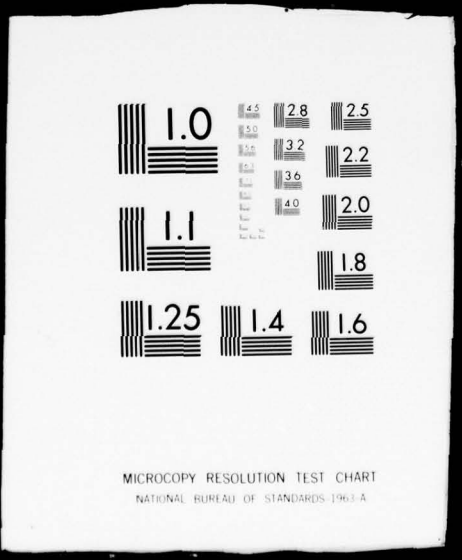
AD-A062 096 ALASKA UNIV FAIRBANKS INST OF MARINE SCIENCE F/G 8/12
GASES IN THE SEA ICE.(U)
SEP 78 T A GOSINK, J J KELLEY N00014-76-C-0331
UNCLASSIFIED NL

1 OF 2
AD A062096

1 OF 2

AD
A062096



AD A062096

DDC FILE COPY

LEVEL II

12

ANNUAL REPORT

to

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

A056115

GASES IN THE SEA ICE

Thomas A. Gosink
and
John J. Kelley

DDC
RECEIVED
DEC 12 1978
A

October 1978

DISTRIBUTION STATEMENT A
Approved for public release;
Distribution Unlimited

78 11 13 104

SECURITY CLASSIFICATION OF THIS PAGE *(When Data Entered)*

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER: A001	2. GOVT ACCESSION NO.
3. RECIPIENT'S CATALOG NUMBER	
4. TITLE *(and Subtitle)*: GASES IN SEA ICE: A Factor Bearing on the Transmission of Sound Energy	5. TYPE OF REPORT & PERIOD COVERED: 10/1/77 - 9/30/78
6. PERFORMING ORG. REPORT NUMBER	
7. AUTHOR(s): Thomas A. Gosink, John J. Kelley	8. CONTRACT OR GRANT NUMBER(s): N000-14-76C-0331
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Institute of Marine Science, University of Alaska, Fairbanks, Alaska 99701	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS: Deapartment of Navy, Arctic Branch, Code 461. Office of Naval Research, Arlington, Virginia 22217	12. REPORT DATE: October, 1978 13. NUMBER OF PAGES: 91
14. MONITORING AGENCY NAME & ADDRESS *(if different from Controlling Office)*: ONR Resident Representative, University of Washington, 3710 Brooklyn Avenue, Seattle, Washington 98195	15. SECURITY CLASS. *(of this report)*: Unclassified 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT *(of this Report)*

DISTRIBUTION STATEMENT A
Approved for public release;
Distribution Unlimited

DDC
DEC 12 1978

17. DISTRIBUTION STATEMENT *(of the abstract entered in Block 20, if different from Report)*

18. SUPPLEMENTARY NOTES

To be published in part in Journal of Geophysical Research Letters.

19. KEY WORDS *(Continue on reverse side if necessary and identify by block number)*

Sea Ice
Gases
Carbon Dioxide
Hydrogen
Ice atmosphere
Gas exchange
Gas chromotography
Carbon Monoxide
Methane

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

See page iii of report.

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102 LF 014 6601

SECURITY CLASSIFICATION OF THIS PAGE *(When Data Entered)*

ANNUAL REPORT

To

Department of Navy
Arctic Branch, Code 461
Office of Naval Research
Arlington, Virginia 22217
Contract Number: N000-14-76C-0331
10 Oct. 1977 - 31 Sept. 1978

Thomas A. Gosink
and
John J. Kelley

From

Institute of Marine Science
University of Alaska
Fairbanks, Alaska 99701

October 1978

(6) GASES IN THE SEA ICE.

(9) annual rept. 1 Oct 77-31 Sep 78,

By

(10) Thomas A. Gosink
and
John J. Kelley

(15) N0001[illegible]4-76C-0331
Sep[illegible]1978
(11)

(12) 98 p.

405 785

ABSTRACT

In the past year we have continued our long standing research on carbon dioxide, and have added several new dimensions. In addition to carbon dioxide, we have some preliminary data on light hydrocarbons, carbon monoxide, nitrous oxide and hydrogen. We have sampled sea ice, sea water, sea ice melt waters, sediment and the troposphere.

We now believe that the arctic plays a significant part in global atmospheric modifications of carbon dioxide by the brine in the sea ice and summer surface waters establishing physical-chemical equilibria. The brine in sea ice has a partical pressure ($\geqslant$ 1000 ppm) of carbon dioxide an uncertain fraction of which escapes to the atmosphere via brine channels and multiple grain bounderies. The size of these channels is determined by temperature and salinity. On the other hand, surface melt waters are depleted in carbon dioxide and act as a large sink during the summer. The tundra is another major source of carbon dioxide in the spring and summer.

Sea water under sea ice in April at ARLIS VII was observed to be depressed to 295-300 ppm in CO_2. This suggests significant biological activity under the ice during the periods of nearly constant illumination. This is clearly in contrast to the winter (dark) values of 330-350 ppm.

Distinct enrichments of methane and nitrons oxide in and over sea ice were noted on several occasions. Again biological activity is suspected.

Some work for collegues in other ONR supported research on aerosols was done. The work is presented in the appendix and deals with basic chemical concepts on gas to particulate conversion.

Preliminary hydrogen work on waters around NARL show typical direct response to light level intensity, with the average concentration being

$3.8X10^{-5}$ml H_2/ℓ. Bering Sea PCO_2 at the surface was mostly low-180-280 ppm high, but high values (400+ppm) were found at 20-40 m. High surface PCO_2 was found west of St. Lawrence Island and confirms past observations.

TABLE OF CONTENTS

ABSTRACT. iii

LIST OF FIGURES vi

LIST OF TABLES. vi

I. INTRODUCTION. 1

II. METHODS 1

III. TOPICAL AREAS - Discussion and Results. 2

1. Restrictec Basin. 2
2. Gases in Sea Ice-Shore Fast 3
3. Gases in Sea Ice-Pack Ice 4
4. Ice/Air Transport of Gases. 6
5. Cooperative Program With Arctic Haze Experiment 17
6. Sediment/Sea Water Exchange of Gases from Subsea Permafrost. 18
7. Injection of Gas to Sea Water from Gas Rich Bed Sediments 18
8. Modification of Arctic Basin Atmosphere from Major Pollution Sources 19
9. Effect of Ozone in Gas Emmersion in Pack Ice from Cover. 19
10. Convection Transport of Ozone to Surface Layers 20
11. Marginal Ice Zone Mixing Processes. 20
12. Hydrogen and Other Trace Gases. 21
    A. *Hakuho Maru* Cruise - July-August 1978. 21
    B. Brine Chemistry. 24

IV. CONCLUSIONS.. 24

V. PROPOSED FUTURE WORK. 25

REFERENCES. 26

APPENDIXES

A. 1978 Science Plan 27
B. Aerosol Formation 42
C. Automatic Gas Sample Resource Controller. 70
D. Equilibrator for Air-Sea Water P_{CO_2} 76
E. The Arctic. A Significant Source-Sink of Carbon Dioxide 79

LIST OF FIGURES

Figure 1. Vertical Profiles of CO_2 North and South of NARL, January, 1978 7

Figure 2. Vertical profiles of CO_2 and temperature over NARL, January, 1978 8

Figure 3. Vertical profiles of CO_2 and ozone north of NARL, January, 1978 9

Figure 4. Vertical profiles of CO_2 and O_3 south of NARL, January, 1978 10

Figure 5. Vertical profiles of CO_2 and O_3 near Deadhorse, Alaska, February, 1978. 11

Figure 6. Vertical profiles of CO_2 temperature and O_3 north of NARL, February, 1978. 12

Figure 7. Vertical profiles of CO_2 temperature and O_3 south of NARL, February, 1978. 13

Figure 8. Horizontal profiles at 100 meters of CO_2 north and south of NARL, June, 1978 14

Figure 9. High and low altitudes horizontal profiles of CO_2 north and south of NARL, September, 1978. 15

Figure 10. Vertical profiles of CO_2 north of NARL, September, 1978. 16

Figure 11. Track of the *Hakuho Maru* cruise in the Bering Sea, July, 1978. 22

Figure 12. *Hakuho Maru* cruise data 23

LIST OF TABLES

Table 1. Oxygen and Carbon Dioxide Recovery in Helium Flushed Chambers on Sea Ice Surfaces. 5

Table 2. Hydrocarbon Analyses, Sea Ice, and Sediment-Head Space Samples 6

I. INTRODUCTION

The overall research at NARL for gases in sea ice is getting to be complex in the number of different tasks that need to be addressed. Furthermore, we have extended help to other ONR supported program and have received cooperation from them. The two principal programs are MIZMEX (Kelly-Hanson at NARL) and the Arctic Aerosol Program (Rahn-Shaw at U.R.I. and U of A). The report of our work on the latter effort is given in appendix C. We have produced an overall, science plan outline to organize our tasks. The plan is given in Appendix A, and the topic will be treated in that order in this report.

II. METHODS

The techniques for analyses of oxigen, nitrogen, carbon monoxide, methane and carbon dioxide are essentially unchanged from the reported in the past. A Perkin-Elmer Model 3920 was borrowed for the nitrous oxide and light hydrocarbon work. The nitrous oxide was determined on the electron capture detector using either a 13 x molecular sieve or Porapak Q column. Light hydrocarbons (C_1-C_4) were determined by the flame ionization detector, using either a chromosorb 102 or the Porapak Q column.

Ozone was determined by the newly acquired Dasibi instrument. The set was calibrated by comparison with the readings at the NOAA-GMCC site located at NARL.

Hydrogen was stripped from sea water by the vacuum expansion method shown to us by Dr. Frank Hall at ONR, Arlington. The Analysis was done on the Reactions Ltd. coulometer described in last years report.

Two recent modifications or the Carle 311 M gas chromatograph enable us to have alternate methods for hydrogen and light hydrocarbon analyses. For hydrogen, substitution of nitrogen for the carrier gas in the gas chromatograph provides adequate sensitivity for analysis of hydrogen stripped from sea water by the vacuum expansion technique. Light hydrocarbon can be analyzed on the Carle 311 M system by replacing columns 1A, and 3 with a 4 ft. Phenylisocyanate Poracil C column, operated at 25°C.

III. TOPICAL AREAS

Discussion and Results

1. Restricted Basins

Many sea water channels and lagoons along the Arctic Coast are either cut off or experience poor circulation because of sea ice growing to or near the bottom of these channels. This afford the opportunity to study sediment influence on sea ice gases, since sediments are almost always high in methane concentrations.

Lack of personnel time prohibited more extensive coverage of the phenomenon as desired, but we observed the following for the area by Niksarook, a point embayment about half way out Point Barrow spit in Elson Lagoon.

There is considerable entrainment of sediment and some organic material in the ice.

Those salinities do indeed rise beyond a normal of about $30°/_{oo}$ to close to $50°/_{oo}$, but usually close to $40°/_{oo}$ in midwinter. This station will be reocupied again this winter for more careful study, but in the embayment area and in the channel instead between the two areas. Other parameters will be monitored as well.

2. Gases in Sea Ice-Shore Fast

Shore fast sea ice in the vicinity of NARL is the most convenient to study for its air sea interaction. Since it is physically near sediment, it may be possible to study the influcence of light hydrocarbons (See subsection 6). Two types of shore fast ice were periodically sampled. Several sites along the coast at NARL provide typical sea ice and the site in Elson Lagoon afford slighly less saline sea ice that has some sediment entrained in it. The underside of both ices were investigated by diving in February (dark) and April (light). There was no visible evidence for bubbles or significant biological growth at those times. Underside ice was smooth slush with occasional stalactites along cracks. No evidence for increased salinity in this ice (see Section 13). However, we did observe high concentration of light hydrocarbons in this slush (see Table II). It is unknown at this time wether this is due to biological activity, or natural frontal zone concentrations of the gases as the water freezes. Then too, there is the question of wether or not this is an accumulation of gases from the sediments which were only 3 m below. The head space gases over the sediments samples (Table II) were however significantly lower. In light of the large diversity in the two slush analyses (head space) it may be that one came from a pocket of microorganisms. Lamontague *et al.* (1973) reported high C_1-C_4 values for antartic sea ice along with visual observations of organisms.

In addition to the carbon dioxide and occasional methane observations in these shore fast annual ices, nitrous oxide was noted to be significantly concentrated in some sea ice samples. This suggests that perhaps facultative anaerobes are operating within the ice matrix. We have contacted micro-

biologists at Oregon State University about this matter, and they have offered to assist in this facet of the study in the coming year.

3. Gases in Sea Ice - Pack Ice

The primary reason for getting away from NARL to other annual ices is to determine wether or not the close proximity of the sediment has a significant effect on the gas content of the ice, and to have the opportunity to find other less saline ice. ARLIS VII (formerly CANBARX) approximately 190 miles northeast of Point Barrow afforded the opportunity. The runway was a large refrozen summer melt lake with salinity of $\sim 1.1°/_{oo}$.

Other multiyear ices in the vicinity were in raised areas, and were very vesicular. This ice was so porous that it was impossible to seal a cuvette to its surface without having it completely open to the atmosphere via the subsurface open lattice. Other refrozen lead ice was similar to that at NARL expect that the prevailing temperatures were colder, and it was less saline.

Finally, there were the observations on early summer rotting ice, and the ice floes of late summer.

The transport of gases from sea ice surfaces to sealed chambers over the ice are shown in Table I. In the first case, the annual ice was 5-10°C warmer than the last two cases, and was more saline. Under those conditions, the carbon dioxide appears to escape much more rapidly than does oxygen.

Furthermore, the brine from the data in Table I is clearly seen to have a bearing on the rate of carbon dioxide escape from the surface as composed to the second and third cases. Both the second and third cases are in the same temperature range, but the multiyear (less saline) ice is significantly slower in outgassing.

Temperature, however, seems to be more important than salinity. There is an order of magnitude difference in outgasing between the two annual ices with 30-50 percent salinity and 5-10°C temperature difference. The second two cases are at the same temperature with a 50-100 percent salinity difference and only 25-35 percent difference in outgassing rate. At -15°C new sea ice contains about 15 percent liquid phase, at -25°C it drops to about 6 percent liquid phase (Richardson, 1976).

In all cases, however, the carbon dioxide load in the sealed chambers exceeded that of the atmosphere. The atmosphere at that time was on the order of 339-341 ppm, and sealed chambers had CO_2 in the range of 351-362 ppm.

TABLE I

Oxygen and Carbon Dioxide Recovery in Helium Flushed Chambers on Sea Ice Surfaces

Identifying Cases	Type of Ice	n	S°/₀₀	Temp.°C	% Recovery O_2	% Recovery CO_2	Time (hrs.)
1	Annual	2	∿3	-15	25	100	3
2	Annual	1	2.0	-20-25	20	70	30
3	Multiyear	2	0.9-1.1	-20-25	25	50	39-42

In the sea ice the source of this CO_2 is the brine, which is about 3 times the concentration of sea water, and has partial pressure of CO_2 $\geq$1000 ppm. The oxygen is rather due to diffusion through the ice or outgassing of the suspected oxygen depleted brines. Brine probably has low concentrations of disolved O_2 because of the salt content and biological activity.

TABLE II

Hydrocarbon Analyses, Sea Ice, and Sediment-Headspace Samples
Approximate ppm Concentrations

Sample	C_1	C_2	C_3	C_4
Shorefast annual ice-underside	400	35	18	2
" " "	65	7	3	tr
Sediment under shorefast ice	10	20	90	-
" " " "	15	7	3	tr
Sediment 71.9°N 152.5°W	100	10	1	tr
Sediment Elson Lagoon	20	tr	-	-
Sediment Offshore-Northeast of NARL	10	tr	-	-

4. Ice/air Transport of Gases with Possible Implication to Climate Modification. See Appendix E for possible publication of this subject.

We have been observing carbon dioxide evolving from sea ice for over two years now, and have other aircraft data from the lower troposphere over sea ice and inland for winter, spring thaw and summer seasons. There is growing evidence that there is a sufficient quantity of carbon dioxide being envolved to cause whole troposphere changes, particularly to the monitor site at Point Barrow located near the source. Aircraft profile data are presented in the following figures.

Aircraft we were depending on for this study became inoperative at the critical period, and thus we only have data for the surrounding periods. Low level flights from Meade River to about 200 miles north of Barrow showed almost continuous levels of CO_2 for the post critical period as did last year.

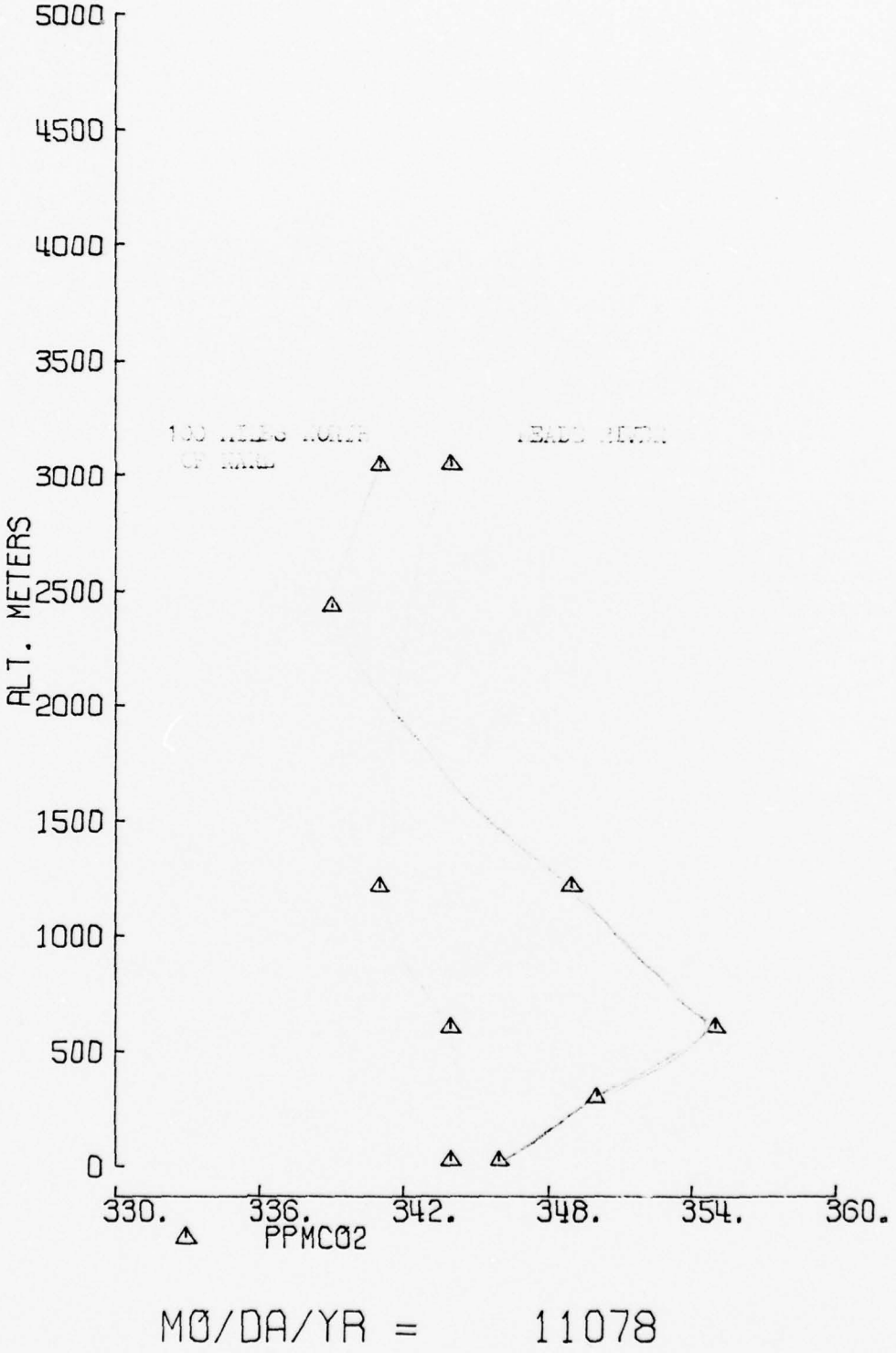


Figure 1. Vertical Profiles of CO_2 North and South of NARL, January, 1978.

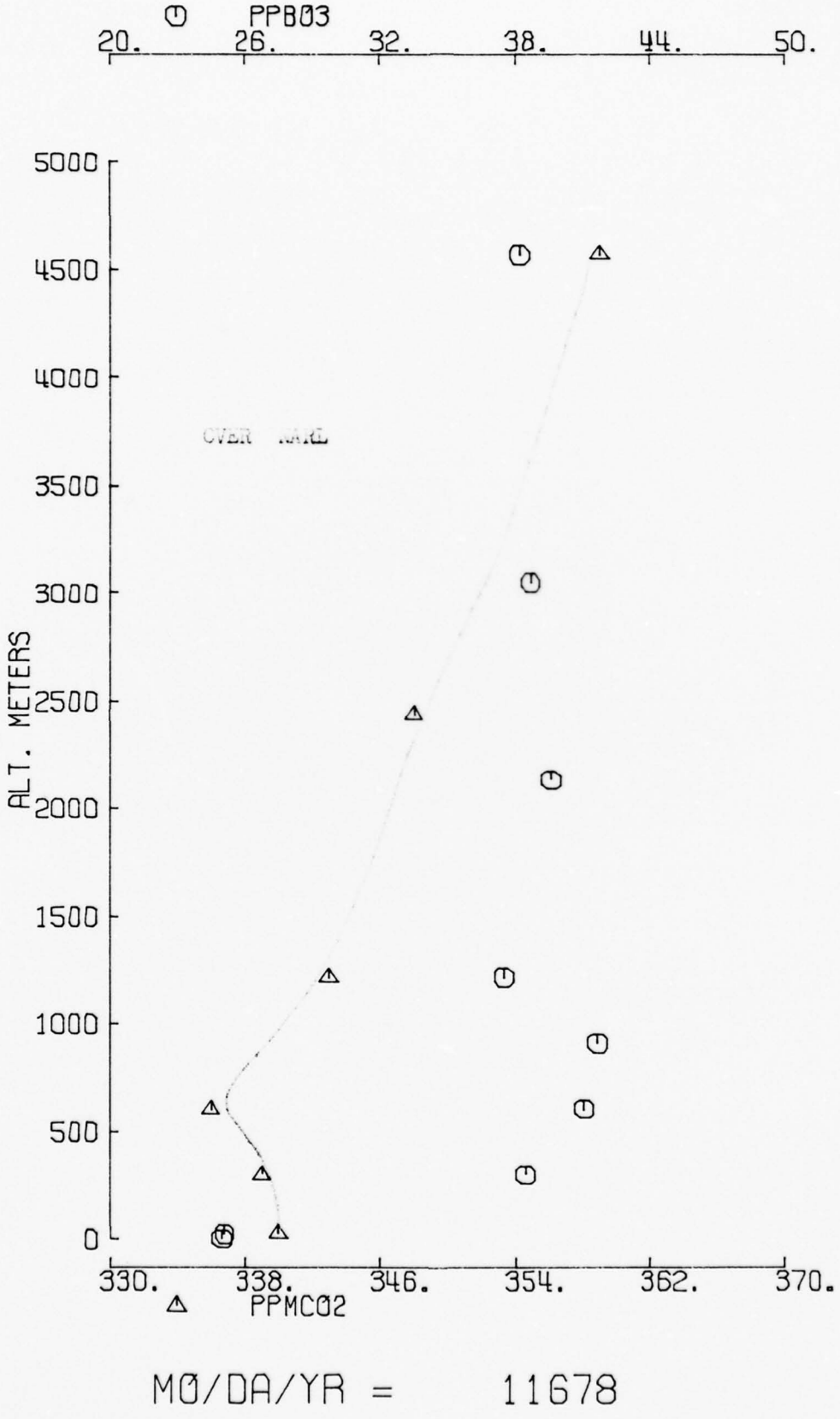
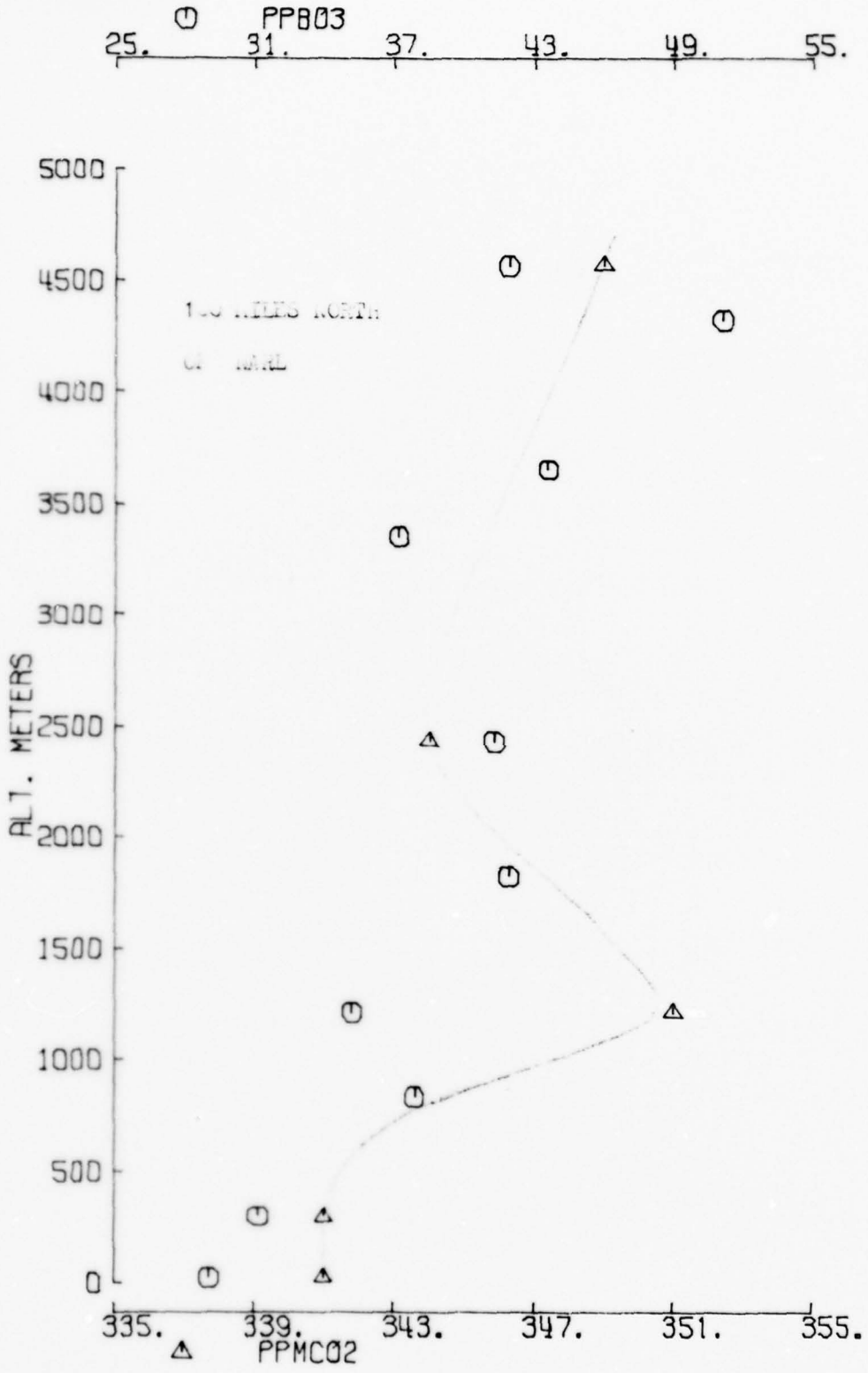


Figure 2. Vertical profiles of CO_2 and temperature over NARL, January, 1978.



MO/DA/YR = 13178-1

Figure 3. Vertical profiles of CO_2 and ozone north of NARL, January, 1978.

78 11 13 10

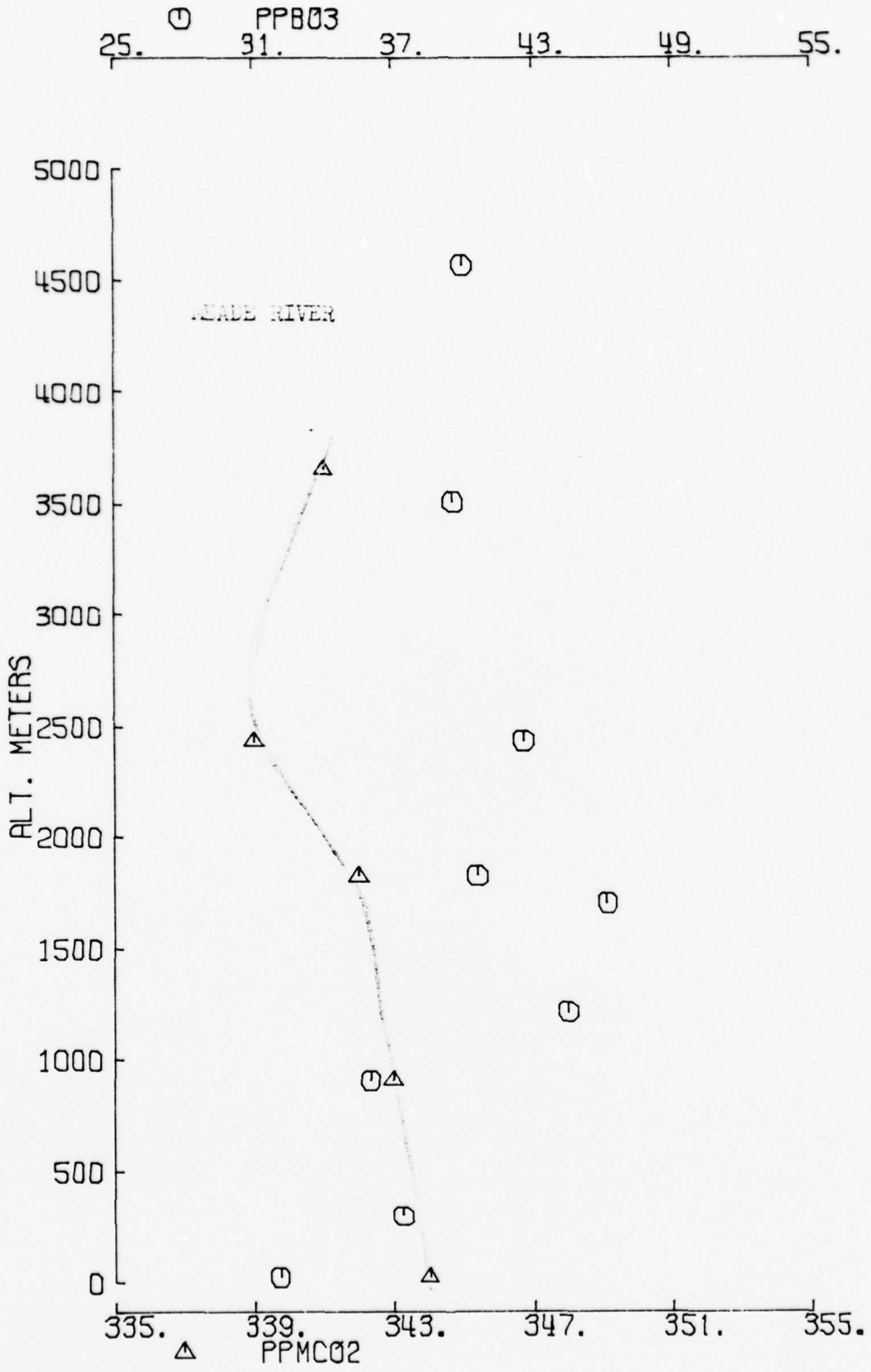


Figure 4. Vertical profiles of CO_2 and O_3 south of NARL, January, 1978.

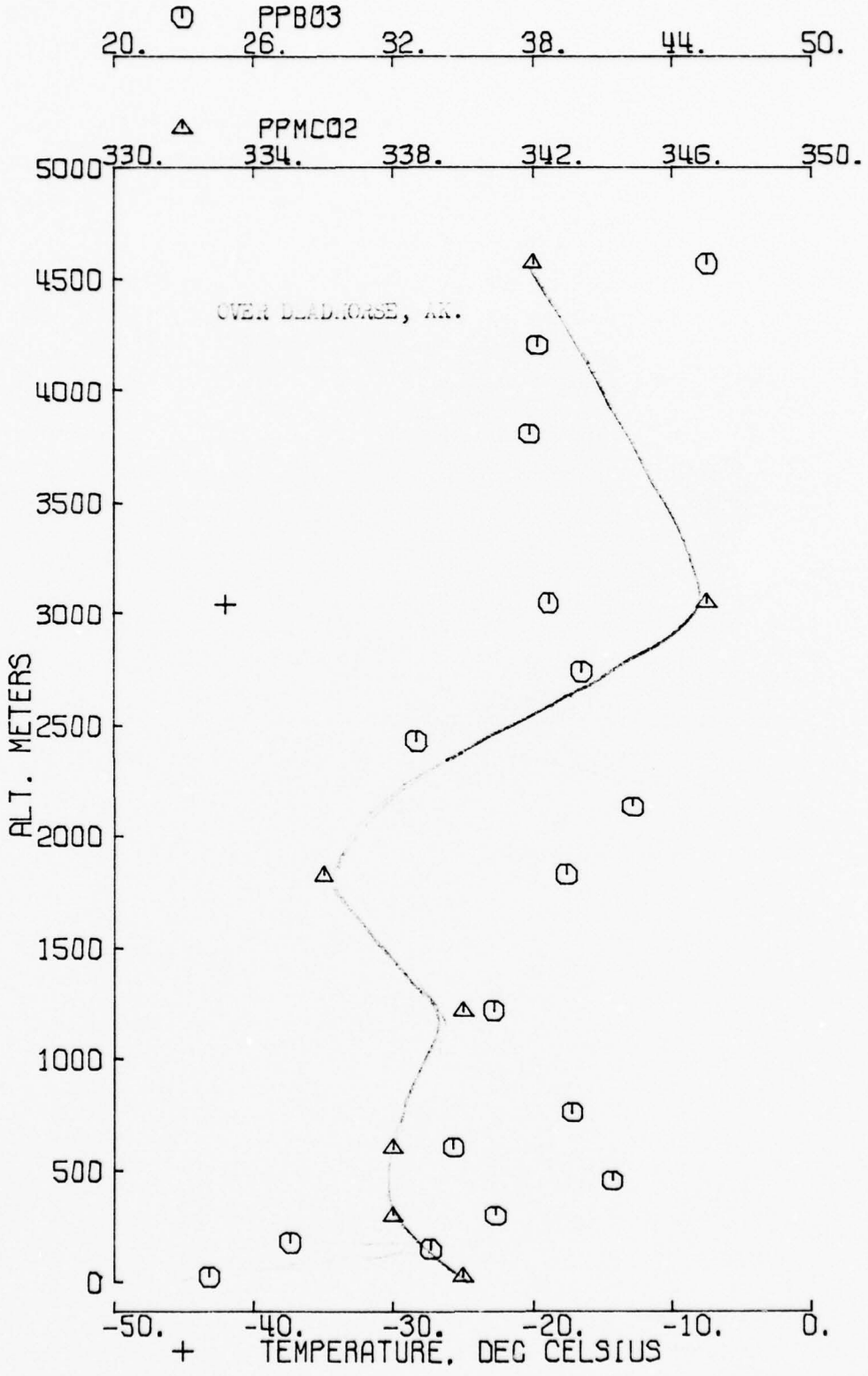


Figure 5. Vertical profiles of CO_2 and O_3 near Deadhorse, Alaska, February, 1978.

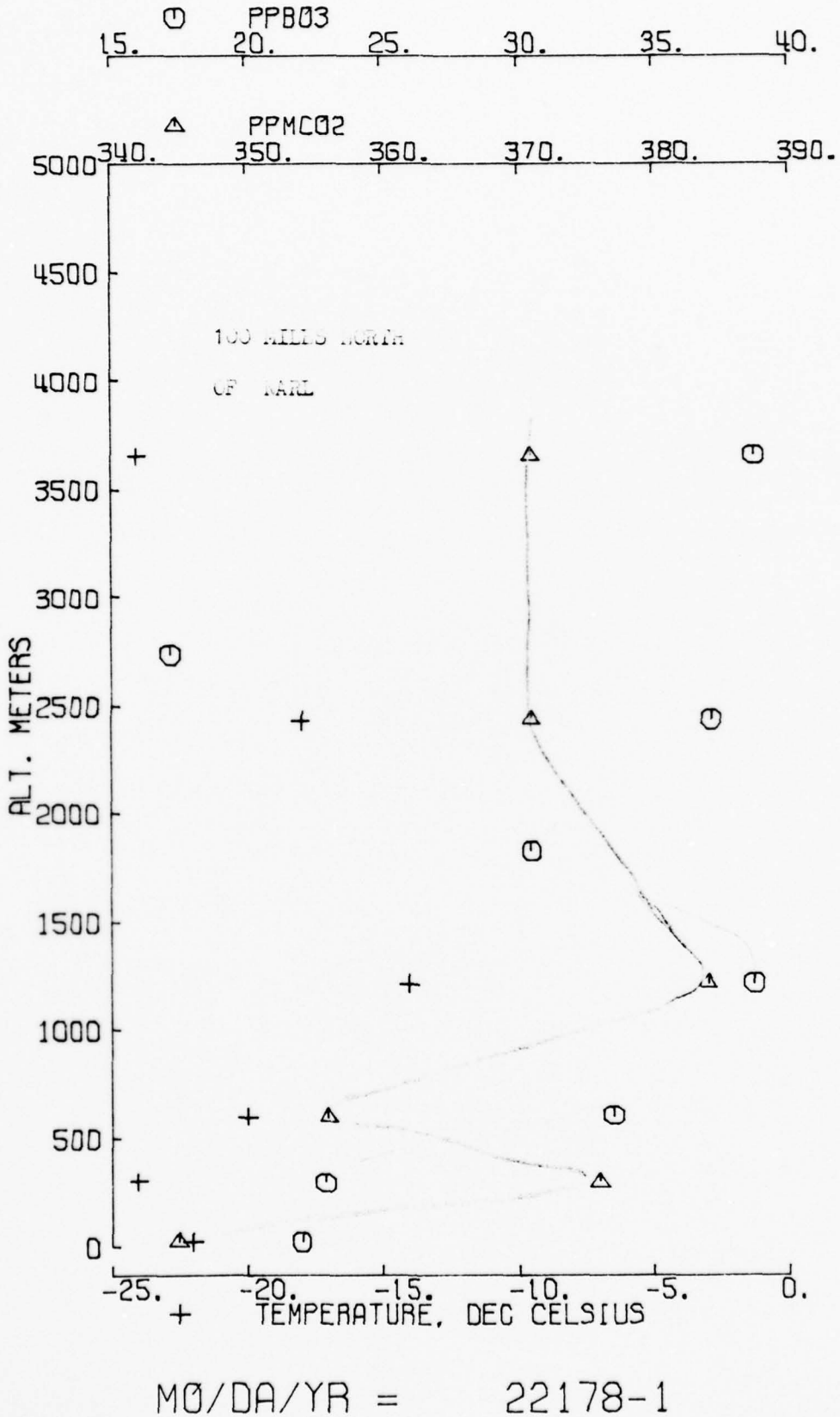


Figure 6. Vertical profiles of CO_2 temperature and O_3 north of NARL, February, 1978.

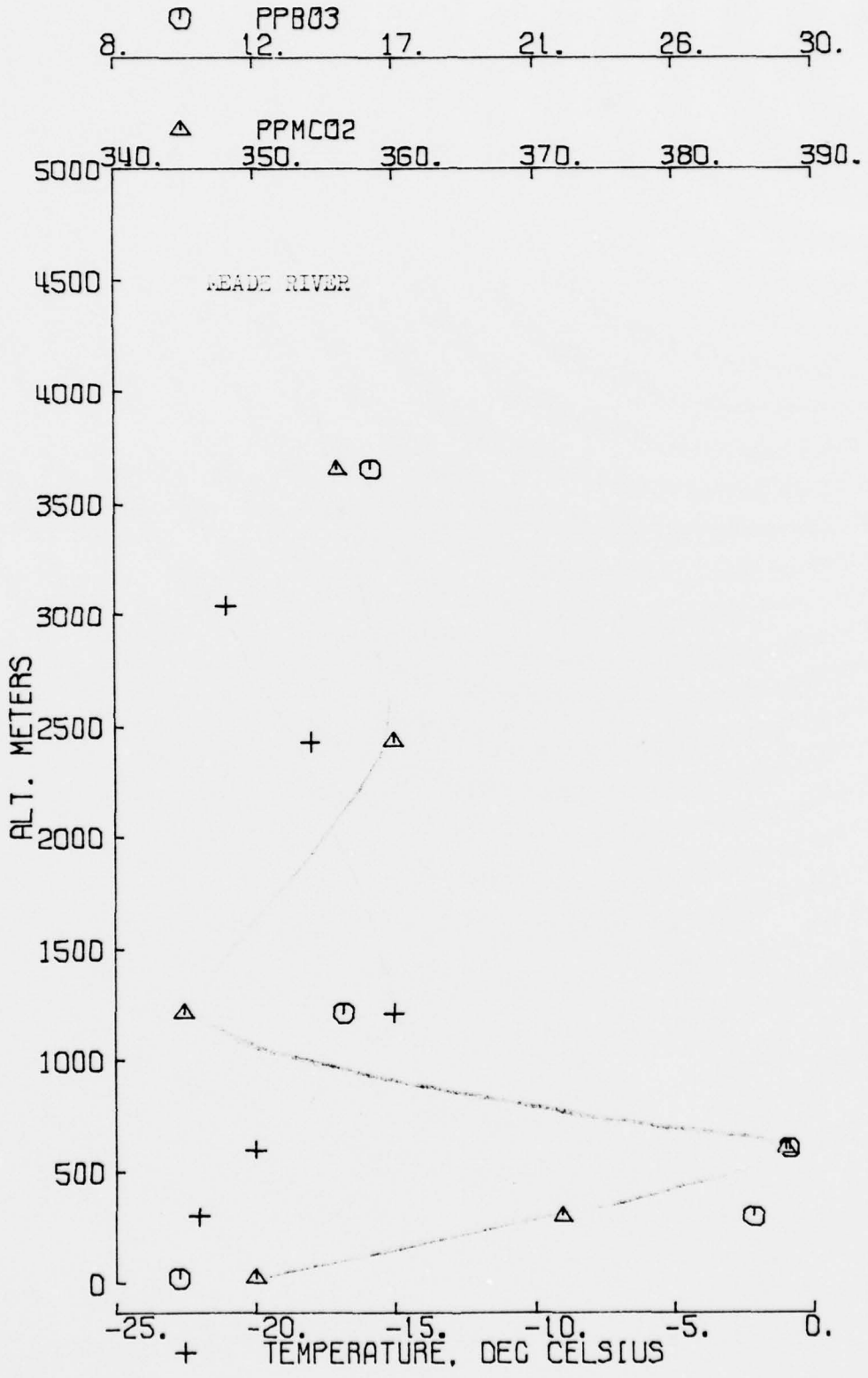


Figure 7. Vertical profiles of CO_2 temperature and O_3 south of NARL, February, 1978.

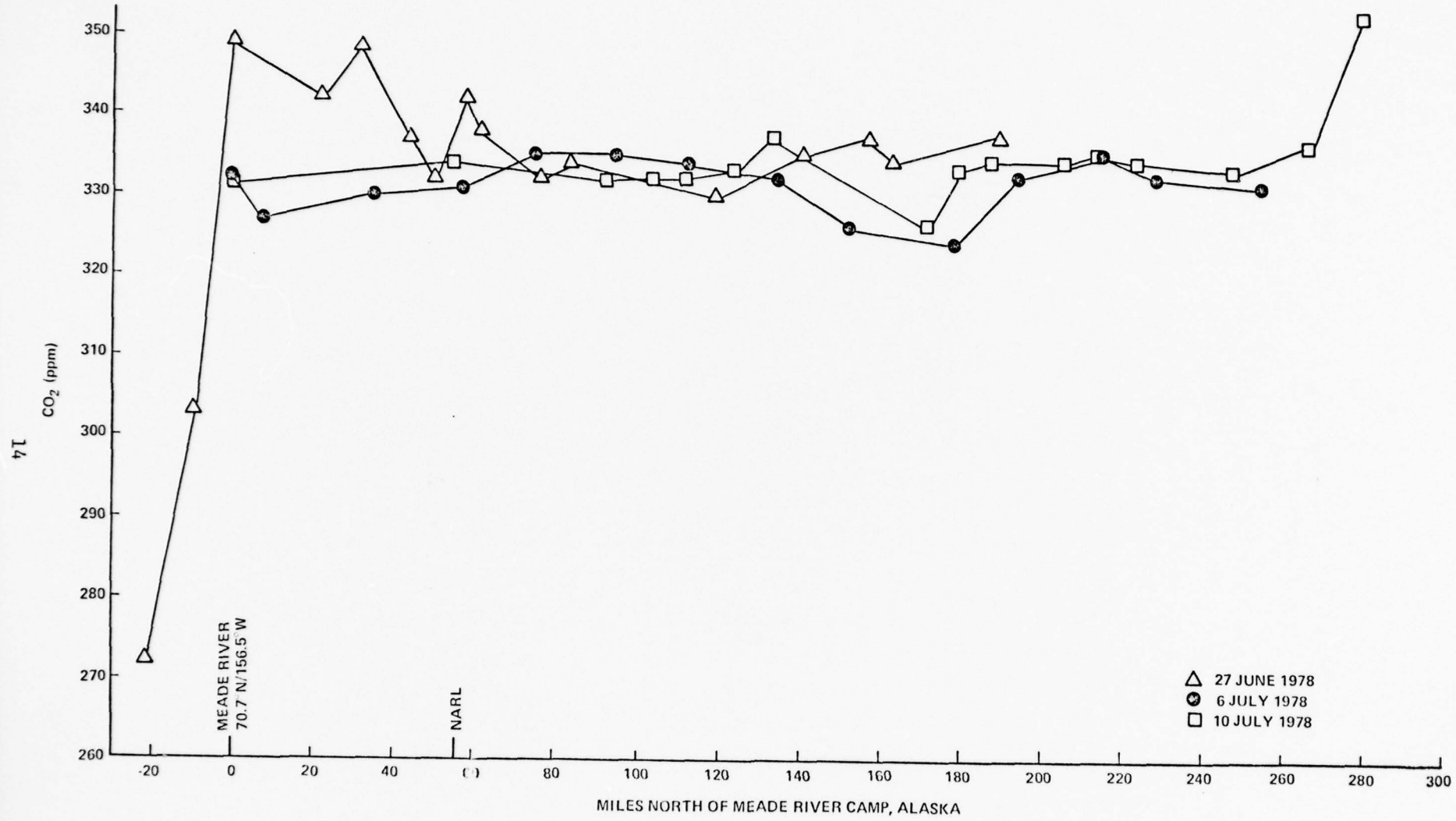


Figure 8. Horizontal profiles at 100 meters of CO_2 north and south of NARL, June, 1978.

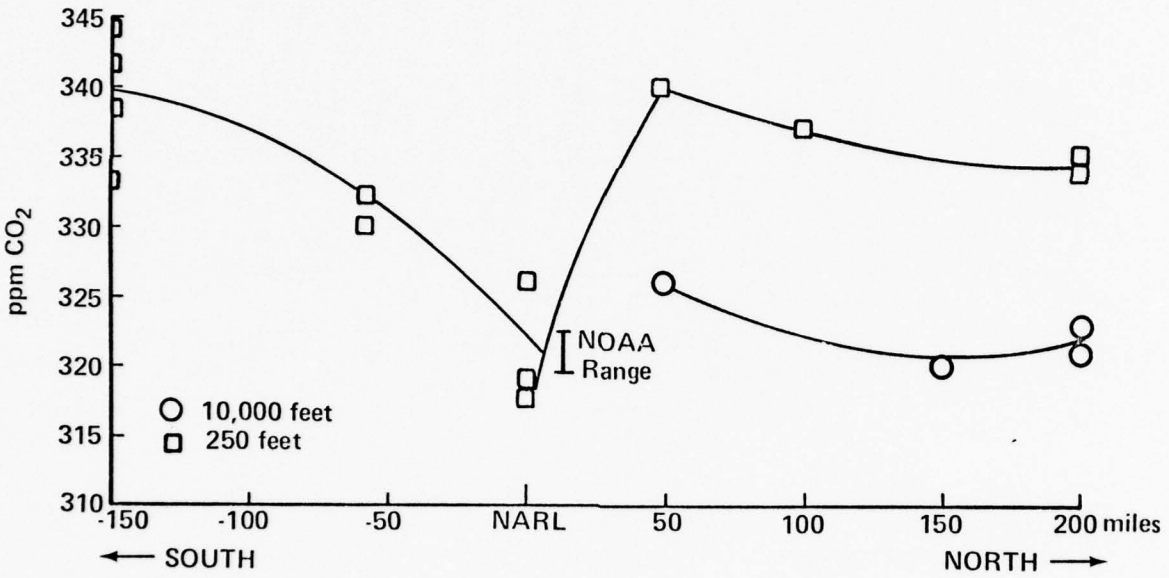


Figure 9. High and low altitudes horizontal profiles of CO_2 north and south of NARL, September, 1978.

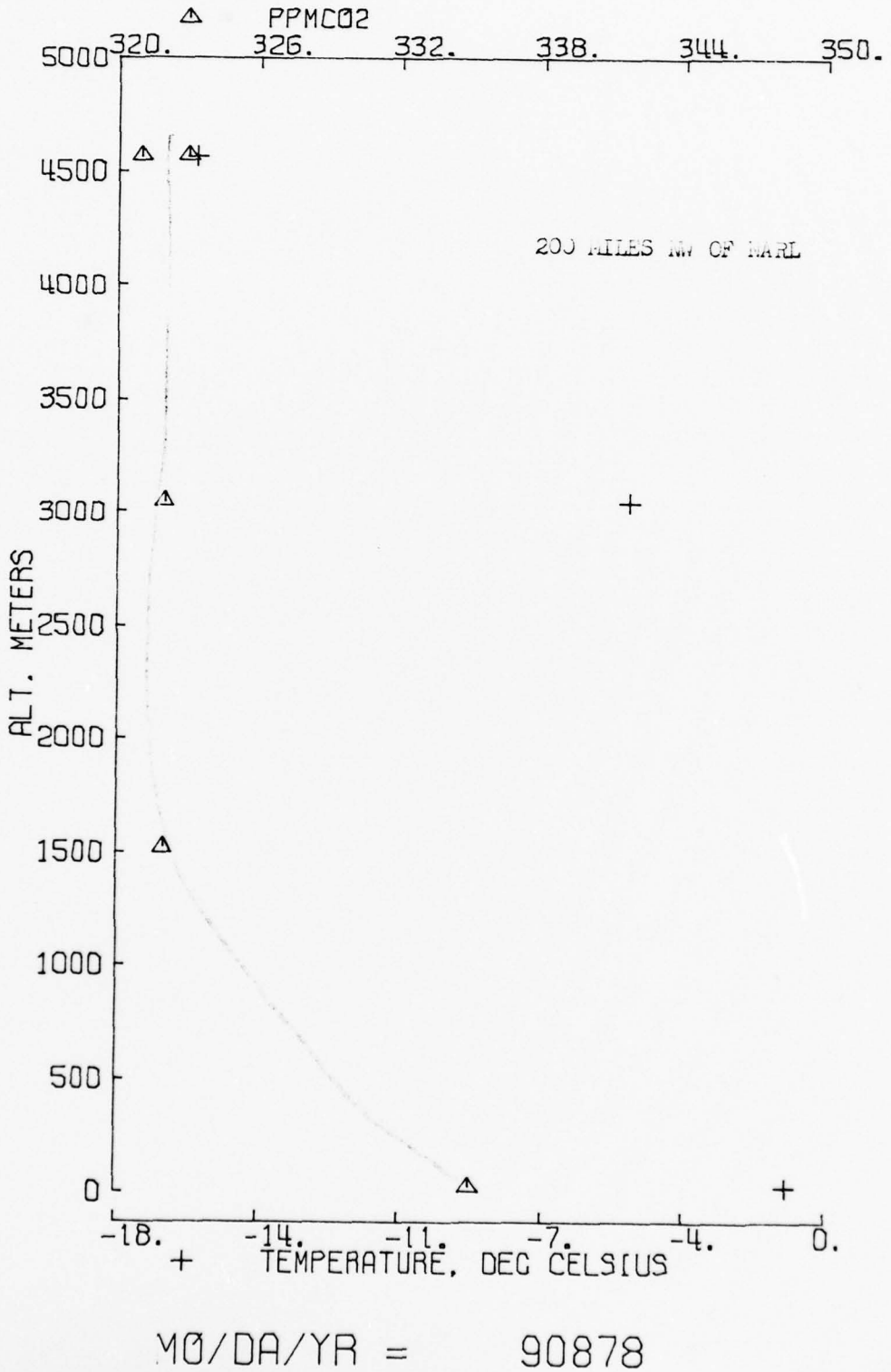


Figure 10. Vertical profiles of CO_2 north of NARL, September, 1978.

There are early flights in June, near, but not at the critical period and it does show some interesting deviations suggesting massive uptake of CO_2 by the biota overland, and possible final bursts of CO_2 for sea ice at the extreme north end of the flight.

The flight in early September shows a clear surface source of CO_2, being nearly 10 ppm greater than values for air collected at 10,000 and 15,000 ft. in the same area. The sea at that time and place (ca. 200 miles NE of Barrow) was ca 90 percent ice cover and new sea ice was forming. There is also evidence of strong terrestrial sources for the inland data due to probable dormancy of the vegetation, and also strong ocean sink action for the ice over the 70-100 miles of open ocean.

Our proposed polar flight also failed because last minute of aircraft inoperability. Our 200 mile flights over the ocean suggest these strong source-sink phenomenon, but require significant penetration either by long rang aircraft or long term ice island work.

5. Cooperative Program with Arctic Haze Experiment.

The bulk of our efforts is to be found in the paper presented in Appendix B of this report. Dr. Glen Shaw asked for assistance in understanding how gases become aerosols in an effort to understand their production in remote areas such as the arctic. In return we have received summaries of his data on aerosol concentrations. We have noted a repeated increased in CO_2 levels at approximately 4000 ft. Dr. Shaw's data shows similar profiles for aerosol counts. The correlation is intriguing, but the full significance is unknown at this time.

6. Sediment/Sea Water Exchange of Gases from Subsea Permafrost.

Last year we saw an ocassional large temporary methane response in our monitoring of gases in sea ice. We thought that perhaps this was being released from the sediments below the shorefast ice, since in the vicinity of NARL there are numerous shallow level gas pockets in the permafrost. This permafrost continues about a km offshore under the sediments, and there is no reason to believe that these subsided sediments do not contain similar gases. The results of a few sampling were presented in Table II earlier. There is only one station (71.9°N 152.5°W) on one occasion that shows any sign of enhanced hydrocarbon content. There were, however, some sample preservation problems. In view of the one large hydrocarbon content of the underside of sea ice, and the apparent lack of it in the sediment under it, it seems more likely that it was produced *in situ* by microorganisms rather than diffusion through the water column. Hydrocarbons in oxygenated waters are usually rapidly consumed. There is too little evidence in any case to tell what the origins of this gas is. Now that we have a grasp of the problems involved in working under the ice, it is hoped that next winter will provide definitive answers to these questions. This topic was one of our low priority interests and was not pursued further. See final comments on section 2.

7. Injection of Gas to Sea Water from Gas-Rich Sea Bed Sediments.

We are attempting to cooperate with the U.S. Giological Survey (Dr. A. Grantz, Menlo Park Calif.) in their search for offshore petroleum deposits. They have seismic records which indicate anomalous areas which may be regions of gas accumulation or clathrates. We have sampled sediments from several of these sites. Again only one (also in Table II) sample shows some promise

of thermogenic rather than biological origin. Earlier gas chemical surveys much further to the east (Macdonald 1976) show only a few promising sites out of fifty samples. Thus our first attempt on only five samples, along with sample preservation problems, are not definitive at this time.

8. Modification of Arctic Basin Atmosphere from Major Pollution Sources.

Since 1973 there has been periodic evidence at the NOAA GMCC site of upwind contamination from their otherwise clean air site. This coincides with increased petroleum production and exploration activities and their location. Visually observed frozen steam plumes from these sites travel many miles from their source before beginning to dissipate. We made one overflight of the Prudhoe area in an attempt to see if there was any unusual concentration of light hydrocarbons in the air. We did not detect any such evidence, however, in retrospect, we may have been at too high altitude over the source rather than a few miles downwind where the gases could rise to us for proper sampling.

9. Effect of Ozone on Gas Conversion in Pack Ice Snow Cover.

We observed very high concentrations of carbon dioxide in the spring, under the snow, both on land (Kelley and Coyne, 1974) and over pack ice (Gosink and Kelley, 1977). One of several possible explanations is photochemical oxidation of methane, and other light hydrocarbons arising from outgassing the tundra and sea ice (higher methane values are usually observed immediately over sea ice, Gosink and Kelley, 1977). Furthermore, in the spring, very high concentrations of carbon monoxide ($\sim$20 ppm) are observed. This may be due to either or both increased biological production of CO, or photochemical oxidation.

At this time, we have acquired the necessary instrumentation, have cross referenced it with the system operated by NOAA at the GMCC site at Barrow,

have test flown it and have indeed seen ocassional burst of ozone at odd intervals that suggest a bolus of upper atmosphere ozone rich air being convected towards the surface. Data is insufficient at this time to further comment. See the next section.

10. Convective Transport of Ozone to Surface Layers.

Past ONR sponsored research (Kelly, 1965-1967) has shown periodic high levels (up to 80 ppb) of 0_3 at the surface. The suspect reason is convevtive transport of 0_3 from aloft, akin to the katabatic flows observed in the antarctic. The other remote possibility is production at the surface by free radical oxidation of hydrocarbons. The latter case may be sufficient to explain the small but measurable increase in the bottom 10 meters, but seems highly unlikely as the source of the high levels mentioned above. Several airborne measurements as well as surface ice measurements were made along with CO_2 observations. See previous section.

11. Marginal Ice Zone Mixing Processes (MIZMEX).

One of the critical times of year for transfer processes is the period of active melt. Very little is known about this time of the year. There is some evidence that gases enter the atmosphere at a greater rate, and that biological effects are pronounced. The former evidence comes from the small but reproducible surge in the maximum atmospheric concentration of CO_2 just before the annual plunge to the summer atmospheric CO_2 minimum.

Preliminary observation in moderate ice flow areas (about 2-3 oktas) show very cold surface temperatures (-0.5 to -2.5°C) and low partial pressures of CO_2 ($\sim$ 280 ppm) salinities are about 18 °/$_{oo}$ in the cold water. Surrounding open water have salinities of about 32°/$_{oo}$ and temperatures of 4-4.5°C. The cold layer extends 0.5-1 m in thickness and a strong thermocline ends at about 3-4 meters where the temperatures are again about 3-4°C.

Biological activity was high and all PCO_2 data for that period were significantly depressed.

Storm activity in September precluded the chance of our supplementing and reporting on this facet at this time.

12. Hydrogen and Other Trace Gases.

At this time we have only a few quantitative observations of coastal waters in the vicinity of NARL for hydrogen, methane and carbon monoxide. Hydrogen appears to show normal direct variations as a function of insolation. The concentration of hydrogen in this area was on the high side of normal, but within the range reported by Hahn for the North Atlantic 3.8×10^{-5} ml/ℓ. Carbon monoxide and methane concentrations are more estimates, but were observed to be 4.8×10^{-5} ml/ℓ and 5.2×10^{-5} ml/ℓ for coastal water in early September. These again are in the range reported by Seiler and Schmidt (1974).

A. *Hokuho Maru* Cruise Data.

We were fortunate to be invited to participate in the cruise of the Japanese Research Vessel *Hokuho Maru* into Alaskan Arctic and Subarctic waters. The cruise track we were involved with is shown in Figure I. We had hoped to enter the marginal ice zone, but unfortunately there was no ice whatsoever at our northern most station. A synopsis of data is shown in Figure II. The PCO_2 data is for surface waters, which, as was to be expected, was in a period of high productivity. The PCO_2 was low, the pH high and the oxygen supersaturated (the latter not shown). In two areas bottom waters clearly had come to the surface. One of the areas was west of St. Lawrence Island as had been observed in the past. Unfortunately regular air analyses had been terminated just before entering those anomalous

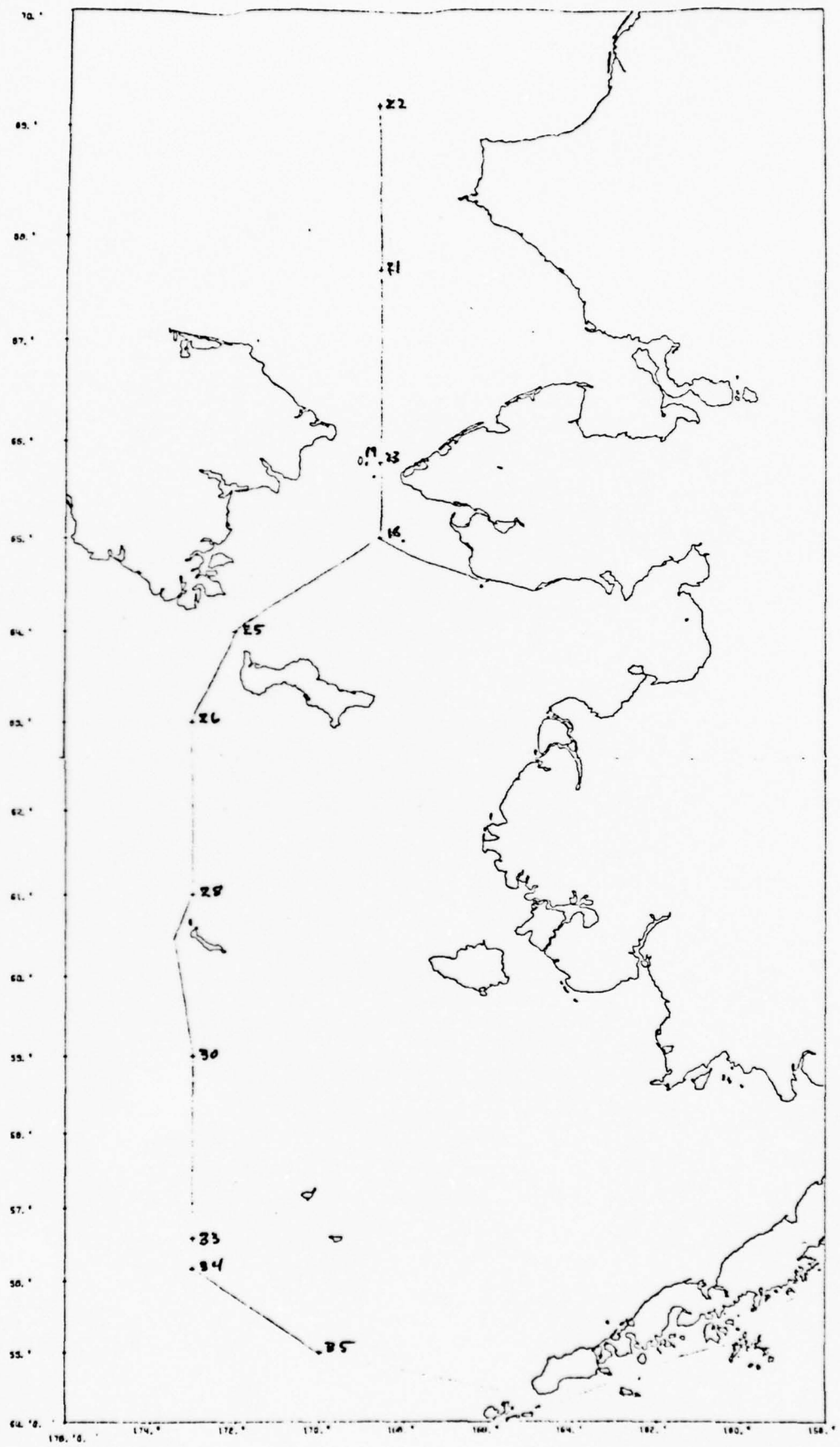


Figure 11. Track of the *Hakuho Maru* Cruise in the Bering Sea. July, 1978.

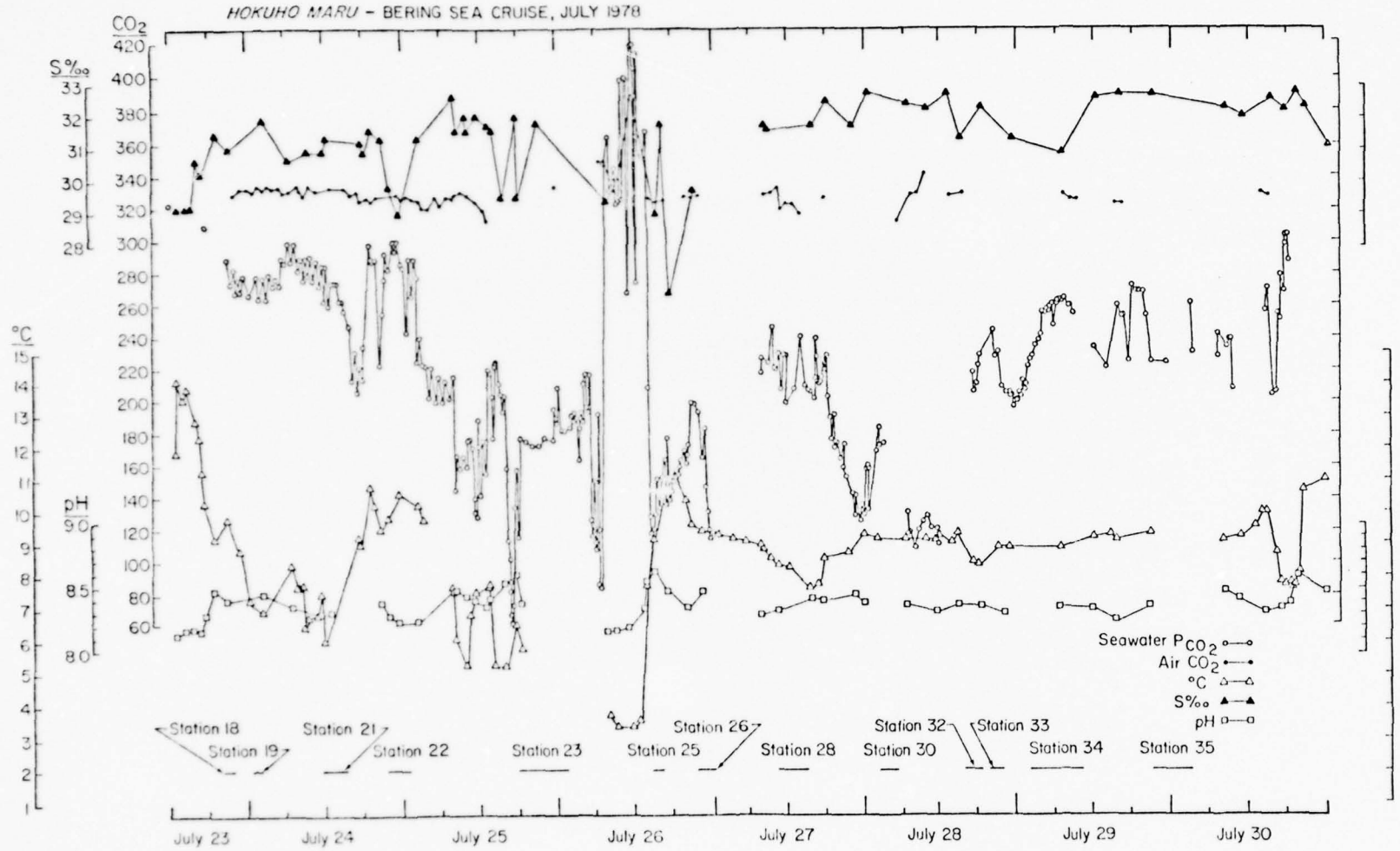


Figure 12. *Hakuho Maru* cruise data.

areas, but the few points there and up and downwind of those areas seem to show significant atmospheric modification of the CO_2 content.

Partial pressures of waters below the thermocline at 20-40 m were all very high >400 ppm.

The pH values appear high because the electrodes were equilibrated with sea water.

B. Brine Chemistry.

Salinities and ion content have been reported for sea ices and brines, both real and laboratory Addison (1977) and Richardson (1976). Sea ices formed in cold weather are more saline as should be expected from normal crystal growth knowledge because occlusions that occur due to rapid formation.

We have been more interested in the brines. Magnesium is enriched in brines and the sea water under sea ice has higher than normal Mg: Ca ratios. This is probably because $CaCO_3$ precipitates and is trapped in the ice matrix, while the Mg flows into the brine areas, and into the relatively quiet sea water under it.

The pH of both sea ice and brine are low in comparison to sea water. Normal sea water has a pH of about 8-8.2, depending on productivity. Melted sea ice has a pH of about 6.8 and brine $\sim$7.7. Both of these values are high because of the sodium ion effect on the glass membrane. So far, we have not found an acceptable literature correction for this salt effect.

IV. CONCLUSIONS

Arctic oceans, and the associated annual sea ice appear to be globally significant in tropospheric modifications of carbon dioxide. The brines in the sea ice certainly play a role, but diffusion of high PCO_2 waters

to the underside of this ice and biological activity are also suspected. Other trace gases, notably CO, CH_4, and H_2 also have apparent sources from these waters and ices. Photosynthesis in the late winter seems to be in progress under the ice. Summer productivity causes the surface waters to be CO_2 sink as is the case in most other oceans.

Without deep water stations from year round, we can not carry our observations too much further on CO_2 except for fall and summer observations. Other trace gases, for example hydrogen, nitrous oxide etc. must also be investigated in detail.

V. PROPOSED FUTURE WORK

A renewal proposal has been submitted to the office of Naval Research to follow through on the points mentioned all of the preceding sections and in the concluding paragraph above. In the subsequent year we must have a year round deep water station such as T-3, and overflights, low and high level of the central arctic basin.

REFERENCES

Richardson, C. 1976. Phase relationships of sea ice as a function of temperature. J. Glaciol. 17, 507-519.

Gosink, T. A. and J. J. Kelley. 1977. Annual Report to ONR.

Kelley, J. J. 1971. Carbon dioxide in the surface water of the Barents Sea: Southwind Expedition-1970. Inst. Mar. Sci. Report R71-20.

Deacon, G. L. R. 1940. Carbon dioxide in Arctic and Antarctic Seas. *Nature* 145:250-252.

Lamontagne, R. A., J. W. Swinnnerton and V. J. Linnenbom. 1974. C-C_4 hydrocarbons in the north and south Pacific. *Tellus*, 26:71-77.

Macdonald, R. W. 1976. Distribution of low-molecular weight hydrocarbons in southern Beaufort Sea. Environ. Sci. and Tech. 10:1241-45.

Seiler, W. and V. Schmidt. 1974. Dissolved nonconservative gases in sea water. *In*: The Sea, chapter 7. Vol. 5. Marine Chemestry. E. Goldberg, Ed. Interscience.

Richardson, C. 1976. Phase relationship of sea ice as a function of temperature. J. Glaciol. 17:507-19.

Addison, J. R. 1977. Impurity concentrations in sea ice. J Glaciol. 18: 117-127.

Coyne, P. I. and J. J. Kelley. 1974. Variations in carbon dioxide across an arctic snowpack during spring. J. Geophy. Res. 79:799-802.

APPENDIX A

1978 SCIENCE PLAN

ARCTIC OCEANOGRAPHIC PROJECTS RELATED TO NAVY NEEDS CONDUCTED AT NARL UNDER ONR PROJECTS

By

Dr. John Kelley
Dr. Thomas Gosink
Mr. Arne Hanson

October 1978

NAVAL ARCTIC RESEARCH LABORATORY

APPENDIX A

1978 SCIENCE PLAN

ARCTIC OCEANOGRAPHIC PROJECTS RELATED TO NAVY NEEDS

CONDUCTED AT NARL UNDER ONR PROJECTS

A. MIZMEX - P78004
(N00014-77-C-0003)
(NARL Base Contract)

B. GASES IN SEA ICE - P76118
(N00014-76-0331)
(IMS, University of Alaska)

INVESTIGATORS:

Dr. John Kelley
Dr. Thomas Gosink
Mr. Arne Hanson

The following projects are in progress or scheduled as tasks for the 1978 season at NARL:

Primary Project Allocation		Subprojects	Page Number
A&B	1.	Restricted Basin	3
B	2.	Gases in Sea Ice-Shore Fast	3
B	3.	Gases in Sea Ice-Pack Ice	4
A&B	4.	Ice/Air Transport of Gases	5
B	5.	Cooperative Program with Arctic Haze Exp.	5
A&B	6.	Sediment/Sea Water Exchange of Gases from Subsea Permafrost	6
B	7.	Injection of Gas to Sea Water from Gas Rich Sea Bed Sediments	7
A	8.	Marginal Ice Zone Melt Experiment	7
A	9.	Ground Truth-Ice and Snow Thickness	8
B	10.	Modification of Arctic Basin Atmosphere from Major Pollution Sources	8
B	11.	Effect of Ozone on Gas Conversion in Pack Ice Snow Cover	9
B	12.	Convective Transport of Ozone to Surface Layers	9
A&B	13.	Marginal Ice Zone Mixing Processes	10
A	14.	Completion of Thesis (A. Hanson) for PhD	11

EXPLANATION OF SUBPROJECTS

1. RESTRICTED BASIN STUDIES
(Primary Project Allocation - A&B)

RATIONALE:

The arctic coastal regions are comprised of many shallow water systems which are composed of restricted basins. These basins are deep sea water channels which are cut-off or exhibit restricted flow during the period of winter ice cover. The western edge of Elson Lagoon offers an experimental area convenient to the NARL to pursue the objectives of this subproject.

Restricted sea water basins offer an opportunity to investigate the exchange of gases from the sediment to the water column and from the water column to the ice and atmosphere during periods under stagnant conditions.

OBSERVATIONS:

1. Observe on weekly basis
   --Salinity at three levels or horizons in the growing/melting ice column.
   --Sea water salinity.
   --pH, alkalinity.
   --Growth of ice.
   --Temperature.

2. Gas analyses
   --Sample ice for gas content (weekly)
   --Sample water for gas content (weekly)
   --Sediment for gas content (three times)

TIME PERIOD: Period of ice cover.

STATUS: In progress

NARL SERVICE: Tracked vehicle; ice drills; laboratory space; sediment grabber; Van Dorn bottle.

2. GASES IN SEA ICE-SHORE FAST
(Primary Project Allocation - B)

RATIONALE:

The shore fast sea ice sheet continues to be an excellent area to investigate mechanisms associated with the exchange of gases across the

water/ice/air interface. Modifications to the experimental method are better accomplished in this region and are cost effective. We have expanded the number of gas compounds that we can measure and use the shore fast ice to provide verification.

The shore fast ice overlays areas of subsea permafrost. We will continue to investigate suspected phenomena related to the capture of gases by the ice from subsea sources.

OBSERVATIONS:

1. Measure gas content and composition in sea ice and snow cover by taking samples and continuous in situ instrumental analysis.

2. Measure rates of exchange across the water/ice/air interface.

TIME PERIOD: Spring 1978.

STATUS: Continuation of previous years' research. Equipment is procured and ready.

NARL SERVICE: Tracked vehicle or snow machine; ice drills; small heated wanigan; generator or camp power; laboratory space; NARL labor assistance.

3. GASES IN SEA ICE-PACK ICE
(Primary Project Allocation - B)

RATIONALE:

The observational rationale is similar to subproject 2. However, the primary purpose of P76118 is to carry these observations to multi-year ice to afford experimental data on gas exchange for the Arctic Ocean. The results of the past years' effort allows us to measure light hydrocarbons and hydrogen. Observations under this subproject will allow for certain Navy relevant application.

OBSERVATIONS: Same as subproject 2.

TIME PERIOD: Spring 1978 plus any other opportunity to make these observations at the convenience of ONR.

STATUS: Same as subproject 2.

NARL SERVICE: At least two weeks on an ice station (i.e., CANBARX) on the distant pack ice; one helohut, heated; power-115Vac/60Hz; subsistence; two investigators; labor assistance in set-up; NARL laboratory space.

4. ICE/AIR TRANSPORT OF GASES WITH POSSIBLE IMPLICATION TO CLIMATE MODIFICATION
(Primary Project Allocation - A&B)

RATIONALE:

It is now strongly suspected, based on the previous season's observations, that there is an efflux of gases from the sea ice which enter the atmosphere. One of these gases, CO_2, is important to questions related to the global atmospheric heat budget. Our results and implications from previous ONR supported research (1961-67) suggest that extensive near-surface atmospheric measurements are required.

OBSERVATIONS:

--Rate of exchange (conducted in conjuction with subprojects 2 and 3)
--Aircraft sampling from 1° latitude south of NARL to as far out over the pack as practical. Light levels are near surface (30m) or at surface by periodic landings and at 3000m.
--Gradient studies over land and at sea from surface to 3000m.
--Intercalibration with NOAA/GMCC, Barrow.
--Ozone measurement made concurrently (see subproject 12).

TIME PERIOD: Monthly.

STATUS: In progress.

NARL SERVICE: Use of C-117 or Twin Otter; aircraft mechanic service, where required; expediter service; NARL laboratory space.

5. COOPERATIVE PROGRAM WITH ARCTIC HAZE EXPERIMENT (with K. Rahn, U of R.I.; Glenn Shaw, Geophysical Institute, U of A)
(Primary Project Allocation - B)

RATIONALE:

The University of Rhode Island program which utilizes the NARL C-117 remote sensing aircraft measures particles and aerosols along predetermined transects to investigate the cause and distribution of arctic haze. Previous discussions with the P.I. led to a cooperative effort to associate our gas measurements with their particulates project. Several cooperative flights have taken place during the past year with data interexchange. It is still desirable for this collaboration and interchange of ideas to promote a more synergistic program in air chemistry and physics.

OBSERVATIONS:

--Collect by means of gas syringes samples of air along the U of R.I. transects. Additional transects or modifications will be made upon agreement between the P.I.'s.
--Measure ozone concurrently and continuously in flight.
--Intercalibration of the ozone analyzers will be made with the NOAA/GMCC, Barrow station.

TIME PERIOD:

STATUS: All systems in operating order for installation in C-117 or Twin Otter.

NARL SERVICE: Flight time; aircraft mechanic where required; expediter service where required; NARL laboratory space.

6. SEDIMENT/SEA WATER EXCHANGE OF GASES FROM SUBSEA PERMAFROST
(Primary Program Allocation - A&B)

RATIONALE:

Recent data on subsea permafrost projects its extent approximately <1 km off the coast of northern Alaska. Associated with permafrost on the land are numerous shallow level gas pockets and gas-filled "ice-poor" sediments. There is little reason to believe that subsea permafrost does not contain gas which may exit the sea bed to the overlying water and, hence, to the ice. Last season's research gave evidence that large bubbles of gas were traversing the underside of the ice; presumably from a sea bed source. These gases entered the ice where they were observed by G.C. analysis.

OBSERVATIONS:

--Transects NW and NE of the Barrow vicinity.
--Collect bottom samples for gas analysis at several locations out to approximately 1 km.

TIME PERIOD: Late spring.

STATUS: All systems in operating order.

NARL SERVICE: Tracked vehicle; flight time, landings on ice; NARL laboratory space.

7. INJECTION OF GAS TO SEA WATER FROM GAS-RICH SEA BED SEDIMENTS
(Primary Project Allocation - B)

RATIONALE:

The U. S. Geological Survey (Dr. A. Grantz) has published reports based on seismic evidence that certain areas of the Beaufort Sea show evidence of high concentrations of gas in the sediments. These gases may continuously evolve small bubbles to the water column which may attenuate acoustic signals. Sampling the water column and sea bed in areas defined by USGS charts may serve to elucidate whether or not these suspected gases are getting out and to what extent. The program will cooperate with USGS if desired.

OBSERVATIONS:

Similar to subproject 6. Will collect samples from short-term (<4 hours) ice stations up to 300 km at sea on the shelf.

TIME PERIOD: Late spring.

STATUS: All systems in operating order.

NARL SERVICE: Flight time, Twin Otter or Cessna 180's; expediter service on ice; NARL laboratory space.

8. MARGINAL ICE ZONE MELT EXPERIMENT
(Primary project allocation - A)

RATIONALE:

The marginal ice zone (MIZ) is a narrow region that encompasses the fringe of the pack ice. The width of the ribbon is variable. In order to understand lateral and bottom melt of sea ice, it will be necessary to make short-term observations from stations of opportunity such as MUMMERS or austere nearby ice camps.

OBSERVATIONS:

--Ice/snow thickness.
--Meteorological regime.
--Salinity.
--Ice geomorphic features.
--Melt from edges of floes.

TIME PERIOD: May/June through August if possible.

STATUS: All equipment procured.

NARL SERVICE: Flight service; expediter/project support service on ice and at Barrow; NARL laboratory space.

9. GROUND TRUTH-ICE AND SNOW THICKNESS ON ARCTIC PACK ICE
(Primary Project Allocation - A)

RATIONALE:

Almost all of the research on ice coverage makes use of satellite imagery. Area is obtained easily but thickness is extrapolated or estimated from very few coastal data. One of the problems in image interpretation is the value to assign a recorded "gray" in an image. In addition, snow cover significantly modifies "gray" values. Ice thickness and snow cover data are not only essential to satellite ground truth, but to any future interpretation of data for the little-known regions of the marginal ice zone and its seasonal transitions.

OBSERVATIONS:

--Aircraft expeditions.
--Land at four to six sites for one to two hours.
--Data reports to be sent to FLEWEAFAC.
--Snow/ice thickness and geomorphic characteristics.
--Salinity.

TIME PERIOD: 28 February 1978; 15 and 31 March; 15 and 30 April.

STATUS: All equipment procurement complete. Project on standby.

NARL SERVICE: Flight service--set transects from near shore to beyond shear zone.

10. MODIFICATION OF ARCTIC BASIN ATMOSPHERE FROM MAJOR POLLUTION SOURCES
(Primary Project Allocation - B)

RATIONALE:

Prior to 1973 the growth of coastal communities and the Prudhoe Bay area were minimal. After 1973 there has been noted periods of contamination suspected to come from local sources and possibly from the vastly developed operations at Prudhoe Bay. It is desirable to investigate this problem so that anthropogenic sources will not confuse data from natural sources.

OBJECTIVE:

--Fly centerline of Prudhoe Bay industrial plume.
--Make observations of gas modification and concentration (and particles--via P76119)

TIME PERIOD: One day in March 1978.

STATUS: All systems on standby.

NARL SERVICE: Flight service--Twin Otter or C-117; expediter service where required; aircraft mechanic services where required.

11. EFFECT OF OZONE ON GAS CONVERSION IN PACK ICE SNOW COVER
(Primary Project Allocation - B)

RATIONALE:

It is suspected from the previous seasons' research that pohtochemical, as well as dark reactions, may take place within the snow layer over the ice in the presence of ozone and gases emanating from the ice. This may be an important mechanism in the interpretation of rates of exchange of gases across the ice/snow/air interface.

OBSERVATIONS:

--Measure gas concentration within snow layer.
--Measure ozone attenuation within snow layer.
--Measure gas compound modification upon increasing the O_3 subnivean level.

TIME PERIOD: March/April 1978.

STATUS: All equipment procured. Project on standby.

NARL SERVICE: Same as subproject 2.

12. CONVECTIVE TRANSPORT OF OZONE TO SURFACE LAYERS
(Primary Project Allocation - B)

RATIONALE:

It has been shown through ONR supported research (Kelley - 1965-67) that atmosphere ozone reaches very high levels (up to 80 ppb) in the surface layer of the arctic atmosphere during winter and spring. This is a variable intensity feature from year-to-year. The suspected reason is convective transport of ozone from aloft.

OBSERVATIONS:

--Vertical and horizontal gradients of ozone.
--Ancillary atmospheric measurements.

TIME PERIOD: 1 January to 1 May 1978 (six flights).

STATUS: Project in progress. All measurements are intercalibrated with the NOAA/GMCC, Barrow program. Data reports and journal articles will be shared with NOAA/GMCC, Barrow observer.

NARL SERVICE: Flight service; aircraft mechanic when required; expediter service when required; NARL laboratory space.

13. MARGINAL ICE ZONE MIXING PROCESSES
(Primary Project Allocation - A&B)

RATIONALE:

The most critical time of the year for the transfer of properties is the period of melt and deterioration of ice in the MIZ. Very little is known about the MIZ during this period. There is evidence that gases enter the atmosphere at a greater rate and that biological effects are pronounced through blooms.

OBSERVATIONS:

--Gas transport at water/ice/sea interface.
--Thermal and salinity microstructure near ice edge.
--Observations of areal extent of thermal and melt phenomena via aircraft remote sensing and ground truth via ship.
--Nutrient gradients.

TIME PERIOD: July-August.

STATUS: Must construct temperature microprobe; must provide heating source to burner radiometer in C-117; all other systems on standby.

NARL SERVICE: R/V NATCHIK, ALUMIAK or IVIK for one to two day trips to nearby ice edge; expediter service; NARL laboratory space.

14. COMPLETION OF THESIS FOR PhD (A. HANSON)

RATIONALE:

Little is known about the flux of dust through the ice canopy. Mass loading of dust in ice is important to melt characteristics and transport of dust through the water column is important to the attenuation of acoustic phenomena particularly in the Marginal Ice Zone which may receive higher dust loads due to wind borne transport from the land.

OBSERVATIONS: No significant field work intended. Data were previously gathered by A. Hanson. Primary task is writing and evaluation.

TIME PERIOD: 1 January to completion--estimated to be by January 1979.

NARL SERVICE: Library, consultation at outside institutions where required; NARL laboratory space.

SUBPROJECT COORDINATION

Many of the subprojects can be accomplished concurrently. They are projected as follows:

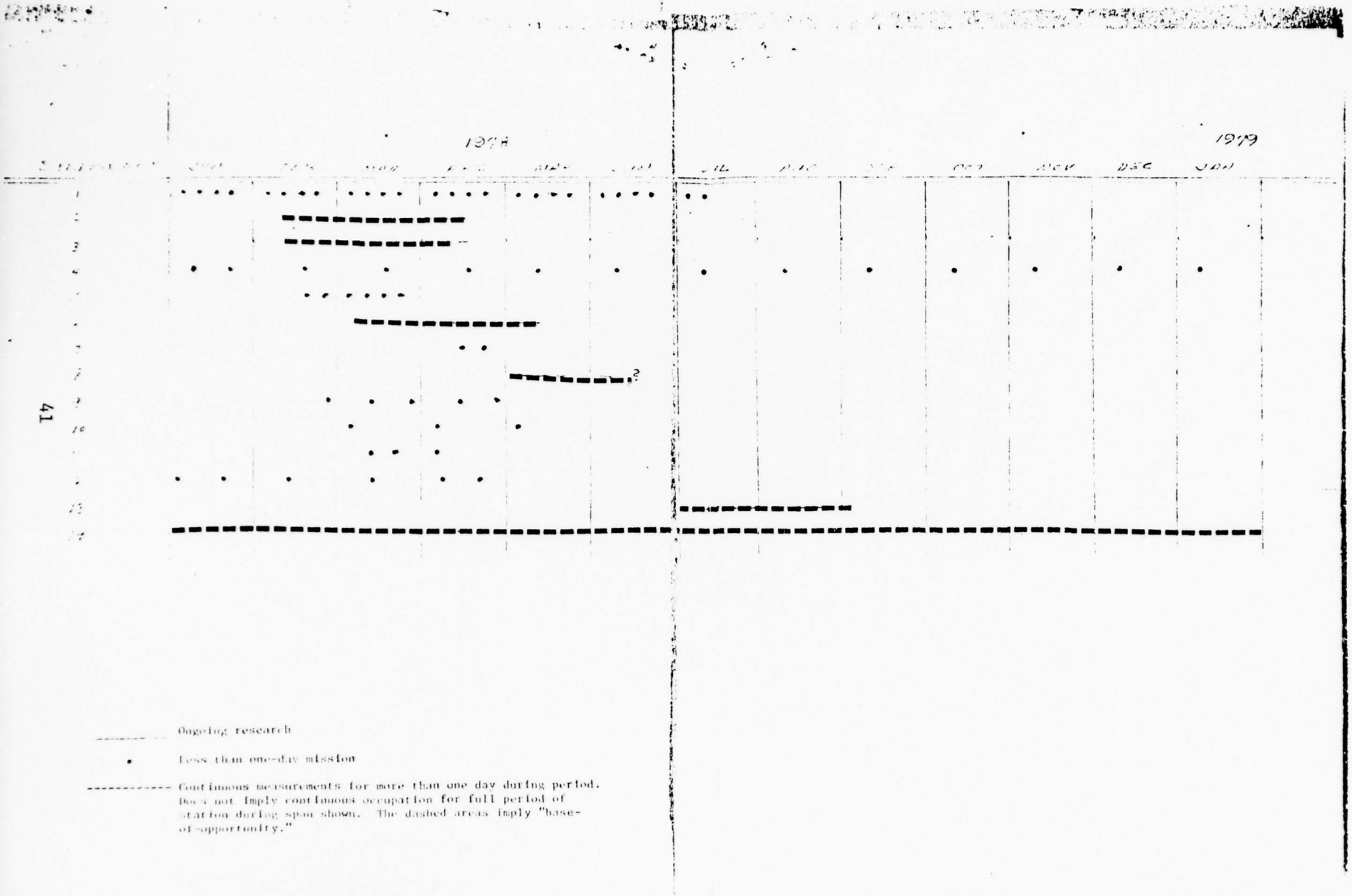
Subproject:	
	1
	2, 11
	4, 5, 8, 10, 12
	6
	8, 3, 6
	13, 8
	14
	3, 7
	9

PROJECT PRIORITY

Priority is assigned subjectively on the basis of critical need to accomplish this season. We assign three ranks (1, 2, 3) where 1 is most critical and 3 could be slipped in time in favor of other more critical subproject tasks.

Subproject	Priority
1	2
2	1
3	1
4	1
5	2
6	2
7	2
8	1
9	1
10	3
11	2
12	2
13	3
14	3

PROPOSED: C-130 flight over Arctic Ocean, June 1978 -- 1
Long-term Ice Station -- 1


1978
1979
Ongoing research
Less than one-day mission
Continuous measurements for more than one day during period. Does not imply continuous occupation for full period of station during span shown. The dashed areas imply "base-of-opportunity."

APPENDIX B

AEROSOL FORMATION

By

Dr. Thomas Gosink

October 1978

AEROSOL FORMATION

Introduction

The intent of this article is to deal with Aitken particle production in simple chemical terms using only some fundamental chemical theory. The concept of formation of particulates from gaseous materials is acknowledged as at least a possibility, and is an accepted fact by chemical researchers, despite the proper scientific reluctance by some when mechanistic details are lacking.

The ubiquitous nature of aerosols is recognized by all, is understandable in most situations, but the mechanism of formation is at best only poorly understood in most situations, and is somewhat puzzeling in others. Direct injections of particulates into the atmosphere, such as volcanic emanations, dust from the earth surface, sea spray etc. are obvious sources, but most of the particulates injected by these processes are too large, settle out quickly, and leave the much larger reservoir of very small or Aitken particles to be explained. Ordinary gas molecules have diameters of about $2\text{-}10\text{x}10^{-8}$ cm. A few, such as a decane molecule, are 2-4 times as large, depending on the conformations imposed on the molecule. Aitken nuclei are the very small particles, and are defined as having diameters greater than 10^{-7} cm (0.001 μm) (a large gas molecule) to about 10^{-5} cm (0.1 μm) or nearly equal the wavelength of visible light. The larger Aitken particles interact with visible light to produce the bluish hazes. Still larger particles generally are mostly water in nature and appear white (e.g. fog).

General Considerations

The atmosphere as a whole is in a reasonable steady state equilibrium. Man has for many centuries affected the local air quality, but it has been only in the past one to two centuries that anthropogenic factors have begun to produce wastes which can influence the massive global natural cycles. While there are sizeable gaps in many areas of our knowledge of sources, sinks and functional mechanisms of trace (<0.1%) gas components of the atmosphere, enough is known so that reasonable estimates of the fate of these components can be made at this time. (e.g. Bach, 1976; Junge, 1977 and Duce, 1977).

Pollutant gases must exit a transient existence from the atmosphere because we know of many globally significant sources for them, yet the atmospheric concentration is essentially constant. There are at least five possible exits: (1) attachment to surfaces of plants, soil, buildings, etc., (2) dissolution into rivers, lakes and oceans, (3) solution in hydrometeors, (4) accretion onto existing nuclei and (5) the formation of new or Aitken nuclei. The first route mentioned above does not lead to either the formation of new nuclei, or to the growth of existing ones. It is highly significant to the lower troposphere, particularly to polar and reactive species such as sulfur dioxide and ammonia. It should be of no particular consequence to non-polar gases such as hydrocarbons. The second exit likewise does not produce new or larger nuclei, but is highly significant to water soluble gases of the lower troposphere such as SO_2 and NH_3, and CO_2. To the extent that the water is not already saturated with the particular non-polar gas in question, a small sink for them as well is available by this second Exit. Hydrometeors play an important cleansing role in the entire troposphere,

by removal of the material dissolved or suspended in then when they impact on surfaces. Hydrometeors are particularly important in their scavenging and concentrating of the highly soluble gases SO_2 and NH_3, where they can react with oxidants to form salts. Individual hydrometeors have very dynamic existences. Droplets are constantly evaporating and the water reforming on other drops or nuclei. Edges of clouds often have significantly higher nuclei counts due to the evaporation of the water to leave the original nuclei material plus any material that was scavenged by the droplet, and which had time to react and form nonvolatile products. The remaining two exits are rather like the chicken and egg problem. At what point is a new particle being formed, or simply absorbing more mass. A single sulfuric acid molecule has a diameter of about 3.3×10^{-8} cm. (0.00033 μm). The smallest Aitken particles have been defined as having diameters greater than 0.001 μm. Therefore a sufuric acid particle of radius 0.001 μm would require 2.2 molecules. A 0.01 μ radius particle is built of $\sim 2.3 \times 10^{5}$ molecules.

Avogadro's number, the number of molecules in a gram-molecular weight of a substance, is very large, 6.02×10^{23}. A single component present at the 0.1 ppbv (per billion by volume; ppb = 10^{-9}) level constitutes 2.7×10^{9} molecules/cc. Even at the 400 mb level there are still 10^{9} molecules/cc of a 0.1 ppbv constituent. Therefore, the theoretical limit on the number of intermediate (r = 0.01 μm) Aitken nuclei that a <u>single</u> reactive gas at 0.1 ppbv concentration could produce is 1.2×10^{4}/cc. Clearly then, the normal range of ∿200-2000 nuclei/cc in clean atmospheres are easily in the realm of possibility given more than one reactive component, a steady state replenishment and probably higher concentrations of each than 0.1 ppbv. In most routine chemical analyses of atmosperic constituents, the limit of detection is around 0.01-0.1 ppbv.

Chemical Reactions

In simplest terms, the rate of any chemical reaction is started by collision theory as:

$$\text{Rate} = \begin{matrix}\text{collision}\\ \text{frequency}\end{matrix} \times \begin{matrix}\text{probability}\\ \text{factor}\end{matrix} \times \begin{matrix}\text{energy}\\ \text{factor}\end{matrix} \qquad (1)$$

(See Frost and Pearson (1953) for more details on most of this section). For ordinary gases at standard conditions, the collision frequency is $\sim 10^{10}$ collisions per second per molecule. Lowering the temperature to 220° K (which approximates temperatures at altitude) won't affect this value by more than about 20 percent, or 0.8×10^{10} collisions/sec/molecule. The probability or steric factor is poorly understood. For gas phase high energy or other nondiscriminate reactions such as proton abtractions involving atoms or radicals, it is fairly high (0.01 to ~ 1). For more complex and discriminate reactions such as polymerization it could be as low as 10^{-5}. Reactions in solution, where hydrating solvent molecules may interfere, the steric factor may go as low as 10^{-9}. Approximations for various steric factors are presented in Table 1.

TABLE 1

Approximate Steric Factors for Gas Phase Biomolecular Reactions.

Type of Collision	Steric Factor
Two Atoms	1
Atom and linear molecule - nonlinear complex	10^{-1}
Atom and linear molecule - linear complex	10^{-2}
Two linear molecules - nonlinear complex	10^{-3}
Two molecules at least one linear	10^{-4}
Two nonlinear molecules - nonlinear complex	10^{-5}

The energy factor is highly variable, depends on the specific reaction, but is exactly stated by term $e^{-Ea/RT}$. Tabulated values for selected energies of activation (Ea) are given in Table 2. The value of Ea for each particular reaction must be determined experimentally by carrying out the reaction at several temperatures and plotting the results. As long as temperature differences are not too large, Ea will remain fairly constant or increase only a few hundred calories with decreasing temperature and molecularity. For reactions involving free radicals and atoms, as is frequently the case for atmospheric chemical reactions, the activation energy is small (7-10 kcal/mole) and the reaction rates consequently are very fast. Second order gaseous reactions between stable molecules, on the other hand, have activation energies that vary between ∿15 and ∿45 kcal/mole., and higher. In order for a reaction of a trace gas component to be of significance to global air chemistry, in the temperature range of 200-300°K, activation energies must be ⩽25 kcal as will be demonstrated below.

TABLE 2

Values of $e^{-Ea/RT}$ for Various Activation energies at 280 and 220°K.

	$e^{-Ea/RT}$	
Ea (Kcal/mole)	280°K	220°K
8	5.69×10^{-7}	1.13×10^{-8}
10	1.56×10^{-8}	1.16×10^{-10}
15	1.95×10^{-12}	1.25×10^{-15}
20	2.44×10^{-16}	1.35×10^{-20}
30	3.82×10^{-24}	1.57×10^{-30}

Given a hypothetical case for a 0.1 ppbv gas (Table 2), realistic steric factor and activation energy of 10^{-2} and 20 kcal/mole, at 280° and 220°K. Substituting these values in Equation (1)

$$\text{Rate}_{280°} = 10^{10} \frac{\text{collis.}}{\text{molec. sec}} \times 2.7\text{x}10^{9} \text{ molec.} \times 10^{-2} \times 2.44\text{x}10^{-16} =$$

65.9 effective collisions/sec

$$\text{Rate}_{220°} = 0.8\text{x}10^{10} \frac{\text{collis.}}{\text{molec. sec}} \times 2.7\text{x}10^{9} \text{ molec.} \times 10^{-2} \times 1.35\text{x}10^{-20} =$$

$2.92\text{x}10^{-3}$ effective collisions/sec.

Other values are tabulated below. These example calculations show that a trace gas under the above conditions would produce several ($\frac{65.9}{2.2} \approx 30$) new small (r = 0.001 μm) nuclei per cm^3 per second in the lower troposphere at 280°K, but would be virtually ineffective at altitudes where temperatures are significantly lower. At 280°K, the time to produce single a 0.01 μm radius particle/cc would be 58.2 minutes. It is evident then, that bimolecular gas phase reactions with activation energies of 25 kcal/mole, or more, are of no consequence to global considerations unless steric factors, concentration, and temperatures are considerably more favorable, all of which are unlikely. In the 280°K range, a 10 percent change in Ea inversely changes the rate by a factor of ∿40. At 220°K, the factor is ∿100.

TABLE 3

Effective Collisions Per Second for 0.1 ppbv Trace Gases, 10^{-2} Steric Factor, Using Selected Values From Table 2.

Ea (Kcal/mole)	280°K	220°K
8	$1.54\text{x}10^{11}$	$2.44\text{x}10^{9}$
10	$4.21\text{x}10^{9}$	$2.50\text{x}10^{7}$
15	$5.27\text{x}10^{5}$	$2.70\text{x}10^{2}$
20	$6.59\text{x}10^{1}$	$2.96\text{x}10^{-3}$
30	$1.03\text{x}10^{-6}$	$3.39\text{x}10^{-13}$

The data in Table 4 indicates the number of intermediate size Aitken particles (r = 0.01 μm) produced per cm^3 in one minute given the reaction efficiencies of Table 3. On another scale for this hypothetical case, the figure of 7.06×10^{-2} in Table 4 translates as ∿70 MT/yr (MT = 10^{12}g) of material if the reaction were homogenous and continuous throughout the entire troposphere.

TABLE 4

Number of Intermediate Sized (r = 0.01 μm) Aitken Particles cc^{-1} min^{-1} for a single 0.1 ppbv Gas Based on Data in Table 3.

Ea (Kcal/mole)	at 280°K	at 220°K
8	4.02×10^{7}	6.37×10^{5}
10	1.10×10^{6}	6.54×10^{3}
15	1.37×10^{2}	7.06×10^{-2}
20	1.72×10^{-2}	7.64×10^{-7}

The Case of Sulfur Dioxide

Most aerosols from clean environments are largely sulfate or sulfuric acid in nature. The usual particle is ammonium sulfate, with a smaller quantity of nitrates, occasionally some persulfate, and about 5 percent of indiscript organic material. Unfortunately, the simple statement of equation 2 is not the case for sulfur dioxide oxidation.

$$2SO_2 + O_2 \rightarrow 2SO_3 \qquad (2)$$

The direct oxidation of sulfur dioxide with oxygen is a slow process, because as equation 2 indicates, it must occur by a rare termolecular collision, and involves a very high energy cleavage of an oxygen molecule. In point of fact, Ea for the reaction in equation (2) is on the order of 40 kcal/mole. In other

words, many orders of magnitude to slow at atmospheric temperatures and concentrations to occur with any significance whatsoever. It will be shown later how the gas phase reaction probably occurs. Sulfur trioxide is produced commercially on a very large scale by the oxidation of sulfur dioxide, but at high temperatures (∿1000°C) and with the aid of nitrogen oxide catalyts. Furthermore, the process is still slow unless a trace of water is present.

Sulfur dioxide is highly water soluble. The reaction between water and sulfur dioxide is frequently shown as that of Equation (3) to produce sulfurous acid.

$$SO_2 + H_2O \rightarrow H_2SO_3 \tag{3}$$

This also is a very misleading statement. Sulfurous acid has never been observed. Sulfur dioxide does indeed dissolve rapidly into water, but it forms a clathrate structure. These caged structures, if they exist independently in the gas phase, would be on the order of 0.002 μm diameter, which is at or below the limit of detection of most particle counters. When the sulfur dioxide does react with the water, the reaction produces a bisulfite anion (Equation 4).

$$SO_2 \cdot xH_2O \overset{K_1}{\rightarrow} HSO_3^-{}_{(aq)} + H_3O^+{}_{(aq)} \tag{4}$$

where

$$K_1 = \frac{[HSO_3^-]\,[H^+]}{[\text{Total dissolved } SO_2] - [HSO_3^-] - [SO_3^{-2}]} = 1.3\times10^{-2} \tag{5}$$

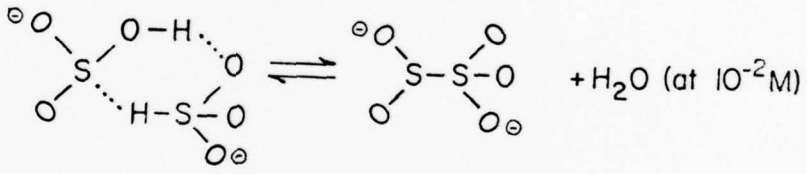
If the acidity becomes too great, an even smaller fraction of the SO_2 reacts to produce the bisulfite anion. Certain trace elements are known to catalyze the oxidation of sulfur dioxide, and it is also known that acid inhibits the oxidation. The observation that the presence of ammonia catalyzes the oxidation of sulfur dioxide is due to the fact that ammonia

reduces the acidity so that more bisulfite and sulfite can form. Bisulfite and sulfite, not sulfur dioxide, are the actual species oxidized in the presence of water.

At concentrations of about 3×10^{-3} M, tautomeric equilibrium becomes important (Equation 6) for bisulfite, and at 10^{-2}M hydrogen bonded dimers and the pyrosulfite anion appear (Equation 7)

(6)

Bisulfite Tautomers

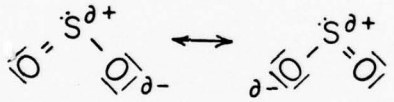


$$\text{Where } K = \frac{[S_2O_5^{-2}]}{[HSO_3]^2} = 7 \times 10^{-6} \qquad (7)$$

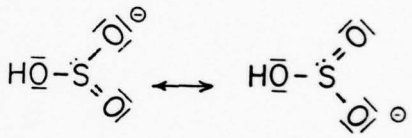
An average cloud with about 0.2 g of water per m^3, and an atmospheric concentration of 0,1 ppb SO_2 would make those droplets $\sim 10^{-3}$M in SO_2, assuming 100 percent efficient scavenging. We know that 100 percent scavenging is not present, because rain water from environments, where background levels of SO_2 are about 1.0 ppb, has a pH of about 5.5-6, and part of that is due to the 320 ppm concentration of CO_2. A 10^{-3}M solution of SO_2, using the equilibrium value (Equation 5) would have a pH of about 4.9. Therefore, rain-drop scavenging must be $\sim$10 percent efficient at these low concentrations. More maybe possible if it is neutralized by NH_3.

Sulfur dioxide is a bent planar molecule which utilizes one of the d orbitals of sulfur in its bonding (Fig 1a). Sulfur trioxide is a trigonal planar molecule, and also utilizes dΠ-pΠ orbital overlap. Sulfuric acid uses two of its 3d orbitals in bonding and is more tetrahedral in shape. One is struck by the similarities of the bisulfite and sulfite structures (Figs. 1b, c) with the sulfut trioxide system (Fig. 1c). All are trigonal plannar structures utilizing the same orbitals except that an extra pair of electrons still belong to the sulfur atom in the bisulfite-sulfite cases.

Figure 1. The canonical forms of sulfur dioxide, bisulfite, sulfite and sulfur trioxide.

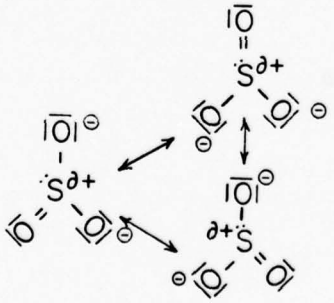


(a) Sulfur Dioxide

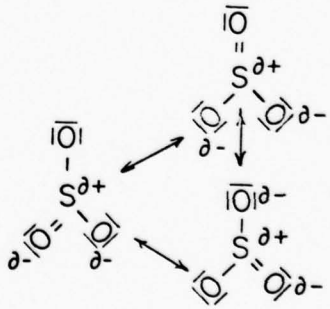


(plus related hydrogen shifted structures)

(b) Bisulfite Anion

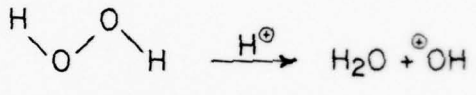


(c) Sulfite Anion



(d) Sulfur Trioxide

Oxidation of sulfur dioxide is known to be faster in hydrometeors than by photochemical oxidations in air. A highly suspect mechanism for bisulfite oxidation in hydrometeors should be its coupling with an oxonium ion, formed by acid cleavage of hydrogen peroxide (Equations 8 and 9)



(8)

Bisulfite Sulfuric Acid

(9)

A paper by Friend *et al.* (1973) describes the laboratory oxidation of sulfur dioxide under a variety of conditions, about which some comments are in order. In those experiments, the water vapor content was frequently at a frost point of -70 to -80°C. This would reduce the water vapor content to about 1 ppm. Air at 220°K and 50 percent humidity, as would probably be found naturally at altitude, would be about 20 ppm. Friend *et al.*'s SO_2 concentrations (0.1-1ppm) were three order of magnitude higher than clean atmosphere concentrations. Sulfur dioxide at 0.1 ppm would require about 1 ppm H_2O at nearly 100 percent scavenging efficiency to form its clathrate structure prior to hydration to produce bisulfite. As discussed earlier, such scavenging efficiencies are not realized. In other words, the system was probably too dry to allow for significant water catalysis in sulfur dioxide oxidation. Furthermore, without sufficient water vapor present, the ammonia catalyst used in some of the experiments could have no effect because bisulfite was not formed.

Finally, their experiments point to the production of more active oxidation species by radiation of <2500Å. Species other than other molecular oxygen are involved in the gas phase mechanism by which sulfur dioxide is oxidized. As mentioned earlier, the oxidation of SO_2 is catalyzed by NO and NO_2. This is because the oxidation of nitric oxide (Equation 10) is both one of those rare termolecular processes, and is very facile (Ea ∿0) possibly due to the free radical nature of all species involved.

$$2NO + O_2 \rightarrow 2NO_2 \qquad (10)$$

Nitrogen dioxide in turn is a supply of oxygen atoms (Equation 11) which is one of the active agent in the gas phase oxidation of SO_2.

$$NO_2 \xrightarrow{h\nu} NO + O \qquad (11)$$

Returning to our simple molecular collision theory for bimolecular gases, and the new reaction shown in Equation (12) we have two basic changes as compared to (2). The first and most important is that a high energy species ·O· (or ·OH) is involved.

$$O + SO_2 \rightarrow SO_3 \qquad (12)$$

The second difference is that the limiting reagent (and the critically active one) is not SO_2, but ·O·. Even though its atmospheric concentration is more than a million fold less than that of SO_2, its energy factor is 10^{23} times greater. (Remember that activation energies for reactions involving free radicals are usually in the 7-10 kcal/mole range). The steric factor is still $\sim 10^{-2}$ for this type of reaction. Using these parameters for reaction (12) in Equation (1) at 295°K, assuming Ea ∿8 kcal/mole and Friend *et al.*'s value [O] = 1.8×10^3 cm^{-3} we obtain 9.7×10^4 0.001 μm radius particles

sec^{-1} cm^{-3}. This estimate figure is in reasonable agreement with Friend *et al.*'s (1973) observations of $\sim 3 \times 10^5$ cm^{-3} ($r \geqslant 0.001$ μ) passing through a reactor for 30 seconds. It should be noted that the concentration of 1.8×10^3 oxygen atoms cc^{-1} would not have been present for the full 30 seconds as stated in Friend's article. If the value of Ea was 7 instead of 8 kcal/mole, the estimated rate increases to 5.3×10^5 0.001 μ radius particle cm^{-3} sec^{-1}.

Another active and variable species in the atmosphere is ·H (Penner *et al.*, 1977; Singh, 1977; Wang *et al.*, 1975, and Perner *et al.*, 1976). The production and consumption of this species occurs by a variety of processes. The concentration in the air varies as a function of the radiation level, so that season, time of day and latitude will have bearing on its concentration.

Concentration variations between about 6 A.M. and noon local time can vary about two or three orders of magnitude. A reasonable daytime average is about 10^5 cm^{-3}. Again, if we assume an activation energy of 10 kcal/mole*, which is probably within a kilocalorie of being exact, and a steric factor of 10^{-2}, the rate of 1.6×10^5 effective collisions/cm/sec. at 280°K. See Equations 13 and 14. This agrees on the high side with the observation in nature ($\sim 2 \times 10^4$). At 260°K the rate is 3.9×10^4 effective collisions/cc/sec. Shaw (1978) reports a bimodal distribution of Aitken paticles in the antarctic. The numbers mode is dominated by the 0.005 μm average radius particles ($\sim$1500/cc) and are presumed to be less than two days old. Shaw also reports (personal communication) that they appear to be essentially all

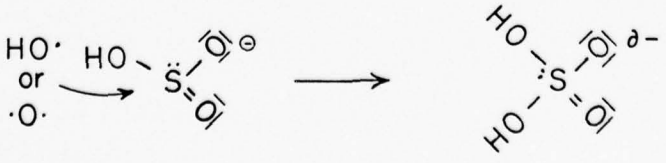
---

*The low end of the range (7-8 kcal/mole) was chosen for the activation energy of ·O·, and here the high end (10 kcal/mole) for ·OH. This is because where ·OH is involved, one side of the radical is blocked by the proton, and the radical as a whole is more stable.

sulfate in nature and that there is an increase in their concentration at sunrise. If we assume that ·OH is the principal agent oxidizing the 0.1 ppb SO_2 (, 19), that the temperature is about 220°K, Ea 10 kcal/mole, and that at in the early A.M. in Antartic (austral summer) that the ·OH concentration is $10^3/cm^3$, then our molecular collision theory predicts $7.3x10^3$ particles (r = 0.005 μm) every two days. This is in good agreement with Shaw's observations if one considers that these particles are coagulating to form large ones during that two day time period, thus lowering the count. In the gas phase, in the high energy upper atmosphere environment, the oxidation of SO_2 does indeed proceed, but as shown in Equations 13 and 14. It is also a reversible reaction until the highly oxidative SO_3 can be hydrated to the considerably more stable sulfuric acid molecule. SO_2 can also be photolyzed in the gas phase to SO and O. Thus water is extremely important to the oxidation of sulfur dioxide even in the dry phase reations.

(13)

Sulfur Dioxide Bisulfite



(14)

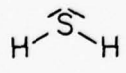
Bisulfite Sulfuric Acid

To summarize this section on sulfur dioxide oxidation, wet chemical processes (in hydrometeors) involves bisulfite and sulfite anions, not the non-existent sulfurous acid, nor the stable clathrate enclosed and oxidative gas SO_2. The reaction may involve an oxonium ion from hydrogen peroxide. In the gas phase, the critical factor is the presence of highly oxidative species such as ·O· and ·OH which are highly dependent on ultraviolet energy for their formation.

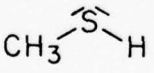
More on Sulfur. Hydrogen and Organic Sulfides.

Anthropogenic sources produce about three times as much sulfur dioxide (∿120 MT) as does nature (∿40 MT) but nature supplies approximately thirty times as much hydrogen sulfide (∿100 MT) as does man (Bach and references therein). Furthermore, there are significant minor contributions by nature to the global atmospheric sulfur budget in the form of organic sulfides. Chief among these is dimethyl sulfide (DMS). Others are indicated with their structures in Figure 2 (Lovelock *et al.*, 1972; Lovelock, 1974; Liss and Slater, 1974; Moroulis *et al.*, 1978; Rasmussen, 1974; and Braman *et al.*, 1978).

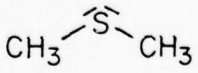
Figure 2. Structures of Sulfides



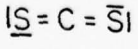
(a) Hydrogen Sulfide



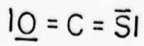
(b) Methyl Mercaptan



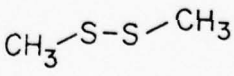
(c) Dimethyl Sulfide



(d) Carbon Disulfide



(e) Carbonyl/Sulfide



(f) Dimethyl Disulfide

The origin of the organic sulfides is biological in nature. Many plants contain significant quantities of amino acids which contain the -SH or $-SCH_3$ group (e.g. cysteine and methionine) which are cleaved by microbial action. Productive areas of the oceans, swamps, etc., generally have significantly higher quantities of the organic sulfides in the atmosphere over them. Dimethyl sulfide may constitute about 5 percent of the global sulfur cycle. Dimethyl disulfide, if only a few data points can be extrapolated, would contribute a little less, and methyl mercaptan, carbon disulfide and carbonyl sulfide all less than 1 percent each. The "other" organic sulfides which have not been specifically identified, may contribute a total of another 5-10 percent.

All of these gases can be oxidized, particularly by the reactive species such as ·O· and ·OH, to produce sulfuric acid (e.g. Cox and Sandals, 1974). Paugam and Coulomb (1975) and Bonsang *et al.*, (1976) ascribe part of the observed particulate matter and sulfur dioxide along the coast of France to the oxidation of DMS. There are, however, certain intriguing intermediate possibilities. Elemental sulfur is a fairly stable entity and should be produced in colloidal form in both hydrometeors and air from hydrogen sulfide oxidation by various oxygen species and by sulfur dioxide (Equation 15). Hydrogen sulfide is, however, much less soluble in water than is sulfur dioxide, particularly in acid media such as is the case with hydrometeors where both CO_2 and SO_2 can lower the pH to $\sim$5.5 (and lower by SO_2 in polluted areas). Hydrogen sulfide oxidation should also occur in gas phase reactions by proton abstraction reactions (e.g. Equation 15b) The facile redox reaction shown in Equation (15a) should lead, at least temporarily, to elemental sulfur particles. Sulfur is a stable product, but may be oxidized under vigorous (e.g. ·OH, ·O·) conditions.

$$2H_2S + SO_2 \rightarrow 2H_2O + 3S \quad (15a)$$

$$2OH + H_2S \rightarrow 2H_2O + S \quad (15b)$$

Elemental sulfur is not normally reported as part of atmospheric aerosols. The question is, is it not present in significant quantities, or was it not specifically looked for in the analysis?

Perhaps the most intriguing factor is the possibility of the sulfides being the principal agents for long range sulfur transport to remote regions (e.g. Antarctica and the Arctic). The half life of hydrogen sulfide in the air is thought to be about 30 hours, whereas that of sulfur dioxide, because of its much greater water solubility, only about 5 hours (Bach, 1976 and references therein). The organic sulfides are relatively water insoluble, and should have comparable half lives with hydrogen sulfide. Consequently they will be transported farther from their source before being converted to sulfate (via other intermediate products) as compared to the highly water soluble SO_2. For example, Flyger *et al.*, (1976) report slightly higher concentrations of sulfur dioxide over the Greenland ice sheet than by the coast. The questions are, was this increase due to volcanic emanations of either SO_2 or H_2S, other distant pollution sources, or by the oxidation of sulfides to sulfur dioxide?

Organic sulfides are insoluble in water because of the hydrophodic organic ligands on them. Consequently, they will largely escape entrapment by hydrometeors and migrate greater distances than sulfur dioxide. However, when oxidation does commence, the products will be polar water soluble ones, and these intermediates will be confined fairly well to the water phase. The first product of the sulfur atom oxidation in DMS is dimethyl sulfoxide

(DMSO) (Equation 16). Other products would involve oxidation of the organic ligands.

$$CH_3\text{-}S\text{-}CH_3 \xrightarrow{[O]} CH_3\text{-}\overset{\overset{O}{\uparrow}}{S} - CH_3 \qquad (16)$$

All such products are unreported, possibly due to the complexity of analytical resolution, minuteness of quantity, or both. Further oxidation of DMSO will produce methane sulfonic acid, via the stable sulfone (Equation 17).

$$CH_3\text{-}\overset{\overset{O}{\uparrow}}{S}\text{-}CH_3 \xrightarrow{[O]} CH_3\text{-}\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}} - CH_3 \xrightarrow{[O]} CH_3SO_3H \qquad (17)$$

Dimethyl disulfide and other sulfur homologs of these compounds will all produce, in part, alkyl sulfonic acids which are not distinguishable from sulfate by normal analytical schemes. They will form insoluble barium salts in the turbidimetric and radio isotope dilution procedures. The material measured by colorimetric methods is actually a derivative of methane sulfonic acid. The ultimate product, with further oxidation of the sulfonic acids or any other intermediates is, however, sulfuric acid. Nevertheless, at least in coastal areas, perhaps 5-10 percent of the material reported as sulfate may actually be alkyl sulfonates.

A purely speculative point is that of a possible correlation between alkyl sulfonic acids and disease. Alkyl sulfonic acids are powerful alkylating agents and thus mutagenic and potentially carcinogenic. There have been weak correlations drawn between aerosols and sulfates and disease, but the question is, what specifically in the aerosol is the correlation with, sulfate, alkyl sulfonates, or some other minor components.

Water Vapors, Photoexcitation and Haze

Tyndal reported nearly a century ago that light photo induced self nucleation of various organic vapors. There have been a few other similar reports, the most recent of which by Wen *et al.* (1978) indicates that pure water self-nucleates by the accumulation of a sufficient number of photo-excited water molecules, This could help to explain a number of phenomenon. For example it could assist in the condensation of water onto small nuclei; to the possible formation of sulfur dioxide clathrates (see section on SO_2); to the appearance of haze in the arctic where surface counts remain near only 400 CN/cc despite the apperance of greater levels of haze.

In the arctic, about half of the winter oceans are covered with relatively thin ice covers (<1 cm to ∿1 m) and about 5 percent is open water in leads and polyni. The open water clearly adds water vapor to the atmosphere, and it is obvious to even the casual observer that large quantities of fog (ice crystals) are in the vicinity of these places. Furthermore, even 1 m thick sea ice maintains a high surface ice temperature due to the essentially in-exhaustable heat source of the ocean under it. Unless the air temperatures have been very cold for a considerable period of time, the temperature of the ice air interface remains ≳ -15°C.* At this temperature, the equilibrium vapor pressure of water over the ice is about 1.24 mm Hg, which is about 1630 ppm H_2O (see Table 5). Photo-induced nucleation has been observed at partial pressures of water vapor as low as 1000 ppm (Wen *et al.*, 1978). If this surface interface air (∿1 cm) is swept up into the lower

*Readers unfamiliar with the arctic should understand that surface temperature extremes, winds etc. are not at all like encountered in the antarctic, nor in the interior of Alaska. An arctic temperature of -55°C is an extreme, and it usually runs about -20 to -35°C during winter.

troposphere where temperatures fall to about -25°C, then nearly two thirds of the available water vapor must go to the particulate ice phase since the equilibrium partial pressure of water vapor at that temperature is only 0.47 mm Hg. If the particulates formed have a radius of 0.1 μm, then just 1cc of air from the ice surface theoretically could produce 10^7 nuclei or an additional 100 nuclei/cc over the bottom km of troposphere where counts usually are around 400/cc in the arctic. In other words, a significant fraction of the whole, and of course it is continually renewable from the surface. These water crystals would not be picked up in routine filter sampling of the air because of evaporation. They would only be detected by optical mothods. Open water, and thin covers of ice from refrozen leads where surface temperatures are between -5°+0°C would provide at least three to four times as many particles. If the radius is only 0.01 μm then the one injection of 1 cm surface air could produce 10^4 nuclei/cc over the bottom 10 km of the arctic troposphere, assuming turbulence and lifetimes sufficient to carry them to that altitude.

TABLE 5

Temp. °C	mm Hg
(over water) 0	4.58
(over ice) -5	3.01
-15	1.24
-25	0.47
-35	0.19

In the arctic spring, when snow and ice still dominate the scene, but insolation intensity and duration has increased dramatically, arctic haze becomes a major phenomenon. This could be due in part to water vapor from a relatively warm surface self-nucleating and freezing out at colder temperatures at altitude. There are of course other alternatives. For example, the increased sunlight could be photooxidizing SO_2 and H_2S *via* $\cdot OH$, which was insufficient in the prior weeks due to low levels of radiation. The albedo of the tundra is not that of pure snow and ice since many dark patches occur due to vegetation and some wind blown debris. Micro-environmental temperatures around these dark and in wind protected patches can become remarkably high even though the air and soil temperatures remain low. In the interior of Antarctica, the situation is different since the surface is always cold with no heat source under it. Thus the increase in nuclei may in part be due to water vapor transported in from the ocean from the previous day and/or the air decends at the pole until the concentration per unit volume increases to a threshold level that can be influenced by the photoexcitation of the rising radiation levels in the morning, or again due to $\cdot OH$ oxidation of sulfur compounds.

Organic Material and Aerosols

The role of atmospheric organic material in the production of aerosols has been intuitively obvious for ages, but only partially scientifically provable for a few score years. We are dealing here with true organic gases being converted to insoluble particulate matter, not the insect wings, pollens and hosts of other fiber particulates. Prior to the availability of modern analytical techniques, the best that resulted was an elemental analysis of the combusted sample since the materials present in aerosols were too small

in quantity, and further broken down into a myriad of diverse categories. The next advance came with the spectroscopic evidence for the presence of oxidized materials. Finally, at the present time, we have only just begun to identify particular organic species in particulates and in the gas phase.

One of the early modern thoughts on the production of organic particulates was to consider polymerization. This, unfortunately is not a likely possibility even though diverse olefinic compounds such as the pinenes are known to be present in most atmospheres; frequently in concentrations of one or two orders of magnitude greater than the hypothetical case at 0.1 ppbv we have been considering. The problem is that most polymerization reactions have activation energies on the order of 25 kcal/mole, moreover it is a sterically unfavorable reaction. The steric factor will be 10^{-4} and probably more like 10^{-5}. If we consider the most favorable case, Ea of 24 kcal/mole, steric factor of 10^{-4} a concentration of 10 ppbv and a higher temperature of 300°K, the quantity that results from Equation (1) is only about 1 effective collision sec^{-1} cm^{-3} (0.1 MT/yr. globally). Organic free radical dimenization may be as much as an order of magnitude greater, but both values are too small to be of global significance. There may, however, be a contribution to particulate production by these polymarization methods in the immediate vicinity of a fire where concentrations and temperatures are higher than those just employed in the example.

In a recent paper, Junge (1977) suggests that for organic material to partition in favor of the particulate phase, its vapor pressure must be on the order of 10^{-7}-10^{-8} mm Hg. Junge further indicates that hydrocarbons must be larger than C_{20} to display such low vapor pressures. As mentioned earlier, spectroscopy clearly indicates the presence of oxidized species

in particulate organic matter. The presence of carboxylic acids, and possibly esters functions, clearly stand out in these infrared spectra, as well as some aldehyde and ether bands. Decane (C_{10}) is a relatively small hydrocarbon, non polar and hydrophobic; thus its vapors will be exclusively in the gas phase. Oxidation to alcohols, aldehyde or ketones still does not appreciably lower its vapor pressure, but it does afford opportunities for removal from the atmosphere by hydrometeors due to the presence of the oxygenated, hydrophillic moieties. However, if one extrapolates the vapor pressure data for capric acid (C_{10}) its vapor pressure is markedly lower than the corresponding alcohol and aldehyde, and is in the range of 10^{-8} mm Hg at 10°C. Dicarboxylic acids (Grossjean *et al.*, 1978) would lower the vapor pressure to the 10^{-7} mm range for smaller hydrocarbon molecules. The fate of organic material in its atmospheric removal therefore appear to lie in its oxidation by the active species such as ·O· and ·OH, O_3, and to a lesser extent by O_2, and not on polymerization reactions.

Other types of oxygenated species are known, for example, the peroxides, epoxides and more notably the nitrated species such as PAN (peroxyacetyl nitrate). Polynuclear materials, where one or more of the rings has a lower aromatic character to it, have also been identified and reported as being nitraded.

The Trace Elements

The consideration of all of the trace elements, or even a careful consideration of a few, is far beyond the intent of this article. There are, however, a few less widely recognized points, that should be brought up in the consideration of how certain elements show up in aerosols in greatly enriched concentrations of over average crustal abundances. Such reports

are for remote areas such as the south pole and the open ocean. (Duce and Zoeller, 1975 and Winkler, 1975).

Several elements are mobilized by biological methylation. This became widely known a few years ago due to the notariety of methyl mercury, although arsenic received similar attention over a century ago when people were poisoned by living in wall-papered rooms where the paste had been treated with arsenic to retard spoilage. Other elements mobilized by microbial methylation have also been reported (Challenger, 1951). These are nitrogen, sulfur, selenium, tellurium and iodide. Since then others have been added to the list, notably chloride. Man adds large quantities of methylated arsenic and alkylated tin to nature in efforts to control pests. Under favorable conditions, these compounds can also be volatilized by biological methylation.

Methylated sulfur and its contribution to aerosols to regions distant from its source was discussed earlier. Similar arguments apply to the other methylated species. Methyl iodide is present in the air in very small quantities, and is generated in certain regions of the oceans. (2.7×10^{11} g/yr - Lovelock *et al.*, 1973 and Liss and Slater, 1974). Nevertheless it is enough to influence the trace components of aerosols. Iodides generated from sea salt spray, or dust from the soil would be large particles confined to the lower troposphere and to relatively short distances from the origin. Rahn (1976) reports an aerosol composition for northern Norway which has a large excess of iodide constituting about 0.05% of the total amount of mass of the material. This could be due to the oxidation or hydrolysis of methyl iodide to produce iodide, and possibly iodate.

Selenium is on the average present in sea water in concentrations of around 10^{-7} g/l. In reality, surface sea waters are practically devoid

of selenium, but it is present in the biota (Gosink, umpublished). The selenium appears to present in the biota in organic form, e.g. the selenium analog of methionine. Biological cleavage of such materials would yield volatile product which could enter the atmosphere where it would be oxidized and scavenged by aerosols to yield the observed enriched values. If it is assumed that only half of the available average selenium in the upper 50 meters of sea water it tied up in the biota, and further that 1 percent of this selenium is eventually released to the atmosphere, it would be sufficient ($2.5 \times 10^{-5} g/m^2$) to account for the 10,000 fold excess of selenium in particulates in the bottom 5 Km of the oceanic trophosphere at the observed average concentration of 5×10^{-9} g/SCM near the surface.

Another source is that some metal salts have appreciable vapor pressures by themselves. Goldberg (1976) has suggested that part of the atmospheric load of several heavy metals is due to the sublimation of surface material.

Finally, compounds like acetylacetone and higher homologs, are known in nature, believed to possibly mobilize trace metals from soils into the plants. Similar compounds have been used by chemists for years to volatilize large numbers of metals for analytical purposes. This in part may account for yet another mechanism whereby plants could inject metals into the atmosphere.

REFERENCES

Bach, W. 1976. Global air pollution and climatic change. *Rev. Geophys. and Space Physics*. 14:429-474.

Bonsang, B., N. B. Cuong and J-Y. Paugam. 1976. Sur la formation de gaz sulfures et noyaux d'Aitken dans l'atmosphere, le long du littoral. C. R. Acad. Ser. D. 283:1285-88.

Braman, R. S., J. A. Ammans and J. L. Bricker. 1978. Preconcentration and determination of hydrogen sulfide in air by flare photometric detection. *Anal. Chem.* 50:992-996.

Challenger, . 1951. Adv. Enzymol. 12:249-

Cotton and Wilkenson. 19.

Cox, R. A. and F. J. Sandalls. 1974. The photo-oxidation of hydrogen sulfide and dimethyl sulfide in air. *Atmos. Environ.* 8:1269-81.

Duce, R. A., and W. Zoeller. 1975. Atmospheric trace metals at remote northern and southern hemisphere sites, Pollution or Natural? *Sci.* 187:59-61.

Duce, R. A. 1977. Speculations on the budget of particulate vapor phase non-methane organic carbon in the global troposphere. Pure and Appl. Geoplp.

Flyger, H., N. Z. Heiden, D. Hansen, W. J. Megaw, E. G. Walther and A. W. Hogan. 1976. The background level of summer tropospheric aerosol, sulfur dioxide and ozone over Greenland and the North Atlantic Ocean. *J. Aerosol Sci.* :103-40.

Friend, J. P., R. Leifer and M. Trichon. 1973. On the formation of stratospheric aerosols. *J. Atmos. Sci.* 30:465-79.

Frost, A. A. and R. G. Pearson. 1953. *Kinetics and Mechanisms*. Wiley and Sons.

Grossjean, D. K. VanCauwenberghe, J. P. Schmid, P. E. Kelley and J. N. Pitts Jr. 1978. Identification of C_3-C_{10} aliphatic dicarboxylic acids in airborne particulate matters. Environ. Sci. Tech. 12, 313-17.

Goldberg, E. 1976. Rock volatility and aerosol composition. *Sci.* 200:128-29.

Junge, C. E. 1977. Basic considerations about trace constituents in the atmosphere as related to the fate of global pollutants. *In: Fate of Pollutants in the Air and Water Environments*, Pt. I., Vol. 8. I. H. Suffet, Ed. J. Wiley and Sons, Inc.

Liss, P. S. and P. G. Slater. 1974. Flux of gases across the air-sea interface. *Nature*. 247:181-84.

Lovelock, J. E., R. J. Maggs and R. A. Rasmusson. 1972. Atmospheric dimethyl sulfide and the natural sulfur cycle. *Nature*. 247:452-3.

Lovelock, J. E., R. J. Maggs and R. J. Wade. 1973. Halogenated hydrocarbon in and over the Atlantic. *Nature*. 241:194-96.

Lovelock, J. E. 1974. CS_2 and the natural sulfur cycle. *Nature*. 248:625-6.

Maroulis, P. J., A. L. Torres and A. R. Bandy. 1978. Atmospheric concentration of carbonyl sulfide in the southeastern and eastern United States. Geophys. Res. Lett. paper 7L789.

Pauling, L. 1964. College Chemistry. Third Edition. W. H. Freeman and Co.

Paugam, J-Y. and J. Coulomb. 1975. Sur la formation de noyaux Aitken dans 1'air au-dessus du littoral. C. R. Acad. Ser. B. 280:821-24.

Penner, J. E., M. B. McElvoy and S. C. Wofsy. 1977. Sources and sinks for atmospheric H_2: A current analysis with projections for the influence of anthropogenic activity. *Planet. Space Sci.* 25:521-540.

Perner, D., D. H. Ehhalt, H. W. Päte, U. Platt, E. P. Röth and A. Volz. 1976. OH-Radicals in the lower troposphere. Geophys. Res. Lett. 3:466-68.

Rahn, K. 1976. The chemical composition of atmospheric aerosol. Technical Report. Grad. School of Oceanog., Univ. of Rhode Island, Kingston, July. See Table A4-4.

Rasmussen, R. A. 1974. Emission of biogenic hydrogen sulfide. *Tellus*. 16: 254-60.

Shaw, G. 1978. Particles in the air at the South Pole. Antarctic Journal (in press).

Singh, H. B. 1977. Atmospheric halocarbons: Evidence in favor of reduced average hydroxy radical concentration in the troposphere. Geophys. Res. Lett. 4:101-07.

Wang, C. C., L. I. Davis, Jr., C. H. Wu, S. Japar, H. Niki and B. Weistock. 1975. *Sci.* 189:797-800.

Wen, F. C., T. McLaughlin and J. L. Katz. 1978. Photoinduced nucleation of water vapor. *Sci.* 200:269-71.

Winkler, P. 1975. Chemical analysis of Aitken particles (<0.2 μm radius) over the Atlantic Ocean. Geophys. Res. Lett. 2:45-48.

APPENDIX C

AUTOMATIC GAS SAMPLE PRESSURE CONTROLLER

By

Dr. Thomas Gosink
Mr. R. L. Seitz

Submitted to the International Journal for Environmental Chemistry. August, 1978.

October 1978

Submitted to the International Journal for Environmental Chemistry. August, 1978.

AUTOMATIC GAS SAMPLE PRESSURE CONTROLLER

ABSTRACT

A system of an absolute pressure transducer, as a part of a wheatstone bridge and amplifier, with a servo controlled valve, automatically controls the pressure in a gas sample loop. The precision of samples controlled by this method is about ±0.2%. The device is applicable to a number of analytical instruments such as gas chromatographs and infrared spectrometers, and should be suitable for aircraft use.

One of the critical steps for accurate and precise measurement of gases is the control of the size of the sample used. Sample loops for many applications provide suitable precision. However, long term repetitive samplings, or systems sampling different sources, pumps, flow rates etc., additional controls, if not more frequent standard samples, are required. We have developed a system for gas chromatography which maintains the absolute pressure in the sample loop to about ±0.2% of the set point. The sample loop is mounted inside the analytical oven where the temperature is controlled to better than 0.1°C, therefore sample size is constant (±0.03%) with respect to temperature. Calibration of the sample loop and valve volume has been described by Cuddeback *et al.* (1975).

The flow scheme for the system is shown in Figure 1. This particular system time multiplexes four different sample sources and standard(s). The gases can be vented as shown for simplicity, or valved back to a closed system. Coarse valves after the pumps are necessary to reduce the pressure to the range of the transducer and fine metering valve which is about ± 40 mm Hg from the set point. The pressure sensor is the Unimeasure® Model P2 which is

a relatively inexpensive piezo-resistive device with a resistance-pressure relationship of $\Omega = 138.4 + 0.205\ P_{mm}$ Hg (absolute), and is good up to about 1000 mm Hg. Other models are available for higher pressures. The electronic system design (Figure 2) will allow for the detection 0.1 mm Hg change in pressure. Whole system response, however, is slow enough so that the pressure control is coarser than this. The ten turn potentiometer is to control the point (or pressure) at which the wheatstone bridge will balance. Similar designs can be found in books on operational amplifiers such as Grame *et al.* (1971).

The precision valve is closed by the stepper motor if the pressure in the sample loop is too low; opened if it is too high. In this work the Nupro SS-2SGD valve was chosen so as to operate in the ranges of 100-200 ml/min flow rate and 50-250 mm Hg pressure differential. Selection of a valve for other applications or control parameters requires the computation of the valve flow coefficient (C_v) which is usually provided by the manufacturer in engineering rather than metric terms.

$$C_v = \frac{Q}{16.05\frac{\left(P_1^2 - P_2^2\right)^{1/2}}{T^\circ}}$$

Q = SCFM (ft^3/min)
P_1, P_2 = PSIA
T = 450° + °F

In the design of the mechanical linkage between the stepper motor and the vernier end of the precision valve, it is important to provide both a slip clutch to avoid jamming and to allow for the travel of the valve stem.

The control point can be measured on the Unimeasure® by switching it out of the system, and using a 4½ digit (or better) digital ohmmeter.

In our work where the coarse valves bring the various sources roughly into line, and there is not too much drift over short periods of time, only a few pulses to the stepper motor are required to stabilize the system.

The maximum pulse rate of the XR220 is determined by the resistor to pin 1 and the capacitor to pins 3 and 5 according to the formula $F = \frac{1}{2} R^{-1} C^{-1}$. Here R = 10 kohms and C = 5 μf so that F = 10/sec. Ninety-six pulses are required for one full turn of the precision valve.

The current cost of the Unimeasure®, electronic components and precision valve is approximately $900. The system should be applicable to other analytical procedures e.g., flow through infrared sample cells. Since the pressure is absolute, it should be adaptable to measurements made from aircraft where profound pressure changes will occur.

This work was supported by the Office of Naval Research, Contract N00014-76C-0331 at the Institute of Marine Science, University of Alaska, Fairbanks, 99701.

T. A. Gosink

R. L. Seitz

References

Cuddeback, J. E., S. R. Birch and W. R. Burg. *Anal. Chem.* 47;355 (1975).

Grame, J. D., G. E. Toby and L. P. Hvelsman. Operational Amplifiers, design and application. McGraw Hill, 1971. Pages 208-212 - Bridge Amplifiers.

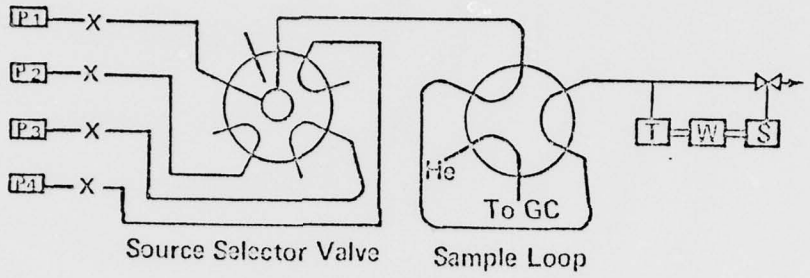


Figure 1. Flow schematic for four different sources being pressure controlled by Unimeasure® transducer (T), Wheatstome bridge amplifier (WA) and servo mechanism (S). P = pump, X = coarse control valve Whitney B-ORM2. Precision valve on servo = Nupro SS-2SGD.

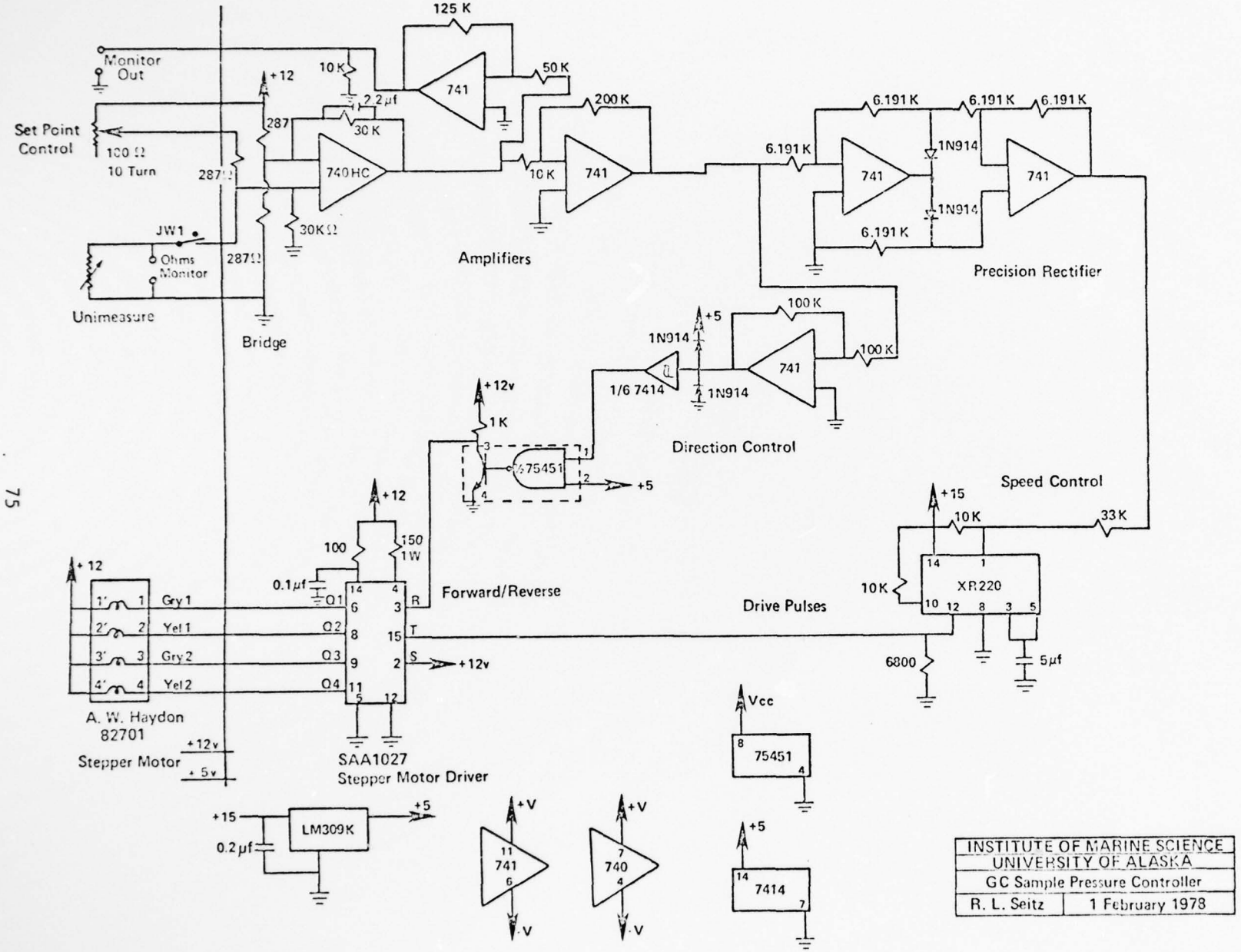


Figure 2. EJectronic schematic for pressure control system.

APPENDIX D

EQUILIBRATOR FOR AIR-SEA-WATER PCO_2

By

Dr. Thomas Gosink

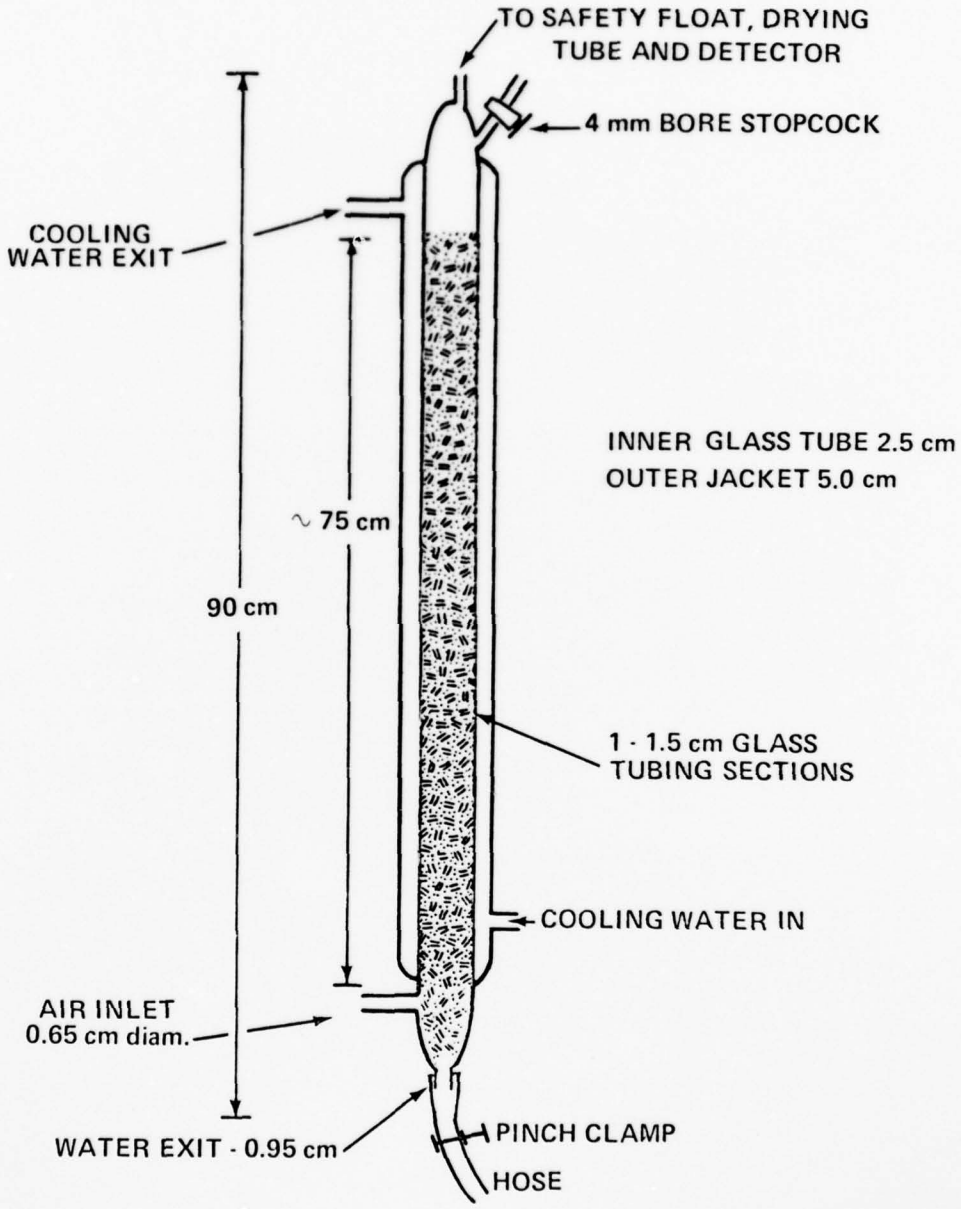
October 1978

EQUILIBRATOR FOR AIR-SEA-WATER P_{CO_2}

A counter current device for the fascile equilibration of air-sea water carbon dioxide is described. Overall length as shown in the figure is about 90 cm. The active CO_2 transfer lenth is about 75 cm which consists of a 2.5 cm diameter glass column filled with short segments of smaller diameter glass tubing to provide a large amount of surface area. The system is thermally jacketed with a 5.0 cm diameter glass tube with auxilliary large flow of the water being equilibrated. The stop cock is adjusted to provide 600-800 ml/min of water to the top of the column. Clean air from a small pump is introduced through the side tube near the bottom at a rate to provide about 100 ml/min escape through the top. The pinch cock on the tubing on the bottom allows the water and excess air to escape. The device will function at atmospheric to slightly elevated pressures (800-1000 mm Hg).

Equilibration is quantitative since slightly shorter columns show no difference when two are hooked in series with the air, and in parallel for the water to be equilibrated.

AIR - WATER CO_2 EQUILIBRIUM DEVICE



APPENDIX E

THE ARCTIC. A SIGNIFICANT SOURCE-SINK OF CARBON DIOXIDE

By

Dr. Thomas Gosink

October 1978

THE ARCTIC. A SIGNIFICANT SOURCE-SINK OF CARBON DIOXIDE

General Introduction

There is growing evidence that the arctic regions are a major source of carbon dioxide in the winter, and both a source and a sink in the spring and summer. These phenomena have been masked by anthropogenic factors in the winter, and by natural events in the spring-summer.

The annual variation of carbon dioxide partial pressures monitored at Point Barrow, Alaska are the largest of all the NOAA-GMCC sites in the world. At Point Barrow, the winter-summer atmospheric carbon dioxide difference is about 12 ppm. At Mauna Loa, Hawaii, the variation is about 6 ppm. The oscillations become even smaller as one proceeds toward the South Pole, where the seasonal differences are only $\sim$1 ppm. These hemispheric differences have been explained, and it remains essentially correct, in the following way. The northern hemisphere has most of the land mass, human population and industry. The winter high values of atmospheric carbon dioxide are due to extensive space heating, and the summer low because of the resurgence of biological activity. The southern hemisphere on the other hand, is largerly an oceanic regime, which is a net sink for carbon dioxide, and it has significantly smaller anthropogenic factors involved.

Considering only the existing northern hemisphere data, there are several features which suggest that there is a high latitude source of carbon dioxide. One of the striking facts is that the carbon dioxide maximum at Point Barrow occurs in May, which is several months after the maximum fossil fuel consumption in December-February. Closer examination of the Point Barrow data show a small but clear and repectable increase in the atmospheric

content of carbon dioxide in May. Furthermore, the carbon dioxide levels at Point Barrow are beginning to climb again by late August, months before any significant space heating occurs. The annual increase in atmospheric carbon dioxide at Mauna Loa does not start until late October.

In this paper we present additional evidence that the arctic is a natural intense source and sink of carbon dioxide, and not an ice sealed passive region.

Sources

A. Sea Ice, Introduction

The principal winter source of carbon dioxide in the arctic is annual sea ice. We have reported (Gosink, Pearson and Kelley, 1976) that sea ice is quite unlike fresh ice (Hemingsen, 1959) with respect to its permeability to gases. Our more recent data show that the partial pressure of carbon dioxide associated with the brine in sea ice is $\geqslant$1000 ppm. This is in agreement with the observations that the salinity of these brines are about three times that of sea water. Physical-chemical equilibration of the carbon dioxide gas in this slightly acid bicarbonate-carbonate containing brine with the atmosphere occurs through brine channels, and multigrain boundaries.

B. A Description of Sea Ice

We include here a description of sea ice because most persons are only familiar with fresh ice, and sea ice is radically different. Sea ice is relatively soft and fluid in comparison to fresh ice. The liquid water content of sea ice is approximately 20, 12 and 3 percent at -10, -20 and -30°C respectively because of the presence of brine. (Richardson, 1976). The free gas content of sea ice varies drastically with depth and age of the ice and

is not the source of the CO_2 in question. The entrained gas in all cases was essentially air at atmospheric pressure. No high pressure bubbles like those found in glaciers or other fresh ice have been oberserved in sea ice.

Brine channels are probably the principle route for gas permeation in sea ice at lower temperatures because of their size. Lake and Lewis (1970) reported these brine channels to be on the order of a few tenths to occasionally several millimeters in diameter. Langhorn (1974) and Lake and Lewis (1970) report significant dye movement through relatively warm fresh and sea ices. We have observed the rapid ($\sim$1 cm/min) movement of ink in sea ice brine through a block of annual sea ice that had been cut out the previous day and set on the surface at ca,-7°C.

Three grain and higher order boundaries are more important to ice of low salt content, and to sea ice at relatively warmer temperatures. The average radius of three grain boundaries varies nearly three orders of magnitude for pure ice within a few tenths of a degree below its freezing point. Based on the formulas and data of Langhorn (1974) the three grain boundary vein radius of pure ice is on the order of 10^{-5} cm at a temperature 0.037°C below the freezing point. This diameter closes to $7x10^{-7}$cm at 0.5°C below the freezing point (A gas molecule is $\sim 10^{-7}$cm in diameter). This explains the inpenetrability reported by Hemingsen (1959) who did all of his work between -0.5 and -9.5°C. Raymond and Harrison's (1975) formula predicts $6x10^{-8}$cm radii for fresh water ice multigrain boundaries at -0.1°C. On the other hand, sea ice at -2°C would have vein radii of 10^{-4}cm, and at -10°C would still have grain boundary veins on the order of 10^{-7}cm radius according to Raymond and Harrison's formula which has a term for the impurity (brine) factor. The veins close by two orders of magnitude at -20°C, which

is in agreement with the approximate factor of 20 decrease in gas flow rate observed and reported below, assuming the much larger brine channels open and close at about the same levels of magnitude as do the multigrain boundaries veins.

Two qualitative descriptions of events surrounding experiments at ca. -7 to 0°C air temperatures in April-May should illustrate the extent and facility with which fluids may move through sea ice. It is difficult to obtain data on gases for *in situ* sea ice at temperatures above -10°C. Bore holes extending no more than half way through annual sea ice will flood to the hydrostatic level within an hour. At -20°C on the other hand, only a few cm of brine will flow into a surface insulated hole in a day or two. During the course of introducing a low pressure gas into one these surface sealed holes in annual ice, a gas leak was heard. The pressure was increased to about 10psi and some water was thrown onto the surface in an attempt to locate the leak. Active bubbling was observed in many places as much as a meter away from the hole. There are also the observations by several different persons at different locations who verbally reported active bubbling of scuba divers air up through ca. 1.3 m of ice in the month of May 1977 and again in 1978.

Eide and Martin (1975) have reported active pumping of sea water well up into sea ice *via* brine channels.

A final important point to remember is that the surface of sea ice remains relatively warm, as does the whole arctic ocean basin, because of the virtually inexhaustable heat source of the ocean water underneath. Average deep winter air temperatures are only -20 to -30°C. A light snow or hoar-frost cover over the ice significantly helps to isolate the surface

ice. A thicker snow cover or drift (ca. 20 cm) will permit the sea ice (ca. 1 m thick) surface to be around -6°C when air temperature are nearly -20°C, provided the wind in not strong.

C. Gases at the Sea Ice-Air Interface

Carbon dioxide, carbon monoxide, methane and sometimes nitrous oxide have all been observed to emanate from sea ice surfaces. We report at this time only on the aspect of carbon dioxide.

Kelley *et al.* (1968) and Coyne and Kelley (1974) reported on the existance of elevated levels of carbon dixide under the snow across the tundra. They were using infrared analytical techniques which required large volumes of air samples being pumped from the subnivean. 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) occurred in May during the annual final rise in atmospheric carbon dioxide mentioned earlier. In this work with gas chromatographic procedures, only 5 cc of air need to be taken and thus, not to disturb the microenvironment. In this manner, small but nearly continuous enrichment of carbon dioxide was noted throughout the winter over the tundra. Likewise, air samples withdrawn from beneath the snow cover over sea ice was enriched in carbon dioxide if the wind velocity was low, or if the sample came from a wind protected area. These subnivean samples tended to be about 30 ppm higher in carbon dioxide than air samples at 2 m taken at the same time. The difference range was 0-80 ppm.

Other ice surface experiments involved air samples withdrawn from cuvettes sealed to the ice surface. Cans of ca. 2L volume covering ca 200 cm^{-2} of sea ice were fitted with a septa port and sealed to the sea ice surface using

snow and fresh water ice packed around the side. In some experiments the increases of carbon dioxide over the original air sealed in the cuvette was followed. In other cases the sealed cuvette was flushed with helium, and the recovery rate of carbon dioxide versus oxygen and nitrogen was followed as a function of time, temperature and ice salinity.

All carbon dioxide measurements were accomplished on a Carle 311M gas chromatograph. Calibration was by means of carbon dioxide standards prepared by Keelings laboratory at the Scripps Institute of Oceanography. Accuracy, as compared to the NOAA GMCC site for air samples, was about ±1 ppm. Samples were taken and held briefly in teflon and glass, gas tight syringes. It is necessary to employ oversized 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 1-2 hours.

A summary of results for the recovery experiments are shown in Table 1. ARLIS VII was an ice camp located approximately 200 mile north of NARL (Naval Arctic Research Lab-Point Barrow).

TABLE 1

Carbon Dioxide and Oxygen Recovery in Helium Flushed Chambers Sealed to Sea Ice Surfaces.

Case No.	Date-Location	Type of Ice	S°/$_{oo}$	Air Temp.	No. Cases	% Recovery CO_2	% Recovery O_2	Hrs.
1	4/77-NARL	Annual	2.4-3.2	-10to-15	1	100	25	3
2	4/78-ARLIS VII	Annual	2.0	-20to-25	1	70	50	30
3	4/78-ARLIS VII	Multiyear	0.9-1.1	-20to-25	2	50	25	39-42

Only five cases are reported here, although numerous other experiments were started. Failures frequently had to do with seal leaks, and lack of time to restart experiment. Still other experiments were systems started with ambient air in the cuvette, rather than being flushed with helium as is reported here.

Temperature appears to be more important than salinity. Experiments labeled cases 2 and 3 above, were caried out at the same time and thus only the salinity is different by $1°/_{oo}$. Carbon dioxide and oxygen recoveries for those two cases differ by 30 and 50 percent and the recovery time by 25 percent. The experiment labeled case 1 was performed a year earlier. The temperature was significantly warmer, thus the brine and multigrain boundary vein sizes should have been larger. The salinity is again different by about $1°/_{oo}$ as compared to case No 2, but this time there is over an order of magnitude difference in the recovery times if one allows for the 30-50 percent variation in the actual recoveries.

Unflushed chambers sealed to the ice at ARLIS VII showed carbon dioxide levels of 351-362 ppm. The ambient air was running between 339-341 ppm. Syringe samples of the subnivean at ARLIS VII generally ran around 350 ppm. The range was 337-374 ppm, with the samples taken over multiyear ice being the lowest.

The partial pressure of carbon dioxide in the sea water under the ice at ARLIS VII was analyzed at 295 and 300 ppm. The light level at that time of year was nearly constant for ca. 18 hrs/day. These low values for Pco_2 suggest that significant biological activity has commenced under the sea ice, and departs from our past observations during the dark winter months when the Pco_2 values ran 340-350 ppm.

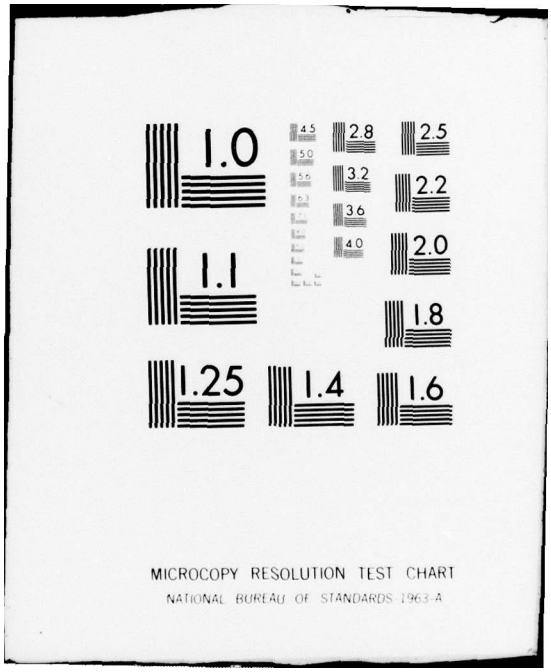
Based on experiments at -10 to -15°C, the rate at which carbon dioxide is being released to the atmosphere from annual ice surfaces is $2\text{-}4\times10^{-3}$ ml $cm^{-2}hr^{-1}$. At -20 to -25°C it apparently drops to about 10^{-4} ml cm^{-2} hr^{-1}. Adequate data is not available for the early May period, but we suggest that a possible cause for the small repeatable atmospheric surge of carbon dioxide before the rapid decline, as mentioned in the introduction, may be due to the brine and multigrain boundary veins opening up with the onset of warmer weather, thus allowing for a final burst of carbon dioxide from the brines in the sea ice before the channels open still farther and are flushed by normal low P_{CO_2} sea water. In late May, the waters on the surface are deceidedly depleted in P_{CO_2}.

We estimate that arctic sea ice covers 1.4×10^{7} km^2. About half of this is annual ice with appreciable brine content to possibly affect the whole atmosphere. If it is assumed that only this annual ice outgasses between mid October to Mid May at a rate of 1×10^{-3} ml cm^{-2} hr^{-1}, then 3.5×10^{17} ml or 0.7×10^{15} g of carbon dioxide will have been added to the northern troposphere. Bolin and Bischof (1970) indicate that most of this carbon dioxide remains in the lower part of the troposphere. If half of this carbon dioxide remains in the northern troposhere during the seasons in which it is emitted, the rest being absorbed by lower latitude oceans, it would amount to an tropospheric change of about 0.2 ppm at Mauna Loa (not allowing for altitude variations) or 8 percent of the Mauna Loa amplitude. The Point Barrow monitor site, on the other hand, being situated by this large area source, should be expected to show larger annual changes. Arctic sea ice covers about 3 percent of the earth's surface. If half of the suggested carbon dioxide evolved from this vast area source remains above 60°N, then

AD-A062 096 ALASKA UNIV FAIRBANKS INST OF MARINE SCIENCE F/G 8/12
GASES IN THE SEA ICE.(U)
SEP 78 T A GOSINK, J J KELLEY N00014-76-C-0331
UNCLASSIFIED NL

2 OF 2
AD A062096

END
DATE FILMED
3-79
DDC


1.0
1.1
1.25
1.4
1.6
1.8
2.0
2.2
2.5
2.8
3.2
3.6
4.0
4.5
5.0
5.6
6.3
MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS 1963-A

it would cause a 2-3 ppm perturbation in that portion of the tropospheric load of carbon dioxide. This is 25-35 percent of the amplitude observed at Point Barrow.

D. Gases from Tundra, Lakes and Ponds

Another large source of carbon dioxide in the arctic is the tundra with its bogs ponds and lakes. Extremely high levels of carbon dioxide and carbon monoxide and other gases can be found at the surface of the tundra and in the lakes and ponds of the arctic in the vicinity of Point Barrow. We will report at this time on the carbon dioxide, and only comment on the carbon monoxide.

During the months of June and October, surface evolved gases are extraordinarily large and variable at least in the vicinity of Point Barrow. The region is dominated by ponds and lakes with organic rich sediment. 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, had an average P_{CO_2} 357 ppm greater than the ambient air. (Coyne and Kelley, 1974). Our observations of gases being evolved from rotting ice at North Meadow Lake near NARL show carbon monoxide levels in those bubbles to be over 100 ppm, methane over 1000 ppm and carbon dioxide estimated to be between 2000 and 3000 ppm. Rotting coastal sea ice was also observed to have carbon monoxide values of about 20 ppm in June of 1977. It is a simple task to find elevated levels of carbon dioxide and carbon monoxide by syringe sampling the air in the vegetation immediately over the tundra. Chambers loosely covering warming spring tundra surface had carbon monoxide levels of 100 ppm and carbon dioxide over 1000 ppm. Based on the lake and pond data of Coyne and Kelley (1974) and our sealed chamber data on tundra,

we estimate both of these surfaces are evolving at least 1g $m^{-2}day^{-1}$ of carbon dioxide. They are known to fix 600+g CO_2/m^2/season in the root system. Given an estimated 200 km perimeter of similar tundra and bogs on the land surrounding the arctic oceans, this would add $1.6x10^{14}$g of carbon dioxide to the troposphere during July-September.

E. Air Samples from Aircraft Overflights of the Summer Arctic Ice.

In order to show the persistant effect of sea ice on the atmospheric load of carbon dioxide, even after the levels monitored at Point Barrow have plunged to their summer low, we have periodically taken air samples from aircraft. The intake is a continuous teflon tube mounted on the copilots step forward of the propeller and ca.0.4m away from the fuselage of a Twin Otter aircraft. Alternatively on a few occasions the tubing was placed up in one of the clean air scoops above the fuselage and forward of the engines of a DC 113. The air scoops were permanent modifications to the aircraft for aerosol research being done at the University of Rhode Island and Alaska. The general flight plan was to fly 150-300 km north of Point Barrow and to take periodic samples at <100m and a vertical profile of samples between <100m and 4500m at the farthest point north of the flight. A second vertical profile of samples would be taken over the Meade River village, about 80 km south of NARL.

SINKS

There is of course the brief intense vegetation growth period of the arctic summer which has been estimated to fix 600+g of CO_2m^{-2} (Coyne and Kelley, 1976; Miller *et al.*, 1977). We wish to report our investigations of arctic ocean surface waters. Sea water under sea ice during the dark

winter months have partial pressures of carbon dioxide of about 330-350 ppm. These partial pressures were observed to have decreased to 295-300 ppm in early April 1978 at a temporary ice station ca. 300 km north of Point Barrow. The winter ice was still forming, but the light level was prolonged (ca. 15 hrs/day). In the summer, after the near shore ice was blown out we sampled the surface water from the R/V Natchick offshore from NARL and ca. 10-15 km north and east of Point Barrow in late July and early September, 1978. In July, there was a shallow (0.5-1m) layer of cold (-0.5 to +2.5°C) sea water (5 16-18°/$_{oo}$) from the melting sea ice. When operating in 2-4 oktas of sea ice cover elsewhere, and by 4m depth in the sea ice area, the salinity was 32-33°/$_{oo}$ and the temperature 3-4.5°C. The partial range of ppm. In the slightly warmer more saline waters it was ppm in September.

Hakuho Maru and Glacier Cruise Data

6 October 1978 - Unfinished

REFERENCES

Bolin B. and W. Bischop. 1970. Variations of the carbon dioxide content of the atmosphere in the northern hemisphere. *Tellus* 22:431-442.

Coyne, P. I. and J. J. Kelley. 1971. Release of carbon dioxide from frozen soil to the Arctic atmosphere. *Nature* 327:407-408.

Coyne, P. I. and J. J. Kelley. 1974. Variation in carbon dioxide across an arctic snow pack during spring. *J. Geophys. Res.* 79:799-802.

Coyne, P. I. and J. J. Kelley. 1974. Carbon dioxide partial pressures in Arctic surface water. *Limnol. Oceanog.* 19:928-38.

Coyne, P. I. and J. J. Kelley. 1976. Carbon CO_2 Exchange over the Alaskan arctic tundra: Meteorological assessment by an aerodynamic method. *J. Appl. Ecol.* 12:587-64.

Eide L. and S. Martin. 1975. The formation of brine drainage features in young sea ice. *J. Glaciol.* 14:137-154.

Gosink, T. A., J. G. Pearson and J. J. Kelley. 1976. Gas movement through sea ice. *Nature*, 263:41-42.

Hemmingsen, E. 1959. Permeation of gases through ice. *Tellus* 11:355-359.

Kelley, J. J., D. F. Weaver and B. P. Smith. 1968. The variation of carbon dioxide under the snow in the Arctic. *Ecology* 49:358-61.

Lake, R. A. and E. L. Lewis. 1970. Salt rejection by sea ice during growth. *J. Geophys. Res.* 75:583-597.

Langhorn, E. J. 1974. Phase equilibria of vains in polycrystalline ice. Can. J. Earth Sci. 11:1280-1287.

Miller, P. C., W. A. Stoner and L. L. Tieszen. 1976. A model of start photosynthesis for the wet meadow tundra at Barrow, Alaska, *Ecology* 57:411-30.

Raymond, C. F. and W. D. Harrison. 1975. Some observations on the behavior of the liquid and gas phases in temperate glacier ice. *J. Glaciol.* 14:213-233.

Richardson, C. 1976. Phase and relationships of sea ice as function of temperature. *J. Geophys. Res.* 17:507-19.