Deuterium Distribution in the Gulf of Mexico

D. J. FRANK

Dept. of Oceanography, Texas A & M University, College Station 77843

ABSTRACT

The variations of the stable isotopes of hydrogen (protium and deuterium) were determined in the various water masses of the Gulf of Mexico. Surface waters of the central Gulf were found to have an average $\delta D = 5.6\%_0$ relative to Standard Mean Ocean Water (SMOW), where

$$\delta D(\%_0) = \{[(HD^+/H_2^+)sample/(HD^+/H_2^+)standard]-1\} \times 1000.$$

The subsurface water masses, Subtropical Underwater, Antarctic Intermediate Water, and Gulf Basin Water, were found to be characterized by deuterium contents of 5.0–5.5, −0.5 and $0.9\%_0$, respectively. In addition, a high deuterium feature ($\delta D = 5.5$–$6.3\%_0$) was shown in the water column at about 100 m depth just above Subtropical Underwater. The δD values for the fresh water contribution to the Gulf via the Mississippi and Coatzacoalcos Rivers were found to be −42.3 and $−19.3\%_0$, respectively. The value for the net fresh water addition to the Gulf was $\sim -33\%_0$. The isotopic composition of near-shore waters is consistent with a simple mixing model of fresh water from runoff with ocean water modified by the mixing of sea waters from distinct sources.

1. Introduction

The proportions of the principal stable molecular species containing hydrogen which are present in the sea and atmosphere are:

H_2O	1,000,000 ppm
HDO	320 ppm

where these values are approximate molecular parts per million in mean seawater as given by Craig and Gordon (1965). Except at a phase boundary, where fractionation occurs, the concentration of deuterium will change only as a result of mixing of waters of different isotopic compositions. Hence the isotopic species of water, H_2O and HDO, provide another conservative property which can be used along with temperature and salinity to characterize water masses. The advantage of deuterium variations over that of just salinity variations in the oceans is that while salinity is a tracer of oceanic fluid, deuterium is a tracer of the water itself in both liquid and vapor phase.

The variations of deuterium in the marine environment can be understood by considering the following factors: 1) evaporation and condensation of water from and to the surface of the ocean, 2) mixing of sea water with fresh water whose isotopic composition is different, 3) the mixing of sea water from distinct sources and diffusion processes, and 4) the formation of sea ice in polar regions. Of these four factors, the most important is that of net evaporation since the fractionation of isotopes during evaporation processes is related to the relative vapor pressures of the molecular species in question. As a result, in the evaporation of sea water, deuterium tends to be concentrated in the condensed phase.

By expressing the deuterium concentration of a water mass as a function of salinity, the mixing of sea water with fresh water can be studied. Horibe and Ogura (1968) found that the surface water above 100 m depth in the South China Sea is formed by the mixing of fresh water with sea water. Redfield and Friedman (1965) show similar results for the mixing of various proportions of fresh water with salt water from the head waters of a number of estuaries to the open sea. In addition, Horibe and Ogura have shown that deuterium-salinity diagrams can be used in the same way as temperature-salinity diagrams to characterize different water masses. They have shown that for the Kuroshio Current, deuterium-salinity diagrams demonstrate more clearly the characteristic features than just temperature and salinity measurements alone.

Consequently, the distribution of deuterium in subsurface water masses is dependent on the processes of mixing and advection of water which first derived its deuterium content at the surface through processes of evaporation and precipitation and by dilution with runoff. Therefore, characteristic values for deuterium content may be assigned to each water mass. Hence the primary objective of this work was to characterize the Gulf of Mexico using concentrations of deuterium and to determine if variations could help in understanding the oceanography of the Gulf of Mexico. In order to accomplish this goal, approximately 160 water samples were collected and analyzed from the Gulf of Mexico, and from two rivers, the Mississippi and Coatzacoalcos.
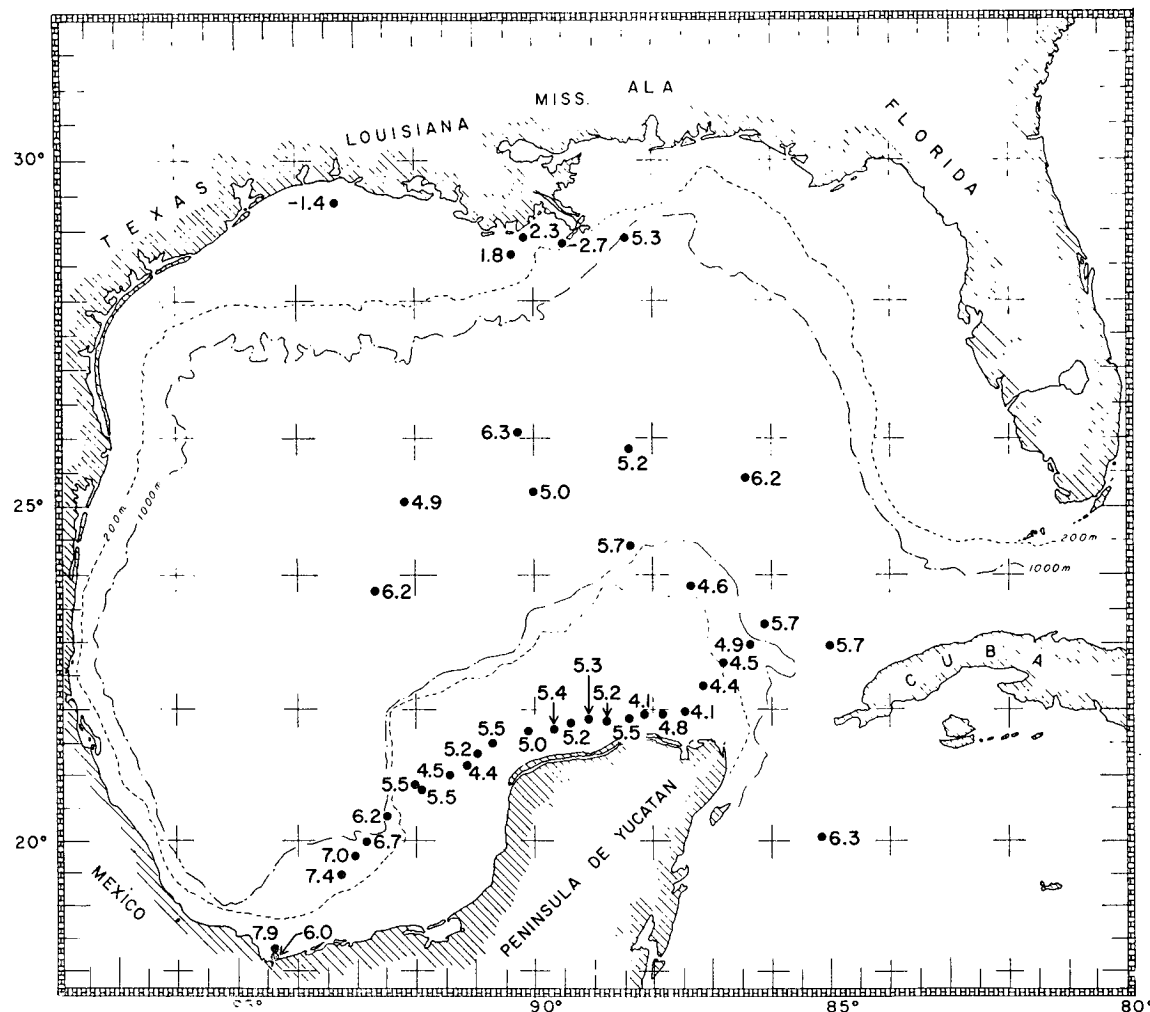
FIG. 1. Deuterium concentrations $\delta D(‰)$ in Gulf of Mexico surface waters relative to SMOW.

2. Experimental procedure

Water samples for the Gulf of Mexico and two of its inflowing rivers (Mississippi and Coatzacoalcos) were collected on four separate cruises of the R/V *Alaminos*. Approximately 10-ml aliquots were sealed in glass ampules for return to the laboratory and subsequent analysis. Care was taken throughout the entire sampling procedure to avoid contamination of the samples with outside water and/or the partial evaporation of the sample resulting in an isotope fractionation. All samples were sealed in ampules within 3 hr after collection. No observable isotopic fractionation, as determined through replicate samples, was detected due to these procedures.

The reduction of the water samples to hydrogen gas was carried out in an all-glass vacuum system following the procedures of Friedman (1953) and Friedman and Hardcastle (1970).

The isotopic composition of the hydrogen gas was measured in a Nier-McKinney type mass spectrometer (Nier, 1947; McKinney *et al.*, 1950) relative to a

standard. This instrument, Nuclide Model RMS-28, is a 60° double collecting mass spectrometer equipped with a split tube. In addition, special modifications in the electronic and gas handling system were made to permit the measurement of small differences in isotope abundances of hydrogen with high sensitivity.

The reported values of isotopic composition are in terms of the per mille (‰) difference between the ratio of the mass-3 and mass-2 ion beams of the sample and standard. This difference is expressed by

$$\delta D(‰) = \left[\frac{(HD^+/H_2{}^+) \text{ sample}}{(HD^+/H_2{}^+) \text{ standard}} - 1 \right] \times 1000,$$

where the standard is Standard Mean Ocean Water (SMOW) (Craig, 1961). The reported δD values include corrections due to the leakage of the magnetic valves and the presence of $H_3{}^+$ ions in the mass-3 ion beam and background. The leakage correction was found to be 1.013 while the mass-3 correction ranged from 1.110 to

1.140 for National Bureau of Standards NBS-1. The overall precision of the measured δD values, including preparation of the samples, was found to be $\pm 1.0‰$.

3. Results and discussion

a. Surface water

Following the analytical procedures described above, the D/H ratios of 51 surface samples from the Gulf of Mexico region were determined. The results of these analyses for the Gulf surface waters are shown in Fig. 1. From this figure it is evident that three major features of the deuterium distribution in the Gulf region exist as follows: 1) low δD values along the northern Gulf coast, 2) δD relatively constant in the central Gulf, and 3) somewhat higher δD values in the Bay of Campeche off the Mexican coast.

The low values of δD along the northern Gulf coast are due to the influx of fresh water via rivers. Friedman *et al.* (1964) have determined the deuterium content of all major U. S. rivers emptying into the Gulf of Mexico and found δD to range from -33 to $+16‰$, except for the Mississippi River which was $-47‰$ at Baton Rouge, La. Values of $-40.5‰$ and $-40.4‰$ for the Southwest Pass (28°58.7′N, 89°22.3′W) and South Pass (29°02.5′N, 89°11.5′W) of the Mississippi, respectively, were determined in this study. The difference in these values and that from the Baton Rouge area are apparently due to the influence of sea water and multiple

Fig. 2. Isotopic composition vs salinity for Gulf of Mexico surface waters.

sources of fresh water. Thus, the value of $\delta D = -2.7‰$ just off the Southwest Pass of the Mississippi is the result of the mixing of ocean water with river water.

If a simple mixing model is assumed between river water and ocean water, then approximate estimates of the factors controlling the distribution of deuterium in coastal waters can be made. If R_r is the D/H ratio of river water, R_o the ratio in ocean water, and R_c the ratio in coastal water, the balance of deuterium requires that

$$xR_r + (1-x)R_o = R_c,$$

where x is the fractional contribution of river water to coastal water. Similarly, the salt balance requires that

$$xS_r + (1-x)S_o = S_c,$$

where S represents the salinity of river, ocean and coastal waters. Thus, an approximate percentage contribution of Mississippi River water ($\delta D = -40.5‰$, $S = 1.2‰$) to mean central Gulf of Mexico water ($\delta D = 5.6‰$, $S = 36‰$) to form the water type having $\delta D = -2.7‰$ and $S = 30.3‰$ just off the Southwest Pass of the Mississippi may be calculated. The result of this calculation using deuterium data indicates that the contribution of the Mississippi River to this water type is $\sim 18\%$. Using salinity data a value of $\sim 16\%$ is obtained. This agreement indicates, as was previously pointed out, that the deuterium content of a water mass is a conservative property.

In support of this mixing model, Nowlin and McLellan (1967) have indicated that runoff from U. S. rivers may give rise to a band of low-salinity water along the northern shore. Furthermore they indicate that this water flows westward over the Texas shelf showing its freshening influence as far south as 26N. Consequently, a simple mixing model between fresh river water and ocean water is adequate to explain low deuterium concentrations along the northern Gulf Coast.

At a depth of 10 m in the Southwest Pass the deuterium content was found to be $-16.5‰$ with a salinity of $19.5‰$. Again, using the same mixing model as above, the contribution of river water ($\delta D = -40.5‰$, $S = 1.2‰$) to mean central Gulf of Mexico water to form the water type at 10 m depth was found to be 48% and 47% from deuterium and salinity data, respectively.

The above calculations were made relative to Mississippi River water of $S \approx 1.2‰$. Thus, for the actual fresh water dilutent at zero salinity the calculated percentage contribution will be somewhat less. Therefore, assuming a minimum value of $\delta D = -44‰$ as the fresh water deuterium content of the Mississippi has the effect of reducing the fresh water contribution by $\sim 6\%$.

Fig. 2 shows a δD-S diagram for all surface water in the Gulf of Mexico. In addition, values for the two rivers studied (Mississippi and Coatzacoalcos) have
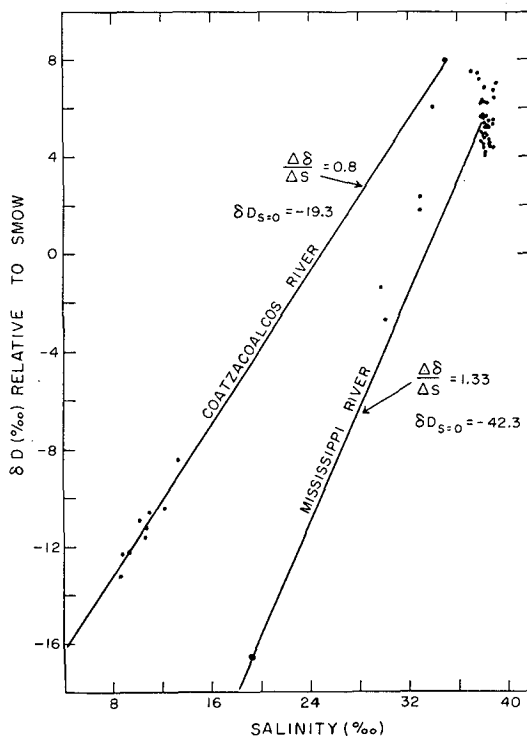
been included. From this diagram it is seen that all ocean values fall into a range of $\delta D = 4.1–7.4\%_o$ at a salinity of $\sim 36\%_o$, except for near-shore samples off Texas and Louisiana. The mean of all central Gulf samples was found to be $5.6\%_o$ at $\sim 36\%_o$ salinity. This value will be taken as the average δD for the surface Gulf of Mexico. With consideration of the above mixing model, a straight line can be drawn through the mean value of Gulf surface water and the two Mississippi samples of $\delta D = -16.5\%_o$ at $S \approx 19.5\%_o$ and $\delta D = -40.5\%_o$ at $S \approx 1.2\%_o$. The slope of this line was found to be 1.33 with an intercept of $-42.3\%_o$ at zero salinity. This value, $\delta D = -42.3\%_o$, is then the mean deuterium concentration for the fresh water dilutent of the Mississippi River. Consequently, all water formed from simple mixing of Mississippi water and central Gulf water should fall on the above line.

Referring to Fig. 2 it can be seen that the water type $\delta D = -2.7\%_o$ and $S = 30.3\%_o$ previously discussed falls on this mixing line within the limits of error of the deuterium measurement of $\delta D = \pm 1.0\%_o$. As a result it must be concluded that this water type is the result of mixing of Mississippi River water and central Gulf surface water. In regard to the three water types along the Texas-Louisiana coast with $\delta D(\%_o)$ of -1.4, 1.8 and 2.3, similar mixing processes must be involved in determining their composition; however, the presence of additional fresh water sources via runoff make interpretation difficult.

For an indication of the deuterium contribution of Mexican Rivers to the Gulf system, a series of samples were analyzed from the Coatzacoalcos River (18°14'N, 94°24'W) which empties into the Bay of Compeche. The results of these analyses are shown in Fig. 3. As was expected these results indicate that the deuterium content increases as you move down river. The salinity range of these samples was from $8.417\%_o$ ($\delta D = -13.2\%_o$) to $13.383\%_o$ ($\delta D = -8.4\%_o$). By plotting S vs δD (see Fig. 2) and extrapolating to zero salinity it was found that the fresh water source of this river had a $\delta D = -19.3\%_o$. Included in the plot were two samples directly offshore from the mouth of the river as shown in Fig. 1. Applying the mixing model discussed above, it was found that the mouth of the river ($\delta D = -8.4\%_o$) was composed of $\sim 60\%$ fresh water, whereas fresh water contributed $\sim 77\%$ at the sampling point farthest up river ($\delta D = -13.2\%_o$). These values are relative to Gulf surface water ($\delta D = +7.9\%_o$) 5 mi out from the mouth of the river.

The high values for sea water off the Coatzacoalcos River (see mixing line for this river in Fig. 2) indicate an excess of evaporation over precipitation in this region as compared to the central Gulf. In addition, latitudinal effects may also contribute to these high values.

Using U. S. and Mexican river discharge data from Hall (1969), deuterium data from U. S. rivers from Friedman et al. (1964), and deuterium data for the
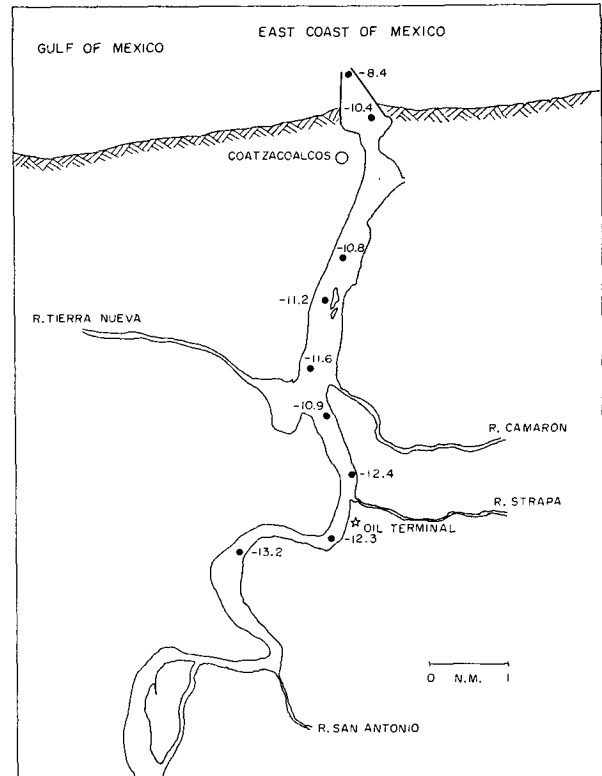

Fig. 3. Deuterium concentrations $\delta D(\%_o)$ in Coatzacoalcos River relative to SMOW.

Mississippi and Coatzacoalcos Rivers measured in this study, a δD value for fresh water addition to the Gulf was calculated to be $-33.2\%_o$. This value is consistent with the δD for average North American precipitation of $-30\%_o$ as determined by Craig and Lal (1961) from a detailed estimate of the isotopic water balance for the North American continent.

b. Subsurface water

In order to characterize the subsurface water masses of the Gulf of Mexico, six vertical profiles were obtained. The locations of these six stations are shown in Fig. 4. In addition, this figure shows the positions of two vertical sections (ABC and ABD) through these profiles. In constructing these vertical sections the data were plotted vs depth and a smooth curve fitted to the data points. Then values were selected from the fitted curves at regular intervals for use in contouring.

Fig. 5 shows the vertical section ABC down to 500 m using both deuterium and salinity. The outstanding feature of these sections is the influx of high salinity and high deuterium water into the Gulf from the Caribbean. This high salinity water has previously been characterized as Subtropical Underwater (Wüst, 1964; Cochrane, 1965, 1966; Nowlin and McLellan, 1967). The origin of this water mass is at the surface maximum in the North Atlantic at 20–25N, 30–50W. From this
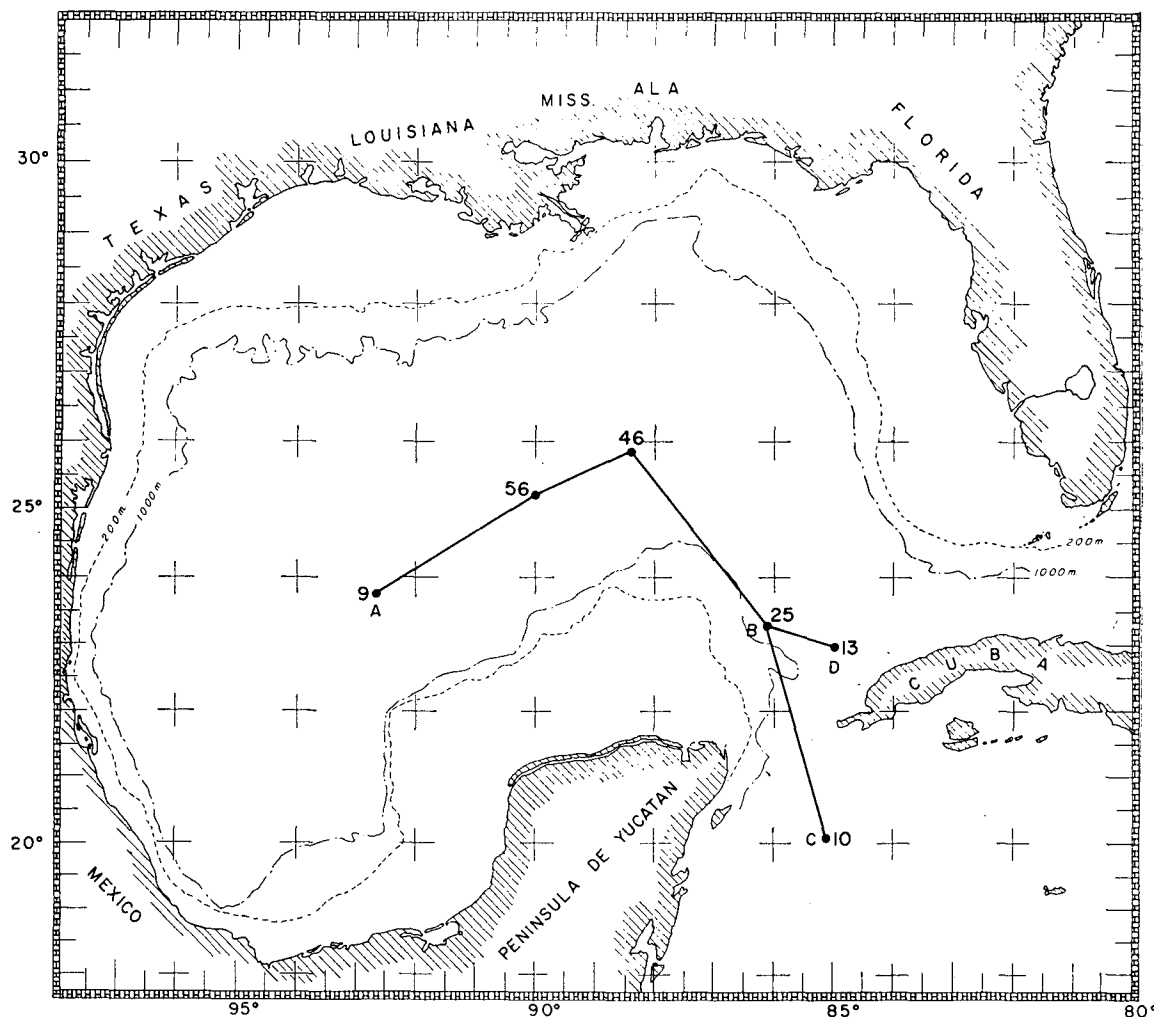
FIG. 4. Locations of subsurface stations and vertical sections.

source area this maximum spreads out westward as an intermediate layer. Redfield and Friedman (1965) have shown that δD for the source region of this water mass has a range of 6.0–8.0‰.

It should be noted that the maximum values of deuterium are centered at about 100 m depth at station 10 in Fig. 5. This core then rises to approximately 50–75 m depth at station 46 in the Central Gulf. This is in contrast to the core of high salinity water characterizing Subtropical Underwater which is centered at ~ 200 m at station 10 and which rises to about 125–150 m at station 25 in the Yucatan Straits. Therefore, a possible conclusion is that this high deuterium feature does not represent Subtropical Underwater. On the contrary, the range of δD that would correspond to the core of this water mass, as determined by the salinity maximum, would be 5.0–5.5‰. The difference in the range of deuterium in the Subtropical Underwater found in the Gulf and at its source region, as discussed above, is not inconsistent with expected changes occur-

ing along the course of the water mass due to mixing processes.

The high deuterium water ($\delta D = 5.5$–6.3‰) shown in Fig. 5 could possibly be explained by two different processes. The first is that this feature is due to evaporation processes within the Caribbean and particularly the Cayman Sea. Therefore, this water mass would not represent Subtropical Underwater which is formed in the North Atlantic. However, another possibility is that this feature is associated with the upper layers of Subtropical Underwater and therefore brought into the Caribbean from some outside source. Due to the lack of data in the Caribbean, the question of whether this feature is from some outside source or due to local effects within the Caribbean cannot be answered at this time. Consequently, this deuterium-rich water will be referred to as High Deuterium Water in the following discussions.

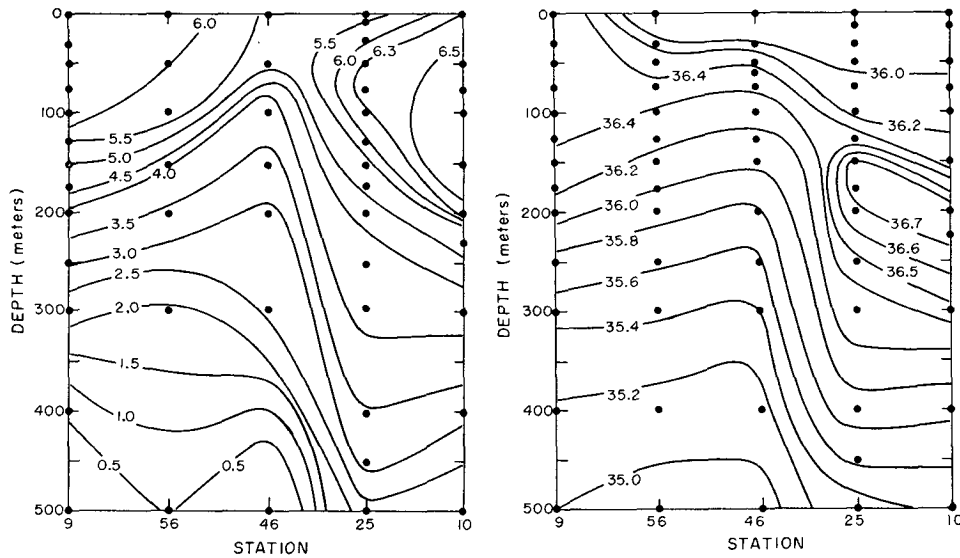Fig. 6 shows the vertical section ABD from the western Gulf to the east side of the Yucatan Straits.

FIG. 5. Vertical section ABC: left, deuterium $\delta D(\%_0)$ relative to SMOW; right, salinity $(\%_0)$.

using both deuterium and salinity. Again the salinity section is included for comparison.

Since deuterium is a conservative property, a deuterium-salinity diagram can be used to characterize the subsurface water masses in a given region. Fig. 7 shows the composite δD-S diagram for the six deep stations discussed above. As was pointed out in reference to the vertical sections, the influence of Subtropical Underwater is shown by a salinity maximum for stations 10, 25 and 13 in the Caribbean, Yucatan Straits, and the eastern edge of the Yucatan Straits, respectively. In addition, the influence of the High Deuterium Water can be seen as far as stations 46 and 56 in the central Gulf as shown by the deuterium maximum.

The presence of the last remnant of Antarctic Intermediate Water (AIW) can be seen from the salinity and deuterium minima. This water mass has been previously described by Wüst (1963, 1964) and Nowlin and McLellan (1967). Redfield and Friedman (1965) have shown that the core of AIW in the South Atlantic may be characterized by a deuterium minimum of $-0.9\%_0$. This value compares favorably with the mean of $-0.5\%_0$ found in the Gulf at 800–1000 m.

The last prominent feature of the δD-S diagram is that of the Gulf Basin Water. This water has the characteristics of $\delta D = 0.7$–$1.1\%_0$ and $S = 34.96$–$34.98\%_0$. According to Wüst (1963), this water mass is predominantly North Atlantic Deep Water (NADW) which has spilled over the sill in the Yucatan Straits.
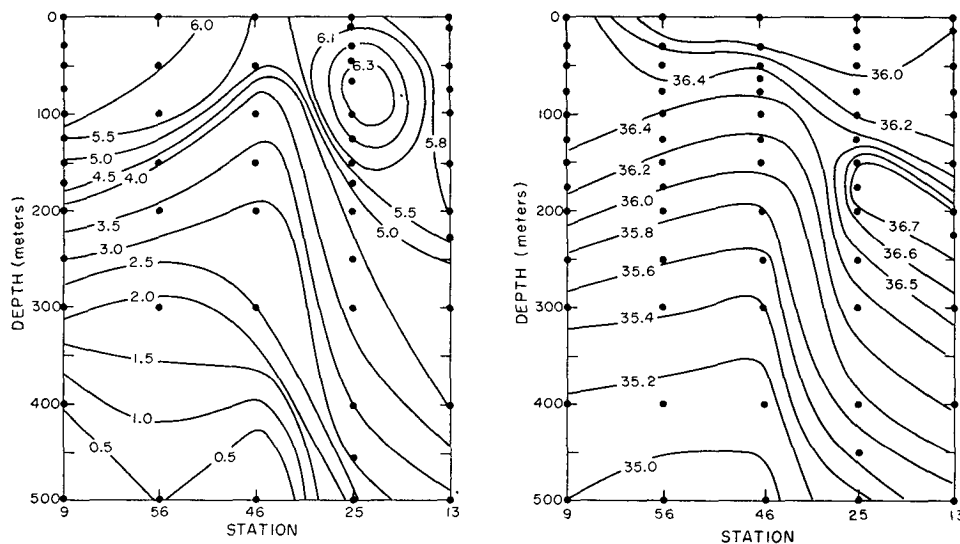

FIG. 6. Vertical section ABD: left, deuterium $\delta D(\%_0)$ relative to SMOW; right, salinity $(\%_0)$.
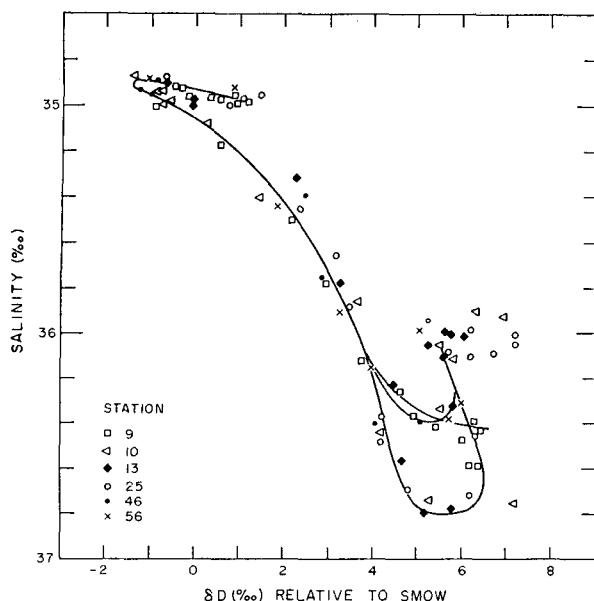
FIG. 7. Isotopic composition vs salinity for stations 9, 10, 13, 25, 46 and 56.

Redfield and Friedman (1969) have reported the δD of NADW as $1.4\%_0$ which is comparable with the mean of $0.9\%_0$ obtained in this study.

4. Summary

The results of this paper have shown that within the limits of the precision of the measurement, $\pm1.0\%_0$, hydrogen-deuterium variations in water can be related to known water mass distributions within the Gulf of Mexico. These results have shown that surface water of the central Gulf are characterized by a $\delta D = +5.6\%_0$ relative to SMOW. In addition, it was shown that the isotopic composition of near-shore water could be explained by a simple mixing model of fresh water from runoff and ocean water modified by the mixing of sea waters from distinct sources. The mean δD composition of fresh water was found to be $-33\%_0$, with the Mississippi and Coatzacoalcos Rivers having values of -42.3 and $-19.3\%_0$, respectively.

The various water masses present (Subtropical Underwater, Antarctic Intermediate Water, Gulf Basin Water) were found to be characterized by deuterium contents of 5.0–5.5, -0.5 and $0.9\%_0$, respectively. These values are comparable with δD values of these water masses in their source regions. The presence of a High Deuterium Water ($\delta D = 5.5$–$6.3\%_0$) was attributed to either local evaporation effects within the western Caribbean or to some water mass associated with the upper layers of the Subtropical Underwater and originating outside the Caribbean Sea.

REFERENCES

Cochrane, J. D., 1965: The Yucatan current and equatorial currents of the western Atlantic. Rept. 65–17T, Dept. of Oceanography, Texas A & M University.

——, 1966: The Yucatan current, upwelling of northeastern Yucatan, and currents and waters of western equatorial Atlantic. Rept. 66–23T, Dept. of Oceanography, Texas A & M University.

Craig, H., 1961: Standard for reporting concentrations of deuterium and oxygen-18 in natural waters. *Science,* **133,** 1833–1834.

——, and L. I. Gordon, 1965: Deuterium and oxygen-18 variations in the ocean and marine atmosphere. *Occas. Publ. Narragansett Marine Lab., Univ. Rhode Island,* **3,** 277–374.

——, and D. Lal, 1961: The production rate of natural tritium. *Tellus,* **13,** 85–95.

Friedman, I., 1953: Deuterium content of natural waters and other substances. *Geochim. Cosmochim. Acta,* **4,** 89–103.

——, and K. Hardcastle, 1970: A new technique for pumping hydrogen gas. *Geochim. Cosmochim. Acta,* **34,** 125–126.

——, A. Redfield, B. Schoen and J. Harris, 1964: The variation of the deuterium content of natural waters in the hydrologic cycle. *Rev. Geophys.,* **2,** 177–224.

Hall, C. S., 1969: An investigation of the water balance of the basin of the Gulf of Mexico. M.S. thesis, Dept. of Meteorology, Texas A & M University, 39 pp.

Horibe, Y., and N. Ogura, 1968: Deuterium content as a parameter of water mass in the ocean. *J. Geophys. Res.,* **73,** 1239–1249.

McKinney, C. R., J. N. McCrea, S. Epstein, H. A. Allen and H. C. Urey, 1950: Improvements in mass spectrometers for the measurement of small differences in isotopic abundance ratios. *Rev. Sci. Instr.,* **21,** 724–730.

Nier, A. O., 1947: A mass spectrometer for isotope and gas analysis. *Rev. Sci. Instr.,* **18,** 398–411.

Nowlin, W. D., and H. J. McLellan, 1967: A characterization of the Gulf of Mexico water in winter. *J. Marine Res.,* **25,** 29–59.

Redfield, A. C., and I. Friedman, 1965: Factors affecting the distribution of deuterium in the ocean. *Occas. Publ. Narragansett Marine Lab., Univ. Rhode Island,* **3,** 149–168.

——, and ——, 1969: The effect of meteoric water, melt water and brine on the composition of polar sea water and of the deep waters of the ocean. *Deep-Sea Res.,* **16** Suppl., 197–214.

Wüst, G., 1963: On the stratification and circulation in the cold water sphere of the Antillean-Caribbean basins. *Deep-Sea Res.,* **10,** 165–175.

——, 1964: *Stratification and Circulation in the Antillean-Caribbean Basins, Part I.* Columbia University Press, 201 pp.