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OCEAN MIXING AS DETERMINED BY RADIOISOTOPES*

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ABSTRACT

Radioactive isotopes provide a time scale for oceanographic studies. The ideal isotopic tracer is an integral part of the water, has a convenient half-life, and is easily measurable. No tracer is ideal for all oceanographic studies. Unless great care is taken in the interpretation, the measurements may tell us that the particular isotope is not suitable for the problem selected rather than that the ocean is behaving strangely.

There are three oceanic regions where isotopic tracers are especially useful as mixing indicators: (1) the thermocline; (2) the ocean floor; (3) intermediate currents. Different isotopes are useful in each area; however, confusion may arise if the geochemical behaviour of the isotope in the ocean is not well understood.

Mixing through the main thermocline is best studied using cosmic ray-produced isotopes (C^{14}, H^3, Si^{32}) and hydrogen bomb-produced isotopes (Sr^{90}, Cs^{137}, H^3, C^{14}). The long half-life (5700 years) and geochemical reactions of C^{14} make results based on it alone rather uncertain. The other isotopes tell us that mixing through the thermocline is an extremely slow process characterised by a diffusion coefficient of $\lesssim 1 cm^2/sec$.

Mixing near the ocean floor is studied using isotopes which naturally leak from deep sea sediments. Koczy attempted to use the diffusion of radium-226 as a mixing indicator; however, the long half-life (1600 years) and geochemical uncertainties have rendered Ra^{226} almost useless. Broecker found that the Ra^{226} daughter, radon-222, does not suffer these difficulties. It is a rare gas with a 3.8 day half-life and is a very convenient indicator of mixing in the lower 100 meters of the water column. Other isotopes that have potential in such studies are radium-228 (half-life = 6.7 years) and lead-210 (half-life = 22 years). Both are undergoing extensive geochemical tests.

Intermediate currents whose waters originate near the surface may also be studied using bomb-produced and cosmic ray-produced isotopes. The outflows from the Red Sea, the Persian Gulf, and the Mediterranean Sea are prime examples of currents that lend themselves to such studies. No one has undertaken this work to date in spite of the rich opportunity for significant contributions.

INTRODUCTION

THE circulation of the world ocean is studied by tracing the paths of water masses through the system. These water masses originate wherever local conditions of temperature and evaporation produce water denser than surrounding surface waters. The densest and hence the deepest water masses are formed at high latitudes and flow toward the opposite pole. North Atlantic Deep Water is formed around Labrador and Greenland and flows toward the South Pole in the Atlantic

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Ocean. Antarctic Bottom Water is formed primarily in the Weddell Sea and flows toward the North Pole in the Atlantic, Pacific, and Indian Oceans. Both of these deep water masses are characterised by their low temperatures.

The Antarctic region also produces an intermediate current which flows northward at a depth of 500-1200 m. It is differentiated from surrounding waters by its low salinity and temperature. In the Indian Ocean, the Red Sea produces a characteristic intermediate current having a very high salinity. This water type is produced by the high evaporation in the Red Sea and, after crossing the Straits of Bab el Mandeb, sinks to a depth of about 700 meters and flows through the Indian Ocean at depths of up to 1200 meters. Similar high salinity intermediate currents are formed in the Persian Gulf and in the Mediterranean Sea.

These characteristic water masses produce a highly stratified ocean, an ocean where the mixing between different water types is highly restricted. It is much easier to move a water mass along a surface of almost constant density than it is to mix two water masses having different densities. Lateral flow is the primary motion ; vertical mixing is much slower.

In general, the water masses of the deep ocean are remarkably similar in density (σ_T) compared to the density difference between the deep and surface ocean. The surface ocean constantly receives energy from the sun and transfers this energy towards the polar regions via surface currents. This results in a warm, low density layer overriding the cold, high density deep water. The sharp gradient of temperature between the surface and deep ocean is known as the thermocline.

Mixing through the thermocline is of major importance. Organisms living in the surface layers of the ocean constantly use nutrients ($PO_4^{\equiv}$, NO_3^{-}, SiO_2, etc.) in their life cycles. A certain fraction of these nutrients are lost from the surface waters when these organisms die and sink to the deep ocean. Fortunately, these nutrients are not completely lost as most of the organic debris is oxidized in the deep ocean and the vital nutrients are released. Now these nutrients must find their way back through the thermocline to the surface ocean where they can be again used in the life process. Mixing through the thermocline thus represents one limit on the productivity of the ocean.

Radioactive Isotopes

There are many places in the general mixing of the oceans where radioactive isotopes may be of use. It is important to recognize that without physical oceanographic measurements on the same waters, the isotopic measurements mean very little. In the ocean there are three types of radioisotopes that may be useful in various oceanographic mixing studies : (1) cosmic ray-produced isotopes [carbon-14, hydrogen-3, and silicon-32] ; (2) hydrogen bomb produced isotopes [cesium-137, strontium-90, hydrogen-3, and carbon-14] ; and (3) natural uranium and thorium series isotopes [radium-228, radon-222, and lead-210].

Carbon-14

Cosmic ray-produced carbon-14 has provided us with most of our knowledge of the overall rate of oceanic circulation. C^{14} is produced in the upper atmosphere by reactions between cosmic rays and nitrogen atoms.

$${}_0n^1+{}_7N^{14}\rightarrow{}_6C^{14}+{}_1p^1$$

The C^{14} is rapidly oxidized to $C^{14}O_2$ which enters the CO_2 cycle of the earth. Within 10-20 years most of this $C^{14}O_2$ enters the ocean. Various models are available to explain the distribution of C^{14} in the ocean (Craig, 1958 ; Broecker, 1963 ; Craig, 1969 ; Broecker and Li, 1970). These models give us an overall picture of oceanic circulation rates ; however, the long half-life (5700 years) and geochemical complications (Craig, 1969 ; Somayajulu *et al.*, 1969 ; Williams *et al.*, 1969) limit the precision of mixing rate studies based on C^{14}. The C^{14} distribution does place certain restrictions on the ocean systems ; e.g. the deep waters mix with the surface ocean only about every 1000 years whereas the surface waters are internally well mixed every 10-20 years (Broecker *et al.*, 1961). Precise ages of various water masses are simply not realistic at this time. Rather than review the extensive literature on C^{14}, I shall discuss other isotopes that show promise in various types of ocean mixing studies.

THERMOCLINE MIXING STUDIES

To study mixing through the main oceanic thermocline, both cosmic ray-produced and bomb-produced isotopes may be used. There is also hope that radium-228, a thorium-232 daughter, may be useful.

Tritium (H^3) is constantly produced in the upper atmosphere by various spallation reactions. As an isotope of hydrogen, it should provide an excellent means of tracing water mixing. However, natural tritium levels in surface waters are quite low and are near the experimental limit of detection ; furthermore, hydrogen bombs and nuclear power plants have released vast amounts of tritium to the atmosphere since 1954 (Table 1). Thus it is not so much cosmic ray-produced tritium as it is man-made tritium that is an effective tracer. Table I shows that tritium produced in the Castle series of hydrogen bomb blasts was rapidly removed in the form of precipitation. This fallout tritium finds its way to the surface ocean as H^3HO where it moves with other water molecules.

TABLE 1. *Tritium concentrations of precipitation samples collected in Palisades, New York, U.S.A.* (Compiled from Giletti *et al.*, 1958)

Dates	No. Samples	$T:H\times10^{18}$
Oct. 25, 1953-Mar. 3, 1954	14	4-17
Mar. 14, 1954	1	1240
Mar. 19-May 11, 1954	10	60-640
May 22, 1954	1	1178
June 1-July 6, 1954	5	150-300
Aug. 13-Nov. 2, 1954	14	11-81
Nov. 6, 1954-Feb. 11, 1955	9	6-20
Feb. 21-July 24, 1955	7	12-37

Recent measurements of tritium in the equatorial Atlantic Ocean have revealed that in 1964 fallout tritium had not penetrated below the thermocline (Östlund *et al.*, 1969). No water samples colder than 12°C (corresponding to a depth of about 100 meters) showed significant tritium activity. Continued measurements of the penetration of H^3 into the thermocline should prove an effective means of studying mixing in this critical area.

Two other fallout isotopes, cesium-137 and strontium-90, have also proved valuable in thermocline mixing studies. There is some question about the penetration of these isotopes into the thermocline (Rocco and Broecker, 1963; Bowen and Sugihara, 1965). Most measurements suggest that by 1961 Sr^{90} and Cs^{137} had penetrated to a depth of 200-300 meters in the Pacific and Atlantic Oceans, but measurements in the Antarctic revealed mixing to a depth of over 1000 meters (Rocco and Broecker, 1963). By 1963 the penetration in the equatorial Pacific and North Atlantic was not significantly greater than in 1961 (Broecker *et al.*, 1966).

These fallout measurements are not at all easy to make. Sr^{90} and Cs^{137} require a water sample of 100-200 liters. To avoid the problem of storage, the chemical processing must be done on the ship, especially if many samples are to be run. Rainwater and surface spray are serious contaminants, as are some of the chemicals used in the separations. For tritium only one liter of sample is required, but the contamination problems are even more serious. Extensive purification or enrichment of all samples is required. Low level beta counting is used to establish activities. Numerous blanks must be run to evaluate the contamination effects.

The overall picture that emerges from the fallout measurements is one of very restricted mixing characterised by a coefficient of vertical eddy diffusion of <1 cm^2/sec. This is in agreement with the general results of the C^{14} measurements.

The recent discovery of large quantities of unsupported radium-228 in the surface ocean has contributed another isotope for thermocline mixing studies (Moore, 1969a and b). Ra^{228} has the advantage of being naturally contributed to the marine environment and not subject to periodic injections like fallout isotopes. Again, large water samples (200-1000 liters), shipboard chemistry, and good counters are required to measure Ra^{228}. Only a few measurements have been made of its depth distribution (Fig. 1) and it is too early to tell if it will confirm the fallout mixing rates or not.

The one cosmic ray-produced isotope available for thermocline mixing studies is silicon-32 (Lal *et al.*, 1960). Because silicon is such a geochemically active element, the ratio (Si^{32}/total Si) is used to normalize the Si^{32} concentration and avoid problems of geochemical removal. Again, the natural levels of activity are extremely low and water samples of over 1000 liters are required along with painstaking chemical separations and the most sensitive counters. Not enough Si^{32} measurements are available for an evaluation of mixing rates using this isotope.

Si^{32} has the advantage of being an isotope of an element closely tied to the nutrient cycle; therefore, studies of its distribution may also be used to evaluate the rate of removal of the vital nutrients from the surface waters.

MIXING NEAR THE SEA FLOOR

Mixing near the sea floor has recently been studied using the natural distribution of radon-222. This isotope is constantly generated from radium-226 present in deep sea sediments. Some of the Rn^{222} leaks from the sediments and dissolves in the overlying waters. It then moves as an integral part of the water and changes in concentration only by radioactive decay. The 3.8 day half-life of Rn^{222} allows for measurements in the lower 30-80 meters of the water column. Broecker *et al.*

(1968) have shown that the distribution of Rn^{222} away from the sea floor should obey the equation

$$C=C_0 \exp [-X\sqrt{\lambda/D_e}]$$

where C=concentration excess Rn^{222} X cm above the bottom
C_0=concentration excess Rn^{222} at the bottom
λ=decay constant Rn^{222}
D_e=rate of vertical eddy diffusion.

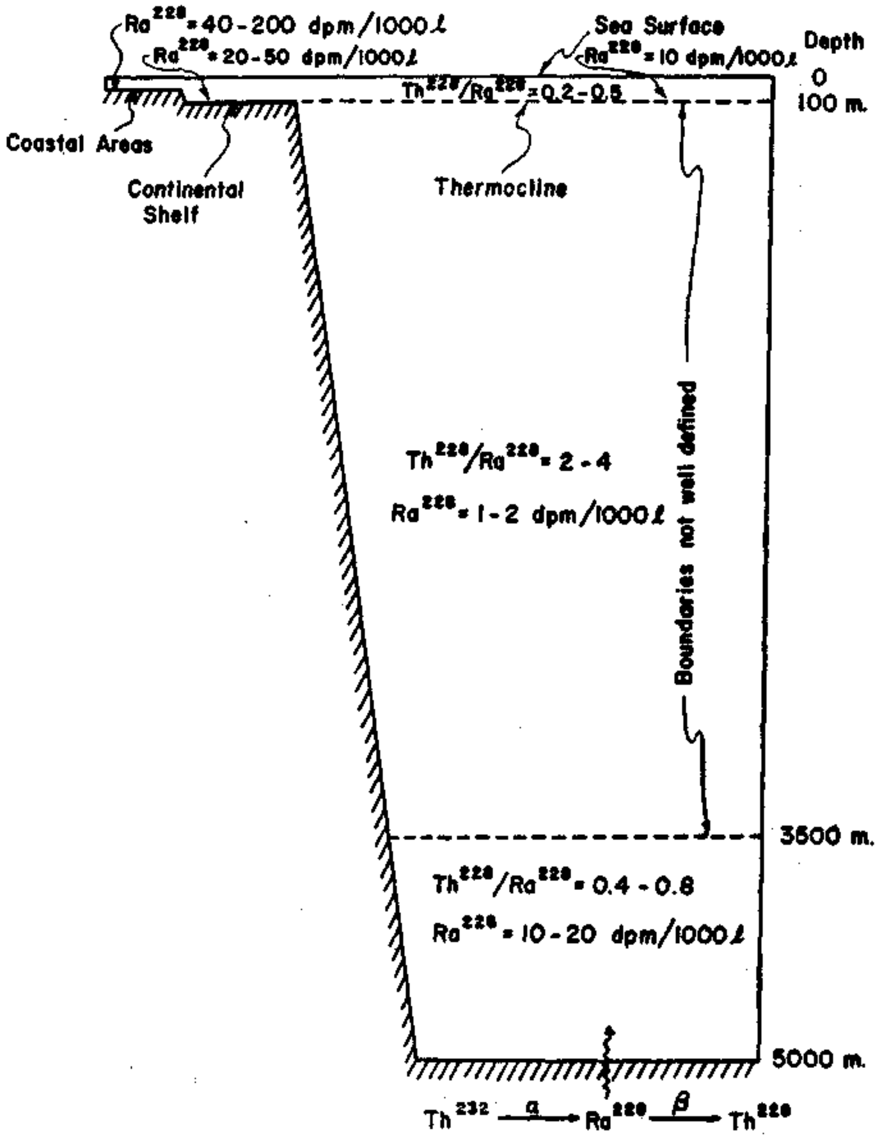

FIG. 1. The distribution of Ra^{228} in the ocean and the activity ratio Th^{228}/Ra^{228}.

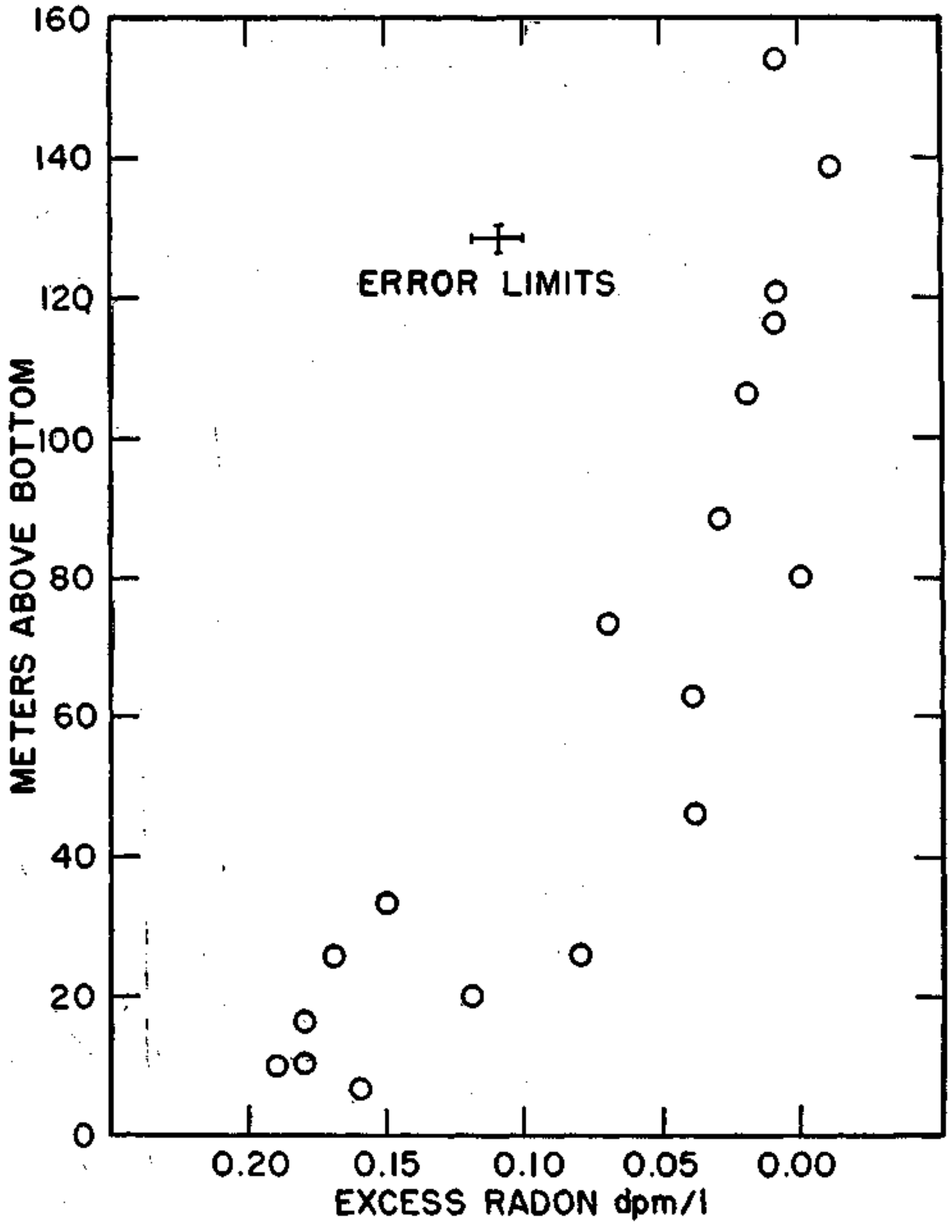

Fig. 2. The concentration of excess Rn^{222} graphed as a function of distance above the bottom for 29° 20′N, 76° 00′W.

For Rn^{222} measurements, 20 liter water samples are required. The radon must be immediately extracted from the water sample, purified in a vacuum line, and counted onboard ship. This requires a rather sophisticated system and liquid nitrogen, a commodity not available in every port. The water samples must also be analyzed for their Ra^{226} concentration because this isotope will contribute supported Rn^{222} activity to the sample. Excess Rn^{222} is calculated by subtracting the supported activity from the total measured.

Radon profiles are available for the Pacific and Atlantic Oceans. The rate of vertical eddy diffusion in the lower 50 meters generally ranges from 5 to 30 cm^2/sec but values as low as 2 and as high as 90 cm^2/sec have been observed (Broecker *et al.*, 1968 ; Moore and Reid, 1970). Figures 2 and 3 are examples of radon profiles that have been measured. The extremely high coefficient of vertical eddy diffusion observed by Moore and Reid (1970) shows that, as one would expect, rapid bottom currents are accompanied by a large amount of turbulent mixing.

The first long-lived isotope in the Rn^{222} decay chain is lead-210. At radioactive equilibrium Rn^{222} will produce a standing crop of Pb^{210} equal in activity to Rn^{222}. Because of its half-life of 22 years, Pb^{210} will mix upward several thousand meters. It should prove to be an effective tracer for a variety of deep water studies. The first measurements are now being conducted at the Tata Institute in Bombay.

Radium-228 is also leaking from deep sea sediments. Its half-life of 6.7 years means that it should be useful in mixing studies in the lower 2000 meters of the water column. Figure 4 is a graph of the predicted Ra^{228} distribution away from the sea floor. Measurements to date have only confirmed the presence of Ra^{228} in the deep ocean (Moore, 1969a and b). Intensive studies will be required to properly evaluate its usefulness.

There is an indication that tritium, strontium-90, and cesium-137, may also be useful in studies of bottom waters. Giletti *et al.* (1958) found measurable tritium activity in the only three samples of bottom water that they measured in the North Atlantic. Rocco and Broecker (1963) and Broecker *et al.* (1966) found Cs^{137} and Sr^{90} in samples they collected near the sea floor in the Atlantic. All of these measurements were very near the blank and carried a 20-50% statistical uncertainty. They may not be real ; however, measurements made above the bottom waters by the same authors showed values much nearer zero. On the basis of bottom current evidence, Schneider (in press) has suggested that the bottom waters in the western North Atlantic may have an age low enough to contain fallout-produced isotopes. This is certainly an exciting field of current research.

INTERMEDIATE CURRENTS

Intermediate currents, especially those derived from semi-enclosed basins, should lend themselves to radioisotope studies quite well. The initial concentration of the isotope in the water should be readily obtained from measurements within the basin. Water samples collected through the water mass at various distances from the source could then be used to evaluate the rate of mixing and the rate of movement of the core of the intermediate current. This is analogous to the use by Wüst of dissolved oxygen decreases along the core of a water mass to determine its rate of movement. All isotopes used in thermocline mixing studies should be useful here also. Two intermediate currents that are ideally suited to such a study

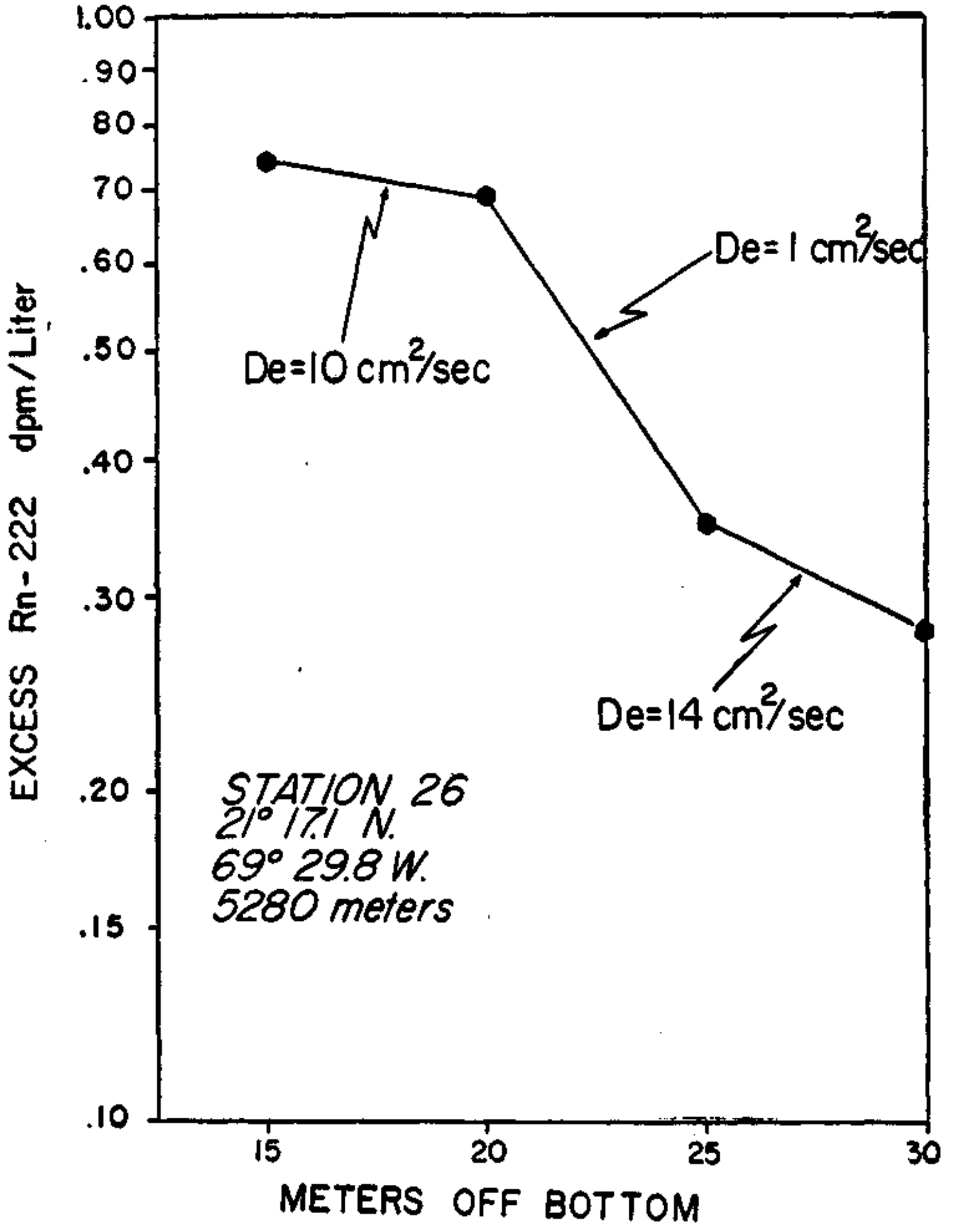

FIG. 3. The concentration of excess Rn^{222} graphed as a function of distance above the bottom for 21°17.1'N, 69°29.8'W.

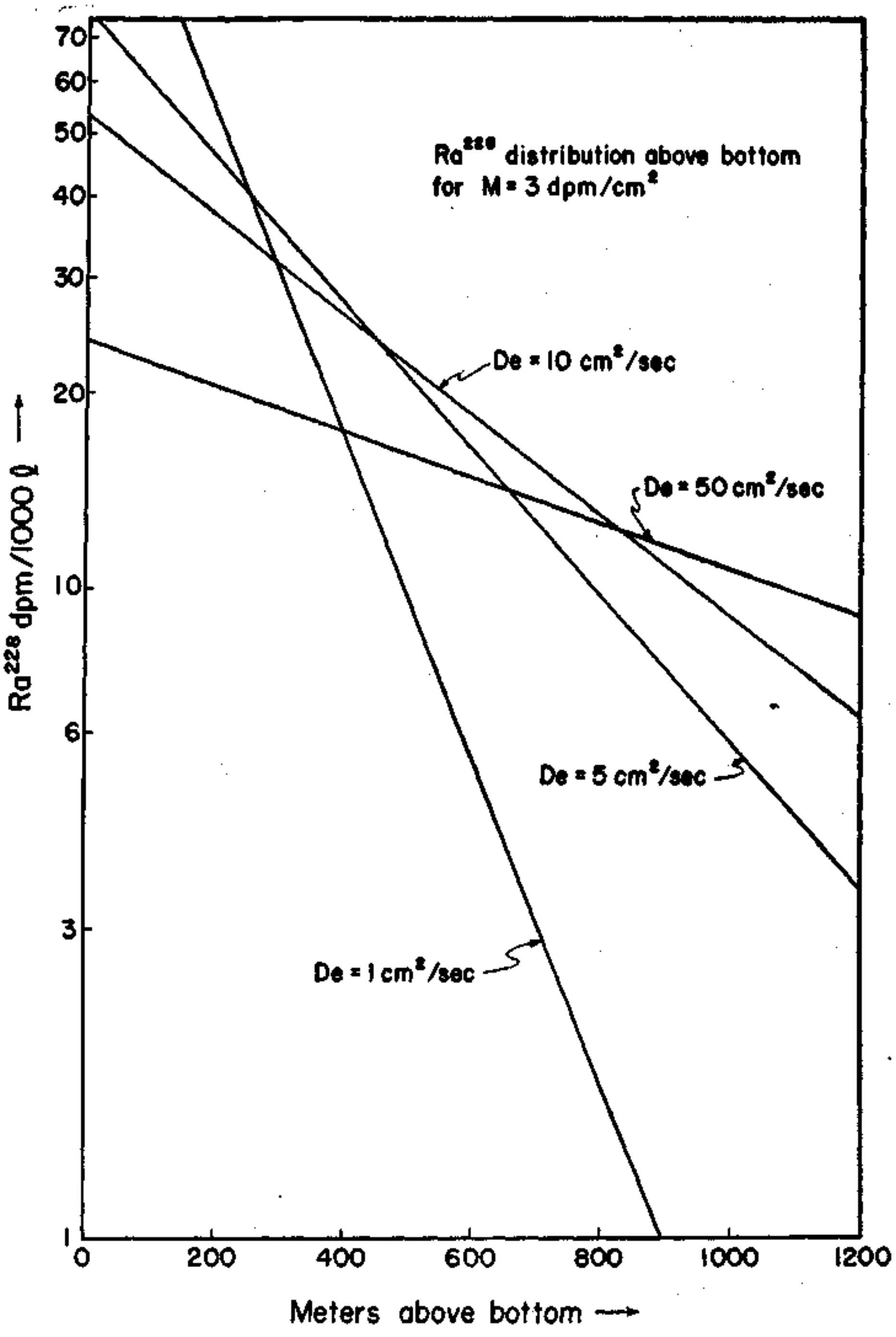

FIG. 4. The predicted Ra^{228} distribution above the ocean floor as a function of various rates of vertical eddy diffusion (De) assuming a standing crop of Ra^{228} of 3 dpm/cm^2.

are the high salinity currents generated in the Red Sea and in the Persian Gulf. Major advances in understanding the circulation of these intermediate currents could quickly be made using radioisotope techniques.

CONCLUSION

It is obvious that many isotopes are available for oceanic mixing studies. What we need are better ways of concentrating these isotopes free of contamination. Increasing emphasis is being placed on using ion exchange type techniques for the *in situ* extraction of isotopes. Professor Lal of the Tata Institute has pioneered efforts of this type. By towing an impregnated fiber or by pumping water through ion exchange materials, isotopes may be concentrated without having to bring a huge water sample to the surface. Problems of contamination are thus considerably lessened.

During the 1960's, radioisotopes came to be an effective tool for oceanographers in evaluating the mixing patterns of the ocean. But the definitive work has yet to be accomplished. Numerous isotopes must be measured at the same location and these measurements must be coupled with extensive physical oceanographic measurements. Only then will radioisotope geochemists realise their full potential in oceanography.

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