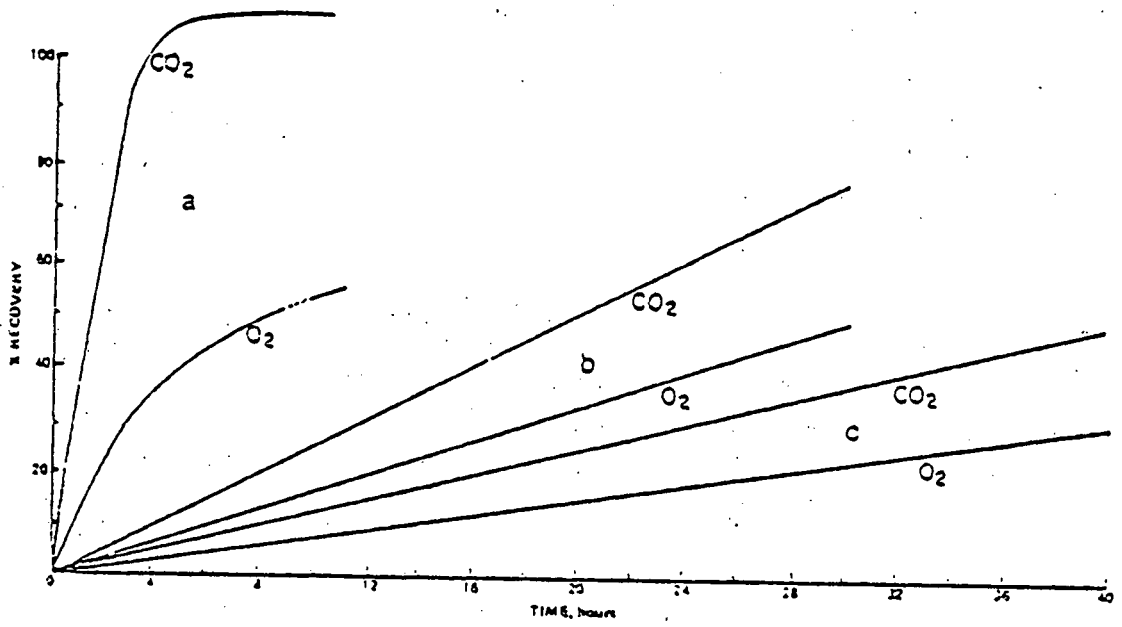

Figure 2

edges. Full (100%) recovery to ambient conditions for CO_2 equals 0.034% (340 ppm) and for O_2, 21%. In all cases (Figures 2: a, b, c) oxygen recovery lags behind CO_2 recovery. The CO_2 partial pressures in the brine in the sea ice matrix have been observed to be in excess of 440 ppm (Gosink and Kelley, 1978). Probably the brines are depleted in O_2 because of the high salt concentration, and because of the suspected slight biological and chemical oxygen consumption within the relatively warm sea ice matrix.

Curve pairs (Figure 2a) denote experiments performed on relatively warm (-10 to -15°C) saline (3-4°/oo) 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°/oo), colder (-20 to -25°C) offshore ice at ARLIS VII (about 220 miles NNE of Point Barrow, Alaska) during 7-11 April 1978. The temperatures in all cases were the ambient air temperatures. The effect of the salinity difference is clearly demonstrated by curve pairs b and c. The ice for cases b and c were, respectively, annual sea ice probably formed late in the previous spring, and 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 was being released to the atmosphere from annual ice surfaces was 2-4 x 10^{-3} ml cm^{-2} hr^{-1}. At -20 to 25°C, it apparently dropped 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 20-40 fold decrease in gas fluxes observed for annual sea ice, assuming the much larger brine channels opened and closed at about the same levels of magnitude as did the much smaller multi-grain boundary veins (Gosink and Kelley, 1981e).

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} discussed shown above. The ambient air CO_2 concentration 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-season ice being the lowest.

There are brief periods in early May when sea ice is begining to rot, when 2 liter chambers covering 200 cm^2 of sea ice were enriched (10-20 ppm) in CO_2 in a few minutes. The PCO_2 of winter sea ice brine was on the order of 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 at the

surface reversed the process. Other possible causes are yeast sporilation on land, as yet thoroughly uninvestigated, and tundra freeze-thaw processes. These facets are mentioned at the end of the next section.

Contact of high PCO_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 exchange on open water. A definite value for this ice resistor effect is unknown at this time, but must be related to the 10^{-3} to 10^{-4} ml cm^{-2} hr^{-1} figures stated earlier. It is this high PCO_2 water rather than the brines in the sea ice that is the probable cause of the continental outgassing of CO_2 from the annual sea ice to the atmosphere. There is insufficient CO_2 in the small amount of brine trapped in annual sea ice to maintain the observed winter-long output of the CO_2.

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

Given a total area of annual sea ice on the order of 6.7×10^6 km^2 (e.g. Barry, 1979) then 101-1190 MT of CO_2 is probably being evolved to the atmosphere over the winter from annual sea depending on the salinity and temperature of the annual sea ice.

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

These considerations of sea-ice-air interfaces alone account for most of the source-sink strengths as shown in Table 2. The net result is to indicate that the Arctic is an annual net sink for CO_2 of more than 1000 MT or an equivalent to 15% of the annual anthropogenic contribution of CO_2 to the troposphere. These figures were derived by the use of our recently observed inversion rate for CO_2 across Barent Sea-Arctic Ocean water. If the lower rate proposed by Keeling (1965) for mid-latitude waters is substituted (0.034 vs. 0.078 mmole atm^{-1} cm^{-2} min^{-1}) then the affect of the Arctic on tropospheric CO_2 is that it still behaves as a sink, but absorbing an equivalent of ca. 7% rather than 15% of the annual antropogenic CO_2. Hood and Kelley's intermediate invasion rate (0.043) provides for a net Arctic CO_2 sink equivalent of ca. 8% of anthropogenic CO_2.

We have recently calculated simple box models (Gosink and Kelley, 1981b) considering CO_2 partial differences for atmospheric CO_2 entering and exiting the Arctic and have arrived at reasonably similar net sink results.

The relatively small but fairly numerous sources and sinks associated with the land portion of the arctic as shown in Table 2 are explained in the following sections.

Gases from Tundra, Lakes and Ponds A large net source of carbon dioxide in the arctic is the tundra with its bogs, ponds and lakes. Extremely high levels of methane and carbon monoxide as well as carbon dioxide were found at the surfce of the tundra and in the lakes and ponds of the arctic in the vicinity of Point Barrow. Kelley et al (1968) and Coyne and Kelley (1974a), reported on the existence of elevated levels of carbon dioxide under the snow 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}, or an almost insignificant 7 MT of CO_2 evolved to the atmosphere over winter.

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.

During the months of June and September, the period of thaw and freeze, the concentration of land surface-evolved gases are large and variable, at least in the vicinity of Point Barrow. The region is dominated by ponds and lakes with organic rich sediment (Brown and Johnson, 1965; Douglas and Tedrow, 1960). Partial pressures of carbon dioxide in the lakes average about 115 ppm higher than that of the ambient atmosphere. The ponds, with warmer bottom sediment and smaller volume dilution, had an average PCO_2 of 357 ppm greater than the ambient aire (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}. Using Coyne and Kelley's evasion rate for tundra lakes and ponds, with an estimated average gradient between lakes and ponds of 300 ppm greater than that of the atmosphere, and that 60% of the 0.6×10^6 km^2 of tundra is involved, then 48 MT of CO_2 is calculated to evolve to the atmosphere over the summer from that interface.

Miller et al, (1976) and Coyne and Kelley (1975), calculate that the vascular plants on the wet tundra fix about 400-770 g 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}. Therefore given the facts and estimates that wet tundra emits more CO_2 than the plants can fix during a portion of this time, i.e. Miller et al's soil source rate for an estimated 8 hours a day over 90 days, Coyne and Kelley's vegetation drawn down values, and that 40% of the tundra and 100% taiga or boreal vegetation are involved then 179 MT of CO_2 are added to the atmosphere

from the soil while the vascular and other plants remove 213-411 MT from the air. This figure is in general agreement with estimated for tundra and alpine ecosystems tabulated by Revelle and Munk (1977).

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

RESULTS

The Arctic emerges from this source-sink analysis to be a source of 1107 MT of CO_2 during the winter period, a sink for 2479 MT of atmospheric CO_2 during the summer to yild a net annual sink effect of 1188 MT. The annual effect is equivalent to 4.6% of the global antropogenic input of CO_2 to the troposphere. The effect is even larger if one considers that half of the antropogenic input of CO_2 to the troposphere remains there while the remainder is withdrawn by the oceans and biosphere throughout the world. High PCO_2 surface waters on the average exist in the equitorial Atlantic and Pacific (Keeling 1968)

which largely offsets much of the low PCO_2 surface waters of the mid-latitudes. Surface waters near Antarctic also display high PCO_2 during the Austral summer. This is due to surface runoff of CO_2 saturated fresh water being affected by the salt of ocean water, plus the upwelling phenomena associated with Antarctic oceans. Therefore the Arctic, which is mostly oceanic in nature, appears to be inordinately important to the removal of atmospheric CO_2 compared to the rest of the world oceans.

Keeling and Bocastow (1977) point out in their models that the ocean-air CO_2 interactions is an equilibrium process. The net removal effect of the oceans an atmospheric CO_2 depends to a large extent on whether or not surface waters, with the absorbed CO_2, are mixed down to about 58 m depth. Winter cooling and salt injection into cold suface water in the Arctic by forming ice fairly well assures that the CO_2 absorbed by surface summer water sinks to depths where it is effectively removed from re-equilibrations with the atmosphere.

If we assume that if only 1/12 of the seasonally absorbed or evolved CO_2 affects tropospheric CO_2 in the Arctic (see arguments in simple box model by Gosink and Kelley, 1981b) then the natural arctic sources and sinks are causing a winter-summer fluctuation of 2.7 ppm, or 22% of the observed average 12 ppm annual variation. However, since both the CO_2 monitor levels, but more importantly that the source-sink effects are at the surface, the apparent effect may be closer to 44%.

CONCLUSIONS

Three conclusions can be drawn from this work.

1. The arctic is not an ice sealed inert surface with respect to atmospheric carbon dioxide balance, but is a viable, essential and substantial part of the whole carbon dioxide question.

2. The natural sources and sinks of CO_2 within the Arctic themselves cause a substantial part of the annual concentration excursion of atmospheric CO_2, particularly at the surface.

3. There are more source-sink data required in three logistically difficult areas if these estimates are to be improved. The most important is the Barents Sea region during the winter because of its tremendously large partial pressure difference, and for which no winter data is available. The next important region is the logistically difficult central Arctic Basin during both the winter and summer. Background data for both the atmosphere and surface water is required. Information about the seasonably variable CO_2 partial pressures in the extensive melt ponds (est. ca. 1-2 x 10^6 km^2) in the Arctic can be expected to have some bearing on temporary source sink strengths. The third need is for the smaller regions for which data is lacking. These are the East Siberian Sea, the Canadian Archipeligo and Baffin Bay.

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FIGURE CAPTIONS

Figure 1. Various rates for transfer of CO_2 across the seas-water-air boundary.

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

CARBON DIOXIDE IN OCEAN SURFACE WATERS: A SIMPLIFIED METHOD OF MEASUREMENT[1]

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RUNNING HEAD: Carbon Dioxide in Sea Water

ABSTRACT

Partial pressures of carbon dioxide in sea water can be estimated with reasonable accuracy by use of the equation: $PCO_2 = 3.98 \times 10^{21} \times pHc^{-19.568}$, where pHc = pHs + (pHs x Sal. x 10^{-3}). It should be possible to equip ships-of-opportunity with relatively simple instrumentation to inexpensively assess ocean surface PCO_2 on a seasonal basis or to derive PCO_2 values from archived pH data if they are of sufficient accuracy.

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INTRODUCTION

A simple relationship between pH and PCO_2 has been found so that PCO_2 in sea water can be calculated with only knowledge of *in situ* pH (pHs) and Salinity (S). The required accuracy of the pH measurement should be better than ± 0.01 pH units in order to maintain an accuracy of ± 6 ppm PCO_2. The accuracy of the salinity measurement needs only to be ± 0.2°/$_{oo}$. Water temperature measurements are not required if pH is measured *in situ*, e.g., at the vessels engine cooling water inlet. Temperature measurements are, however, required (± 0.2°C) in order to calibrate the pH meter against temperature dependent pH standards.

An important sink for atmospheric carbon dioxide is the ocean. Partial pressure differences between the ocean and the atmosphere usually are on the order of ± 0-40 ppm concentration mixing ratio (approximately ± 0-40μ atmospheres) with extreme ranges of ± ∿150 ppm. In order to determine PCO_2 in sea water, direct methods such as infrared or gas chromatographic analysis of clean air equilibrated with the sea water are used, or it is calculated from pH and alkalinity titration data. The latter indirect method produces data which are usually about 5% (or more) higher than the former methods (about 15 ppm with air values at 300 ppm) when performed simultaneously. The indirect method, furthermore, is variable depending on the values of K_1, K_2 and K_B employed for the apparent ionization constants for carbonic and boric acids (Gieskes, 1974; Millero, 1979). In order to perform any of these measurements, skilled personnel are usually necessary, and thus data for only limited areas and seasons are available from various scientific cruises.

DISCUSSION

The pH of pure rain water in equilibrium with atmospheric CO_2 should be about 5.7 (with no contribution from SO_2). The pH of a pure calcium carbonate solution is about 9.9, but when in equilibrium with atmospheric CO_2 (carbonic acid production) it is about 8.4 (e.g., Garrels and Christ, 1965). Sea water not only is essentially a calcium carbonate system in approximate equilibrium with carbonic acid produced from atmospheric CO_2, but also has additional acid contributions due to boric, silicic and phosphoric acids etc. and thus its "normal" pH is closer to 8.1. The contributions of the additional acids are proportional to the salinity of the water. Edmond (1970) calculated that in $35°/_{oo}$ sea water, bicarbonate and carbonate account for 96.5% of the conjugate base present. Therefore 3.5% is the contribution of the other conjugate bases (borate, etc.). Assuming a reasonable constancy of composition, the correction factor for alkalinity titrations (and for pH) is $\frac{0.035}{35}$ x Salinity, or Salinity x 10^{-3}. This factor can be applied either to the pH in an additive fashion as in this work, or to the total alkalinity as a substrative term in place of the borate term to obtain an estimate of the carbonate alkalinity (Gosink and Kelley, 1980). Thus, K_B and ΣB, uncertain terms in the calculation (Millero, 1979) are not required. Silicates etc. are usually ignored, but are important for occurrences of $\leq$ 0.008 pH units.

The observed sea water pH is lower than the theoretical calculated carbonic acid-carbonate pH due to the presence of other acids in sea water. Thus, if the pH is corrected by adding the term pHs x Sal. x 10^{-3}, then the PCO_2 of the sea water can be calculated by the formula $PCO_2 = a\ pHc^n$.

The subscripts on the pH term refer to *in situ* (s) and corrected (c) terms. The least squares fit for [a] and [n] based on observations from a summer cruise (*Hakuho Maru*, 1978) to the Bering Sea (Gosink and Kelley, 1980) are $a = 3.98 \times 10^{20}$ and $n = -19.568$. An initial emperical fit (Fig. 1) for data based only on calculations of PCO_2 from pH and alkalinity titrations, and randomly selected to cover a limited pH range from 7.9 to 8.2 are $a = 6.34 \times 10^{21}$ and $n = -20.83$. The slopes of the two curves (n) are essentially the same. The intercepts (a) differ because of the differences between observed and calculated PCO_2 which is treated elsewhere (Gosink and Kelley, 1980). Comparison of this method to PCO_2 calculated for sea water at 2000 m to the surface from alkalinity data also appears to be good. The method, however, fails below 20°/$_{oo}$ salinity. We calculated the *in situ* and pressure corrected aH and pH by the thermodynamic methods reported by Millero (1979) and are related to NBS rather than tris buffer calibrations. Table 1 may be used with interpolation for the determination of the partial pressure of CO_2 in sea water from *in situ* pH (NBS buffer reference) in the salinity range of 26 to 36°/$_{oo}$. This range should cover nearly all expected observations in the near surface to 400 meters of sea water.

CONCLUSIONS

Careful measurements of pHs along with salinity and temperature should make it possible, with reasonably simple periodic calibrations, to economically employ any ship of opportunity to more easily assess PCO_2 in ocean surface waters during all seasons or to retrieve PCO_2 information from

archived pH data. This should provide a more extensive data base, for example, for models related to global climate change in response to CO_2 changes in the natural environment.

Further observations of PCO_2 by direct (gas chromatography) and indirect (alkalinity titrations) measurement will be necessary to refine the values of a and n. A more detailed comparison of the methods is to be published elsewhere (Gosink and Kelley, 1980).

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Table 1. Partial pressures on CO_2 (ppm) in sea water for *in situ* pH between 7.9 and 8.4 and 26 to 36°/$_{oo}$ salinity.

	PCO_2 (ppm)					
s °/$_{oo}$	7.90	8.00	8.10	8.20	8.30	8.40
36	543	424	333	262	206	157
34	564	441	346	272	214	163
32	585	458	359	282	223	169
30	608	475	373	293	231	177
28	632	494	387	305	240	185
26	565	513	402	316	250	192

FIGURE CAPTION

Figure 1. Empirical fit of ln pH_c versus ln PCO_2 where the solid circles are for calculated PCO_2^c from randomly selected stations in the Bering Sea (*Hakuho Maru*, 1978) and the solid squares represent the observed PCO_2 data.

ARCTIC TROPOSPHERIC CARBON DIOXIDE. LOW ALTITUDE AIRCRAFT SAMPLING

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Barrow, Alaska 99723

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 PCO_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 1a, 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 1c 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 PCO_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 PCO_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 PCO_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 PCO_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 PCO_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 ($\sim$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.

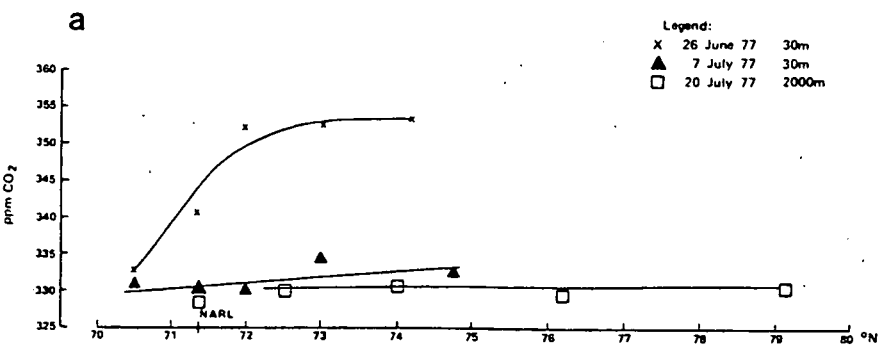
Figure 1b. Horizontal profile of atmospheric CO_2 at low altitude north and south of Point Barrow, Alaska, June-July 1978.

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.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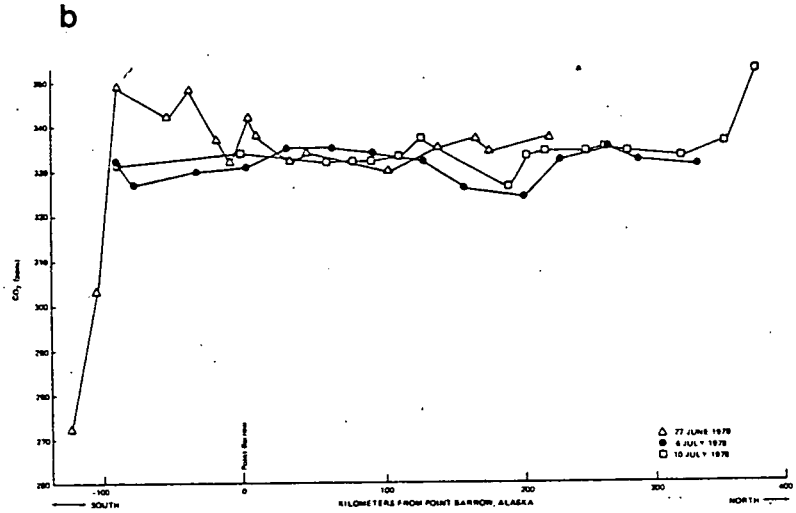
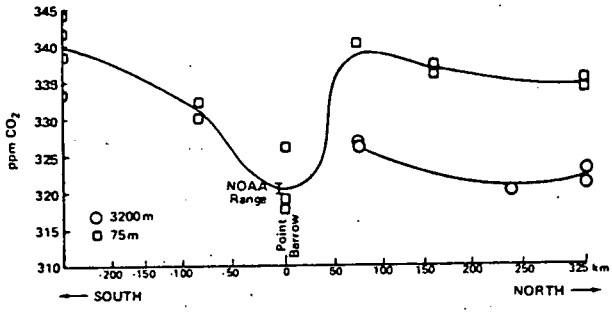
▲ 7 July 77 30m
□ 20 July 77 2000m
ppm CO2
NARL
°N


b
SOUTH
NORTH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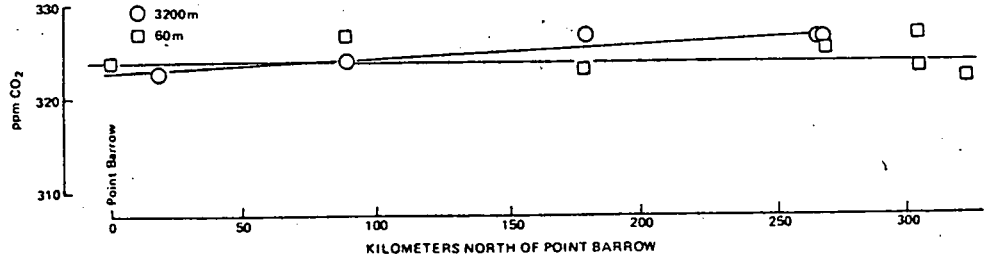
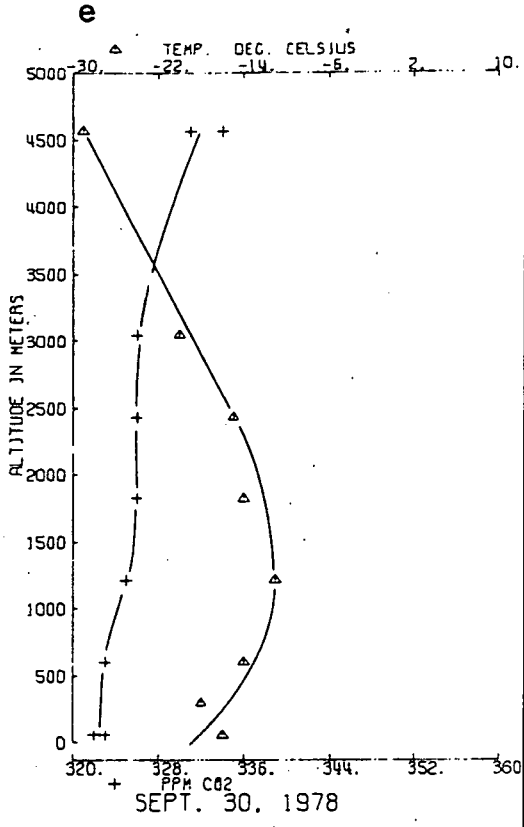
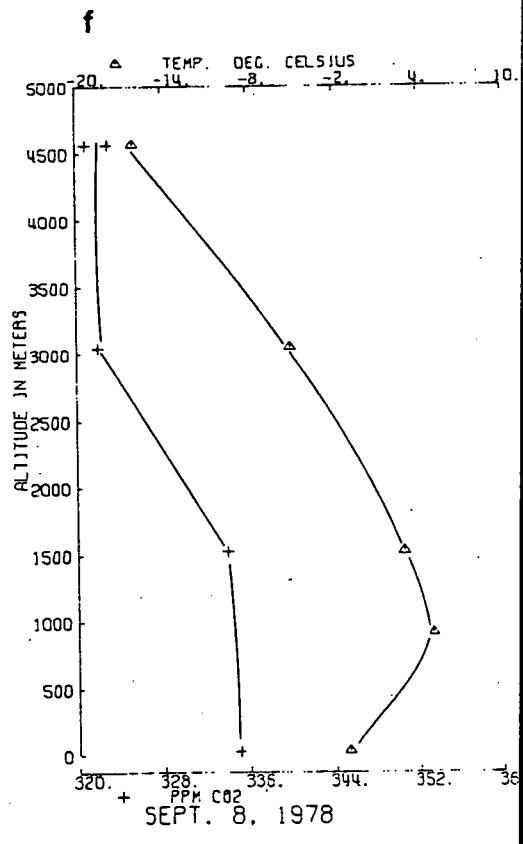
NOAA Range
Point Barrow
3200m
75m
SOUTH
NORTH
km


d
3200m
60m
ppm CO2
Point Barrow
KILOMETERS NORTH OF POINT BARROW


e
TEMP. DEG. CELSIUS
ALTITUDE IN METERS
PPM CO2
SEPT. 30, 1978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TEMP. DEG. CELSIUS
ALTITUDE IN METERS
PPM CO2
SEPT. 8, 1978

APPENDIX 7

List of manuscripts (with titles) in preparation or partial completion.

1. Observations and calculations of PCO_2 in sea waters: A new approach.
2. An explanation for the extremely low partial pressure of carbon dioxide in surface sea waters of the Barents, Kara, and Greenland Seas.
3. Annual Sea Ic. An air-sea gas exchange moderator.

Prospectus to the U.S. Department of Energy Carbon Dioxide and Climate Division for support of a working group on the past, present, and future interactions with CO_2 induced climatic change among the atmosphere, land, sea, snow, and ice in polar regions

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We propose a small working group to synthesize existing information on the interactions among the atmosphere, land, sea, snow, and ice in order to evaluate the hypothesis that with CO_2 induced climatic change the polar regions will become stronger carbon sinks than they are currently and that they will function significantly to damp out the global rise in atmospheric CO_2 and temperature. As CO_2 contents and temperatures rise within the northern polar regions, terrestrial ecosystems will become stronger sinks, the polar ice cap will become a CO_2 source, and open water will become a stronger CO_2 sink. The net result will be a northern sink for CO_2.

The hypothesis will be evaluated by reviewing and synthesizing the current data on the current carbon budgets, past carbon budgets, and future carbon budgets with CO_2 induced climatic change. To develop these carbon budgets, the polar region will be divided into geographic units consisting of ice, snow, land, and open sea. The region under consideration will be that dominated by the polar air mass or underlain by permanent or discontinuous permafrost, i.e., with an annual mean temperature of about -2°C. The working group will also develop a preliminary model of the three-dimension fluxes of CO_2 in the polar regions which can be used to project the current understanding into future conditions.

We propose to include 12-20 scientists actively involved in polar research or atmospheric CO_2 questions. Some possible participants are: G. Kukla, J. Kelley, P. C. Miller, T. A. Gosink, W. C. Oechel, W. O. Heal, L. C. Bliss, C. D. Keeling, Thomas Rosswall, John Andrews, Roger Barry, Kenneth Hare or Ritchie, P. Webber, V. Alexander, J. Hobbie, M. Miller, Joyce Harris, Brian Halter, Ken Rahn. The workshop should involve 5 days since the group has not worked together on this sort of problem and some

time must be spent on developing a common background for productive discussions. Prior to the workshop J. Kelley and P. Miller will develop the format for data from the workshop, which should expedite the processing of the data, the development of conclusions, and publication of the workshop report. The basic data will involve current areal extents of the geographic units, carbon contents, and carbon fluxes, and future areal extents, carbon contents, and carbon fluxes with CO_2 induced climatic change. Consideration of the transient responses must be given.

The proposed budget will be about $17,000, including about $10,000 for travel, $5,000 for local arrangements, and $2,000 for preparation and publication of the report. The workshop might best be held in Boulder, Colorado, to be centrally located and make use of the facilities of INSTAAR or NOAA. Alternatively, it could be held in San Diego.