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NRL Report 6249

Postulated Anomalous Dissolved Atmospheric Gas Concentration in the Arctic Ocean

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April 19, 1965

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ABSTRACT

The possibility of anomalous concentrations of dissolved atmospheric gas in certain Arctic Ocean waters is theorized. The unique geometry of the Arctic Basin and its permanent ice cover create a gigantic "zone-refiner" that could lead to this condition. The application of a previously developed NRL instrument to an investigation of this phenomenon is indicated and recommended.

PROBLEM STATUS

This is an interim report; work is continuing.

AUTHORIZATION

NRL Problem C05-20
ONR RR 001-01-43-4756

Manuscript submitted January 19, 1965.

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POSTULATED ANOMALOUS DISSOLVED ATMOSPHERIC GAS CONCENTRATION IN THE ARCTIC OCEAN

INTRODUCTION

The ingenious utilization by oceanographers of the various self-contained "tracers" in the world's oceans is documented in every text and reference related to this burgeoning field. Chemical, physical, and biological entities, singly and in concert, have been used to explain the impact of the oceans on such diverse subjects as climate, commerce, marine warfare, and even life on earth as regards the makeup of our atmosphere.

One of the more frequently used tracers, the usefulness of which overlaps nearly all of the oceanographic disciplines, is the dissolved oxygen content of sea water (1). The concentration of this gas, under unsaturated but quasi-equilibrated conditions, defines and names a nearly worldwide layer of intermediate water, the oxygen minimum layer, whose low-oxygen content results from its function as the oxidative zone for the chemical and biological constituents of the upper hydrosphere (2,3). The physical oceanographer has used this tracer to delineate ocean currents and circulation; e.g., Richards and Redfield(4) traced a core of low-oxygen Gulf Stream water from off New England to its origin in the Caribbean Sea, coincidentally establishing the fact of actual water transport as opposed to momentum transfer. The fact that most deep ocean waters exhibit a degree of oxygen saturation that could have been attained only by surface exposure in polar regions lends credence to certain circulatory models for the entire oceanic system (2).

Other, nonatmospheric, gas content data, such as for methane and hydrogen sulfide, have been used to establish the relative stagnancy of the waters off the east coast of Africa and in the Cariaca Trench (2).

In spite of the generalized examples above, dissolved gas analysis has far from realized its potential as an oceanographic tool. The mere magnitude of data required, combined with the relative difficulty of sampling and analysis, is rather overwhelming. Local biological activity, particularly in the case of oxygen, can obscure the proper interpretation of data. For the delineation of physical phenomena, a more inert material would make a better tracer. One of the more inert gases present in sea water in sufficient concentration to make it attractive for this purpose is nitrogen. Unfortunately, present data indicate that this gas is present in essential saturation in all waters, thus leaving no "handle" for its use. Additionally, nitrogen analyses have been tedious and difficult, which, coupled with a lack of interest, has prevented the accumulation of a significant volume of data on this element.

NEW INSTRUMENTATION

The development of an instrument for the continuous sampling and gas chromatographic analysis of water for its dissolved gas content (5) obviated one of the principal deterrents to nitrogen data collection – that of difficulty. With this instrument, recently successfully sea-tested aboard an operating submarine (6), oxygen and nitrogen are simultaneously determined, essentially in situ, with equal ease and accuracy. The technique of direct sampling from a submerged platform eliminates the error-fraught cast methods,

with subsequent wet analysis after exposure to changing temperature, pressure, and container effects. Present submersibles do not allow for vertical profiling to the significant depths that are desired for general application, but the emerging generation of vehicles will. There is one body of water, however, that lends itself uniquely to this technique even at moderate depths – the Arctic Ocean.

Recent interest in the polar regions has served to emphasize the dearth of our knowledge concerning these increasingly important areas. The present method of data collection in the Arctic is the establishment of manned, drifting ice stations by both the United States and the Soviet Union. A supplementary "laboratory" was added when this ocean was conquered by the nuclear submarine. This feat opened a new and exciting avenue for a more rapid (and comfortable) accumulation of information. The incorporation of an instrument for dissolved gas analysis on a research-oriented arctic mission of a nuclear submarine could provide much useful information. The new knowledge gained could be very surprising and significant to many disciplines.

POSTULATED DISSOLVED GAS ANOMALY

When one considers the age and immensity of the polar ice pack and the fate of dissolved gases under the influence of cyclic freezing and thawing, one cannot avoid the surmise that there MAY be a considerable volume of water under the ice cover which is less than saturated with the atmospheric gases. Every cloudy or transluscent ice cube demonstrates that the process of freezing water liberates and segregates a certain amount of previously dissolved gas, not all of which may be trapped in the bubbles. The geometry of the ice pack and its supporting water column, the annual freeze-thaw cycle, combined with long-term diffusion processes, could result in a considerable volume of "gas-poor" water in the confines of the high-sill basin which delineates the Arctic Ocean. Candor requires that an assumption of equally questionable validity can be made as to the possibility that the same conditions could produce supersaturated water – supersaturated at atmospheric conditions, but in hydrodynamic equilibrium with respect to the depth of the sample. In either event, an anomalous concentration of dissolved gas would be present, and if of the latter type, would not be detected by cast sampling techniques.

Meager and somewhat contradictory literature on this subject tends to militate against, but does not deny, the above possibilities. Coachman et al. (7), in a study of Norwegian glacial ice, reported no general loss of gas with age, but a depletion of oxygen and argon and an increase of carbon dioxide in entrapped gas bubbles was reported. Hemmingsen (8) reported no detectable penetration of oxygen through ice, while carbon dioxide diffused at a measurable rate. No mention of nitrogen is made in either article. Untersteiner (9) in his Arctic sea-ice study for the IGY, reports bottom accumulation and surface ablation as the primary, but not the sole, model for annual ice equilibrium.

Another contributing factor is the magnitude of plant and animal life under the ice pack. Johnson (10a), English (10b), and Hill (2) all report a very low level of phytoplankton production under the permanent ice. The area is not devoid of life, however, and the peripheral waters are relatively abundant in both plant and animal species. While biological activity and nutrient oxidation could affect or even obscure an oxygen anomaly, present data on this element are the sole experimental evidence that such a condition may exist. Coachman (10c) states that meager data indicate that all arctic water masses are more than 70% saturated with respect to oxygen. Why only 70%? English (10b) presents data (Fig. 1) from the North Polar Sea taken on Drift Station Alpha in 1958 (Fig. 2) showing a remarkably stable column of oxygen-saturated water to a depth of about 50 meters with a precipitous drop to about 70% saturation in the next 50 meters and below. If the oxygen minimum layer in other oceans results from extensive oxidation, why a similar minimum where oxidation is presumed to be much less? (It is pertinent to note here that the depths involved above are admirably suited to direct sampling from a submarine.)

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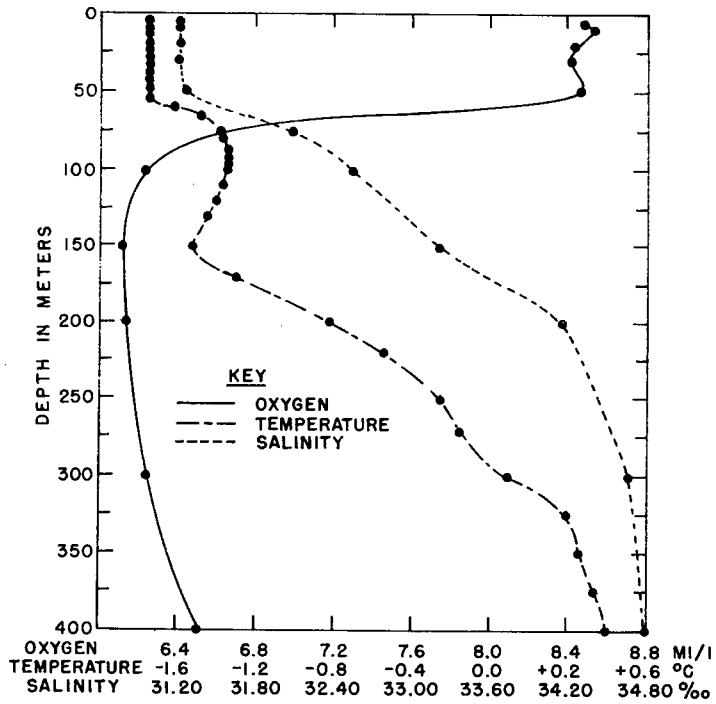

Fig. 1 - Temperature, salinity, and dissolved oxygen, Drift Station Alpha, 23-24 June 1958 (taken from Ref. 10b)

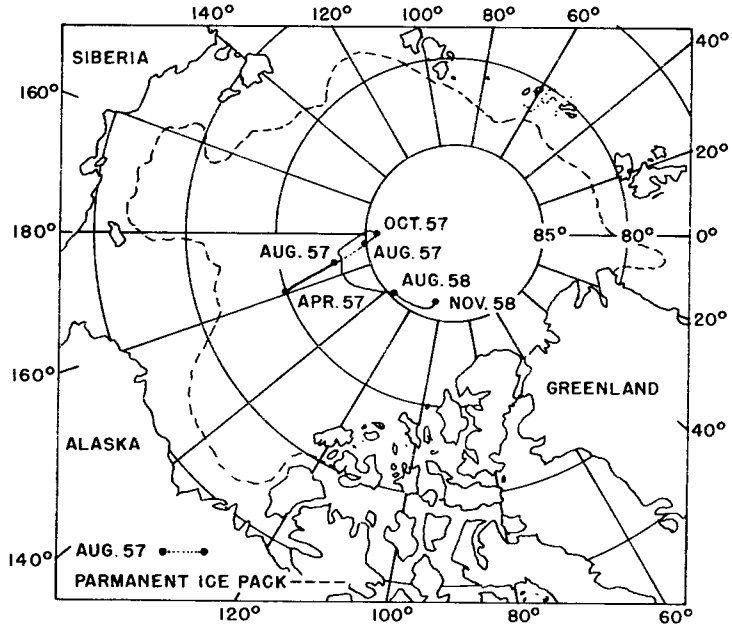

Fig. 2 - Track of Drift Station Alpha, April 1957 – November 1958 (taken from Ref. 10b)

The role of water exchange between the Arctic, Atlantic, and Pacific Oceans has not been integrated into the preceding picture. One reason for this omission is the contradictions that appear in the literature. Some texts refer to a relatively permanent "pool" of water below the Atlantic sill depth, while others have calculated bottom water residence times of 50 years and less. Coachmen (10d) stated, "The movement of bottom water has been impossible to trace. We need some sort of specific tracer, or direct current measurements." The intent of this report is to suggest the possibility of such a tracer.

Assume then that an atmospheric gas content anomaly exists and that a rapid, accurate method for nearly continuous analysis is available. Submarine tracking of nitrogen – "traced" water masses to define the limits or movement within or out of the arctic basin becomes both feasible and informative. Depending upon the magnitude of the anomaly and the ability of the submarine to define its location, much valuable information on water currents and masses could be derived. Important insights into flow patterns, heat balances, seasonal effects, etc., would result. Even if anomalous concentrations were not found, the collection of this type of data would be an important contribution to our chemical knowledge of this forbidding but increasingly important region.

While the final answer will necessarily await actual analyses in the region of interest, a number of laboratory investigations can be executed. The fate of dissolved gas under controlled cycles of freezing and thawing, the residual gas content of "clear" ice frozen bubble-free, and further investigation of diffusion in or through ice are immediately obvious approaches. The shore analysis of sub-pack-ice water samples is also indicated, although such samples suffer all the fates of the obvious environmental changes and can be very misleading. This Laboratory is proceeding with experiments of the above nature and has submitted a request for participation in a research-oriented nuclear submarine mission under the arctic ice.

REFERENCES

1. Sverdrup, H.U., Johnson, M.W., and Fleming, R.H., "The Oceans," Englewood Cliffs, N. J.:Prentiss-Hall, Inc., 1942

2. Hill, M.N., "The Sea," Vol. 2, New York, N. Y.:Interscience Publishers, 1963

3. Harvey, H.W., "The Chemistry and Fertility of Sea Waters," London:Cambridge University Press, 1955

4. Richards, F.A., and Redfield, A.C., Deep-Sea Research 2:182-199 (1955)

5. Williams, D.D., and Miller, R.R., "An Instrument for 'On-Stream' Stripping and Analysis of Dissolved Gases in Water," NRL Report 5678, Sept. 1961, and Anal. Chem. 34(No. 6):657 (May 1962)

6. Williams, D.D., and Miller, R.R., "Submarine Application of Gas Chromatography for the Analysis of Dissolved Gases in Sea Water," NRL Report 6245 (in press), 1965

7. Coachman, L.K., Enns, T., and Scholander, P.F., Tellus 10:493-5 (1958)

8. Hemmingsen, E., Tellus 11:355-9 (1959)

9. Untersteiner, N., Trans. Amer. Geophys. Union 39:601-5 (1958)

10. "Proceedings of Arctic Basin Symposium, Oct. 1962," Washington, D. C.:Arctic Inst. of N. Amer., 1963

    a. Johnson, M.W., "Arctic Ocean Plankton," pp. 173-83
    b. English, T.S., "Some Remarks on Arctic Ocean Plankton," pp. 184-96
    c. Coachman, L.K., "Water Masses of the Arctic," pp. 143-67
    d. "Discussion of Dr. Coachman's Paper," p. 170

Security Classification

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY *(Corporate author)*

U.S. Naval Research Laboratory
Washington, D.C. 20390

2a. REPORT SECURITY CLASSIFICATION

Unclassified

2b. GROUP

3. REPORT TITLE

POSTULATED ANOMALOUS DISSOLVED ATMOSPHERIC GAS CONCENTRATION IN THE ARCTIC OCEAN

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

An interim report on one phase of the problem.

5. AUTHOR(S) *(Last name, first name, initial)*

Williams, D.D., and Miller, R.R.

6. REPORT DATE

April 19, 1965

7a. TOTAL NO. OF PAGES

9

7b. NO. OF REFS

10

8a. CONTRACT OR GRANT NO.

C05-20

b. PROJECT NO.

ONR RR 001-01-43-4756

c.

d.

9a. ORIGINATOR'S REPORT NUMBER(S)

NRL Report 6249

9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*

10. AVAILABILITY/LIMITATION NOTICES

Unlimited availability
Available at CFSTI

11. SUPPLEMENTARY NOTES

12. SPONSORING MILITARY ACTIVITY

Dep't of the Navy (Office of Naval Research)

13. ABSTRACT

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DD FORM 1 JAN 64 1473

Security Classification

UNCLASSIFIED

14. KEY WORDS	LINK A ROLE	LINK A WT	LINK B ROLE	LINK B WT	LINK C ROLE	LINK C WT
Oceanographic "tracers" Dissolved atmospheric gas in ocean waters Arctic Ocean Nitrogen Dissolved gas analyzer						

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