Molecular hydrogen in the atmosphere

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ABSTRACT

The distribution of molecular hydrogen in the troposphere, the lower stratosphere, as well as ocean surface waters of the Atlantic Ocean region was studied. A rather constant mixing ratio of 0.548 ± 0.015 ppmv was found in the southern troposphere and in the lower stratosphere of the northern hemisphere. Statistically significant higher levels of 0.558 ± 0.019 ppmv and 0.585 ± 0.029 ppmv have been obtained in the northern hemisphere in the upper troposphere and in surface air respectively. The data do not indicate any change in the H_2 mixing ratio in the lower stratosphere up to 4 km above the tropopause. Surface waters of the Atlantic Ocean appeared to be supersaturated by a factor of about 3. Vertical profiles showed distinct maxima between 500 and 1 000 m depth. The discussion of sources and sinks leads to a tropospheric residence time of about 4 to 7 years.

Introduction

Our knowledge about the distribution of molecular H_2 in the atmosphere is quite patchy. The first reliable analyses were made by Schuftan (1923, see Paneth, 1937), who found 0.50 ± 0.10 ppmv in air samples from different liquid air plants in Germany. Since that time, this concentration was considered to be constant and to be representative for atmospheric air. This value and all data published later are combined in Fig. 1, in which we tried to give a complete historical survey of all measurements in the troposphere.

Most of these studies employed different methods of limited accuracy. Since all previous authors analysed individual air samples, their data sets are rather restricted in number so that the average values are not very representative. Furthermore, most of these measurements were performed in the vicinity of populated areas and it is very likely that the scatter of the data is due to local contamination. Accordingly, these data cannot be considered a very reliable basis for any conclusions about the H_2 distribution in the troposphere.

Measurements of H_2 mixing ratios in clean air were performed by Bainbridge (1964), who analysed distinct samples of surface air over the Pacific Ocean, and by Ehhalt & Heidt

(1973), who collected samples of tropospheric air at different altitudes over Palestine, Texas and Scottsbluff, Nebraska, USA. Parallel to continuous measurements, which we will report on in this paper, Ehhalt (1971) collected several air samples over the North Atlantic.

It has been pointed out by Junge (1972) that, together with CH_4, CO, and N_2O, H_2 belongs to a group of atmospheric constituents, influenced strongly by microbiological sources. On the other hand, there is some evidence that the photochemical oxidation of CH_4 provides a source for H_2 and CO thus also coupling the tropospheric cycles of these gases (Levy, 1972; Wofsy et al., 1972). Therefore, data on the large scale distribution, as well as on the sources and sinks of H_2, will also provide information on the cycles of CH_4 and CO and vice versa. In this paper the results of an extensive study on the abundance of H_2 in the atmosphere and the first (somewhat) quantitative evaluation of the tropospheric budget of this gas will be reported.

Measurements

Two years ago a program was started that emphasized the determination of the atmospheric H_2 background level. Fig. 2 illustrates
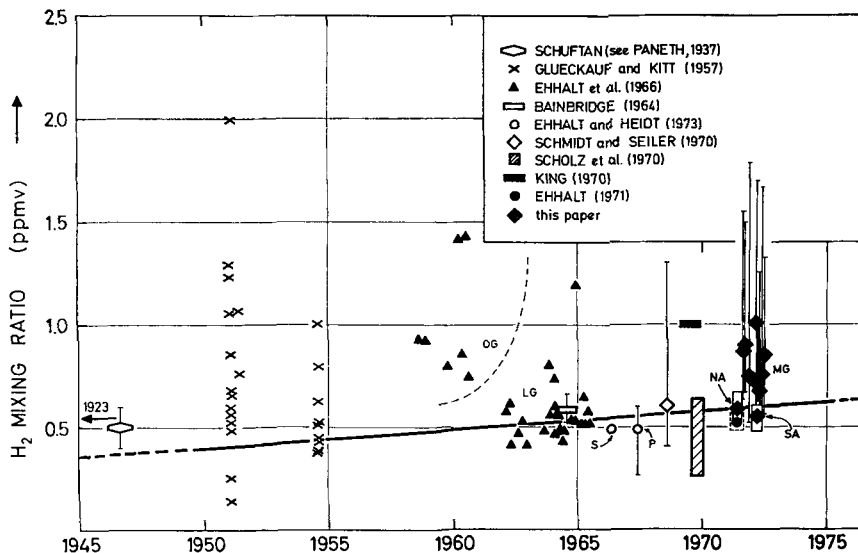
Fig. 1. Historical survey of H$_2$ measurements in tropospheric air. Glueckauf & Kitt (1957) analysed two sets of 200-1 samples collected at Harwell, Great Britain. Ehhalt et al. (1966) determined the H$_2$/He ratios in liquid air samples collected at Oberhausen (OG) and Lohhof (LG), Germany. The plotted values are calculated from these ratios assuming a He mixing ratio of 5.24 ppmv. All further data are plotted as averages with vertical lines or rectangles representing the range of H$_2$ mixing ratios observed during periods of one or several months, respectively. These measurements were performed by Bainbridge (1964) on the Pacific Ocean, by Ehhalt & Heidt (1973) at Scottsbluff, Nebraska (S) and Palestine, Texas (P), USA, by Schmidt & Seiler (1970) at Mainz, Germany, by Scholz et al. (1970) near Boulder, Colorado, USA, by King (1970) at Bayway, New Jersey, USA, by Ehhalt (1971) on the North Atlantic, and during this work on the North Atlantic (NA) and South Atlantic (SA) as well as at Mainz, Germany (MG). The thick line represents the suggested increase of the H$_2$ mixing ratio due to anthropogenic activity (see text).

the cruises of several expeditions. Continuous registrations of the H$_2$ mixing ratio in surface air over the Atlantic Ocean have been performed for about 80 days during cruises on board the R.V. *Meteor* (Cruise No. 23) in May and June 1971 on the North Atlantic and on board the R.R.S. *Shackleton* (Antarctic Cruise) in November and December 1971 on the North and South Atlantic.

Parallel to these expeditions, continuous registrations in the upper troposphere were performed during several flights with commercial aircrafts type Boeing 707 of the Deutsche Lufthansa from Frankfurt to New York in June and July 1971 and from Frankfurt to Rio de Janeiro in November 1971 and March 1972.

These large scale measurements were complemented by vertical profiles of the H$_2$ mixing ratio, obtained during one flight with chartered aircraft over West France, as well as by several months of monitoring H$_2$ in polluted air at Mainz/West Germany.

In addition, the H$_2$ content in ocean surface waters and about ten vertical profiles of the H$_2$ content in deep water samples were measured during both cruises on the North and South Atlantic.

Experimental

The H$_2$ was measured with a continuously recording instrument based on the mercury oxide technique. The method has been developed at this laboratory and was described previously (Schmidt & Seiler, 1970). The relative error of the improved instrument, now in use, is 1–2 % for a H$_2$ mixing ratio of 0.60 ppmv. The lower limit of detection is 3.0 ppbv. The instrument performs automatic zero checks and calibrations at time intervals of one and three hours, respectively. Calibration gases are supplied from steel cylinders containing air with various H$_2$ mixing ratios, which are checked in the laboratory against primary standards.
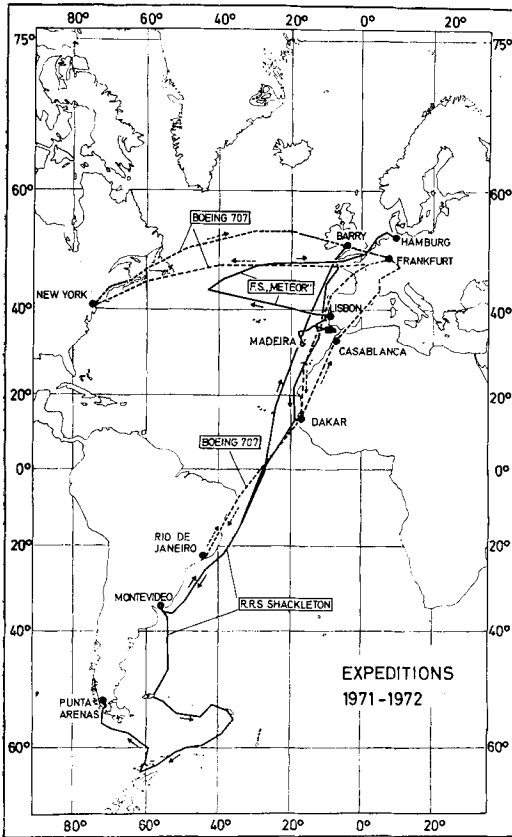
Fig. 2. H_2 measurements over the North and South Atlantic: ——, on board the R.V. *Meteor* and R.R.S. *Shackleton*; – – –, on board commercial aircraft Boeing 707 of the Deutsche Lufthansa.

On board of ships the ambient air was sampled at the bow or at the top of the mast and then pumped at high flow rates through copper tubing to the laboratory. This procedure was carefully checked for contamination on board the R.V. *Meteor*, where one instrument was installed in a laboratory located about 10 m above the foredeck. No difference in the H_2 mixing ratio was detected when ambient air passed alternatively through 50 m long copper tubing and 1 m long glass tubing.

On board commercial (Boeing 707) and chartered (Hawker-Siddeley 125) aircraft the air was taken from the ventilation system. It has been pointed out previously by Seiler & Warneck (1972) that in both types of aircraft CO, and even O_3, is well preserved in ambient air,
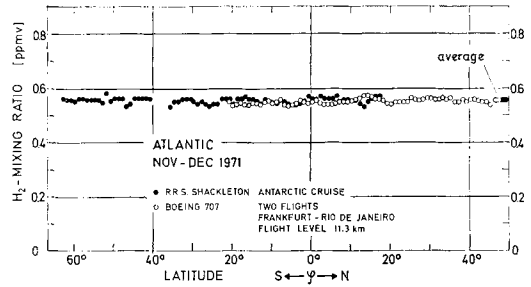

Fig. 3. H_2 mixing ratio in surface air and upper tropospheric air during two expeditions over the Atlantic.

passing the ventilation system. The same should be true for H_2.

Additional instrumentation was required for the analysis of H_2 in ocean water. The method for continuous registration of H_2 in surface waters employed a vertical glass cylinder in which a downward flow of seawater is purged with an equivalent recycled flow of H_2 free air entering at the bottom of the cylinder. In this manner about 98 % of the H_2 dissolved in the seawater is transferred into the gaseous phase. The H_2 mixing ratio of this air is subsequently recorded in the same way as ambient air. The relative error for the water samples is $\pm 15\%$.

For analyses of deep water samples about 5 l of water are sucked into an evacuated 10 l glass flask. A very rapid equilibration between the liquid and the gaseous phase is obtained by this procedure. The flask is then filled up to ambient pressure with H_2 free air before the entire air sample is fed into the H_2 analyzer.

H_2 mixing ration in atmospheric air

The very first measurements in clean air over the North Atlantic already demonstrated that there are no large fluctuations of the H_2 mixing ratio. For periods of several hours the variations often hardly exceeded the standard deviation of the instrument. Similar results have been obtained in the course of all further measurements over the oceans. The data from the southward trip on board the R.R.S. *Shackleton* and from the first flight on board a Boeing 707 aircraft from Frankfurt to Rio de Janeiro are given in Fig. 3 to demonstrate these general features of the H_2 distribution in tropospheric air. Unfortunately, there are no data available
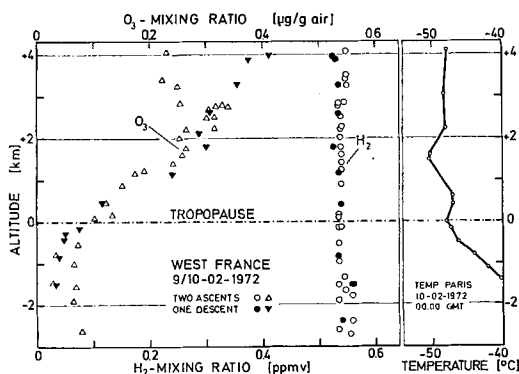
Fig. 4. H_2 and O_3 profiles from one flight with chartered aircraft. Altitudes are given relatively to the tropopause, which was located at 8.5 km height. Temperature profile from sounding at Paris/France.

for the southern upper troposphere beyond 23° S. However, the constant values in surface air— observed on days with quite different weather conditions—strongly suggested that the southern troposphere is well mixed with respect to H_2 both vertically and horizontally.

During several flights on board Boeing 707 the aircraft happened to penetrate the tropopause, especially over the European area while cruising at a constant flight altitude of 10 to 11 km. In such situations simultaneous registrations of both CO and O_3 were used to identify stratospheric air. Whereas the CO mixing ratio dropped down to values of about 0.05 ppmv, which can be considered to represent stratospheric air as shown by Seiler & Warneck (1972), we could never detect any changes of the H_2 mixing ratio.

From these flights with commercial aircraft it was not possible to derive any vertical profiles because of the lack of information on the exact altitude relative to the tropopause. Therefore, we have measured separately three profiles during one flight mission over West France using chartered aircraft (Hawker-Siddeley 125). The results are given in Fig. 4 and are in harmony with the Boeing 707 data. There is no evidence for any gradient in the H_2 mixing ratio either increasing or decreasing up to 4 km above the tropopause.

All data obtained over the Atlantic Ocean as well as a portion of the continuous registrations at Mainz from May to July 1972 are en-

tered in Table 1. From this table we can draw the following conclusions:

(1) There seems to be no difference in the H_2 mixing ratios between the lower stratosphere of the northern hemisphere and the upper troposphere of the southern hemisphere.

(2) There seems to be a statistically significant higher H_2 level in the upper troposphere of the northern than in the southern hemisphere, although the values are only slightly outside the range of the standard error of the averages.

(3) The surface values from the North Atlantic are quite clearly higher than those from the South Atlantic. The apparent vertical gradient of the H_2 mixing ratio within the troposphere is statistically significant over the North Atlantic, but hardly visible over the South Atlantic.

(4) The values from Mainz are definitely the highest.

These data show that for a trace gas like H_2, significant data can only be obtained with recording instruments because only in this case sufficiently large numbers of data with a high relative accuracy can be expected to ensure the necessary statistical significance for the small differences observed. We feel that our results are valid, nevertheless, it would certainly be very desirable to have these results confirmed by an even larger set of data, particularly also from other parts of the world.

The apparent hemispheric difference in the H_2 mixing ratio is also indicated by the data of Bainbridge (1964). Although his data cover only the latitudinal range from 30° S to 30° N, he found about 2.3 % higher values in the northern than in the southern hemisphere over the eastern Pacific Ocean, compared with a difference of 6.0 % for our data from the region between 60° S and 50° N over the Atlantic Ocean.

The H_2 content of seawater

The role of the oceans on the tropospheric H_2 budget has been elucidated by continuous analyses of surface waters. A more detailed summary of the measurements so far available is given by Seiler & Schmidt (1973). A short section of data obtained on the South Atlantic near the island South Georgia is shown in Fig. 5. In the course of all measurements no diurnal trends or any systematic variations could be

Table 1. *Comparison of atmospheric data in the northern and southern hemisphere*

Separate sets are given for data obtained from measurements at the surface (*a*) on board R.V. *Meteor* and R.R.S. *Shackleton* and in the upper troposphere (*b*) and lower stratosphere (*c*) during several flights with commercial aircraft (Boeing 707 of the Deutsche Lufthansa). The numbers of data represent averages for one degree of latitude or longitude. In addition the data for the northern lower stratosphere include 5-min averages obtained during one flight with chartered aircraft (Hawker-Siddeley 125). The data from Mainz are given as 6-h averages

Location	No. of data	Average (ppmv)	Std. dev. of all data (%)	Std. error of average (%)	Range of avg. values within std. error (ppmv)
N. Atlantic					
(*a*)	132	0.585	4.9	0.43	0.5825–0.5875
(*b*)	290	0.558	3.3	0.20	0.5569–0.5591
(*c*)	81	0.548	2.5	0.29	0.5464–0.5496
S. Atlantic					
(*a*)	94	0.552	1.8	0.21	0.5508–0.5532
(*b*)	45	0.545	2.7	0.32	0.5433–0.5467
Mainz (Germany)	300	0.800	20.1	1.16	0.7907–0.8093

detected. The H_2 content of surface waters in the North and South Atlantic varied from 0.8 to 5.0×10^{-5} ml/l H_2O, corresponding to saturation factors of $f = 0.8$ to $f = 5.4$, where $f = 1$ represents equilibrium conditions between surface water and air and $f < 1$ or $f > 1$ indicates under- or supersaturation, respectively.

Several vertical profiles from the North Atlantic showed H_2 contents decreasing with depth to equilibrium values compared with surface air and distinct layers slightly enriched in H_2. Very high supersaturations approaching a factor of $f = 20$ were found in layers with high nutrient supply and high bacteria concentrations, especially in the Gulf of Cadiz (Fig. 6).
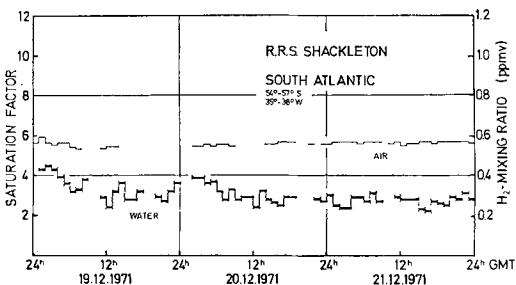
Different strains of bacteria isolated from

water samples collected at these depths have been positively identified at this laboratory to produce hydrogen (Junge et al., 1972). Microbiological activity, therefore, might be a probable explanation for H_2 supersaturations in ocean waters.
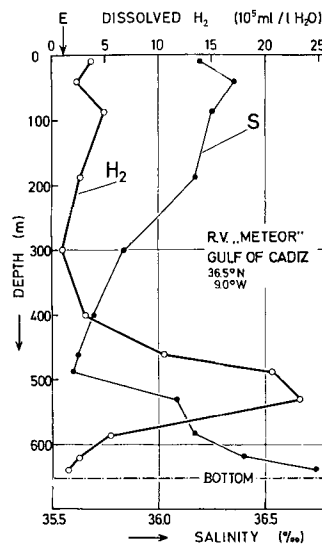
Fig. 6. Vertical profiles of the H_2 content (open circles) and salinity (closed dots) in the Gulf of Cadiz. The increase in salinity below 500 m depth is caused by the outflow of mediterranean water at the bottom. Salinity data by Roether (1972).

Fig. 5. H_2 content of surface water (thick line) and surface air (thin line) obtained from continuous analyses. A saturation factor of $f = 1$ would represent equilibrium conditions between air and water.

Sources and sinks

The significant difference between the average H_2 mixing ratios in both hemispheres suggests either additional, though not major, sources in the northern hemisphere, or equivalent sinks in the southern hemisphere.

The first possibility is strongly supported by the data compiled in Table 1. The apparent vertical gradient of the H_2 mixing ratio in the northern troposphere must be caused by sources located near the earth's surface. Such sources can be:

    (a) anthropogenic activity,

    (b) the oceans,

    (c) the soil,

    (d) photochemical production in the troposphere.

The suggestion of a major sink in the southern hemisphere must be rejected. So far as photochemical reactions are concerned, there is as yet no indication for any process in the stratosphere or in the troposphere which is dominant in the southern hemisphere. We know that the oceans act as a source, thus leaving the continents to be the only part of the earth's surface, which can act as a sink. However, due to the distribution of land and water this sink should be even much larger in the northern than in the southern hemisphere.

Possible sinks for H_2 are:

    (e) photochemical destruction in the troposphere,

    (f) the stratosphere,

    (g) the soil.

We will now discuss the individual sources and sinks in detail.

SOURCES

(a) Anthropogenic activity

The data from Mainz, given in Table 1, show considerably higher values and larger fluctuations than the data obtained for surface air over the North Atlantic. In Fig. 7 the Mainz data are plotted as a windrose.

The institute is located on the southwestern fringe of the city. Big industry and regions with high traffic densities occur only to the north and northeast. The other parts of the vicinity are predominantly rural areas. Therefore, the
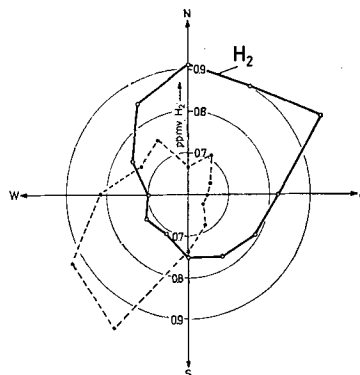
Fig. 7. H_2 mixing ratio at Mainz/Germany from May to July 1972 as a function of wind direction (solid line) and the frequency distribution of wind directions in relative units (dashed line). Note that the center value of the H_2 scale is 0.6 ppmv. Data accompanied with wind speeds below 2 m/sec are excluded.

higher mixing ratios accompanying winds from the north and northeast are a definite proof for an anthropogenic H_2 production while lower values accompanying southwesterly winds indicate less polluted air.

There is only very little information available from the literature on H_2 production rates of different anthropogenic processes. The H_2 content of automotive exhaust gases is in the range of 1–5 % by volume, depending on the operation conditions of the engine (see e.g. D'Alleva & Lovell, 1936; Jones et al., 1971). No quantitative data on industrial processes are available. However, it appears reasonable to utilize the known anthropogenic CO production rates to obtain an estimate of the total anthropogenic H_2 production on the basis of simultaneous registrations of CO and H_2 at Mainz during May and June 1972.

The average H_2 mixing ratio at Mainz during this period was $m_M(H_2) = 0.780$ ppmv, i.e. 0.195 ppmv higher than the North Atlantic background value $m_{NA}(H_2) = 0.585$ ppmv. The corresponding values for CO were $m_M(CO) = 0.63$ ppmv and $m_{NA}(CO) = 0.18$ ppmv (Seiler, 1972).

For the purpose of this discussion we assume that the North Atlantic background values are similar to those in Central Europe. Since the major anthropogenic sources for H_2 and CO are exhaust gases, the distribution of sources for both gases can be assumed to be similar too.

Under these assumption the total flux from a source to the surroundings for any two gases, which can be considered sufficiently conservative outside the source area, such as H_2 and CO, must be proportional to the gradients of the concentrations $(m\varrho)$ in the vicinity of the source. Since the total flux is equal to the total anthropogenic production rate Q_A within the source area, we have:

$$\frac{Q_A(H_2)}{Q_A(CO)} = \frac{(m(H_2)\,\varrho(H_2))_M - (m(H_2)\,\varrho(H_2))_{NA}}{(m(CO)\,\varrho(CO))_M - (m(CO)\,\varrho(CO))_{NA}} \quad (1)$$

where $\varrho(H_2) = 0.089$ mg/cm^3 and $\varrho(CO) = 1.25$ mg/cm^3 are the densities of H_2 and CO, respectively. If Mainz can be considered representative for the global production rates Q'_A, we obtain

$$\frac{Q'_A(H_2)}{Q'_A(CO)} = \frac{Q_A(H_2)}{Q_A(CO)} \quad (2)$$

and with $Q'_A(CO) = 4 \times 10^{14}$ g/yr (Jaffe, 1972) we obtain $Q'_A(H_2) = 13 \times 10^{12}$ g/yr. This annual production is equal to 8 % of the total tropospheric reservoir and is located for at least 80 %, in the northern hemisphere, due to the population distribution.

(b) The oceans

Due to the general supersaturations of surface waters with respect to H_2, the oceans must be regarded as a source of atmospheric H_2 in both hemispheres.

The net transfer J of H_2 from the surface water to the air was estimated by Seiler & Schmidt (1973) on the basis of the model for the exchange of gas between water and air through a laminar boundary layer at the water surface, developed by Broecker & Peng (1971) as

$$J = \frac{D}{z}\varrho(H_2)\,(C - \alpha p) \quad \text{g/cm}^2\text{sec}$$

where D is the diffusion coefficient of H_2 in water $= 5.8 \times 10^{-5}$ cm^2/sec (Davidson & Cullen, 1957), assuming a water temperature of $t = 20°$C, and z is the thickness of the laminar boundary layer, which may be reasonably assumed to be 25 μ for a global estimation (Münnich, 1972). The solubility coefficient of H_2 in seawater, α, was calculated for $t = 20°$C from data on the salting-out constants for a 3.5 % NaCl solution,

given by Morrison & Billett (1952), to be 1.6×10^{-2} cm^3 H_2/cm^3 H_2O at.; p is the partial pressure of H_2 in surface air, $= 0.56 \times 10^{-6}$ at. for a global estimation.

For an average H_2 content of $C = 2.5 \times 10^{-8}$ cm^3/cm^3 of seawater, corresponding to a supersaturation by a factor $f = 3$, the global oceanic source strength is 4.0×10^{12} g H_2/yr for the total surface of the oceans $A_0 = 3.6 \times 10^{18}$ cm^2.

Because of the fact that measurements of H_2 in ocean surface waters are somewhat restricted until now, and because of the uncertainties concerning the different parameters involved in this model, this number is a rough estimate only.

According to the distribution of the oceans in both hemispheres the oceanic H_2 production is larger in the southern hemisphere but the excess is less than 10^{12} g/yr, compared with the northern hemisphere. This amount is too small to balance the anthropogenic source in the northern hemisphere.

(c) The soil

Several processes at the land surface are known that might produce significant amounts of H_2. Among these, bacterial fermentation seems to be of major importance. A study by Kojama (1964) on production rates of a variety of fields is not very reliable because he extrapolapolated the results of laboratory tests to the whole earth's surface. For the same reason any quantitative correction of his estimate of 10^{11} g/yr—about 80 % of which are even volcanic exhalations—must be considered speculative. Moreover, under natural conditions, H_2 often appears to be only an intermediate product of fermentation processes and is probably consumed by other species of the microbial population. In addition it is known that H_2 is rapidly consumed by microbial processes at the soil surface, as we will discuss later.

(d) Photochemical production in the troposphere

In recent years comprehensive studies tried to develop a chemical model of the troposphere and it was postulated that H_2 should be a product of the CH_4 oxidizing chain reactions (see e.g. Wofsy et al., 1972; Levy, 1972). Starting with the reaction of CH_4 with OH radicals, CH_2O is formed as an intermediate product, from which H_2 is produced by photolysis (Cal-

vert et al., 1972) at wavelengths between 3 000 and 3 600 Å according to the reaction

$$CH_2O + h_\nu \rightarrow H_2 + CO \qquad (4)$$

With an improved model Levy (1973) calculated a tropospheric H_2 production rate of 8.7×10^{10} molecules/cm^2 sec, corresponding to a global source strength of 46.0×10^{12} g/yr, if this rate is extrapolated to the whole troposphere. However, based on other considerations, it appears that the rate of the CH_4 oxidation is overestimated by a factor of 5 to 10. For example, it is suggested by Warneck (1974) from NO_3^- budget calculations that the OH radical concentration is much smaller than assumed in these models. Accordingly this would reduce the rate of H_2 formation from CH_4 oxidation.

In addition, the interhemispheric distribution of CO, which is the major product of the CH_4 oxidation mechanism, again is not in harmony with the production rates provided by these models (Seiler, 1974). The photochemical H_2 production, therefore, should be reduced by a factor of 5 to 10 to an amount of 4.6 to 9.2 × 10^{12} g/yr.

SINKS

(e) Photochemical detruction in the troposphere

Tropospheric chemistry also suggests a sink for H_2. The H_2 consuming reaction is

$$OH + H_2 \rightarrow H_2O + H \qquad (5)$$

(Greiner, 1969). The destruction rates, as calculated by Levy (1973, Tab. 9) suggest an average tropospheric H_2 mixing ratio of $m = 0.75$ ppmv for photochemical steady state. If the same rates are employed for the actual mixing ratios, the photochemical sink is 37×10^{12} g/yr or about 80% of the photochemical source. Since the above reaction also depends on the OH radical concentration, the resulting sink again should be reduced—to an amount of 3.7–7.3 × 10^{12} g/yr.

(f) The stratosphere

The role of the stratosphere, which acts as a sink for many trace gases, is not quite clear with respect to H_2. From our data the stratosphere does not seem to be a potential sink due to the lack of any vertical gradient of the H_2

mixing ratio in the lower stratosphere up to 4.0 km above the tropopause.

Measurements by Ehhalt & Heidt (1973) showed a maximum H_2 mixing ratio at 27 km indicating that the stratosphere might be a source rather than a sink for atmospheric H_2.

(g) The soil

Several tests performed at this institute by Liebl (1971) have definitely proved that different types of soils act as very effective sinks for H_2. He used a glass box placed upside down on the surface of the soil and filled with air containing ambient H_2 mixing ratios. The decrease of the H_2 content in the glass box was then measured for different soil temperatures. In addition to these laboratory tests, similar in situ measurements with desert type soil were performed near Albuquerque, New Mexico, USA. The results are plotted in Fig. 8.
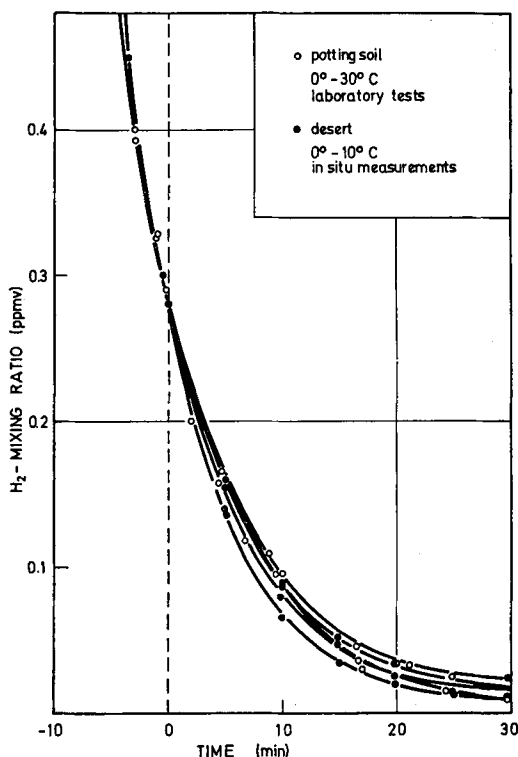

Fig. 8. H_2 consumption at the surface of soils. In situ measurements were started with different H_2 mixing ratios. Therefore, all curves are standardized to $m = 0.28$ ppmv for zero exposure time. Laboratory tests made by Liebl (1971).

The H_2 mixing ratio within the glass box drops down rapidly in an exponentiell manner to a value in the range of about 20–30 ppbv. Therefore, the uptake mechanism can be characterized as a first order reaction of H_2 at the surface of the soil, i.e. the uptake *rate* is proportional to the H_2 concentration. Undoubtedly the H_2 consumption by soil is due to microbiological activity.

The mathematical equation for the decrease of the H_2 mixing ratio m with the time T is

$$(m - m_\infty) = (m_0 - m_\infty)e^{-cT} \qquad (6)$$

m_0 is the initial value and m_∞ is the final value of the H_2 mixing ratio observed during an experiment; the coefficient c is directly proportional to the exposed surface area F and inversely proportional to the amount M of H_2 in the glass box, $M = Vm_0\varrho(H_2)$, where V is the volume of the glass box. Thus we have

$$c = P\frac{F}{Vm_0\varrho(H_2)} \quad \text{sec}^{-1} \qquad (7)$$

where P represents the H_2 uptake rate at the surface. From eq. (6) and (7) we obtain

$$P = \frac{m_0\,V\varrho(H_2)}{FT}\ln\frac{m_0 - m_\infty}{m - m_\infty} \quad \text{g/cm}^2\text{ sec} \qquad (8)$$

Our measurements provided values of P in the range from 2×10^{-12} g H_2/cm² sec to 4×10^{-12} g H_2/cm² sec for different types of soil (e.g. potting soil, loess, desert type soil) rather independent of the temperature of the soil. Although these data must be considered very preliminary and should be confirmed by more detailed studies, an average uptake rate of $P = 3 \times 10^{-12}$ g H_2/cm² sec may be used to estimate the global effect of this sink. The annual H_2 consumption by the earth's surface—excluding the polar regions—i.e. $A_1 = 1.2 \times 10^{18}$ cm², is obtained to be 12.0×10^{12} g/yr or about the same as the anthropogenic sources.

Due to the distribution of the land mass between the two hemispheres, the major amount of H_2 is consumed in the northern hemisphere.

In Table 2A a summary of all sources and sinks so far known is given. The amounts are subdivided for both hemispheres in accord with the following considerations. We denote with Q the sources, with S the sinks, and their type and location with the index

A: anthropogenic
O: oceanic
S: soil surface
C: photochemical
N: northern hemisphere
S: southern hemisphere

(e.g. Q_A is the global a thropogenic H_2 production of which Q_{AN} is the northern hemispheric portion).

The industrial activity is concentrated within the northern hemisphere to at least 85 %, thus

$$Q_{AN} = 0.85Q_A. \qquad (9)$$

The oceanic source is divided according to area

$$Q_{ON} = 0.40Q_O. \qquad (10)$$

Due to the 10 % higher CH_4 mixing ratio in the northern hemisphere (Lamontagne et al., 1973), we assumed

$$Q_{CN} = 0.525Q_C. \qquad (11)$$

The H_2 mixing ratio was found to be about 4.5 % higher in the northern hemisphere. Therefore, the photochemical sink is

$$S_{CN} = 0.51S_C. \qquad (12)$$

For latitudes below 60° the land surface area in the northern hemisphere is about twice that in the southern hemisphere:

$$S_{SN} = 0.66S_S. \qquad (13)$$

According to the data in Table 2 A the global H_2 production is $21.6 - 26.2 \times 10^{12}$ g/yr or 13.5–16.5 % of the tropospheric reservoir. Correspondingly, the H_2 residence time in the troposphere should be 6 to 7 years.

Taking into account the considerable uncertainties of the estimates of sources and sinks, including even the most uncertain effect of photochemistry, the tropospheric H_2 cycle—from these direct estimations—seems to be balanced for about 75 %.

A very important result of these estimations is that the anthropogenic source seems to be about 50 % of the global H_2 production. Unless important additional *natural* sources will be detected in the future, H_2 must be regarded as a "pollutant" in the atmosphere. This forces to the conclusion that the H_2 content in atmo-

Table 2.

	A Northern Southern Hemisphere		B Northern Southern Hemisphere	
Sources × 10^{12} g/yr				
Anthropogenic activity Q_A	11.0	2.0	21.7	3.8
Oceans Q_A	1.6	2.4	1.6	2.4
Photochemistry Q_C	2.4–4.8	2.2–4.4	3.7	3.3
Various fields	> 0.1^a			
Volcanoes				
Sinks × 10^{12} g/yr				
Photochemistry S_C	1.9–3.7	1.8–3.6	2.8	2.7
Soils S_S	8.0	4.0	20.7	10.3
Global production $Q × 10^{12}$ g/yr	21.6–26.2		36.5	
Global consumption $S × 10^{12}$ g/yr	15.7–19.3		36.5	
Average mixing ratio m (ppmv)	0.575		0.550	
Average concentration n (ug/m³)	51.2		49.0	
Atmospheric reservoir $M_A × 10^{12}$ g	104.0		100.0	
Tropospheric reservoir $M_T × 10^{12}$ g	81.5		78.0	
Tropospheric residence time yr	6.1–7.4		4.4	

^{a} From Kojama (1964).

Fig. 9. Anthropogenic production Q_A (– – –) and microbiological sink S_S (–·–) as functions of the photochemical and the oceanic production Q_C and Q_O as given by the equations (22) and (23). The vertical lines accentuate distinct values of Q_C: Levy's (1973) results = L/1 and the range of the estimated reduced production rates L/5 to L/10 as discussed in this paper.

spheric air must have inreased with time in correlation with the increase of the global fuel consumption, because industrial and automotive fuel combustion most probably are the major anthropogenic H_2 producing processes.

The world's consumption of gasoline, gas oil, and fuel oil was doubled from 1951 to 1965 (OECD, 1967). On the basis of these figures we expect the H_2 mixing ratio to have been 0.40 ppmv in 1950.

In Fig. 1 this suggested H_2 increase is compared with the observations. Unfortunately the data so far available are not good enough to detect such a trend. This is primarily due to the lack of measurements in uncontaminated air at earlier times and also to the limited accuracy of the different methods employed. We feel that the low accuracy is also responsible for the occurrence of values as low as 0.13 ppmv.
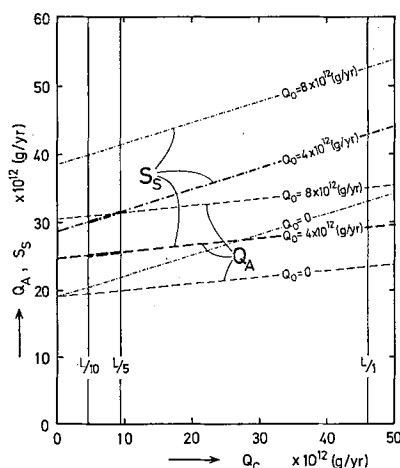
Although it cannot be excluded that some of these low values are caused by sinks at the earth's surface during very stagnant weather conditions, they are quite difficult to understand on the basis of our present data. During all our continuous registrations the H_2 mixing ratio never decreased below 0.52 ppmv.

The tropospheric H_2 budget

There is still another important information which can be used for budget considerations: the difference between the hemispheres. It can be shown that for steady state conditions and for residence times of the constituent of more than one year the hemispheric behavior of a trace constituent may be approximated by a simple two box model, employing an exchange rate between the hemispheres of about one per year (Czeplak and Junge, 1973).

On the basis of such a model we obtain the balance equations

$$Q_{AN} + Q_{ON} + Q_{CN} - S_{CN} - S_{SN} - k(M_{TN} - M_{TS})$$
$$= 0; \tag{14}$$

$$Q_{AS} + Q_{OS} + Q_{CS} - S_{CS} - S_{SS} + k(M_{TN} - M_{TS})$$
$$= 0; \tag{15}$$

for steady state conditions in the northern and southern hemisphere, respectively. We have assumed that the source strength of the soil is negligible as indicated in Table 2A, i.e. S_{SN} and S_{SS} are the net sinks. Furthermore, any influence of the stratosphere either as a source or a sink is neglected in accord with the above discussion.

The terms KM_{TN} and kM_{TS} represent the interhemispheric exchange of air between both hemispheres, where k is the exchange rate = 1 yr^{-1} and M_{TN} and M_{TS} are the tropospheric H$_2$ reservoirs in grams. M_{TN} and M_{TS} can be calculated from the data in Table 1; because of the vertical density profile in the atmosphere we attach twice the weight to the surface values of the mixing ratio as compared with the values for the upper troposphere. The average H$_2$ mixing ratios are then

$\overline{m}_N = 0.575$ ppmv in the northern troposphere

$\overline{m}_S = 0.550$ ppmv in the southern troposphere

with a difference of 4.5 %. The average height of the tropopause is about 11 km and thus the troposphere contains 78 % of the global air mass. The height of the homogeneous atmosphere is $H = 8 \times 10^5$ cm and according to

$$M_T = 0.78 \times H \times \varrho(H_2) \times \overline{m} \qquad (16)$$

we obtain $M_{TN} = 81.5 \times 10^{12}$ g, $M_{TS} = 78.0 \times 10^{12}$ g, and the difference $M_{TN} - M_{TS} = 3.5 \times 10^{12}$ g.

Addition and subtraction of (14) and (15) lead to the global balance equations

$$(Q_{AN} + Q_{AS}) + (Q_{ON} + Q_{OS}) + (Q_{CN} + Q_{CS})$$
$$- (S_{CN} + S_{CS}) - (S_{SN} + S_{SS}) = 0; \qquad (17)$$

$$(Q_{AN} - Q_{AS}) + (Q_{ON} - Q_{OS}) + (Q_{CN} - Q_{CS})$$
$$- (S_{CN} - S_{CS}) - (S_{SN} - S_{SS})$$
$$= 2k(M_{TN} - M_{TS}) \qquad (18)$$

the latter relating the distribution of sources and sinks to the difference of the H$_2$ mixing ratios in both hemispheres. We may now employ the equations (9) through (13) in connection with equation

$$S_C = 0.79 Q_C \qquad (19)$$

according to the calculations reported by Levy

(1973, Table 9) as we have discussed previously, and the equations (17) and (18) transform into

$$Q_A + Q_O + 0.21 Q_S - S_S = 0; \qquad (20)$$

$$0.7 Q_A - 0.2 Q_O + 0.034 Q_C - 0.33 S_S$$
$$= 2k(M_{TN} - M_{TS}). \qquad (21)$$

For four quantities we have only two independent equations. However, we may express any two quantities as functions of the two others. Choosing Q_O and Q_C as independent variables we obtain:

$$Q_A = 1.43 Q_0 + 0.10 Q_C + 5.41(M_{TN} - M_{TS}); \qquad (22)$$

$$S_S = 2.43 Q_0 + 0.31 Q_C + 5.41(M_{TN} - M_{TS}); \qquad (23)$$

The graphic resolution of these equations is plotted in Fig. 9 for $k(M_{TN} - M_{TS}) = 3.5 \times 10^2$ g/yr and values of Q_0 ranging from 0.0 to 8.0×10^{12} g/yr.

We see that both Q_A and S_S should be by a factor of about two or three higher than the direct estimates in Table 2A. Even if the photochemical production Q_C and the oceanic source Q_O are neglected, both Q_A as well as S_S must exceed values of 19×10^{12} g/yr to satisfy the interhemispheric difference in the H$_2$ mixing ratio. If we now introduce the estimated values for Q_0 and Q_C from Table 2A we obtain an anthropogenic production rate Q_A in the range of 25.0 to 26.0×10^{12} g/yr and the sink at the surface of the soil S_S results in 30.0 to 30.0×10^{12} g/yr.

Fig. 9 shows that with increasing values for Q_C—up to the results given by Levy (1973)—Q_A and S_S do not increase very much. This considerations on the interhemispheric exchange, therefore, do not allow to draw any conclusions with respect to Q_C and S_C on the basis of the assumption used. Since the values of Q_A and S_S in Fig. 9 are already higher than those directly estimated (Table 2A), we feel that low values of Q_C and S_C are more likely.

We suggest, therefore, to regard as best values of Q_A and S_S those, which relate to $Q_0 = 4.0 \times 10^{12}$ g/yr and $Q_C = 7.0 \times 10^{12}$ g/yr (Table 2B). The corresponding H$_2$ residence time is about 4 years. The reported values certainly will be subjected to revision if better data on the distribution of the sources and sinks—equations (9) through (13)—and more detailed information on the production rates

Q_O and Q_C become available. Nevertheless, we feel confident that the distribution and the strength of the sources and sinks as given in Table 2 are of the correct magnitude to agree with the observed difference of the H_2 mixing ratio in both hemispheres.

Concluding remarks

Because the H_2 residence time might be affected by the strength of the photochemical source, more accurate information is needed on this item. On the other hand, measurements of the H_2 mixing ratio in the stratosphere, preferably in the southern hemisphere, would be valuable for more quantitative calculations of the atmospheric H_2 budget. Since the H_2 cycle is coupled to the CH_4 and CO cycles via microbiological and/or photochemical processes, simultaneous measurements of these gases in various environments would provide much needed information to attain a better understanding of the cycles of each of these gases.

The importance of such measurements has been demonstrated in this work with respect to the role of the stratosphere as well as for estimating the anthropogenic H_2 source.

It has been suggested by various authors that the origin of tropospheric H_2 might be the photolysis of water vapor in the upper atmosphere (see e.g. Suess, 1966). However, the almost constant H_2 mixing ratio in the tropopause region indicates that the new flux of H_2 between the troposphere and the stratosphere is very small compared with the estimated tropospheric sources and sinks, if it exists at all (see e.g. also Junge, 1972). Undoubtedly the rather fast tropospheric cycle with a residence time of about 4–7 years determines the tropospheric and the lower stratospheric H_2 level.

Acknowledgements

REFERENCES

Bainbridge, A. E. 1964. Variations and production rates of hydrogen and methane in the southern and northern hemisphere. Unpublished data.

Broecker, W. S. & Peng, T. H. 1971. The vertical distribution of radon in the Bomex Area. *Earth. Planet. Sci. Letters 11*, 99–108.

Calvert, J. G., Kerr, J. A., Demerjan, K. L. & McQuigg, R. D. 1972. Photolysis of formaldehyde as a hydrogen atom source in the lower atmosphere. *Science 175*, 751–752.

Czeplak, G. & Junge, C. 1973. Studies of interhemispheric exchange in the troposphere by a diffusion model. Paper presented on the "*Second IUTAM-IUGG Symposium on Turbulent Diffusion in Environmental Pollution*, Charlottesville, Virginia, USA.

D'Alleva, B. A. & Lovell, W. G. 1936. Relation of exhaust gas composition to air-fuel ratio. *SAE Journal (Trans) 38*, 90–98, 116.

Davidson, J. F. & Cullen, M. A. 1957. The determination of diffusion coefficients for sparingly soluble gases in liquids. *Trans. Instn. Chem. Engrs. 35*, 51–60.

Ehhalt, D. H. 1971. Private communication.

Ehhalt, D. H. 1973 and Heidt, L. E. The concentration of molecular H_2 and CH_4 in the stratosphere. *Pure Appl. Geophys. (PAGEOPH), 106–108*, 1352–1360.

Ehhalt, D. H., Roether, W. & Stich, W. 1966. Der Anstieg des Tritiumgehaltes im atmosphärischen Wasserstoff seit 1960. *Z. Naturforschung 21a*, 1703–1709.

Glueckauf, E. & Kitt, G. P. 1957. The hydrogen content of atmospheric air at ground level. *Quart. J. R. Met. Soc. 83*, 522–528.

Greiner, N. P. 1969. Hydroxyl radical kinetics by kinetic spectroscopy. V. Reactions with H_2 and CO in the range 300–500°K. *J. Chem. Phys. 51*, 5049–5051.

Jaffe, L. S. 1972. Carbon monoxide in the biosphere: Sources, distribution, and concentrations. Paper presented at the *Meeting on Sources, Sinks, and Concentrations of Carbon Monoxide and Methane in the Earth's Environment*. St. Petersburg, Florida, USA.

Jones, J. H., Kummer, J. T., Otto, K., Shelef, M.

& Weaver, E. E. 1971. Selective catalytic reaction of hydrogen with nitric oxide in the presence of oxygen. *Environ. Sci. Technol. 5*, 790–798.

Junge, C. 1972. The cycle of atmospheric gases—natural and man-made. *Quart. J. R. Met. Soc. 98*, 711–729.

Junge, C., Seiler, W., Schmidt, U., Bock, R., Greese, K. D., Radler, F. & Rüger, H. J. 1972. Kohlenmonoxid- und Wasserstoffproduction mariner Mikroorganismen im Nährmedium mit synthetischem Seewasser. *Naturwissenschaften 59*, 514–515.

King, W. H. 1970. The monitoring of hydrogen, methane, and hydrocarbons in the atmosphere. *Environ. Sci. Technol. 4*, 1136–1141.

Kojama, T. 1964. Biochemical studies on lake sediments and paddy soils and the production of atmospheric methane and hydrogen. In *Recent Researches in the Field of Hydrosphere, Atmosphere, and Nuclear Geochemistry*. Maruzen, Tokyo, Japan.

Lamontagne, R. A., Swinnerton, J. W. & Linnenbom, V. J., 1973, Methane distribution in the world oceans. Paper presented at the *CACGP Symposium on Trace Gases*, Mainz, W.-Germany.

Levy, H. 1972. Photochemistry of the lower troposphere. *Planet. Space Sci. 20*, 919–935.

Levy, H. 1973. Photochemistry of the troposphere. In *Advances in Photochemistry*, Vol. 9 (ed. J. N. Pitts, G. S. Hammond & W. A. Noyes). Wiley Interscience, New York, USA (in press).

Liebl, K. 1971. Der Boden als Senke und Quelle für das atmosphärische Kohlenmonoxid. *Master thesis*, Institut für Meteorologie, Johannes-Gutenberg-Universität, Mainz, West Germany.

Morrison, T. J. & Billett, F. 1952. The salting-out of non-electrolytes. Part II. The effect of variation in non-electrolyte. *J. chem. Soc. 1952*, 3819–3822.

Münnich, K. O. 1972. Private communication.

OECD, 1967. Basic statistics of energy 1951–1965. *Statistical Bulletins*, Paris, France.

Paneth, F. A. 1937. The chemical composition of the atmosphere. *Quart. J. Roy. Meteorol. Soc. 63*, 433–438.

Roether, W., 1972. Private communication.

Schmidt, U. & Seiler, W. 1970. A new method for recording molecular hydrogen in atmospheric air. *J. Geophys. Res. 75*, 1713–1716.

Scholz, T. G., Ehhalt, D. H., Heidt, L. E. & Martell, E. A. 1970. Water vapor, molecular hydrogen, methane, and tritium concentrations near the stratopause. *J. Geophys. Res. 75*, 3049–3054.

Seiler, W. 1972. Unpublished data.

Seiler, W. 1974. The cycle of atmospheric CO. *Tellus*, this issue.

Seiler, W. & Warneck, P. 1972. Decrease of the carbon monoxide mixing ratio at the tropopause. *J. Geophys. Res. 77*, 3204–3214.

Seiler, W. & Schmidt, U. 1973. Dissolved nonconservative gases in seawater. In *The sea*, Vol. V (ed. E. D. Goldberg). Wiley Interscience, New York, USA (in press).

Suess, H. E. 1966. Some chemical aspects of the evolution of the terrestrial atmosphere. *Tellus 18*, 207–211.

Warneck, P. 1974. The role of OH and HO_2 radicals in the troposphere. *Tellus*, this issue.

Wofsy, S. C., McConnell, J. C. & McElroy, M. B. 1972. Atmospheric CH_4, CO, and CO_2. *J. Geophys. Res. 77*, 4477–4493.

МОЛЕКУЛЯРНЫЙ ВОДОРОД В АТМОСФЕРЕ

Изучалось распределение молекулярного водорода в тропосфере, нижней стратосфере, также как и в поверхностных водах Атлантического океана. Найдено, что в тропосфере и нижней стратосфере южной части северного полушария объемное отношение смеси довольно постоянно и составляет $(5,48 \pm 0,15) \cdot 10^{-7}$. Статистически значимые более высокие концентрации $(5,58 \pm 0,19) \cdot 10^{-7}$ и $(5,85 \pm 0,29) \cdot 10^{-7}$ были получены в северном полушарии для верхней тропосферы и в приземном слое, соответственно. Данные не указывают на какие-либо изменения в отношении смеси H_2 в нижней стратосфере до уровней вплоть до 4 км над тропопаузой. Поверхностные воды Атлантики представляются примерно втрое перенасыщенными. Вертикальные профили концентрации H_2 показывают два определенных максимума на глубинах между 500 и 1 000 м. Обсуждение источников и стоков приводит к оценке времени жизни H_2 в тропосфере от 6 до 7 лет.