New tritium and deuterium measurements in atmospheric hydrogen

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ABSTRACT

Tritium and deuterium analysis were made on samples of atmospheric hydrogen collected in 1961. A positive correlation exists between tritium and deuterium. The heaviest samples yield a value of about +18 % S.M.O.W. for atmospheric hydrogen. The deuterium concentration of the industrial hydrogen varies from −18 % to −22 %. The industrial hydrogen is partially ascribed to hydrogen from automobile exhaust gas.

The corrected tritium concentration in atmospheric hydrogen continues to increase, doubling every two years. Several large tritium peaks are correlated with Soviet weapons tests.

As it is well known, the atmosphere contains about 1/2 part per million of gaseous hydrogen. In a sample of atmospheric hydrogen taken in 1948 FALTINGS & HARTECK (1950) discovered tritium and measured a concentration of 3.8×10^3 T.U. One T.U. (i.e. Tritium Unit) corresponds to a tritium concentration of one tritium atom per 10^{18} H-atoms. Of another sample, again collected in 1948, BAINBRIDGE, SUESS & FRIEDMAN (1961) reported a T-concentration of 3.5×10^4 T.U.; these two measurements differ by one order of magnitude. In the sample mentioned last the D-concentration was stated at −9.6 % in relation to S.M.O.W.

Tritium, produced by cosmic radiation in the stratosphere, is an indicator for exchange processes between stratosphere and troposphere; still open is the question, whether some tritium is induced into the earth's atmosphere from interplanetary sources, e.g. from the sun. Investigation of this latter problem has been complicated since the beginning of nuclear test explosions. These man-made injections of radioactive substances as well as of tritium into the atmosphere, on the other hand, opens ways and means to improve the chances to investigate exchange processes in the atmosphere.

During the last ten years research by BISHOP & TAYLOR (1960) has shown that since 1954 tritium concentration has doubled every two years; this rise, due to atomic bomb explosions, is superposed by variations that are relatively high and of short duration. Additional measurements of deuterium concentration by BEGEMANN & FRIEDMAN (1959) demonstrated that some of these variations could be explained by a variable admixture of industrially produced hydrogen. This hydrogen admixture is, for all practical purposes, free of tritium and low in deuterium, which means that the hydrogen admixture leads to a lowering of both tritium and deuterium-concentration, so that these variations show a positive correlation between tritium and deuterium. Therefore, the measured tritium values must be corrected on the basis of deuterium measurements in order to get the true conditions of an atmosphere undisturbed by any admixture. Furthermore, it has been found by GONSIOR & FRIEDMAN (1962) that some of these tritium peaks cannot be explained in this way; those peaks are due to the addition of man-made tritium into the atmosphere by Soviet nuclear test explosions or by other artificial tritium injections. These tritium peaks show no correlation with deuterium values, because deuterium, in these cases,

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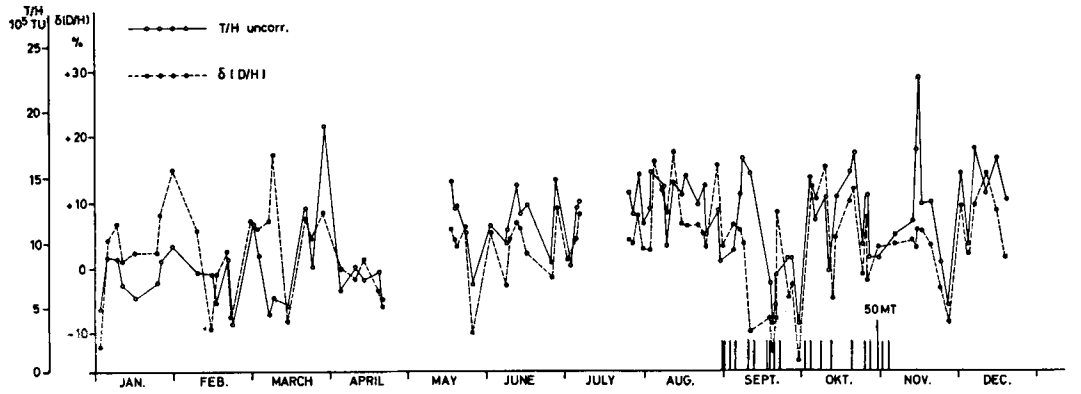


FIG. 1. Tritium and deuterium analysis of atmospheric samples from 1961, plotted as a function of date of collection of samples. The uncorrected tritium values (open dots) are given in 10^5 T.U., the deuterium values (full dots) are given in per cent deviation of standard mean ocean water (S.M.O.W.).

has not been injected into the atmosphere in quantities large enough to be detected.

In a 1960 sample EHHALT *et al.* (1963) found a tritium concentration of about 10^6 T.U. and in two samples of 1962 they found about 1.8×10^6 T.U.

In this paper, we want to report on tritium and deuterium measurements which we made on samples of atmospheric hydrogen taken in 1961. At that time we were especially interested in the question whether tritium concentration is still rising during the test moratorium.

BEGEMANN (1963), in some samples collected in 1961, could not find any significant rise in tritium concentration and also no good correlation between tritium and deuterium. This might have been due to his having taken his samples in the Ruhr Valley, an area densely industrialized; therefore the chance of contamination from many and different sources of hydrogen may have been rather high.

In September 1961 the Soviet Union resumed nuclear weapon experiments, and we believed that it would be quite interesting to gain some knowledge of the influence of these newly started experiments on the changes of tritium activity in atmospheric hydrogen. As usual the samples were taken at the He outlet of a large industrial liquifaction plant; the noble gas mixture, together with the H, was led through a CuO oven, so that the H could be collected in the form of water. Contrary to our former measurements (GONSIOR *et al.*, 1962), we used a liquid scintillation counter for measuring tritium activity. Deuterium was measured, as we did before, by mass spectrometer.

The advantage of using liquid scintillators is mainly that one is able to bring the tritium in form of water into the detector. In this way one can measure large amounts of material and consequently get high counting rates. For a scintillator we used a mixture of 120 grams naphthalene, 4 grams PPO and 0.05 grams POPOP dissolved in one liter of dioxan. A maximum of 23% of water can be admixed. At this maximum admixture the efficiency, however, is relatively low. We, therefore, added no more than 2% water and attained efficiency of about 20%. In order to suppress the dark current pulses, we channeled the light pulses through two multipliers with preamplifiers, amplifiers, and discriminators on slow coincidences. In this way the coincidence counting rates and the single rates were measured. In addition, the coincidence rates were recorded as a function of time, whereby differential counting rates can be obtained. Furthermore, occasionally we sent our pulses through a linear gate into a multi-channel analyzer. The background of the apparatus amounted to about 43 c.p.m.; the tritium counting rates were a few thousand c.p.m.

The results of the tritium and deuterium measurements are shown in Fig. 1. As in former investigations we attempted to make the sample intervals as short as possible, so that we might not miss any short time variations. The solid line shown in Fig. 1 represents the tritium

concentration of the samples. The dashed line gives the deuterium concentration in % S.M.O.W. (For example, a value of +5% indicates that the sample had 5% more deuterium than the Standard Mean Ocean Water reference standard.) It is obvious that these samples show a correlation between tritium and deuterium concentration similar to former samples (BEGEMANN *et al.*, 1959; GONSIOR *et al.*, 1962).

With the exception of the tritium peaks of September 10 and November 10, both of which will be discussed later, the deuterium and tritium concentrations show a good positive correlation.

A similar correlation has been explained by BEGEMANN & FRIEDMAN (1959) as being due to an admixture of industrially derived hydrogen. Applying a correction for this industrial hydrogen should yield the true concentration of tritium in the undisturbed atmosphere. Other measurements have shown that the deuterium concentration of the free atmosphere contains about +10% on the basis of S.M.O.W. In our samples we found a deuterium concentration up to +18%, and this is remarkably higher.

In Fig. 2*a–d* we have plotted the deuterium concentration in % S.M.O.W. versus the tritium concentration in T.U. $\times 10^5$ for various wind directions. Since we are concerned with a relatively short time interval (1 year), we can, for this plot, ignore the slow rise in tritium (doubling every 2 years). However, in the early part of the year the increase is more rapid so that correlation considerations may be somewhat critical. The extrapolation of these T vs. D plots to zero Tritium should give the deuterium value of the "industrial" admixed hydrogen δ_{pr}. In Fig. 2*a–d* the least square lines have been drawn and extrapolated to zero T. The extrapolated deuterium values of the different quadrants are

$\delta_{pr} = (-22.4 \pm 4)\%$ for the NE quadrant

$\delta_{pr} = (-18.5 \pm 3)\%$ for the SE quadrant

$\delta_{pr} = (-19.1 \pm 5)\%$ for the SW quadrant

$\delta_{pr} = (-14.7 \pm 5)\%$ for the NW quadrant

Previously BEGEMANN & FRIEDMAN (1959) found that in samples collected in Buffalo, New York, the "industrial" hydrogen was −25% S.M.O.W.

GONSIOR & FRIEDMAN (1962) found a value of −26% for samples collected in Hamburg.

Automobile exhaust gases are a possible source of hydrogen. On the average these contain 2% hydrogen by volume (on a dry basis). As a check on the isotopic composition of auto exhaust gas, we collected H_2O and hydrogen gas from a motor car. The water was −8.5% S.M.O.W., while the hydrogen analyzed −69%, corresponding to equilibrium between H_2 and H_2O at 70°C. EHHALT (1965) has found values on other engines and fuel as low as −29%. Obviously auto exhaust gas hydrogen can vary widely in deuterium content depending mainly upon the temperature at which the isotopic equilibrium

$$H_2O + HD \rightleftharpoons HDO + H_2$$

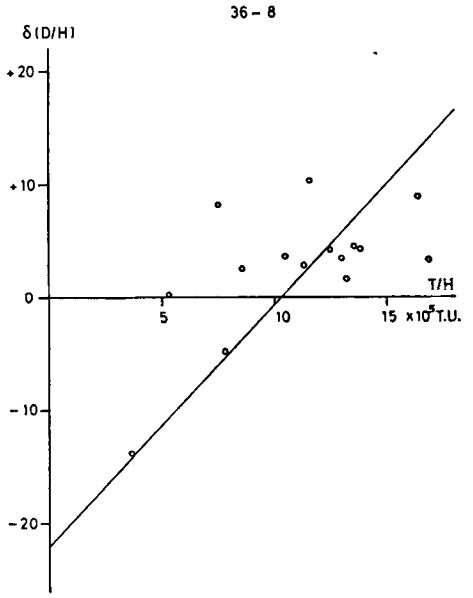
is established. However, at any reasonable temperature (less than 800°C) the hydrogen will be depleted in deuterium. Automobile exhaust gas, then, is a likely source of the "industrial" contamination discussed by BEGEMANN & FRIEDMAN (1959) and GONSIOR & FRIEDMAN (1962). A further discussion of this problem will be given in a subsequent paper.

The corrected tritium values are given in Fig. 3. In making the correction for "industrial" hydrogen, we have assumed that this hydrogen has a deuterium concentration of −20% (a mean of our results). For the natural hydrogen (free atmosphere hydrogen) uncontaminated by man, we have used our heaviest value, +18%. This high value is higher than those previously reported.

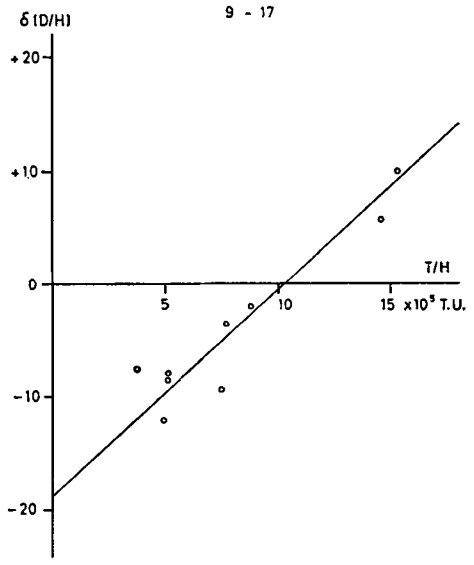
Despite the test-moratorium the medium tritium concentration rose. In 1959 the tritium concentration was about $5–7 \times 10^5$ T.U.; in 1960 according to the measurements of EHHALT *et al.* (1963) it was about 10×10^5 T.U.

Line *A* in Fig. 3 shows the tritium concentration as a function of time, as predicted by BISHOP & TAYLOR (1960). It is obvious from an examination of the data of Fig. 3 prior to September that the mean tritium value has risen as predicted by BISHOP & TAYLOR (1960) and EHHALT (1963). They recognized the importance of both nuclear testing and nuclear industrial leakage.

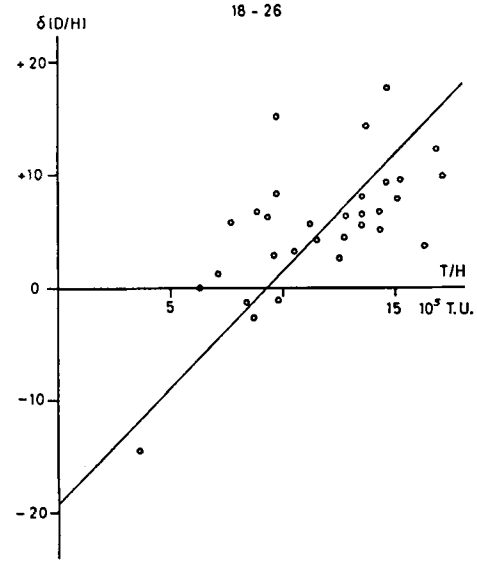
The large tritium peak in the sample of March 28 might be explained by the fact that the trajectory of this air was such that it



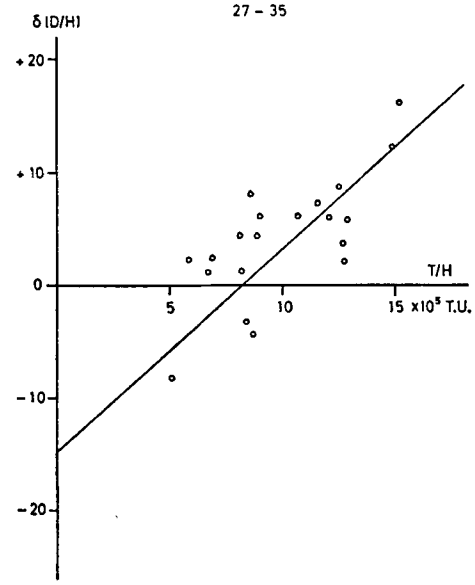
2*a* = North to East. Extrapolated deuterium content of locally produced hydrogen $\delta_{pr} = (-22.4 \pm 4)$ %.



2*b* = East to South. Extrapolated deuterium content of locally produced hydrogen $\delta_{pr} = (-18.5 \pm 3)$%.



2*c* = South to West. Extrapolated deuterium content of locally produced hydrogen $\delta_{pr} = (-19.1 \pm 5)$ %.



2*d* = West to North. Extrapolated deuterium content of locally produced hydrogen $\delta_{pr} = (-14.7 \pm 5)$ %.

FIG. 2. Tritium vs. deuterium concentrations related to different wind directions. The straight lines give the least squares fit for the data. The intercepts of these lines with the ordinate represent the deuterium content of the locally produced hydrogen δ_{pr}. The standard deviations of these extrapolated values are due to the random errors in the tritium and deuterium measurements.

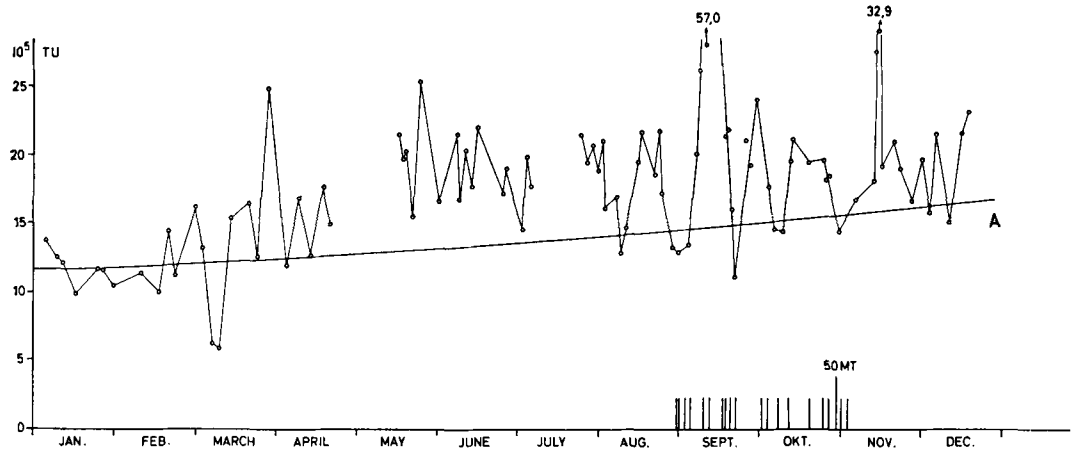


FIG. 3. Tritium values corrected for industrial hydrogen admixture, plotted as a function of the date of collection. The corrected tritium values are given in 10^5 T.U. Line *A* shows the tritium concentration as a function of time, as predicted by BISHOP & TAYLOR (1960). The signs at the abscissa represent the Sovietic bomb tests with the 50 MT bomb at the end of October.

passed through the region north of 60° N latitude, where the springtime stratospheric-tropopause break is known to have occurred. Fig. 4 gives a plot of the trajectory of this air mass from meteorological data. The rapid increase in the first part of the year with a doubling time of about 7 months may be due to the common spring rise. From May on the further rise is compatible with the doubling time of 2 years.

The Soviet Union resumed nuclear testing on September 1. The trajectories of the air masses from the test sites, calculated by MACHTA *et al.* (1962), are shown in Fig. 5. They show that the air masses, which at the time of explosion on September 1 were located at the central Asian test site, drifted over our collection station in Europe during September 10. This is the time that we recorded the first large tritium peak. The second peak, at September 29, may be due to the Stalingrad test. However the deuterium corrections for this

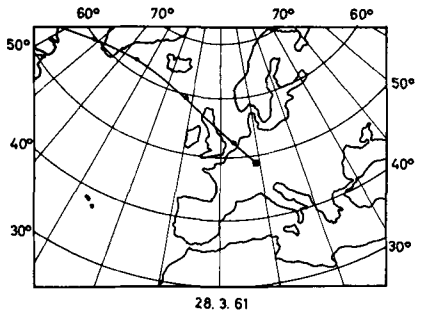


FIG. 4. Trajectory of air collected in Ludwigshafen, Germany, on March 28. The full square represents the sampling station. The full dots indicate mean positions of the air masses on the days before the sampling date in order to represent the trajectory of the air masses from March 24 to March 28, 1961.

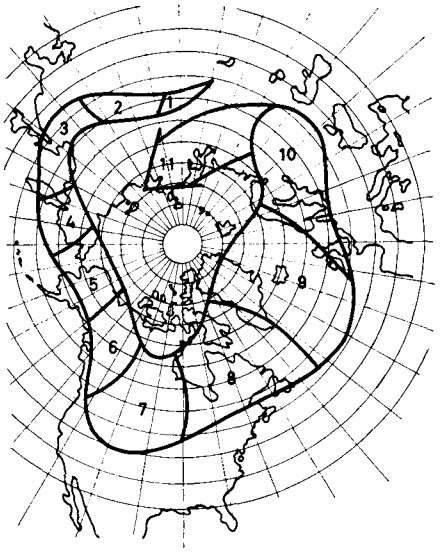


FIG. 5. The area covered by an air mass which may have contained radioactive debris from the first Russian test in 1961 at 9 km. Figures indicate the dates during September 1961 when the cloud passed over the indicated regions. From MACHTA *et al.* (1962).

peak are very large and the extrapolated D-concentration may vary around our mean value of -20% by about $\pm 5\%$, so the peak may not be real.

We discovered another tritium-maximum around mid-November which most probably was caused by the 50 MT-bomb, fired at the end of October. We are in the process of verifying this by means of trajectory calculations. In due time we hope to be able to give further details on these trajectories as well as on the deuterium-value deviations.

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НОВЫЕ ИЗМЕРЕНИЯ ТРИТИЯ И ДЕЙТЕРИЯ В АТМОСФЕРНОМ ВОДОРОДЕ

Содержание трития и дейтерия анализировались на пробах атмосферного водорода, собранных в 1961 г. Существует положительная корреляция между тритием и дейтерием. В самых тяжелых пробах концентрация дейтерия в атмосферном водороде была около 118% от стайдартного среднего значения в океанной воде. Концентрация дейтерия в индустриальном водороде меняется от 78% до 82%. Индустриальный водород является в частности водородом из выхлопных автомобильных газов.

Скорректированная концентрация трития в атмосферном водороде непрерывно увеличивается удваиваясь каждые два года. Отдельные большие пики связаны с ядерными испытаниями.