Tritium in atmospheric hydrogen

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ABSTRACT

The radioactivity of tritiated hydrogen (HT) in the atmosphere in Westwood, New Jersey was measured at approximately weekly intervals from August 1971 to August 1973. The background level remained constant at approximately 80 tritium atoms per milligram of air. Frequent increases in the activity level of up to an order of magnitude were observed until January 1973. The source(s) of HT which was responsible for the frequent increases apparently ceased as a tropospheric source in January 1973. Possible sources of HT may result from the production and storage of tritium for military purposes or from gaseous releases by the nuclear power industry.

Introduction

The existence of tritium in the form of HT in the atmosphere was first measured in 1948 by Faltings & Harteck (1950). The measurements of HT activity in the atmosphere during the period 1948–1964 have been summarized by Ehhalt (1966). Although the method of sample collection, proximity of collection site to industrial areas (such areas are possible sources of hydrogen which may perturb the T/H ratio), meteorological parameters, and related factors, vary among the investigations summarized, the HT activity increased continuously over the period studied from approximately 0.08 T atoms/mg of air to approximately 80 T atoms/mg of air. In tritium units the increase was from 4×10^3 T.U. to 4×10^6 T.U. The sources of the hydrogen samples for the various atmospheric HT studies were from air liquefaction factories. The hydrogen was extracted from the crude-neon fraction which also contains neon, helium, and a variable amount of nitrogen. The reliance on air liquefaction factories as sources of hydrogen has several disadvantages. First, the factories are usually located in industrial areas, consequently the natural hydrogen extracted may be contaminated by locally produced industrial hydrogen. The specific activity of the tritium in the natural hydrogen may still be determined but only after applying a corrective factor to eliminate the industrial hydrogen contribution. The procedure described more thoroughly by Ehhalt is briefly outlined here. The crude-neon fraction preserves the original concentration ratio of hydrogen, helium and neon in the sample. The natural abundances of the three elements are well known in uncontaminated surface air samples, and only the hydrogen concentration may be appreciably affected by industrial sources. The measured value of the specific activity of tritium is based on the volume of the natural hydrogen and the admixed industrial hydrogen. The measured specific activity may be corrected to correspond exclusively to the natural abundance of hydrogen by multiplying the measured value by the H_2/He ratio of the sample and dividing by the natural H_2/He ratio.

Another disadvantage to the dependence on air liquefaction factories is the limited flexibility in choosing the time, and time duration, of collecting an air sample from a particular air mass. The use of tritium as a tracer may provide meteorological information about the transport and mixing of air masses and may provide a technique for identifying anthropogenic sources of tritium. A third disadvantage is the limited number of sampling locations from which to chose.

Since 1964, Layton (1969), Östlund et al. (1972), and Östlund & Mason (1974) have reported atmospheric HT measurements. From

July 1963 to December 1966 Layton measured the HT activity in air collected by the Linde Company in Indiana. The majority of the values were observed to be in the range of 20 to 40 T atoms/mg of air; the total range included values from 12 to 80 T atoms/mg of air. More recently Östlund and coworkers have been measuring the HT activity of three ground stations and from several aircraft flights. Briefly summarized, the results of Östlund and coworkers show a rather constant activity level between 40 to 50 T atoms/mg of air at the Miami, Florida station from October 1968 to May 1972 and at the Mauna Loa, Hawaii station from August 1971 to July 1972 with occasionally higher values. In Fairbanks, Alaska in November 1970 the HT activity increased suddenly to 100 T atoms/mg of air but has steadily decreased over the period of a few months to the range of 50 to 60 T atoms/mg of air. Samples collected by an aircraft flying at altitudes between 16 and 23 km from Honolulu, Hawaii (21° N) to 68° S and return showed HT activity levels between 34 and 53 T atoms/mg of air in the upper troposphere. In the section of the flight path in which the aircraft was in the lower stratosphere (the latitudinal positions were south of 48° S) the HT values ranged between 47 and 83 Tatoms/mg of air.

The most probable natural formation of atmospheric tritium is due to cosmic ray interaction with atoms and molecules in the stratosphere. Other suggested, but unproven at present, sources of tritium are production by solar protons in the stratosphere and tritium influx into the atmosphere with solar corpuscular streams. Investigations of these sources are difficult by themselves and are further complicated by anthropogenic injections due to such sources as: (1) the atmospheric nuclear weapons testing in the 1950's and early 1960's, (2) possible leaks occurring during the production and storage of tritium for military purposes, or (3) possible gaseous releases by the nuclear power industry. The objective of the present study was to investigate whether variations in the tropospheric HT activity exist, and if so, to determine the time scale of variations. Since it is generally accepted that the time scale of general mixing of tropospheric air in the northern hemisphere is on the order of a few weeks, the time increment of one week was chosen between air samplings in Westwood, New Jersey as a practical interval to investigate general mixing times.

Experimental procedure

In the present study surface air samples of between two to three standard cubic meters were each compressed into a 15-liter steel sphere using an air compressor powered by either an electric motor or gasoline engine. Multiple analyses were performed in some cases on a single sample for measurement of the radioactivity of several elements, the chemical speciations of which include HT, HTO, $^{14}CO_2$, ^{37}Ar, ^{85}Kr, and $^{131m,133m,133}Xe$.

The procedure for measuring the tritiated hydrogen activity in atmospheric air consists of first adding two liters of nontritiated hydrogen to 400 liters of the air sample. The resultant mixture is passed, at a regulated flow of 4.0 liters/minute, through two traps maintained at −75°C to remove water vapor and hydrocarbons. The air then passes through a hydrogen combustor which consists of a 40 micron mesh stainless steel cylindrical plug impregnated with palladium as the catalyst. The plug is 25 cm in length and 0.6 cm in diameter and is enclosed in a quartz tube. A heating element maintains a temperature of 80°C on the exterior surface of the quartz vacuum wall. The air stream is at −75°C as it enters the combustion region. Although the reaction of hydrogen and oxygen in the presence of the palladium is exothermic, it is doubtful that the resultant combustion temperature is as high as 80°C. The water vapor produced is collected in a plain glass cold trap at −75°C. The remainder of the sample is expelled from the system through a 0.33 psig check valve. At these operating conditions methane and other hydrocarbons are not combusted to a measurable extent. Further dicussion of efficiencies of combustion will follow in a later paragraph.

At the completion of the combustion, the trap containing the water is detached from the system. The water is extracted with a hypodermic needle and injected through a silicone stopper of a second processing system into a small glass bulb containing a port. The water is converted to hydrogen by passing the water, heated to its vapor state, over a granular zinc conversion column heated to 400°C. The hydrogen is collected in an activated charcoal trap, cooled to −196°C by liquid nitrogen. Upon completion of the collection, the liquid nitrogen is removed and the hydrogen is allowed to

expand into a one-liter proportional detector. The pressure is recorded and the quotient of the volume of hydrogen in the proportional detector at this point divided by the volume of initial hydrogen carrier added to the air sample represents the yield of the entire processing of the hydrogen (or more specifically, of the protium). Nontritiated hydrogen is then added to the proportional detector to a pressure of 2.4 atmospheres. The final pressure of 3 atmospheres in the proportional detector is accomplished by adding nonradioactive methane. This procedure permits operating the proportional detector at essentially the same voltage and with the same gas composition for each sample. Correcting the observed count rate for the proportional detector background is more reliable with this procedure. The proportional detector is then inserted into an anticoincidence shield which in turn is surrounded by a passive shield of lead and iron. The one-liter detectors have backgrounds of approximately 3 cpm and nominal counting times are 1 000 minutes.

Tests were performed to check for possible (1) combustion of hydrocarbons, particularly methane, (2) passage of water vapor through the system from the initial air sample, and (3) differences in the processing yields of H_2 versus HT (or T_2). A brief discussion follows of each of these aspects.

The possible combustion of methane was investigated in the following manner. A few cubic centimeters of methane with a tritium activity of 262 ± 8 dpm were added to 2 liters of hydrogen carrier and 156 liters of ambient air collected outside the laboratory. The volume of methane was purposely kept small relative to the carrier and air sample volumes in order to maintain essentially the same composition as is present with a normal air sample. The sample was processed in the manner described earlier; no measurable activity could be attributed to the tritiated methane. A conservative upper limit of $< 0.5\%$ may be assigned to the efficiency of combustion of methane. A few cubic centimeters of a mixture of ethane, propane, and *n*-butane, all with measured tritium activities, were added to a second air sample; the processing and counting showed that hydrocarbons are not combusted in the system.

The collection of water vapor from the original air sample into the plain glass, cold trap following the selective combustor would present two problems. The water vapor may have an appreciable tritium activity which would perturb the measured activity attributed to HT. A second source of error would be due to the addition of the volume of condensed water vapor to the volume of water produced from the hydrogen combustion. The retention of water vapor in the two cold traps preceding the combustor was investigated by passing an air sample to which water vapor with a tritium activity of 641 ± 82 dpm had been added through the combustion system. The temperature of the two traps preceding the combustor was maintained at 0°C, a higher temperature than maintained during normal processing. One milliliter of nontritiated water, to serve as a carrier, was added to the glass condensing bulb. After the sample had been vented through the check valve, the carrier water was counted in a liquid scintillator. The efficiency of retention of water vapor in the two cold traps preceding the combustor was determined to be greater than 99%

When processing a sample of unknown HT activity, the yield that is directly determinable is a net processing yield of H_2. As described earlier, the net processing yield is the quotient of the volume of H_2 carrier loaded into the proportional detector divided by the total volume of the H_2 carrier originally added to the air sample (the natural content of H_2 in the sample is negligible). The net processing yield of HT (or possibly tritium as T_2) must be determined in a separate measurement. This was accomplished by processing several prepared air samples containing high HT activities and comparing the net processing yields of HT versus H_2 in each sample. The result was that the net processing yield for HT was determined to be less than for H_2 by the averaged ratio of 0.846 ± 0.042.

Results

Ambient tropospheric air samples in Westwood, New Jersey have been collected at ground level and analyzed for HT on approximately a weekly basis since August 1971; the results are shown graphically in Fig. 1. Systematic measurement errors are within $\pm 10\%$.

A number in parentheses to the right of a data point indicates identical results of multiple analyses. Data points in a vertical line are also

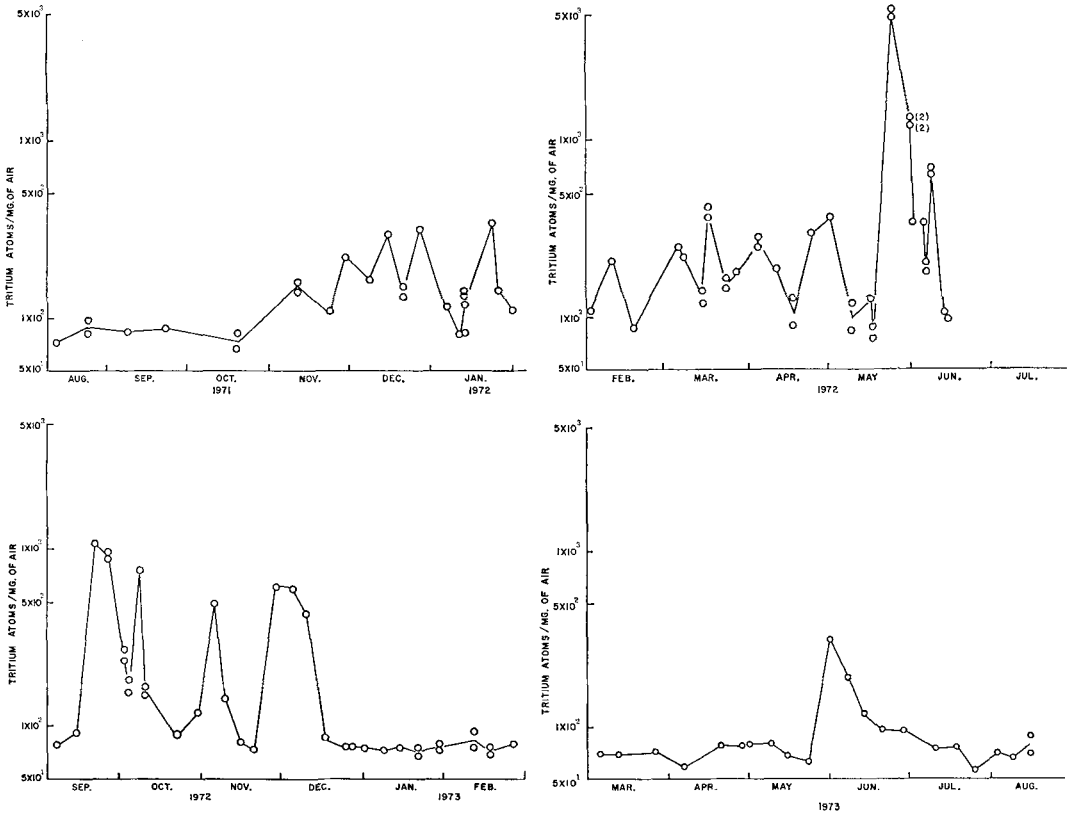

Fig. 1. HT activity measurements in air in Westwood, N.J. from August 1971 to August 1973.

multiple analyses. The lines connecting data points are for convenience of following the time sequence of activity levels; the lines are not necessarily intended to depict time distributions of HT activity levels. As is evident from the figure, there are large variations in the HT activity level until January 1973; some are approximately an order of magnitude greater than the lowest values, and in one case, on May 25, 1972, the activity level was nearly a factor of 10^2 greater. After each increase in the HT level, the ambient level consistently returned to approximately 80 T atoms/mg of air.

In the first eight months of 1973, except for one three-week period, the HT activity level was quite constant in Westwood with values predominantly between 70–90 T atoms/mg of air. Perhaps the source of HT which gave the large activity variations prior to 1973 ceased as an input of HT into the troposphere. The sample collected May 31, 1973 had a HT activity of 316 T atoms/mg of air, nearly a factor of four above the background level. The activity decreased monotonically during the next two to three week period. To be assured that the large variations in the pre-1973 HT activity levels were not laboratory-induced, several precautions were taken. The steel spheres were evacuated, heated to 150°C, and continuously pumped on, for several hours between samples. Only Westwood air samples are stored in the spheres. Aliquots of air from one sphere or from two spheres pumped simultaneously have been processed for more than 25% of the samples collected in order to check reproducibility of results. Most of the duplicate analyses were performed on two combustion systems in order to check for systematic errors. The one combustion system using the palladium catalyst has been described. The second system used a heated coiled platinum wire as the catalyst. As in the case of the palladium system, the net processing yield of HT relative to the net processing yield of H_2 was determined for the

platinum system in separate experiments using prepared air samples of known HT activities. The HT is less efficiently converted to HTO than H_2 is to H_2O by the ratio 0.663 ± 0.047. As further consideration of the precautions described, the analysis of the air collected June 1, 1972 is illustrated. In June 1972 two aliquots were processed, one on the platinum system, the other on the palladium system. The results were 1 290 and 1 310 T atoms/mg of air for the platinum and palladium systems, respectively. For each combustor the unique relative net processing yield for HT versus H_2 was used in the calculations. The consequence resulted in good agreement between combustors. Two more aliquots of the same air collected June 1 were processed three months later, in September. The results were 1 360 and 1 270 T atoms/mg of air for the platinum and palladium combustors. The four analyses are in good agreement and provide a degree of reliability of the technique and the high HT activities observed pre-1973.

There in no readily apparent correlation between the HT activity and wind direction, as measured by the US Weather Bureau at Newark and LaGuardia airports, both of which are within 30 kilometers of Westwood. Factors which may complicate the search for a correlation include various meteorological conditions, possible variations in length of release times of HT, time between releases, and total activity released, from unknown anthropogenic sources. An approximate yearly anthrogenic input of HT can be calculated, however, from the following considerations. First, from the data of Östlund and coworkers, the stratosphere is probably not at present a significant source of HT to the troposphere, although it undoubtedly was in the 1950's and early 1960's; nor, apparently, is there a significant stratospheric sink of HT. Second, from at least August 1971 to August 1973, the ambient level of HT in Westwood consistently returned to approximately 80 T atom/mg of air after measurements of increases in the activity level. The inference may be that the source (or sources) of HT contributes, averaged on a global scale, a total activity sufficient to offset that lost by radioactive decay and other possible sinks which are not sufficiently well understood to include in the present calculation. One possible tropospheric sink of H_2 is, as observed by Schmidt (1974), uptake by soil. Schmidt has calculated an upper limit of soil uptake of H_2 to be approximately 1.2×10^{13} g/year. Radioactive decay accounts for a HT loss from the atmosphere of 5.5% per year, or approximately 4.4 T atoms/(mg·yr). Extrapolating to the entire atmosphere, the total anthropogenic injections of HT per year necessary to maintain an average HT activity of 80 T atoms/mg is estimated to be 1.2×10^6 curies. This value would represent a lower limit if other sinks of HT are included in the calculation.

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ТРИТИЙ В АТМОСФЕРНОМ ВОДОРОДЕ

С августа 1971 по август 1973 года в Уэствуде, Нью Джерси, приблизительно с недельными интервалами измерялась радиоактивность молекул атмосферного HT. Фоновый уровень оставался постоянным и равным приблизительно 80 атомам трития на миллиграмм воздуха. До января 1973 г. наблюдались частые увеличения уровня активности вплоть до порядка величины. Источник (*и*) HT, ответственный за частые увеличения концентрации, по всей видимости прекратил свое действие по выпуску HT в тропосферу в январе 1973 г. Возможными источниками HT могут являться производство и хранение трития для военных целей или выпуск газа в воздух индустрией ядерной энергии.