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Dissolved hydrogen in Eurasian Arctic waters

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ABSTRACT

The distribution of dissolved hydrogen was studied during YMER-80 in the Arctic Ocean and the northern Barents Sea. Water samples were analyzed from a variety of Arctic environments including stations under complete ice cover and along the retreating ice-edge as well as vertical and horizontal sets obtained apart from the ship. The results show localized hydrogen concentrations well below air–sea equilibrium. Levels of undersaturation resemble those found in the Norwegian Sea, 3–8 nl/l (0.13–0.36 nM). Deep water in the Polar Basin contains 4.5 nl/l (0.20 nM). A section northwest of Franz-Joseph Land contains a prominent subsurface maximum with levels above saturation between 75 and 300 m. Supersaturation is also found in surface waters among ice floes at two coastal sites. In the Barents Sea, hydrogen in surface water is near equilibrium and is highly correlated with salinity. Below the surface, the hydrogen level quickly drops to half the H_2 concentration contained in Norwegian Sea water. This distribution suggests that hydrogen is being consumed throughout the Barents while excess H_2 is added to surface waters by low salinity intrusion from the retreating ice pack with secondary fluxes across the air–sea interface and from river runoff. The hydrogen mixing ratio in air samples north of Svalbard is 16% below the mixing ratio measured over the Baltic Sea.

1. Introduction

Recent work on the Atlantic H_2 distribution has shown that tropical North Atlantic surface waters contain just over twice the air–sea equilibrium concentration (Seiler and Schmidt, 1974; Herr and Barger, 1978; Scranton et al., 1982). Levels at intermediate depths vary from station to station, and maxima occur in the thermocline. North Atlantic water deeper than 1500 m is uniformly below the equilibrium level (Herr and Barger, 1978). This deep water undersaturation is identified with widespread undersaturation in the North Atlantic deep water source region, the Norwegian Sea–Labrador Sea. At higher latitudes, the North Atlantic surface water is 70% saturated. In the Norwegian Sea, surface water contains 40–80% of the equilibrium level, and the deeper water is only 30–40% of equilibrium (Herr, 1981). The evidence implies that in this region near surface consumption of H_2 sources within the water column are overshadowed or are absent.

The observation of widespread undersaturation in the Norwegian Sea seems to separate H_2 studies into tropical and arctic subsets, and suggests the following questions. (a) How widespread is H_2 undersaturation in the Arctic and Antarctic? (b) Can regions of production be found? (c) Is there a lower limit to the H_2 undersaturation? (d) Does the presence of ice cover lead to greater undersaturation as the atmospheric source is partially restricted? (e) Does high productivity observed directly under sea ice lead to areas of H_2 production? (f) How well does the net H_2 distribution match chemical parameters such as nutrients and other microbiological indicators?

During the summer of 1980, an invitation to join the Swedish Arctic Expedition, YMER-80, presented a unique opportunity to attempt to answer some of the above preliminary questions about the nature

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of hydrogen production and consumption in high-latitude waters. Hydrogen analyses were performed on leg 1 of YMER-80 at stations shown in Fig. 1. Hydrogen data are tabulated (Herr, 1982) and are available along with the exact station positions and other chemical parameters measured during leg 1 of YMER-80 either from the author or from Department of Marine and Analytical Chemistry, Chalmers Institute of Technology, Göteborg, Sweden.

2. Analytical and sampling methods

The analysis for dissolved H_2 was carried out onboard ship using the hot mercuric oxide technique (Schmidt and Seiler, 1970). The method was similar to that previously described (Herr and Barger, 1978). Briefly, a 10 ml sample of gas stripped from seawater was introduced into a purified air carrier stream. Hydrogen in the sample was oxidized over hot HgO, releasing Hg vapor which was in turn detected optically at 254 nm by flameless low temperature atomic absorption. This reaction is quite reproducible with a 2% precision for injections of standard calibration gases. Carbon monoxide, which also reacts strongly with HgO, was retarded by molecular sieve and then oxidized by Ag_2O to undetectable CO_2. The heated (260 °C) HgO reactor bed and optical cell were built onto a commercial atomic absorption spectrophotometer to take advantage of the intensity and stability of a hollow cathode lamp. In each injected sample, trace organic impurities which absorb light at 254 nm (such as aromatics), and thus interfere with the Hg vapor measurement, were adsorbed on the

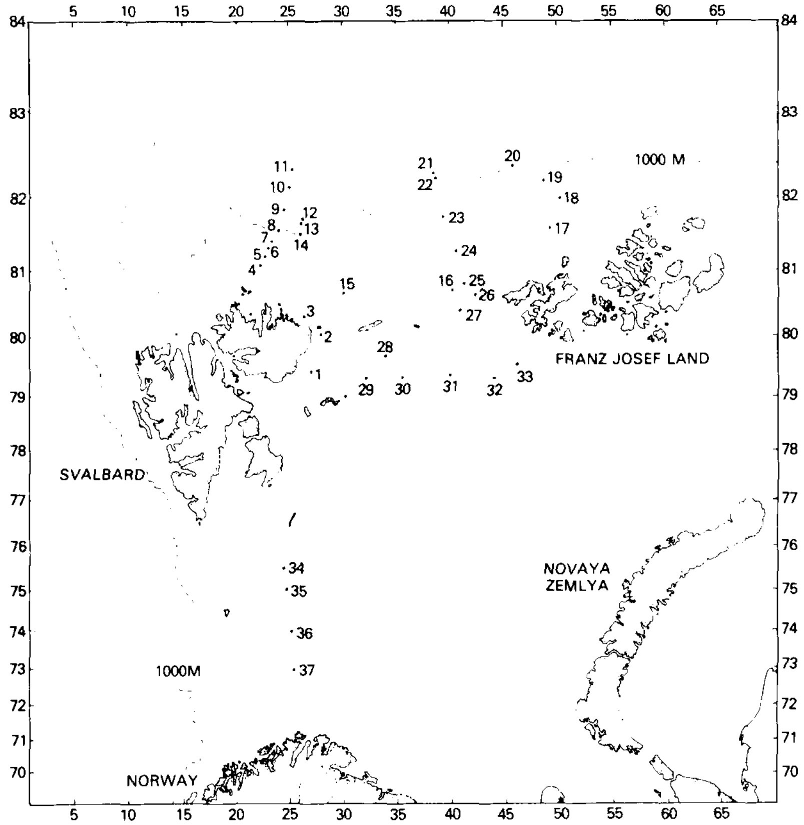

Fig. 1. Hydrogen stations occupied along the YMER-80 cruise track, leg 1. Exact location of each station is available from Herr (1982). Additional CTD and biological stations are not shown.

molecular sieve. Those impurities not adsorbed, as well as any broadband absorptive species, were eliminated by using two hollow cathode lamps (Fe at 243 nm and Hg at 254 nm) pulsed alternately at 140 Hz. All analyses were compared to a H_2-in-N_2 primary standard prepared commercially and calibrated in our laboratory by a single step dilution technique. Each sample was compared to a standard injected just prior to it.

Seawater samples were transferred to 1200 ml glass storage bottles directly from 2.5 l Niskin bottles. Precautions were taken to minimize contact with air. The sealed sample was placed in warm (35–40 °C) water for 30 min to bring it to room temperature before analysis. Poison was not used to stop biological activity in the sample since previous work (Herr, unpublished results) showed that samples can be stored at 18 to 20 °C for up to 12 h with less than 10% change in hydrogen concentration. Temperature equilibrium was begun immediately upon collection and all H_2 samples were analyzed within 6–8 h of collection.

An improved static vacuum extraction technique was used to remove dissolved gas from the seawater. The redesigned extraction vessel uses a fluorocarbon needle valve which allows the water sample to enter the evacuated (3 Pa, 20 mtorr) glass chamber and to spray down the sides. The fine spray combined with a relatively long exposure to the low pressure allows extraction efficiencies of 88–90% to be obtained for N_2 and H_2. The efficiency was determined for the extraction vessel from the amount of H_2 removed from a seawater sample saturated with calibration gas (0.998 p.p.m.v. H_2 in N_2). An aliquot of the total volume of extracted gas was injected into the analyzer at room temperature. The peak heights for sample and standard were recorded and the concentration of H_2 was corrected to STP volumes for 1.00 l of seawater. The following equation was used.

$$C_{H_2}\,(\text{nl(STP)/liter seawater}) = \frac{C_b V_b A V_t\, 1000}{E B V_a (V - V_s)}$$

where C_b is the concentration of the calibration gas (0.998 p.p.m.v. H_2), V_b is the injected volume of calibration gas corrected to STP, E is the H_2 extraction efficiency, 0.88, A/B is the ratio of peak heights of sample to standard, V_t/V_a is the ratio of total extracted gas to injected sample, both at ambient conditions, and V is the extraction bulb volume, 989.6 cm^3. The overall uncertainty for each seawater analysis has been determined (Herr and Barger, 1978; Herr et al., 1981) to be 8% or ± 0.6 nl/l (0.027 nM), whichever was larger.

The major problem for environmental hydrogen analyses is contamination from the small but significant amounts of hydrogen generated by marine corrosion. Strict isolation of the seawater sample from metallic surfaces is necessary to obtain unambiguous results. Samples obtained close to ships' hulls are unreliable, thus off-ship stations were taken for samples less than 10–15 m in depth. Standard PVC Niskin samplers have shown no contamination after they have been used repeatedly; however, the rosette sampler system has to be used with great caution. The rosette was coated with fluorocarbon and the protective zinc anodes were removed. Exposed steel clamps and the first 2–3 m of hydrowire were covered by electrical tape.

Air sampling was performed along the cruise track. Extensive sampling was not possible, but at various locations series of 10 ml air samples were analyzed. These samples were obtained with a polypropylene syringe sealed with a nylon ball valve. The time between collection and analysis was never more than 2 min. Care was taken to avoid the ship's influence; all samples were taken to windward and 20 m above the sea or ice surface.

In addition to onboard sampling, water sampling was performed on four occasions off the YMER. Twice, hydrographic profiles were taken through the ice to 50 m with a single Niskin bottle, polyester line, acrylic-coated lead sinkers, and a fluorocarbon-coated messenger. These samples were obtained 100–120 m upwind from the ship at the end of a small lead. Also, 2 trips were taken away from the ship in a rubber boat to sample the surface water around ice floes. In these excursions, water samples were taken directly into a glass sample bottle held 10 cm below the surface. Both of these sampling methods allowed hydrogen samples to be obtained close to the sea surface, a region which is generally inaccessible in the open ocean due to the corrosion problem and difficulties working from small boats.

Data from the first few H_2 stations reflect initial difficulties with sampling and analysis procedures. Until station 12, the Niskin bottles were not tightly closing due to relaxation of the elastic closures in the cold weather and subzero water. Some air exchange occurred in a number of samples and many were lost altogether. The closure problem was solved by filling the Niskin bottles with hot water (65 °C) prior to use.

3. Hydrography

The hydrography of the region surrounding the Svalbard and Franz-Joseph Land archipelagoes separates the stations shown in Fig. 1 into two groups. Those stations north of the island groups were under complete ice cover during leg 1 of the expedition. Subsurface water characteristics are dominated by the West Spitzbergen current which flows around the northeastern side of the Svalbard group and then eastward along the continental slope of the Eurasian Basin. The core depth of this current is 220–320 m, and it is the single largest source of heat transported into the Arctic (Aagaard and Griesman, 1975). In this region north of Svalbard and Franz-Joseph Land heat is removed from the incoming Atlantic water and polar water is formed (Coachman and Aagaard, 1974). Fig. 2 shows the T–S characteristics for stations 9–27 north of the archipelagoes. The temperatures and salinities were read from CTD lowerings accompanying the rosette sampler, and are courtesy of B. Rudels, University of Göteborg. In the summer, the salinity of water between the surface and 30 m is lowered by river runoff to the east of the Eurasian Basin (Hanzlick and Aagaard, 1980), and the temperature remains near freezing point (Fujino et al., 1974) as heat is lost to melting ice. The influence of the West Spitzbergen current is evident as both salinity and temperature rise towards 2 °C and 34.0 × 10^{-3}. The formation of polar water, after Coachman and Aagaard (1974), occurs as mixed subsurface water, near freezing and with salinities >34.5 × 10^{-3}, flows southward in continental canyons rising and mixing with northward flowing water at shallower depths which has lower salinity and is losing heat. The mixture is lowered to near freezing point by climatic conditions and flows back into the basin. The result is the nearly constant salinity (34.9 × 10^{-3}) deep water in Fig. 2 at depths greater than 500 m.

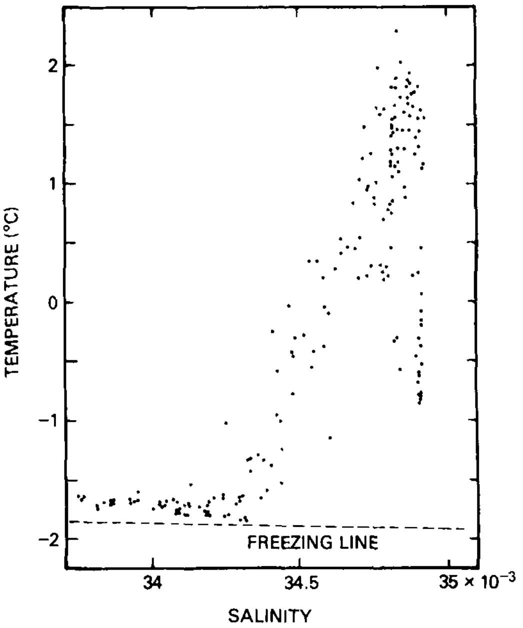

Fig. 2. Temperature–salinity relationships from depths at which H_2 samples were collected. Data include H_2 stations 9–27 north of the Svalbard–Franz-Joseph Land archipelagoes. Courtesy of Rudels, University of Göteborg.

To the south of the Svalbard–Franz-Joseph Land archipelagoes, the Barents Sea is shallow (<400 m), and ice-free during summer months. The line of stations 29–33 coincides with the location of the retreating ice-edge the first week of August, 1980. Consequently, the surface water along stations 29–33 were 1–2 degrees warmer than the freezing point. Along stations 34–37, the polar front (Johannessen and Foster, 1978) was crossed and surface temperatures rose above 6 °C. The circulation in the Barents Sea consists of an input of Atlantic water entering the trough south of Bjornoya, flowing eastward and northward filling the central sea. Hanzlick and Aagaard (1980) indicate this now modified Atlantic water merges in the east, north of Novaya Zemyla with additional Atlantic water flowing southward into the northeast Kara Sea. A surface counterflow in the western Barents, the East Spitzbergen current, exists south of the Svalbard archipelago. The polar front south of Bjornoya is thus maintained by warm (6–8 °C), highly saline (34.92 × 10^{-3}) water flowing in on the southern side of the deep water channel and colder (2°) and less saline (34.2 × 10^{-3}) water exiting along the northern side of channel. This cooler, fresher water appears not to originate north of the archipelagoes. An analysis of

YMER-80 CTD data has recently shown that, contrary to previous estimates of transport (Aagaard and Greisman, 1975), the Barents Sea is a source of dense water flowing northward into the Eurasian Basin below the pycnocline, adding to the formation of polar water (Aagaard et al., 1981). Thus, southward flow between the archipelagoes may be only a minor influence in the Barents and the directionality of flow through the Franz-Joseph Land–Novaya Zemyla gap is highly uncertain. Coachman and Aagaard (1974) and later Aagaard (1982) conclude that annual mean transport through the gap is probably from the Barents to the Kara Sea. Meltwater from the retreating ice-edge appears to be the major source for the fresher water north of the Bornoya polar front. However, exchange of Arctic Ocean water with the Barents is not well understood and river runoff cannot be excluded entirely as yet.

4. Results

4.1. *Air measurements*

Table 1 gives a summary of the H_2 air measurements made along the ship's track. Air sampling commenced as YMER left Stockholm. It continued as the ship made its way through the Baltic Sea and then northward into the Arctic. While in the influence of European air masses, the H_2 levels are higher than further north where the air masses are coming from the north polar region. These results are similar to sea level results obtained in the Norwegian Sea in 1979 (Herr et al., 1980; 0.62 ± 0.20 p.p.m.v.). Earlier tropospheric H_2 measurements made from aircraft (Schmidt, 1978; 0.551 ± 0.015 p.p.m.v.) at higher northern latitudes (50°–70° N) are lower than the present Baltic and Norwegian Sea data and are in closer agreement with the Arctic measurements. Schmidt (1978) remarked that a strong H_2 sink at the earth's surface must be present at higher latitudes to explain the observed decrease in the H_2 mixing ratio in tropospheric profiles below 3 km.

4.2. *Seawater measurements*

An attempt was made to sample as many different Arctic environments as possible. Thus, stations were selected which were near-shore (stations 1, 2, 3), apart from the ship (stations 2, 11, 12, 28), along CTD sections in the West Spitzbergen current (stations 4–10, 17–24), at the ice edge (stations 29–33) as well as in areas of ice cover, and in open water well away from the region of sea ice (stations 34–37). The results in these many areas show the arctic H_2 distribution is varied and complex. Undersaturation of H_2 (air–sea exchange equilibrium is 11.5 nl/l at −1.7 °C, 34 × 10^{-3}; 11.0 nl/l at ±1.6 °C, 34.9 × 10^{-3}; and 10.6 nl/l at 6.0 °C, 34.9 × 10^{-3}; Gordon et al., 1977) predominates in near-surface waters throughout the region north of Svalbard and Franz-Joseph Land. The surface water down to 50 m is, with exceptions, 30–50% undersaturated, and levels are

Table 1. *Hydrogen mixing ratios in air samples during YMER-80*

Date	Samples	Average mixing ratio	Standard deviation	Position
24 June	14	0.630	0.007	Baltic-Stockholm
25 June	15	0.628	0.015	Baltic-Copenhagen
26 June	5	0.593	0.009	Baltic-Göteburg
27 June	10	0.581	0.019	North Sea-Bergen
28 June	6	0.599	0.009	Norwegian Sea-Trondheim
29 June	10	0.571	0.012	Norwegian Sea-Bodö
03 July	14	0.578	0.017	Barents-Tromsö
05 July	6	0.582	0.005	Svalbard–Kong Karls Land
09 July	6	0.525	0.036	North of Svalbard
15 July	6	0.550	0.009	North of Svalbard
16 July	2	0.553	0.003	North of Svalbard
31 July	15	0.575	0.024	East of Svalbard
05 August	10	0.568	0.027	North Cape, Norway

comparable to those seen in the Norwegian Sea (Herr et al., 1981).

Table 2 lists the results of two stations occupied on the ice 200 m away from the ship. The hydrocasts were performed with a single Niskin bottle over a period of 30 min. These results show H_2 is undersaturated at all depths to 50 m including between the surface and the bottom of the sea ice. Both profiles show little in the way of structure, although at station 12, the H_2 concentration decreases sharply at the bottom of the 15 m mixed layer. These two stations suggest that a 10 m sample obtained conventionally by the rosette sampler is representative of the surface mixed layer.

On the other hand, two notable instances of the surface H_2 concentration contrasting with deeper values are seen in horizontal samples from stations near the islands of Storoya (station 2) and Kvitoya (station 28): see Table 3. High H_2 variability in these samples taken from 10 cm depth in shallow waters around ice floes correlates with some high carbon monoxide values (obtained qualitatively by the HgO system when the Ag_2O trap is overwhelmed) and algal colonies associated with the ice. A sample from 10 m at station 2 was 7.0 nl/l. Unfortunately, only a few opportunities were afforded to sample close to the surface in water unambiguously never in contact with the ship, so it is impossible to say how widespread is the surface supersaturation. However, these samples suggest that in some coastal areas a source for H_2 is present quite near the surface. The patchiness implied by the variability between samples separated by 50 ± 10 m may be evidence of either a noncontinuous *in situ* source or a complicated mixing pattern formed from elevated H_2 levels in meltwater. These samples were checked for a correlation with salinity but none was apparent. Gosink and Kelley (1979) have found that annual ice can be a source for trace gases in the arctic. This surface source for H_2 is interesting and needs to be pursued.

Table 2. *Shallow water column profiles of dissolved hydrogen off ship*

Depth (m)	Station 11 (nl/l)	Station 12 (nl/l)
0	4.7	6.7
5	4.9	6.7
10	5.8	6.8
15	4.2	3.2
20	6.5	5.0
25	5.8	5.0
30	7.0	4.2
40	6.5	3.8
50	5.0	3.7

Table 3. *Horizontal surface (10 cm) H_2 samples*

Station relative distance apart (m)	28b(82) horizontal (nl/l)	2(Storoya) horizontal (nl/l)
0	7.2	11.4
50	26	8.3
100	19.2	22.1
150	9.1	50.4 high CO
200	9.1	7.6
250	9.1	15.5
300	18.7	25.5
350	13.5	29.1 high CO
400	16.9	14.8
450	8.5	45.4 high CO
500	7.8	

Fig. 3 shows H_2 concentration contours drawn from profiles along the section from stations 21 to 26 northwest of Franz-Joseph Land. Above 70 m, H_2 is 30–50% undersaturated with values between 6 and 8 nl/l. Undersaturation increases with depth in the southernmost stations closest to the Barents Sea with H_2 values decreasing to 3–5 nl/l below the pycnocline. Further north the mid-depth H_2 distri-

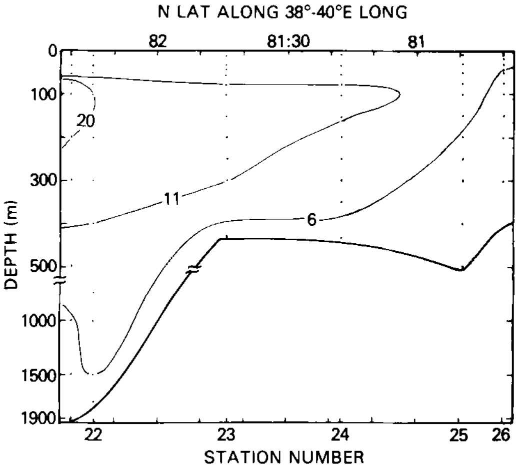

Fig. 3. Hydrogen section running north–south between Svalbard and Franz-Joseph Land. Eleven nl/l is the approximate air–sea equilibrium level. Note the depth discontinuity.

bution is quite different. At stations 21–24, supersaturation (H_2 >11 nl/l) coincides with the warmer water of the West Spitzbergen current. At stations 21 and 22, H_2 concentrations reach 2- to 3-fold supersaturation in the region above the temperature maximum of the current (200–340 m). In this region, surface waters are mixing with the warmer Atlantic water below, and the temperature gradient is intense, to 0.025 °C/m. The region of supersaturation extends southward to station 24 well onto the continental shelf.

The deepest water ($\sigma_T = 28.04$) in all stations of the section contain H_2 concentrations below 6 nl/l. This is polar water (Coachman and Aagaard, 1974), and from the deepest samples taken from station 9 (4.5 nl/l for 2000, 2500, 3230 m depths) it can be inferred that the central arctic Eurasian Basin is at least 60% undersaturated in H_2.

Space does not permit an extensive listing of the individual analyses from which the sections presented here are taken, nor can many profiles be plotted. However, Fig. 4 shows representative profiles from three shallow stations north of Franz-Joseph Land. Station 16, closest in position to station 25 in the arctic section but separated in time by one week, shows a pronounced subsurface maximum at 40 m. A maximum also appears at station 17 further east, but station 18, 40 km north, shows only little evidence of this feature. Below 50 m, H_2 levels progressively decrease and below 100 m have similar values extending to the bottom in spite of their variability at shallower depth.

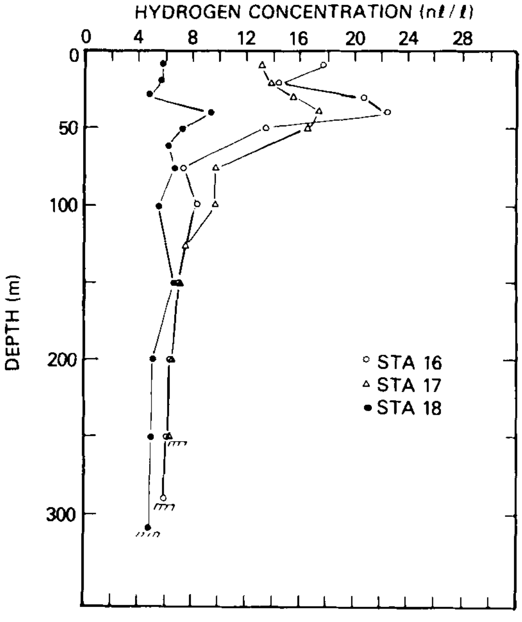

Fig. 4. Hydrogen profiles north of Franz-Joseph Land illustrating oceanographic continuity. In spite of upper water column variability, the H_2 levels below 100 m are quite similar.

Fig. 5 shows a very different H_2 distribution in the northern Barents Sea. There, the H_2 levels are near saturation in the upper 15–20 m. The 11 n/l contour represents the approximate air–sea equilibrium level; data from 10 m along the section match or exceed this contour within the stated uncertainty. Ice coverage ranged from 4–6 octaves for station 32 to 3–4 octaves for stations 29 and 30. Open water was present for stations 31 and 33 but ice was as near as the horizon. The H_2 levels decreased monotonically and fell below 3 nl/l at 100 m for station 29 and at 30 m for stations 32 and 33. The lowest H_2 concentrations yet recorded in the Atlantic and its surrounding seas are the values near 2 nl/l recorded along this section.

Fig. 6 shows the H_2 distribution along a section across the channel south of Bjornoya through which Atlantic water enters the Barents. In this region of open water the H_2 levels remain much like the concentrations further north in the Barents Sea. The values above 4 nl/l on the southern side of the channel are similar to H_2 levels found in the eastern

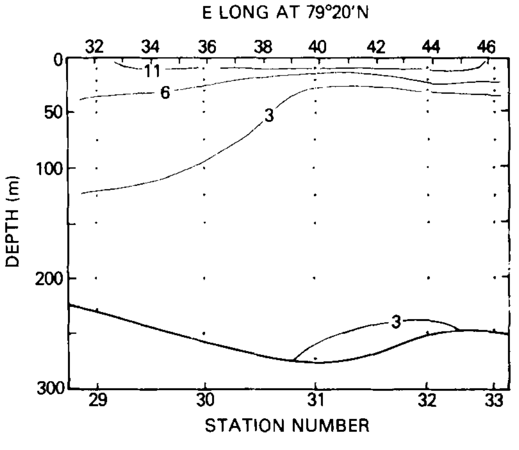

Fig. 5. Hydrogen section running east–west along the ice edge in the northern Barents Sea. Hydrogen levels above 50 m correlate with salinity, while deep water within the less than 3 nl/l field reaches 2 nl/l, the lowest value recorded in the Atlantic region.

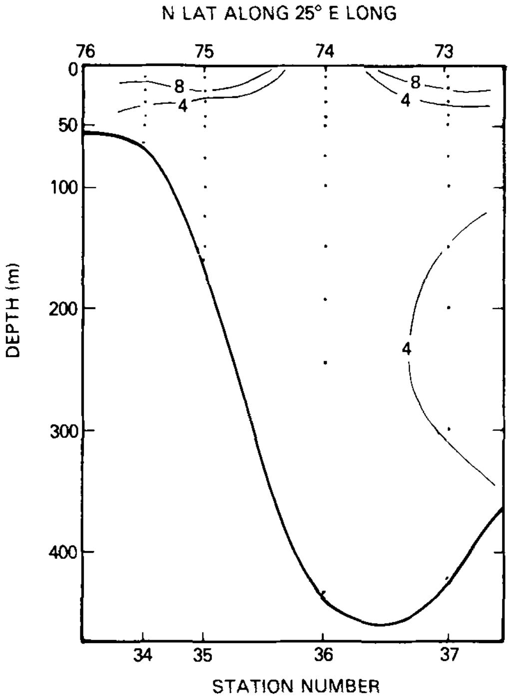

Fig. 6. Hydrogen section running north–south at the entrance to the Barents Sea north of Norway and southeast of Bjornoya. The polar front occurs along the north side of the channel. Values above 4 nl/l on the southern side reflect inflow from Norwegian Sea. Upwelling is evident at station 36.

Norwegian Sea (Herr et al., 1981), the source of this inflow to the Barents. The polar front, which is topographically controlled (Johannessen and Foster, 1978) along the northern side of the channel, results in upwelling at station 36 as the 27.45 isopycnal rises to the surface from 30 m at station 34 and from 20 m at station 35. At the southern edge of the section the 27.45 isopycnal has submerged again to 40 m. This upwelling displaces water near the air–sea equilibrium H_2 concentrations with highly undersaturated deeper water.

5. Discussion

The widespread undersaturation of H_2 in surface waters of the Norwegian Sea and the apparent absence there of H_2 sources in either surface or deeper waters (Herr et al., 1981) contrasts sharply with results from the tropical ocean where increasing evidence is being found linking surface sources of H_2 production to photosynthetic processes (Bullister et al., 1982; Setser, et al., 1982). Scranton et al. (1982) found in the Mediterranean that elevated H_2 levels did not extend to the euphotic zone below the mixed layer, suggesting sources near the surface. The discovery that H_2 levels follow a diurnal period in oligotrophic waters of the South Atlantic (Herr, et al., 1983) is further evidence of the dynamic nature of H_2 in the mixed layer. The emerging picture of ocean H_2 processes shows net H_2 production in surface waters of the tropical ocean which yields to net H_2 consumption in colder northern waters. The arctic data described here confirms that H_2 is generally consumed in high latitude surface water, thus accounting for the widespread undersaturation of the upper layers seen in Figs. 3 and 4. On the other hand, local H_2 sources are present and can produce H_2 to levels comparable with the tropical values. The horizontal samples show such a local source, but since the mixed layer surrounding these sources is undersaturated, local consumption must overwhelm the H_2 which is produced. The time scales for these processes are unknown.

The most likely source of H_2 in tropical waters is microbiological production. Hydrogen can be formed by hydrogenase in eukaryotic algae (Kessler, 1974) or by nitrogenase during N_2 fixation (Burns and Hardy, 1975) and by photosynthetic bacteria (Greenbaum, 1977). Hydrogenase activity is strictly anerobic, and microenvironments free of O_2 are necessary for H_2 production. Thus, a major problem for a hydrogenase mechanism is the location of suitable reducing environments. Many organisms which fix N_2, including cyanobacteria, are aerobic and photosynthetically active, and may produce H_2 as a by-product to the formation of ammonia. Hydrogen and ammonia are formed by O_2-sensitive nitrogenase, and many cyanobacteria contain their own ability to protect the nitrogenase activity by creating O_2-free zones. Further, H_2 production and its subsequent hydrogenase-mediated consumption (requiring O_2) may form a protective mechanism for the nitrogenase (Saino and Hattori, 1982a, b). Recent work by Scranton (1982) has shown that the cyanobacterium, *Oscillatoria thiebauti*, commonly found in the tropical oceans, can produce sufficient H_2 while fixing N_2 to account for the locally observed H_2 levels during collection.

However, this species of cyanobacteria, since it is found only in warm water, cannot account for the elevated H_2 levels observed below the pack ice in transitional water above the West Spitzbergen current (Fig. 2). Sources producing this excess H_2 are likely associated with the current than with the process of mixing warmer water from the current with colder overlying surface waters (Coachman and Aagaard, 1974). Data from other stations along the continental shelf do not show similar regions of supersaturation associated with the West Spitzbergen current. Fig. 4 shows subsurface maxima at stations 16, 17 and 18, but H_2 concentrations at stations 19 and 20 to the east are not supersaturated between 75 m and 300 m. At these depths the data remain between 4.5 nl/l and 7.0 nl/l. Elevated H_2 concentrations have been observed before in the Norwegian Sea in regions of mixing along the polar front (Herr et al., 1981); however, data were insufficient to identify a source.

Bacterial counts and ATP analyses performed during YMER-80 by the Department of Microbiology, University of Göteborg show this region of the Arctic Ocean to contain an active microbial biomass. The total number of bacteria ranged between 10^4 ml^{-1} and 10^5 ml^{-1} (Dahlback et al., 1982). However, the H_2 levels do not correlate with either indicator of total biomass. Twelve coincident samples of H_2 and bacterial counts give a correlation coefficient of 0.007, and eleven coincident samples of H_2 and ATP give a correlation coefficient of 0.23. Nutrient data (Valderrama, 1982), also show little correlation with H_2 analyses performed on the same Niskin samples.

This lack of correlation between H_2, nutrients and biomass appears in tropical data sets as well. Hydrogen data from the North Atlantic (Herr and Barger, 1978) correlated with neither nutrients nor ATP. Scranton et al. (1982) found no correlation between H_2, nutrients and suspended matter in the Mediterranean. In controlled ecosystem experiments (CEPEX), using 9.5 m × 29 m bags, H_2 showed a possible relationship to chlorophyll at dissimilar depths, and no correlations with nutrients or bacteria counts (Bullister et al., 1982). In the Pacific, higher H_2 values and fluorescence appeared associated in warm, surface waters. However, in colder surface waters where H_2 levels were lower, there was no correlation. Neither water type showed a correlation between H_2 and nutrients (Setser et al., 1982); this individual behaviour for H_2 in regions where its concentration is maintained far from equilibrium argues against a single species, or maybe even a single family of microorganisms, being responsible for H_2 production or consumption. Recycling of H_2 within a single cell, as in cyanobacteria (Burns and Hardy, 1975), or within interdependent individuals, as in anaerobic bacteria (Zehnder, 1978), may cause a cell's or colony's net H_2 release to be dependent on local environmental conditions which affect the cellular energy balance (Evans et al., 1981). In view of the 3- to 4-order-of-magnitude disparity between bulk nutrients and H_2, it is not surprising that local variations at subanomolar levels in nutrients or other indicators might go unnoticed.

The similarity between H_2 profiles at station 26, Fig. 3, and those at the stations in Fig. 5 combined with evidence in Fig. 6, of the Norwegian current and upwelling along the polar front, suggests an identification of H_2 levels with water type in the Barents Sea. Fig. 7 shows the correlation of the H_2 gradient with salinity in the near surface waters of stations 30 to 37 (salinity data for station 29 are unavailable). In all these stations H_2 decreases monotonically with depth. Hydrogen is uniformly higher in less saline surface waters, 10–60 m, of stations 30–34. However, the correlation extends only to 20 m for station 35 near the polar front and breaks down at stations to the south of the polar front in warmer water of similar salinity. Hydrogen

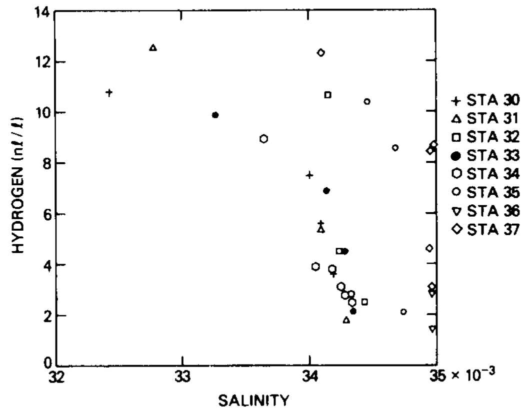

Fig. 7. Correlation between H_2 and salinity in near-surface waters, 10–60 m, of the Barents Sea. The correlation breaks down for stations 35–37 in warmer water south of the polar front where low salinity water is absent.

in the surface waters of the Barents contrasts with surface values from under the ice north of the Svalbard–Franz-Joseph Land archipelagoes where the H_2 concentration is often undersaturated. The two regions are subject to different hydrographic conditions which are apt to affect agents of H_2 production or consumption.

The correlation between H_2 and salinity in the Barents Sea argues against rapid *in situ* processes controlling the surface concentration. In tropical waters where biological production is the only likely source, H_2 levels are maintained despite mixing (Herr et al., 1983; Scranton et al., 1982). Near-surface consumption which has been advanced as an explanation for H_2 profiles in the Norwegian Sea (Herr et al., 1981) is also sufficiently rapid to prevent an atmospheric source from replacing the H_2 in surface water. The near-equilibrium H_2 found at 10 m in Fig. 5 seem to suggest an apparent absence of both active biological production or consumption in the water column. In this case, the atmosphere may be the source of H_2 to the surface water. However, just below the surface, the H_2 concentration falls rapidly until below 60 m it is 2 nl/l, half the 4–5 nl/l value contained in water entering the Barents from the Norwegian Sea; see Fig. 6. Thus, H_2 is apparently being consumed in the deeper water. If infusion of atmospheric H_2 to surface water controls the observed near-surface H_2 concentration in the Barents, oxygen in surface water may be expected to show similar behaviour. However, O_2 does not correlate with temperature or salinity (Valderrama, 1982). It remains supersaturated over the depth range H_2 decreases monotonically with salinity, and then abruptly becomes undersaturated. The H_2 gradient does not follow either a solubility relationship as salinity varies nor does it match the O_2 behavior. Therefore, it is unlikely that the only source of H_2 to the surface waters of the Barents Sea is the atmosphere.

The higher H_2 values associated with low salinity water in the Barents Sea may have as sources either meltwater containing high levels of H_2 from the retreating ice pack, or surface water with moderately supersaturated H_2 levels advected from river sources. Tritium data (Östlund, 1982) show that while river runoff is the principal source of freshwater to the ice-covered arctic, at least one fifth of the freshwater in the upper 10–60 m originates from melting ice. Lewis (1982) reports this meltwater to runoff ratio may even approach unity. On the other hand, near the retreating ice edge, stations 29–33, the proportion of meltwater to river runoff ought to be high. Table 3 shows the high concentrations of H_2 which can exist in the nearest of surface waters. Secondly, the presently available hydrographic information indicates that little if any Kara Sea water containing a high proportion of river runoff reaches these stations in the Barents Sea. The introduction of wind stress in open water will tend to deepen the mixed layer, and thus dilute the surface meltwater H_2 values. Other local effects such as upwelling (Buckley et al., 1979), may be influential as well to modify the near-surface H_2 concentration. Low salinity water originating from the freshwater discharge of Siberian rivers entering the Barents with elevated H_2 concentrations may contribute to the near-surface salinity–H_2 correlation. Advected freshwater would in this case modify locally produced H_2 concentrations from meltwater to produce the observed H_2 surface values.

6. Conclusions

The distribution of H_2 off the Eurasian Arctic Continental Shelf and in the northern Barents Sea is a complex assortment of localized H_2 sources overlying a general pattern of H_2 consumption throughout the water column. Based upon data collected from widely dissimilar arctic environments, the following conclusions are drawn.

Profiles and sections show surface water to be undersaturated beneath pack ice and in open water. Near the ice edge, surface water is near equilibrium. Levels of undersaturation are similar to those found in the Norwegian Sea where H_2 concentrations are between 3 and 8 nl/l. Deep water in the Polar Basin contains 4.5 nl/l, and in the Barents Sea, bottom water reaches 2 nl/l. While the common feature of supersaturation makes the surface waters of tropical oceans a source of H_2 to the troposphere, Arctic waters are undersaturated; and thus, are a sink for tropospheric H_2. Air measurements along the YMER-80 station track show a 16% decline in the H_2 mixing ratio between the Baltic Sea, with air masses from industrialized Europe, and the region north of Svalbard with air masses from the North Pole.

The water column northwest of Franz-Joseph

Land contains a prominent subsurface H_2 maximum reaching 3-fold supersaturation. This maximum, between depths of 75 and 300 m, overlies the West Spitzbergen current, but there is insufficient evidence to associate the maximum with the warmer Norwegian Sea water. Also, suites of surface samples at two stations in coastal waters show highly varied, supersaturated H_2 concentrations at 50 m spacings. In these regions of apparent *in situ* net H_2 production, no correlations with nutrients or biomass, including bacterial counts, have been found. This lack of correlation suggests H_2 has multiple biogenic sources.

Hydrogen in surface waters of the Barents Sea is near air–sea equilibrium and strongly correlates ($R = 0.9$) with salinity. Below the surface, H_2 concentrations drop rapidly to the lowest levels recorded in the Atlantic or its surrounding seas. This distribution implies that half of the H_2 entering the Barents from the Norwegian Sea is consumed by a sink below the pycnocline. Further, H_2 is apparently added to surface waters by low salinity intrusion from the retreating ice pack with secondary influxes across the air-sea interface and from river runoff.

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