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Distribution and variability of dissolved hydrogen in the Mediterranean Sea

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ABSTRACT

Hydrogen is one of the most interesting of the oceanic reduced gases because of its important role in both microbial nitrogen fixation and the anaerobic microbial food chain. A recent investigation in the Mediterranean Sea and Gulf of Cadiz on the USNS *Bartlett* has confirmed previous studies showing warm ocean waters to be supersaturated relative to atmospheric equilibrium in the mixed layer and undersaturated at depth. Waters in the 20-30 m deep mixed layer have hydrogen concentrations up to four times saturation while deep water concentrations are at or near equilibrium. Surface waters (20 m) have much more variable hydrogen distributions on horizontal scales of hundreds of meters than do waters below the euphotic zone (100 m), suggesting that the hydrogen excesses in the mixed layer have a patchy biological source. We also observed a dramatic and unusual hydrogen maximum at two stations in the Mediterranean near the sill at the Strait of Gibraltar. The larger and sharper maximum was seen at the station nearest Gibraltar. The source for these unusual features appears to be associated with the strong density gradient between North Atlantic Water and Mediterranean Deep Water.

1. Introduction

The distribution of reduced gases (CH_4 , H_2 , CO , N_2O) in the oceans is of interest to the oceanographic community because of the importance these gases have as chemical probes for microbiological activity. Biogenic in nature, the reduced gases all show oceanographic vertical distributions with significant deviations from air-sea equilibrium concentrations. However, their low concentrations have frustrated many attempts at correlation with microbiological activity. This is particularly true for hydrogen, and for many years analytical difficulties limited the amount and quality of data available for interpretation (Williams and Bainbridge, 1973). More recently, techniques have been developed which overcome contamination and interferences. The environments now successfully studied for H_2 include the subtropical Atlantic (Herr and Barger, 1978) and Pacific (Bullister *et al.*, 1979; Bullister, 1980) the Norwegian Sea (Herr *et al.*, 1981), and an anoxic fjord (Lilley and Gordon, 1978).

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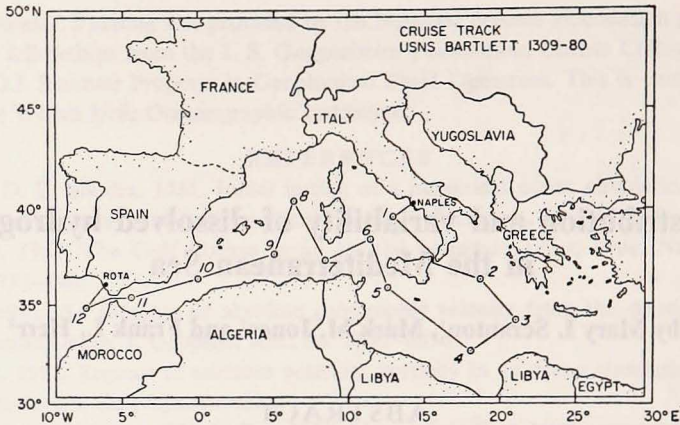


Figure 1. Cruise track for USNS *Bartlett* 1309-80.

The data have suggested that the subtropical oceans are sources for atmospheric hydrogen and that the polar regions represent either regions of widespread under-saturation or systems where surface conditions are close to that predicted from atmospheric equilibrium. It has been suggested (Herr *et al.*, 1981) that this pattern reflects the distribution of nitrogen-fixing cyanobacteria (blue-green algae) in the open ocean, as it is well known that many species of cyanobacteria are important hydrogen producers (Burns and Hardy, 1975). Other workers have proposed correlations between hydrogen and such parameters as near-surface particle maxima which are associated with concentrations of organisms at the bottom of the mixed layer (David Reid and John Schwarz, personal communication). In warm coastal waters off southern California, Setser and coworkers (in preparation) have found good correlations between hydrogen and *in vivo* fluorescence. However, no strict correlations between hydrogen and this or other chemical and biological parameters have been found in other studies, although hydrogen has been measured on cruises along with methane, CO, chlorophyll *a* and oxygen, among other parameters.

We had an opportunity to extend the data base for oceanic hydrogen concentrations as well as to test some of the hypotheses related to hydrogen sources and sinks during a cruise on the USNS *Bartlett* (1309-80) to the Mediterranean during August and September, 1980 (Fig. 1). Our goal for the cruise was to determine whether the Mediterranean had hydrogen distributions similar to those found in other warm oceans and to begin an assessment of the importance of biological activity on hydrogen concentrations.

2. Materials and methods

Water samples, and temperature and salinity data for *Bartlett* 1309-80 were obtained using a Neil Brown CTD and rosette system fitted with 12 Niskin bottles

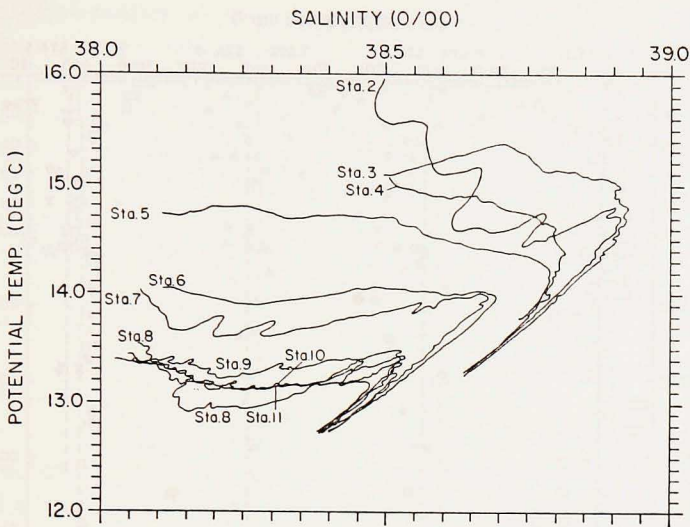


Figure 2. Temperature-salinity diagram for stations occupied on *Bartlett* 1309-80. Data are from the continuous CTD records.

(twelve or thirty liter). Discrete data plotted in this paper are the temperatures, salinities and depths obtained from the CTD directly after the bottle was tripped. As seas were very calm and ship's drift and roll were negligible in most cases, the T - S data and depths accurately represent those of the water sample. Data plotted in Figure 2 represent θ - S plots obtained from the continuous CTD records (David Reid, personal communication).

Hydrogen was analyzed in 1-liter samples, using the gas extraction procedure and mercuric oxide reduction method of Herr and Barger (1978) and Herr *et al.* (1981). Samples were poisoned with 1 ml of saturated mercuric chloride solution at stations 9, 10, 11 and 12 but were unpoisoned during the rest of the cruise. Comparisons of poisoned and unpoisoned replicates indicate the presence of mercuric chloride has no effect on the analysis. In all cases, samples were analyzed within 24 hours of collection and more typically within 1-8 hours. The standard used was a nominal 1 ppm H_2 in N_2 standard obtained from Scott Specialty Gas Co. and calibrated to contain 0.99 ppmv H_2 by a one-step static dilution procedure at NRL. A 10 ml standard was injected after every sample. The limit of detection of analysis is about 0.2 nl/L for a one liter water sample.

In order to determine the precision of our data, a large number of duplicate samples (samples drawn from the same Niskin) were run. All data are plotted in the vertical profiles in Figures 3, 4, 5 and 6. Precision for air analyses is comparable to reproducibility of standards or about $\pm 3\%$. Precision for analysis of water samples is generally 8-10% or $\pm 1 \text{ nl L}^{-1}$.

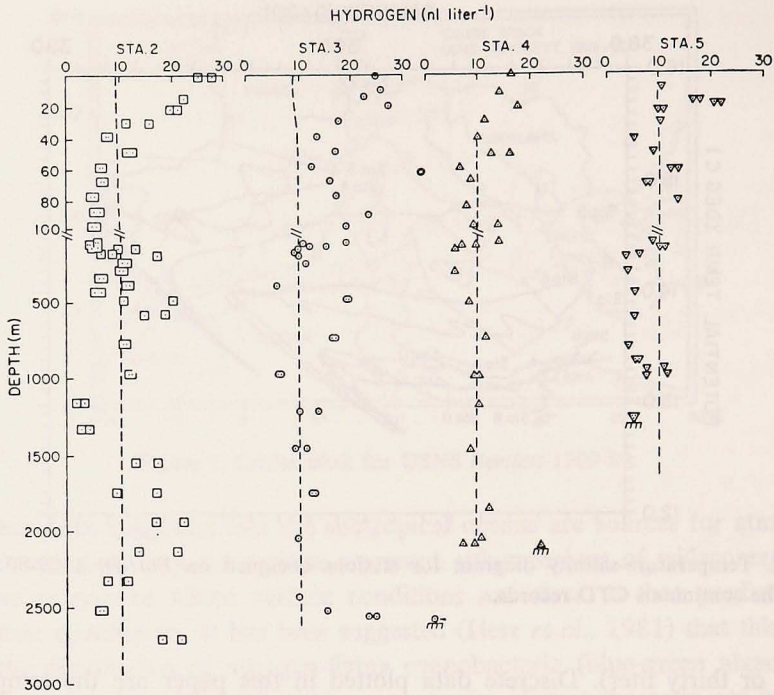


Figure 3. Vertical profiles of hydrogen from stations in the eastern Mediterranean. The dotted line represents the hydrogen value predicted from solubility considerations.

A number of precautions were taken to avoid possible sample contamination from the CTD rosette. The sacrificial zinc anode was removed from the CTD rosette for the duration of the cruise, and the entire rosette body was painted with black enamel paint to reduce the amount of bare metal which could corrode and thus generate hydrogen. The wire termination and about 3 to 5 m of the hydrowire were carefully taped with electrical tape to reduce the possibility that the samples would trap water in which corrosion had been occurring. Finally water samples were triggered and closed with the rosette moving slowly upward, or just as the rosette stopped. In all cases the rosette stopped very shortly after the bottle was triggered, to read pressure and *T-S* data at the point where the sample was taken. In no case did the rosette remain at the sample depth for more than a few seconds before closing (except as noted below). Experiments on the *Bartlett* during which the rosette was stopped for a time before bottle closure indicated that this final procedure (making sure that the rosette was moving into clean water as it was closed) was essential to maintaining the quality of the data. We feel lack of attention to this precaution may be reflected in the increased scatter present in station 2 as compared with later stations (Fig. 3).

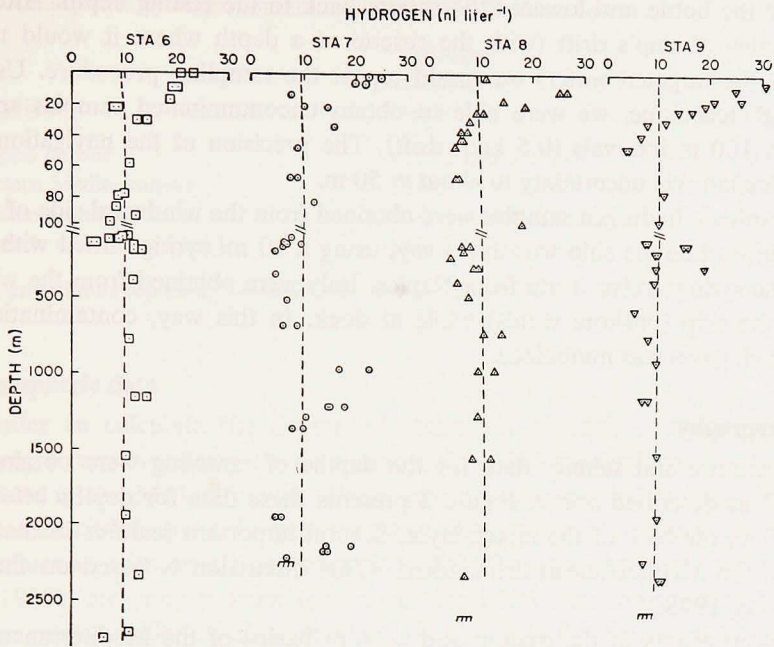


Figure 4. Vertical profiles of hydrogen from stations in the western Mediterranean. The dotted line represents the hydrogen value predicted from solubility considerations.

In spite of the above precautions it will be noted that a number of replicate sample pairs (39%) fell outside the accustomed limit to the analysis precision (8-10% or 1 nl/L). Scrutiny of these data and analytical procedures suggests that inhomogeneities within the Niskin bottles during the period of sampling, probably due to local corrosion of exposed steel fittings from poorly coated handles and vents, was the major source of the larger uncertainties. It is also possible that biological hydrogen production or consumption might be occurring within the Niskins. However, we feel that our rapid sampling and analysis has minimized possible H_2 artifacts. Because of our uncertainty about the source of these errors, we have conservatively omitted discussions of those maxima and minima (Figs. 3 and 4) which are small or are present in only a few stations.

Two sampling schemes were employed to collect hydrogen samples. The first represented traditional vertical hydrocasts from which hydrogen samples, as well as samples for salinity, chlorophyll *a*, nutrients and other parameters were drawn. The second sampling scheme was designed to determine the degree of horizontal variability present in oceanic hydrogen distributions. To obtain horizontally spaced samples, we lowered the rosette to a depth about 10 m below the desired sampling depth. With the ship drifting, we then raised the sampler to the required depth,

triggered the bottle and lowered the rosette back to the resting depth. After about five minutes of ship's drift (with the rosette at a depth where it would not contaminate the targeted water) we would repeat the sampling procedure. Using this "yo-yoing" technique, we were able to obtain uncontaminated samples spaced at less than 100 m intervals (0.5 knot drift). The precision of the navigation system limited the interval uncertainty to about ± 50 m.

Atmospheric hydrogen samples were obtained from the windward side of the bow of the ship, while the ship was underway, using a 10 ml syringe fitted with a polypropylene syringe valve. Data from Naples, Italy were obtained from the windward side of the ship (onshore winds) while at dock. In this way, contamination from ship's stack gases was minimized.

3. Hydrography

Temperature and salinity data for the depths of sampling were obtained from the CTD as described above. Figure 2 presents these data for depths below about 20 to 30 m, the base of the mixed layer. Several important features in the hydrography of the Mediterranean are evident. (This discussion is based on the review of Hopkins, 1978.)

The deep waters of the eastern and western basins of the Mediterranean, while quite distinct from one another in terms of salinity and temperature, are very homogeneous within each basin. The eastern basin deep waters are systematically warmer and more saline than waters at similar depths from the western basin. This reflects the smaller Atlantic influence and greater evaporation within the eastern basin.

Another important feature is the marked salinity maximum present at mid-depth (200-700 m) at stations throughout the Mediterranean. This maximum represents the presence of Levantine Intermediate Water (LIW) which forms in February and March near Rhodes (Hopkins, 1978). Above the LIW, at a number of stations especially in the western Mediterranean, a temperature minimum associated with Intermediate Waters formed south of France or in the Tyrrhenian Sea is also present (Hopkins, 1978).

At still shallower depths, ranging from about 20 m near Gibraltar to 70 m in the eastern Mediterranean, a salinity minimum associated with inflowing NAW (North Atlantic Water) was seen in the CTD profiles from individual stations although the data reflecting this salinity minimum are not plotted in Figure 2.

In spite of the importance of such features as the NAW, the LIW and the eastern and western basin deep waters to the hydrography of the Mediterranean, no widespread correlation between hydrogen concentrations and temperature, salinity or density has been found in the Mediterranean. Correlations which may be suggested by Figures 3 and 4 are rendered tenuous by the relatively high variability of the data.

Table 1. Atmospheric hydrogen concentrations from the Mediterranean.

Location	Hydrogen concentration (ppmv)*	Number of samples
Naples harbor	0.79 \pm 0.04 (5.8%)	9
Eastern Mediterranean	0.66 \pm 0.02 (3.0%)	68
Western Mediterranean	0.66 \pm 0.02 (3.0%)	31
Atlantic (Gulf of Cadiz)	0.65 \pm 0.02 (3.1%)	20

* The error limits represent 1σ values for the number of points indicated.

4. Atmospheric data

In order to calculate the degree of saturation of surface ocean water with hydrogen, it was necessary to determine values for atmospheric hydrogen concentrations in the Mediterranean. These data are presented in Table 1. Although samples taken while the ship was in port in Naples indicate substantial anthropogenic influence, with an air concentration of 0.79 ppmv, (compare with Scranton *et al.*, 1980), air samples from the rest of the Mediterranean indicate a uniform hydrogen concentration of about 0.66 ppmv. Similarly the air in the Gulf of Cadiz has a hydrogen concentration of 0.65 ppmv, not significantly different from the value observed for the Mediterranean.

Few data are available for comparison except for that of Herr and Barger (1978) who reported that Gulf of Cadiz air contained 0.65 ppmv hydrogen in 1977 and that of Schmidt (1978) who reported an average of 0.56 to 0.58 ppmv for North Atlantic air. The earlier results of the NRL group are essentially identical with those reported here in spite of the use of different standards, calibrated independently. Schmidt's data (collected in 1973 and 1974) are slightly lower than ours. Because no intercalibration between the NRL group and the German group has been carried out, we are unable at this point to define the source of the discrepancy between the values obtained by the two groups in and near the Gulf of Cadiz. The most probable source of discrepancy is a calibration difference between the groups.

5. Vertical profiles

Our major effort on this cruise was devoted to making an exploratory study of hydrogen throughout the Mediterranean. The cruise track (Fig. 1) was designed to permit sampling in most of the major basins of the Mediterranean, and we obtained an excellent over-view of the hydrogen distribution. Due to replicate variability, data in any one basin are insufficient to determine to what degree hydrographic processes control small regional variations in hydrogen profiles. The several dominant patterns noted in the data are discussed below.

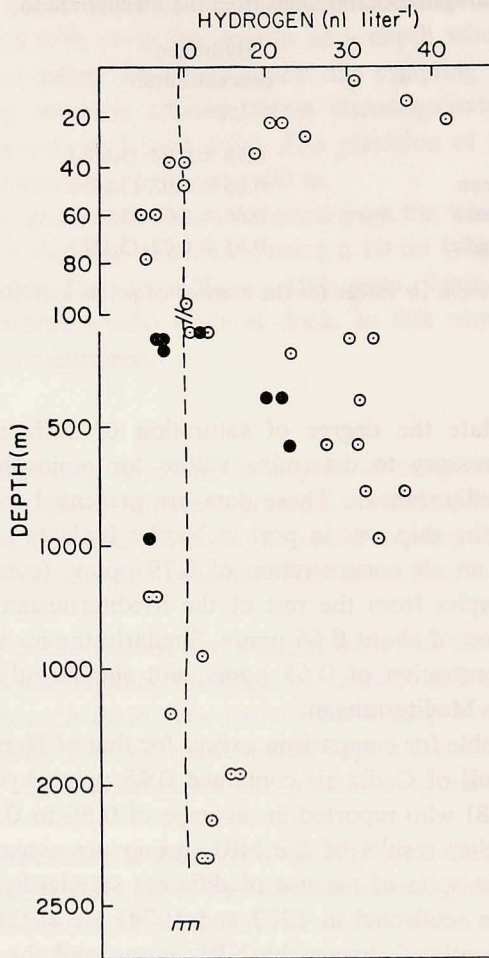


Figure 5. Hydrogen distribution at station 10 in the Alboran Sea. The heavy dots represent samples taken from a third cast to confirm the existence of the large hydrogen maximum. The dotted line represents hydrogen concentrations predicted from solubility considerations.

Hydrogen profiles for stations occupied in the Mediterranean are presented in Figures 3, 4, 5, and 6. (Tabulated data from *Bartlett 1309-80* are available from the first author.) A line representing the calculated air solubility (based on potential temperature and salinity of the water and using an atmospheric value of 0.66 ppmv and the solubility data of Wiesenberg and Guinasso (1979)) is presented in each graph. At all stations sampled throughout the Mediterranean, hydrogen concentrations in the upper twenty or thirty meters were considerably higher than the "predicted" air-sea equilibrium values. Maximum concentrations ranged from about two times equilibrium to greater than four times the values predicted from solubility

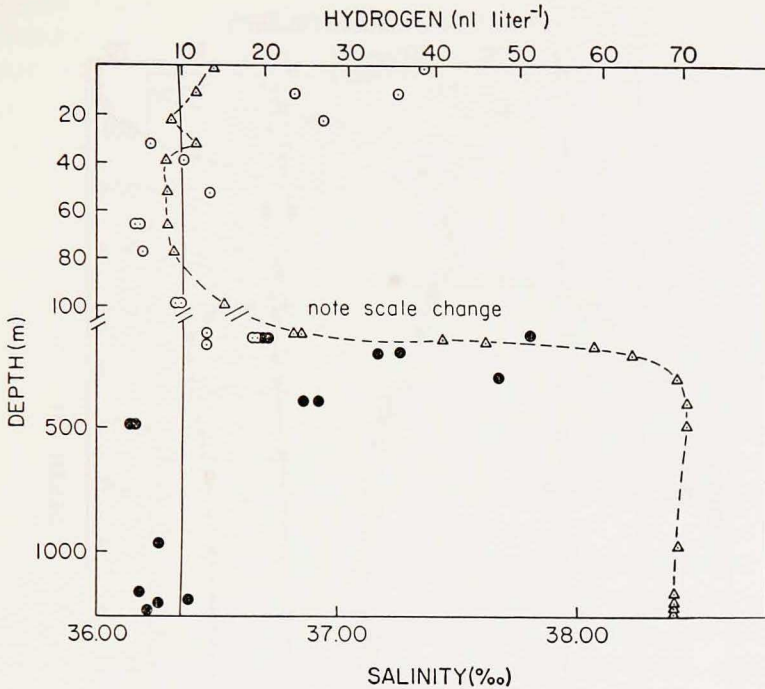


Figure 6. Hydrogen distribution at station 11, in the Alboran Sea. The heavy circles represent samples from the deep cast; open circles represent samples from the shallow cast. Open triangles represent salinity data. The solid line represents hydrogen concentrations predicted from solubility considerations.

considerations. In general, the highest hydrogen concentrations were found within a few meters of the surface, but at stations 5, 8 and 10, distinct subsurface maxima were observed in the mixed layer. The depth range over which elevated hydrogen levels were found corresponds closely with the depth of the mixed, or nearly mixed, layer in these stations (see Fig. 7 for an example).

It is also clear that the deep waters of the Mediterranean are at or near solubility equilibrium with the atmosphere. (The maxima appearing in stations 10 and 11 are discussed below.) In stations 3, 5 and 7 sampling was extended so close to the bottom that the samples could not be taken with the rosette in motion upward and therefore may be contaminated with corrosion-produced hydrogen. The hydrogen maximum present near the bottom in stations 4 and 7 may be real although data are insufficient to determine the source of the hydrogen.

The pattern of elevated hydrogen concentrations within the mixed layer and equilibrium or lower hydrogen concentrations at depth is very similar to hydrogen distributions described for the North Atlantic (Herr and Barger, 1978) and for the East Tropical North Pacific (Bullister *et al.*, 1979) in spite of the substantially

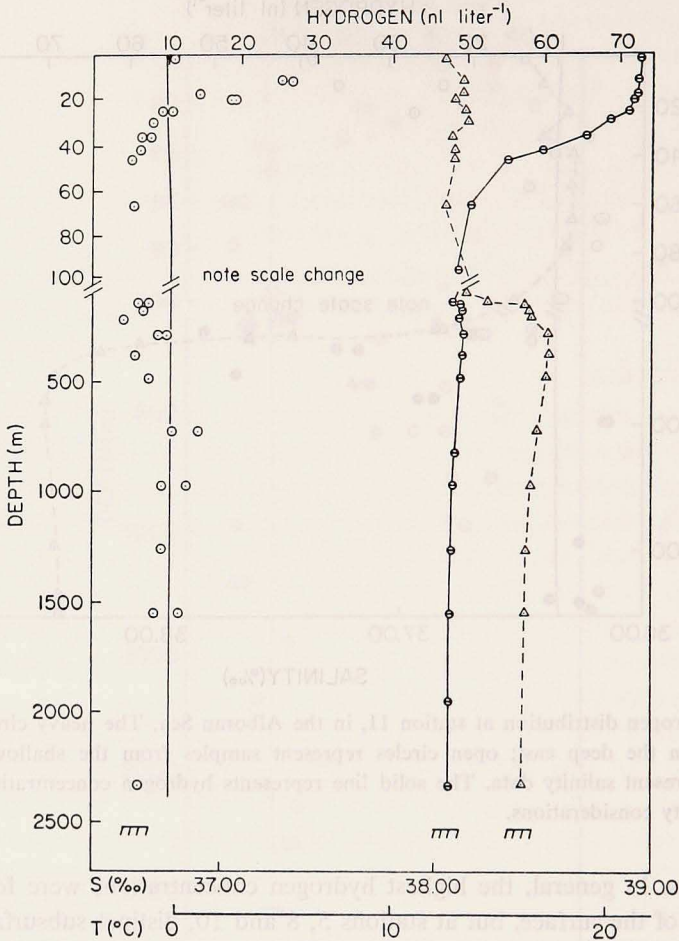


Figure 7. Hydrogen (\odot), temperature (\ominus) and salinity (Δ) data from station 8. The light solid line represents hydrogen concentrations predicted from solubility considerations.

shallower mixed layer depth in the Mediterranean. Data from *Bartlett* 1309-80 indicate that the euphotic zone in the Mediterranean Sea extends to depths of 90 to 100 m compared with mixed layer depths of 20 to 30 m, and that nutrient depletion extends to comparable depths. Hydrogen concentrations are also low in the submixed layer euphotic zone. It appears that the process responsible for net hydrogen production (indicated by consistently supersaturated waters) is restricted to the brightly-lit and nutrient-depleted mixed layer. (It should be noted that we can identify *net* hydrogen-production only. It is therefore possible that production and consumption just balance at depths below the mixed layer.)

At stations 10 and 11, in the Alboran Sea (Figs. 5 and 6) an additional feature in the hydrogen distribution was observed. At both stations, beginning at a depth of

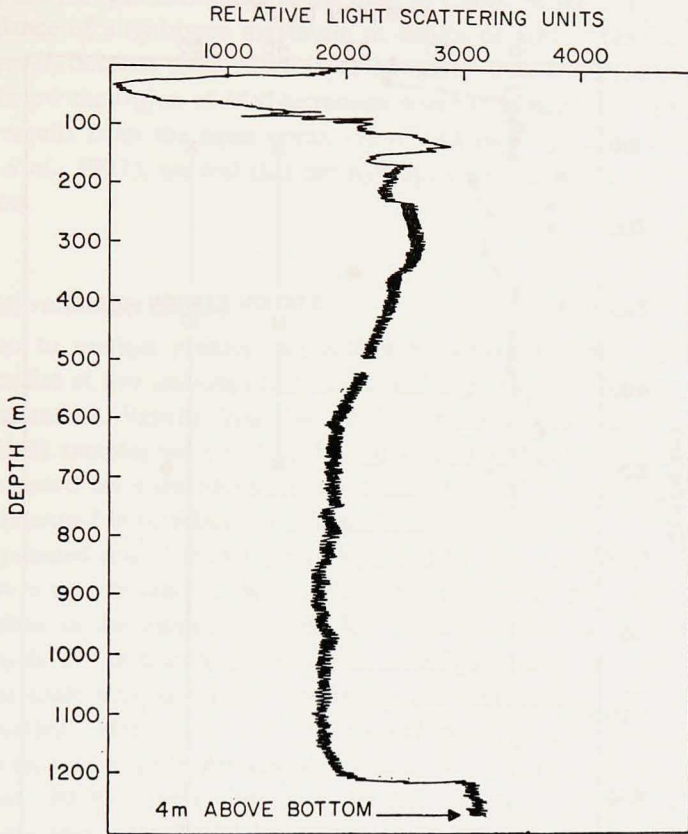


Figure 8. Light scattering profile from station 11 in the Alboran Sea. The surface maximum is due to the fact that the cast was made in daylight.

about 150-200 m and extending to a depth of 1000 m at station 10 and 400 m at station 11, a dramatic hydrogen maximum was found. Although cast to cast variability was substantial at station 10, the maximum was observed on several casts, and the concentrations measured are so high compared with typical values from these depths that the presence of the maximum is unequivocal. The depth of the top of the hydrogen maximum in both stations corresponds to the depth of the transition from incoming North Atlantic Water at the surface to outgoing Mediterranean water at depth. Because the maximum is so much sharper at station 11 than at station 10 it appears that the origin of the feature is near the sill at the Strait of Gibraltar (depth about 200 m). The top of the feature corresponds to a nephelometer maximum (see Fig. 8) which presumably indicates the presence of sinking particles held up at the sharp density discontinuity between the two water types. Therefore, it seems possible that the feature is related to biological activity within

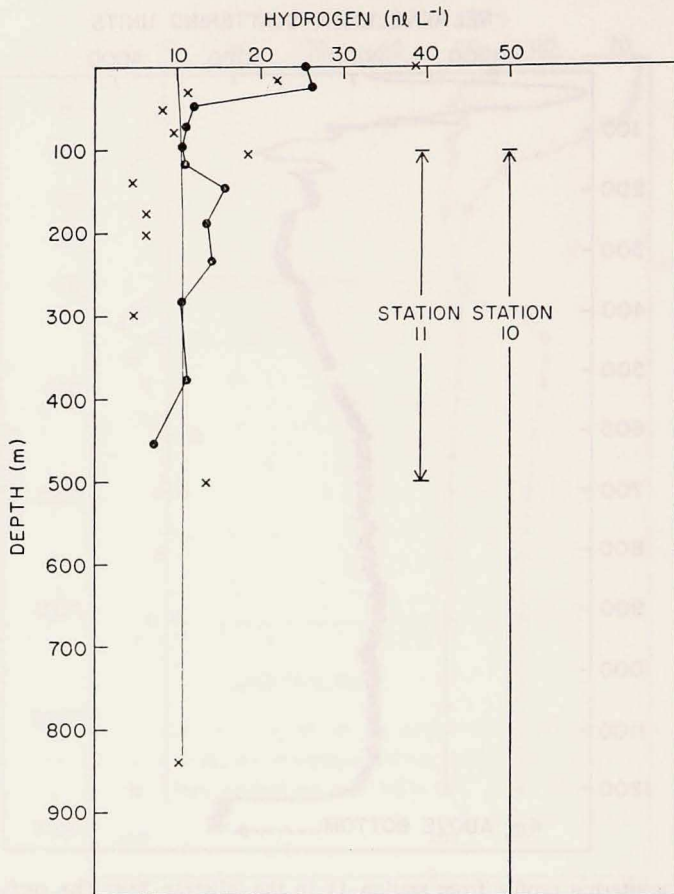


Figure 9. Hydrogen data from the Alboran Sea collected by F. L. Herr and W. R. Barger in 1977. Data from 35.51N 5.03W are shown by \times . Data from 36.10N 4.54W are shown by \bullet . Depth ranges for the Bartlett 1309-80 maxima are also indicated.

the active shear zone, followed by mixing. Much of the cast to cast variability observed may reflect horizontal variations in the details of the maximum.

Earlier data obtained by Herr and Barger and shown in Figure 9 suggest that this feature may persist from year to year, although with variable intensity. Stations occupied by them in the Alboran Sea in 1977 show elevated hydrogen concentrations (about 1.5 to 1.8 times equilibrium values) at depths of 100 m at one station and 144, 187 and 233 m in another station in the Alboran Sea.

In contrast to the dramatic hydrogen maximum found in the Alboran Sea, data from the Gulf of Cadiz do not show evidence of a similar feature, in spite of the possibility of advection of water with elevated hydrogen content out of the Mediterranean. Neither our data nor data of Herr and Barger (1978) indicate the presence

of a mid-depth hydrogen maximum in the Gulf of Cadiz. Seiler and Schmidt (1974) did find evidence of a hydrogen maximum at depths of 400 to 600 m in the same region. However, because their mixed layer hydrogen data and their hydrogen data from water below the region of Mediterranean water influence are so high compared with recent results from the open ocean (Herr and Barger, 1978; Bullister *et al.*, 1979; Herr *et al.*, 1981), we feel that the hydrogen maximum found may represent contamination.

6. Horizontal variability studies

In addition to vertical profiles, we collected hydrogen samples for horizontal variability studies at five stations (3, 7, 8, 11 and 12). Tabulated data are available from the first author. Results from two of these stations are presented in Figures 10 and 11. Drift samples were collected from 20 and 100 m to provide a comparison between mixed layer distributions and distributions at a depth where biological activity was expected to be relatively unimportant.

We have pursued this alternate sampling mode to gain an appreciation for how representative a sample taken in a vertical cast is relative to other water parcels at similar densities in the immediate area. We expect the biological processes controlling the hydrogen distribution to vary horizontally: in other words to be patchy. However, the scale lengths for this variability are unknown in areas of high hydrogen productivity. Herr *et al.* (1981) attempted to determine mesoscale horizontal variability in an area of hydrogen consumption near the Faroe Islands. They found, in some areas, 20-30% variations over 10 km distances, while less than 10% variations were seen over 20-30 km distances in other areas. It is important to know how hydrogen concentrations vary over fine scale lengths, as well as among basins, in order to evaluate relationships between hydrogen distributions and biological activity in the Mediterranean.

Several patterns were noted in the data. Firstly, it was obvious that the pattern of supersaturation and undersaturation (relative to atmospheric equilibrium) seen in the vertical profiles is reflected in the drift data as well. At all stations except station 7, the 100 m hydrogen concentrations were well below equilibrium with at most one or two samples giving values above saturation. On the other hand, at all stations except station 8, the mixed layer values were well above those predicted from solubility considerations. Station 8 was occupied immediately following a storm accompanied by high winds, so it might be expected that any excess hydrogen in the mixed layer would have been lost to the atmosphere. Therefore, the fact that we found hydrogen concentrations close to equilibrium at station 8 is not surprising.

The major difference between drift stations was the extent of variability observed over the course of each experiment. For example, station 12 (Fig. 10) represents a

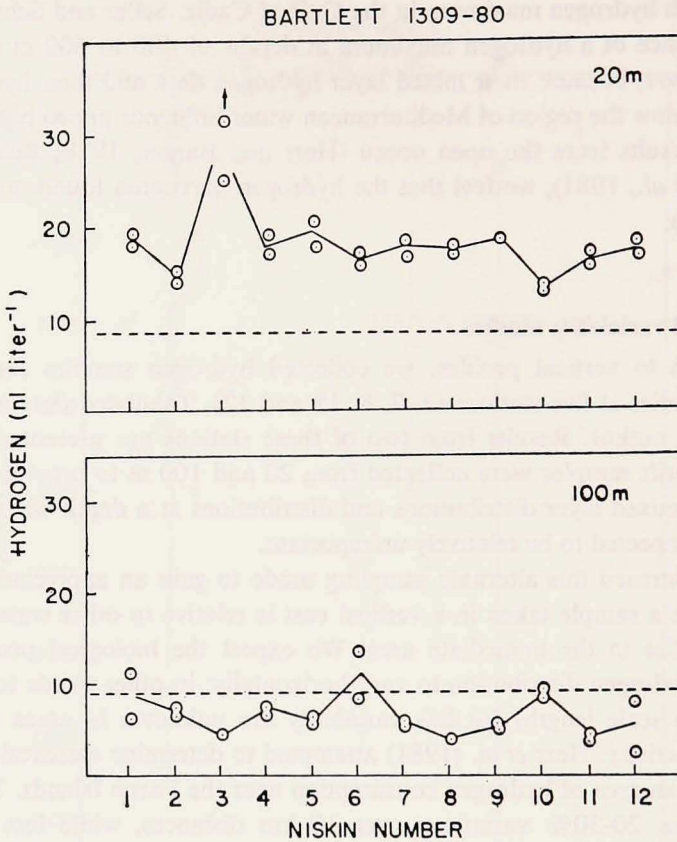


Figure 10. Hydrogen data from a horizontal variability study in the Gulf of Cadiz at station 12. These data are characteristic of a "low variability" situation. The dashed line represents hydrogen concentrations predicted from solubility considerations.

low variability station in the Gulf of Cadiz in which no systematic trends in hydrogen could be seen. In contrast, Figure 11 shows data from a high variability station in the waterway between Sicily and Tunisia (station 7). At this latter site, hydrogen concentrations changed by a factor of from 2-3 at 20 m and by even more at 100 m (from 35 nL/L to 6 nL/L). Other stations showed trends but none as large as at station 7. The presence of such large variations in hydrogen concentrations over short (1-2 km) horizontal distances suggests the presence of a patchy source. We do not have sufficient data to explain why station 7 was the only station to show hydrogen production at 100 m.

7. Discussion

The goal of our research in the Mediterranean Sea was to identify the sites of

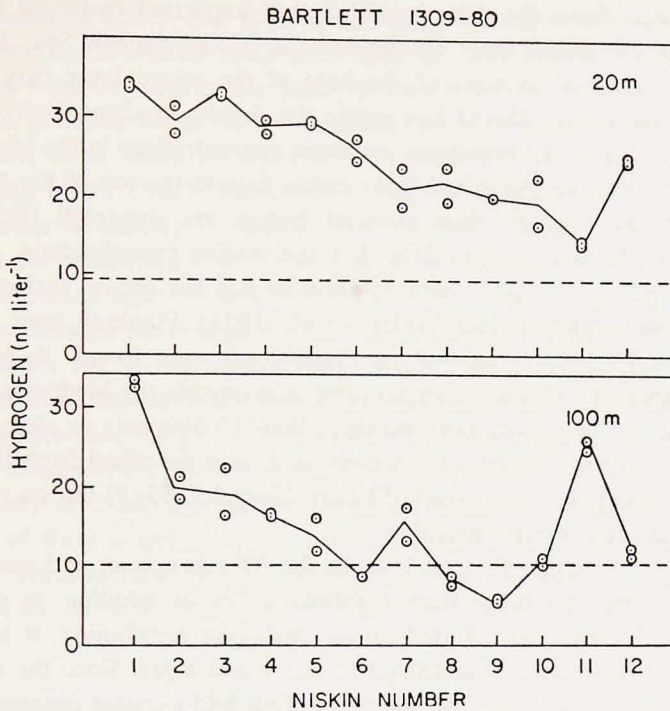


Figure 11. Hydrogen data from a horizontal variability study between Sicily and Tunisia, at station 7. These data reflect an unusually high degree of horizontal variability. The dashed line represents hydrogen concentrations predicted from solubility considerations.

hydrogen production and consumption in that ocean. Our results indicate that the deep waters exhibit hydrogen undersaturation, probably reflecting the same sort of sink for hydrogen as is present in the North Atlantic. This may either be consumption *in situ*, or net consumption in surface waters during water mass formation (as was seen in the Norwegian Sea by Herr *et al.*, 1981). The pattern of hydrogen excesses seems more complex in the Mediterranean than observed in other parts of the ocean. This is particularly true with respect to the large hydrogen maxima present near the mouth of the Mediterranean (Figs. 5 and 6). The Alboran Sea maxima seem to be confined to depths below the density gradient between North Atlantic Water and Mediterranean Water and appear to originate at or near the sill. There may be a correlation between hydrogen and a nepheloid maximum observed in the density gradient in this special system (compare Figs. 6 and 8) although elevated hydrogen concentrations are also observed at depths well below the particle maximum. Low rates of hydrogen production in this zone may result in significant concentration gradients because of the limited vertical mixing permitted by the strong density stratification.

It is also clear from the data presented that important hydrogen sources are present within the mixed layer throughout the Mediterranean Sea. It has been suggested that methane maxima at the base of the mixed layer may be due to uniform production but reduced loss within the density gradient. Unlike the situation observed for methane, maximum hydrogen concentrations in the Mediterranean are usually found within the mixed layer rather than in the top of the thermocline, suggesting biological rather than physical factors are dominant (Scranton and Brewer, 1977). We had hypothesized that the marine cyanobacteria, *Oscillatoria thiebautii* and *O. erythraeum*, were responsible for the excess surface hydrogen values in the subtropical Atlantic (Herr *et al.*, 1981). Plankton tows were taken throughout the Mediterranean, but no *Oscillatoria* were found. A few colonies (individual filaments and small clumps) were seen outside the Mediterranean in the Gulf of Cadiz, but they were rare (no more than 10 filaments or clumps in a 30-minute plankton tow at 15 m). *Oscillatoria* have been described from the Mediterranean as occurring along the coast of Spain (Margalef, 1969) but no evidence for this activity was seen during our cruise.

Therefore, we conclude that, at least in the Mediterranean and probably elsewhere, some organisms other than *Oscillatoria* (or in addition to *Oscillatoria*) must be producing hydrogen. Based on the hydrogen distribution, it appears that the greatest net production is restricted to the mixed layer. Since the mixed layer in the Mediterranean is so shallow, the two to four fold excesses observed represent substantial production rates. Based on the thin film model (Danckwerts, 1970) and assuming a thin film thickness of about 100 μm (characteristic of wind speeds of about 1-5 m/sec according to Emerson (1975)), and a diffusivity of hydrogen at 25°C of 4.6×10^{-5} cm^2/sec (Broecker and Peng, 1974), in the absence of production, hydrogen concentrations should return to equilibrium levels on a time scale of one or two weeks. Since this does not appear to occur (samples throughout the entire Mediterranean show the same patterns) production must be a persistent phenomenon.

The source of the hydrogen excess could be either anaerobic organisms such as fermentative bacteria (Zehnder, 1978) or nitrogen-fixing bacteria (Burns and Hardy, 1975), many of which are aerobic in the sense that they can survive and be active in an environment containing oxygen. We do not favor the hypothesis that hydrogen is produced anaerobically in the open sea. Anoxic conditions in the mixed layer must be associated with reducing microenvironments such as the guts of fish or in fecal pellets. Oremland (1979) has shown that methane-producing bacteria can be isolated from the intestines of certain fish, suggesting that these systems are rigorously anaerobic. However, although hydrogen is produced by fermentative bacteria it may be rapidly reconsumed during interspecies hydrogen transport (Zehnder, 1978). Large amounts of hydrogen will not accumulate. This is supported

by observations of Lilley and Gordon (1978) in Saanich Inlet where hydrogen concentrations in the anoxic zone were near the atmospheric equilibrium value, and by data from an anoxic salt pond in which waters remained highly anoxic ($H_2S > 1$ m mole/L) for periods of months and where hydrogen concentrations reached levels of at most 10 times those predicted from solubility equilibrium (Scranton and Loud, 1982). Therefore, a large anaerobic source of hydrogen to the mixed layer is unlikely. In addition no correlation was found during *Bartlett* 1309-80 in the Mediterranean between hydrogen concentrations and nepheloid layers in the mixed layer. (Particles large enough to be anaerobic on the inside must be concentrated (as in nepheloid layers) if they are to be a significant source of hydrogen for the mixed layer.) Therefore, we do not believe that anaerobic microenvironments should be invoked to explain the surface H_2 maxima.

Instead we feel that the gas is most probably produced by one or several species of nitrogen-fixing bacteria. Johnson and Sieburth (1979) have reported identifying a large variety of cyanobacterial-like organisms from seawater, and although the importance of these organisms as oceanic nitrogen fixers has not been evaluated, many other cyanobacteria produce hydrogen and fix nitrogen in large quantities. Thus we feel they may be significant to the oceanic hydrogen cycle.

8. Conclusions

The hydrogen distribution in the Mediterranean is similar to hydrogen distributions found in other oceans. Based on our experiments, including drift tests designed to determine the horizontal variability of hydrogen concentrations, we can make the following conclusions.

(1) An important hydrogen source exists in the oceanic mixed layer. Variability studies suggest that this source is patchy on a distance scale of a few hundred meters. Vertical profiles suggest that net production of hydrogen is favored in the well-lit shallow mixed layer, but that production decreases and/or consumption increases in the euphotic zone below the bottom of the mixed layer in the Mediterranean Sea. These observations indicate a biological origin for the hydrogen, probably in association with a photosynthetic process which requires high light levels.

(2) A sink for hydrogen exists in the deep Mediterranean which may be associated with consumption at depth or with consumption in surface waters during periods of water mass formation.

(3) A large source for hydrogen exists at sill depth in the Straits of Gibraltar. The maximum produced by this source appears to be more diffuse further into the Mediterranean, and in addition appears to constitute a temporally and/or spatially variable plume.

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