The Production Rate of Natural Tritium

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Abstract

A detailed evaluation is made of the production rate of natural tritium in the pre-thermonuclear epoch. Deuterium and tritium analyses on the same precipitation samples are used to establish the uncontaminated tritium levels in precipitation sampled before the Castle tests, and the tritium balance is calculated for the North American troposphere. The global mean production rate $\overline{Q}$, calculated from the geochemical inventory, is found to be 0.5 ± 0.3 atoms T/cm² sec. This value is three to four times smaller than values found previously by such calculations because of the following developments:

1. The deuterium and tritium data show that the increases in tritium content observed during early thermonuclear tests before Castle are due to addition of synthetic tritium rather than to random fluctuations. The deuterium-tritium relationships are used to establish the general pattern of tritium variations over the North American continent and to evaluate the uncontaminated tritium levels.

2. The mean stratospheric residence time for tritium is found to be about 1.6 years from studies on fission product fallout and from the latitudinal variation of stratospheric cosmic ray production.

3. Stratospheric tritium is preferentially injected into the troposphere at high latitudes, as shown by fallout observations. The tritium influx into the North American troposphere is therefore higher than the mean global value.

The predicted production rate is calculated from cosmic ray and nuclear cross section data using the star production rates in the atmosphere. The predicted mean global tritium production rate during an average solar cycle is found to be 0.25 ± 0.08 atoms T/cm² sec. The variation in the production rate over an average solar cycle is found to be ± 4.5 %.

Within the uncertainties of the data and calculations, the production rates calculated from the geochemical inventory and from the cosmic ray data are in agreement, and there is thus no observational evidence for accretion of tritium from an extra-terrestrial source.

Introduction

The geochemistry of tritium is a subject which has been much discussed during the decade since the discovery, by Faltings and Harteck and by Libby and his associates, that this isotope is continuously formed in the atmosphere by cosmic radiation. By 1956 Libby and his coworkers had analyzed a large number of natural waters and had found that there was general agreement between the global production rate computed from the natural inventory of tritium and that calculated from the cosmic ray flux and nuclear cross section data, namely about 0.14 atoms T/cm² sec. However in 1957 one of us showed that previous calculations of the production rate from observed tritium concentrations had neglected several essential factors, the most important of which was transport of water vapor out of North America, and that the most likely value was a production rate $\overline{Q}$ of about 1.3 atoms/cm² (CRAIG, 1957). It was also shown that with the observed concentrations in the atmosphere and sea, the mixing rates deduced from the better-known radiocarbon

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data required a figure of similar magnitude. BEGEMANN and LIBBY (1957) calculated $\overline{Q} = 2$ from a study of the Mississippi valley water balance.

Since 1957 on the average of two papers per year have been published in which tritium production rates ranging from $\overline{Q} = 1$ to 2 have been calculated from data on natural concentrations, suggesting that the cosmic-ray production rate is too small by an order of magnitude to account for the pre-bomb tritium inventory. The present paper breaks the chain. Our treatment of the problem is essentially that given by CRAIG (*op. cit.*), modified however by consideration of several important factors and new data which have since been developed. Because the comparison of the cosmic ray production rate with observed natural concentrations, and the possibility of accretion of tritium from extraterrestrial sources as suggested by several authors, are important geophysical problems, we have attempted to evaluate as carefully as possible the production rate of natural tritium from the small amount of available data. In what follows, we first discuss the associated deuterium-tritium variations in precipitation samples and eliminate pre-Castle precipitation affected by thermonuclear contamination. We then calculate the natural production rate from the observed tritium concentrations, and finally compare this value with the most accurate calculation we can make based on the cosmic ray flux and cross section data.

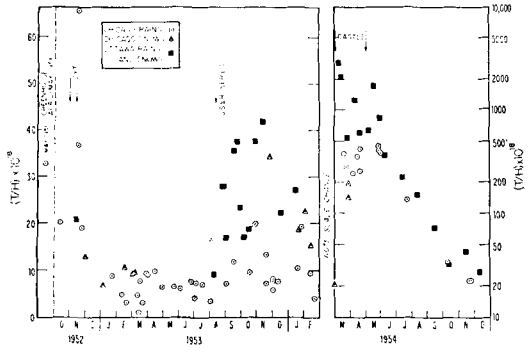

Fig. 1. Tritium concentration in Chicago and Ottawa precipitation up to the end of 1954. The dates of announced thermonuclear explosions are indicated. (Tritium data: Kaufman and Libby, 1954; von Buttlar and Libby, 1955; Brown and Grummitt, 1956; Begemann and Libby, 1957).

Deuterium and tritium analyses of precipitation

Tritium analyses of Chicago precipitation make up by far the major part of the data on natural waters and we therefore begin with an evaluation of these measurements (KAUFMAN and LIBBY, 1954; VON BUTTLAR and LIBBY, 1955; BEGEMANN and LIBBY, 1957).[1] The Chicago data, as well as the analyses of Ottawa precipitation (BROWN and GRUMMITT, 1956) up to and including the year 1954 are shown in Figure 1.[2] The most prominent feature of these data is the large injection of artificial tritium as a result of the Castle tests in the spring of 1954 (BEGEMANN, 1956).

Figure 1 also shows, however, that there are significant increases in the natural level associated with the thermonuclear tests carried out before Castle by U.S. and the U.S.S.R.[3] It is unfortunate that there are no Ottawa data for the period January 1 to August 1, 1953, but as we show below it does not seem possible that the natural uncontaminated level in Ottawa can have been anywhere near as high as the values of 20—40 T.U. found from August 1953 to the Castle tests. If these levels represent artificial injection, as we believe, they are significantly higher than those observed in Chicago during the same period, but this phenomenon is definitely observed during the Castle injection and the pattern is therefore significant. It should be noted that after the Castle shots the tritium level in Ottawa precipitation decayed to a level of about the same magnitude as observed in Chicago at that time.

Because the Chicago data do not for the most part show increases to levels as high as those seen in Ottawa during the seven months before Castle, and because of the lack of Ottawa data prior to this period, Figure 1 does not in itself constitute proof of pre-Castle artificial tritium injection and it is necessary to seek more definite evidence. This can be done by

[1] Hereafter these papers are referred to as K-L, VB-L, and B-L, respectively.

[2] We use the abbreviation 1 tritium unit (1 T.U.) = 1×10^{-18} atoms T/atom H hereafter.

[3] Our source of information on dates and locations of thermonuclear detonations is the paper by TELEGADAS (1959). We believe, however, that the tritium data indicate that the dates announced for some of these tests are not precisely accurate, as we note later on.

a method of "isotopic renormalization" based on the comparison of deuterium and tritium analyses on the same precipitation samples. Deuterium variations in precipitation are due to preferential concentration of HDO in the liquid phase because of its lower vapor pressure relative to H_2O, so that in atmospheric water vapor passing over a continent the ratio D/H decreases as moisture is removed by precipitation. The removal rate of HDO is greater at lower temperatures because of the increase in the isotopic vapor pressure difference with decreasing temperature. The precipitation process affects the HTO/H_2O ratio in the same way but to a greater extent because of the larger vapor pressure difference in the case of HTO.

Figure 2 is an isohydrogram of Chicago, Greenland, and Pacific island precipitation, in which the tritium content in T.U. is plotted vs. the deuterium content of the same samples. The deuterium data were measured by one of us (H. C.) by mass spectrometric analysis of H_2 obtained by quantitative reduction of the original precipitation samples using zinc or uranium. The δ values plotted are the per cent deviations of the D/H ratio from that of an arbitrary "standard mean ocean water" (SMOW)[1] which is the composite of ocean water samples taken from 500—2,000 meters depth used as a standard for O^{18} measurements by EPSTEIN and MAYEDA (1953). That is,

$$\delta D\,(\%) = \left[\frac{D/H_{sample}}{D/H_{SMOW}} - 1\right] \times 100$$

The data plotted in Figure 2 are accurate to about $\pm$ 0.2 %.

A complete discussion of the isohydrogram and the deuterium, tritium, and oxygen data in these and other samples will be given elsewhere. At present, we wish only to compare the tritium-deuterium relationships during the possible periods of contamination indicated in Figure 1. However as we refer to various aspects of Figure 2 in later discussions in this paper, we shall briefly describe the properties of this diagram. The trajectories of points in the isohydrogram representing precipitation samples derived from an idealized air mass moving across a continent are in general governed by the following factors:

1. Preferential removal of the heavy isotopic species HDO and HTO relative to H_2O during precipitation because of the lower vapor pressures of the heavy isotopic species. These effects are given by the well-know Rayleigh distillation equations—see calculations and discussion for HDO and H_2O^{18} by CRAIG, BOATO, and WHITE (1956).
2. Continuous injection of cosmic ray produced tritium as HTO.
3. Injection of HTO from thermonuclear explosions.
4. Mixing with extraneous water vapor, addition of water from continental evaporation, etc.

In general, it has been found that the D and O^{18} content of Chicago precipitation reflects the dominant source and trajectory of the water vapor from which the precipitation is derived. Precipitation which can be identified as coming from polar air is relatively light, values of δD ranging down to $-$ 16 %, while precipitation from maritime tropical air which has suffered little loss of moisture prior to its arrival ranges up to $\delta D = 0$ or even somewhat higher. The distribution of deuterium in precipitation samples taken over the two-year period 1953—54 in Chicago is shown in Figure 3, in which the lower D concentrations in the winter snow samples are quite evident. These lower values also reflect to some extent the lower temperature of precipitation as described previously. Oxygen 18 measurements on these samples correlate with the D data according to the equation given above which seems to hold true for precipitation from all over the world, for climates ranging from the tropical Pacific Ocean to the Arctic and Antarctic.

Assuming no artificial injection of tritium, tropical maritime air should begin a trajectory

[1] On this scale the δ values for the NBS water standards vs. SMOW are:

$$\delta D\,(\text{NBS-1}) = -\ 4.76\ \% \pm 0.02$$
$$\delta D\,(\text{NBS-1A}) = -18.33\ \% \pm 0.20$$

The relative enrichment of NBS-1A vs. NBS-1 taken as the standard is then $-14.25\ \% \pm 0.25$.

Oxygen 18 analyses were also made on these samples and the O^{18} data correlate precisely with the D/H data according to the relationship: $\delta D = 8\,\delta O^{18} + 1$ (both δ's in per cent) in agreement with the general relationship which has been established for precipitation from all over the world (H. CRAIG, 1961).

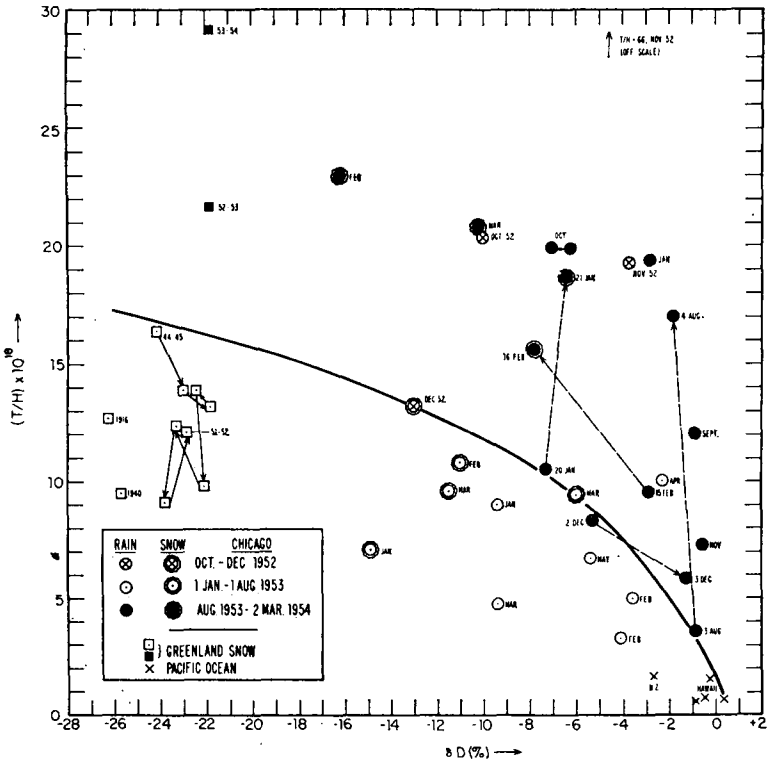

Fig. 2. Isohydrogram showing tritium and deuterium variations in Chicago, Greenland, and Pacific island precipation. Deuterium data (H. Craig, paper in preparation) are per cent deviation of D/H ratio from "standard mean ocean water" (SMOW). Tritium analyses by K-L, VB-L, and Begemann (1959). The Greenland core samples consist of yearly precipitation from summer to summer; the connecting arrows and indicated dates show the time sequence from 1944—52 according to Begemann. We believe the actual precipitation dates may be a year earlier than shown (see text).

at a point close to the origin of Figure 2, with a D/H ratio representing approximate isotopic equilibrium of the vapor with surface ocean water (which has a δ value of about + 1 due to evaporation) and a T/H ratio reflecting the approximate steady state balance between the tendency to reach isotopic equilibrium and the gradient imposed by continuous atmospheric production with a finite exchange rate with the sea. As the vapor moves to higher latitudes and inland over continents the factors (1) and (2) above will impose various slopes upon a trajectory of points plotted in the isohydrogram, depending on the varying importance of these two effects (we neglect the minor complications imposed by item 4 in this discussion). On the average, however, a rather continuous spread of discrete points may be expected as the vapor moves from the ocean, let us say, northward and/or eastward into and over continents.

In Figure 2 the following data have been plotted:

1. Chicago precipitation, identified as to the periods (see Figure 1) (a) prior to January, 1953; (b) 1 January to 1 August, 1953; and (c) from 1 August, 1953 to the Castle test series. The tritium data for these samples are given in K-L, VB-L, and B-L.

2. Samples of Greenland snow from a core taken about 320 km east of Thule at altitude 2,300 meters, by H. Bader and E. W. Marshall of SIPRE. These samples were divided by year of precipitation according to the summer melt layer, and each sample shown represents a year of precipitation from

summer to summer. Two additional samples from Thule, of summer snow from 1916 and winter snow from 1940—41 are also shown. Tritium analyses of these samples have been made by BEGEMANN (1959).

3. Several samples of rain from the Hawaiian Islands and one from New Zealand (tritium data given in K-L and VB-L).

The most prominent feature of the isohydrogram is the tendency toward a rather continuous trend from the Hawaiian samples, through the Chicago samples of group 1 (b) above, to the Greenland samples of pre-Ivy precipitation. On the other hand one sees that the samples of Chicago precipitation from groups 1 (a) and (c), taken during periods of possible artificial injection of tritium, have on the average much higher T concentrations compared to samples of the same D concentrations in group 1 (b) taken from 1 January to 1 August 1953 when no thermonuclear tests were made. We have drawn an arbitrary line in the isohydrogram as the approximate envelope of these latter samples. If we now compare the δ D values for Chicago precipitation from 1953 and from 1954, as shown in Figure 3, we see that there is no apparent tendency for a systematic difference in D content, either for rain or for snow, so that there is no reason to expect a systematic difference in the HDO-HTO relationship from one year to the next. Yet the T contents for samples of quite similar δD values may differ by as much as a factor of 5 and by much more in the case of one sample from November, 1952 which plots off the diagram.

In Figure 2 we have also shown the month in which the Chicago samples were collected, and one sees that even in samples from the same season of the year the T levels in the different periods can be quite different for the same δD values. Moreover, we have indicated by connecting arrows samples separated by not more than a day in time, and in two cases, August 3—4 and January 20—21, 1954, there is a striking sudden increase in tritium while the deuterium concentration remains practically constant. Such a phenomenon requires the existence of relatively large tritium gradients in moisture which is arriving with a homogeneous D (and O^{18}) concentration, and which would therefore be expected to have had a uniform history of precipitation and trajectory.

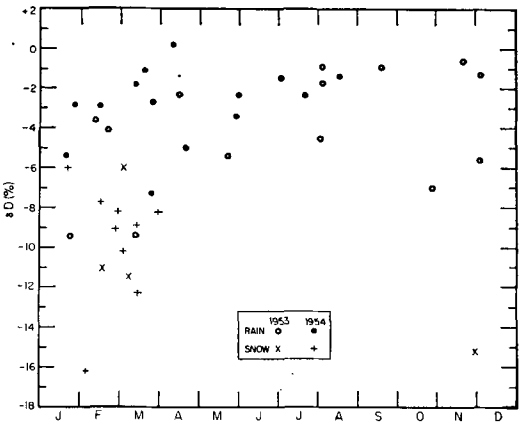

Fig. 3. Deuterium variations in Chicago precipitation for two years, showing δD relative to SMOW (cf. Figure 2). Not all precipitation was analyzed. (From a paper in preparation by H. Craig.)

By far the easiest way to achieve such gradients is by the sudden injection of tritium into a portion of a relatively uniform system. On the other hand, the points shown for December 2—3, 1954, represent the type of change which may well be entirely meteorological in origin, regardless of whether any artificial T is or is not present.

The U.S.S.R. thermonuclear test of August 12, 1953 was announced by the U.S. as "part of a series" (TELEGADAS, 1959) and if our interpretation is correct, the August 3—4 points indicate a shot somewhat earlier. We have no explanation for the point shown for October 14, 1952, just prior to the announced date of the Ivy shot.

Thermonuclear tritium in Ottawa and Greenland

The importance of the conclusions obtained from the isohydrogram lies in the strong evidence of appreciable contamination during the period of Ivy and the U.S.S.R. thermonuclear tests (and possibly during Greenhouse). The first Ivy shot (Mike) was a refrigerated fusion device which presumably contained a liquid deuterium-tritium mixture and thus released directly a relatively small amount of pre-synthesized tritium (CAMERON, 1959). The amount of artificial T injected into the atmosphere was much less than in the Castle and subsequent shots, which probably produced tritium by the Li^6 (n, α) T reaction. No

information is available to us on the mechanism of the 1953 U.S.S.R. shots. The Greenhouse mechanism was presumbly even more primitive than Ivy, and it seems fair to conclude that Chicago precipitation levels from 1 January to 1 August 1953 can be taken as fairly representative of the natural level, especially when we consider the rapid removal of artificial tritium from the troposphere after Castle (Figure 1).

The Ottawa samples from 1 August 1953 to Castle show much higher values than the T levels observed in Greenland snow. The deuterium content of precipitation and river samples taken from British Columbia and Alaska through northern Canada to the east coast and into Greenland is very uniform at about the average value found in the Thule samples, or a little lower (H. CRAIG, paper in preparation). On the other hand, a sample from the Ottawa River, 4 August 1954, gave $\delta D = -7.9$ %, while the lightest sample found in this general area, from the Rivière à Claude on the Gaspé Peninsula, 25 June 1954, gave $\delta D = -10.4$ %. Since average Chicago precipitation will plot on the isohydrogram at about $\delta D = -5$ %, T/H = 6 T.U., Ottawa precipitation would normally be expected to plot somewhere between the Chicago and Greenland averages, whereas it actually contains about twice as much T as Greenland precipitation during the period in question. These data thus provide further evidence for pre-Castle contamination.

Tritium variations in the Greenland samples shown in Figure 2 have been discussed by BEGEMANN (1959) who pointed out that the high value found for summer 1952—summer 1953 precipitation is most probably due to artifical contamination from the Ivy tests, so that the layers for the following years contain the tritium injected by Castle. In addition to the data shown in Figure 2, there were two more layers in the core which are not plotted; the dates and observed T concentrations for these are: 1954—55, 212 T.U.; and 1955—56, 101 T.U. (BEGEMANN, 1959). Deuterium measurements on these two samples gave $\delta D = -23.6$ % for each, very close to the values found for the samples plotted in Figure 2. Thus the D/H ratio is practically constant throughout the core, indicating that the high T concentrations from 1952 on are indeed due to artificial tritium. This evidence from the isohydrogram is further strengthened by the fact that the core data plotted cover a complete sunspot cycle from the minimum in 1944 to the following minimum in 1954.[1]

Pre-thermonuclear tritium levels

We conclude that the isohydrogram presents a reasonable picture of the pattern of tritium-deuterium variations in North America when injection of artificial tritium is not of major importance. The effect of contamination in Chicago precipitation from August 1953 to the Castle tests is shown in Table 1, in which we summarize the data for the period 1 January to 1 August, 1953, during which no tests were held and the Chicago level was relatively constant, together with the data from August 1953 to the Castle tests. Weighted means are not available for the latter period, but the unweighted means indicate that during this time the Chicago tritium levels were increased by about 1.7 in rain, 2.4 in snow, and by an overall average of about a factor of 2. The higher increase factor observed in snow is in agreement with the very low δ values often found in snow (see Figure 3) indicating the presence of vapor derived from high latitudes and therefore more subject to con-

[1] It appears, however, than the dating given by Begemann is incorrect by one year, at least in the upper part of the core. The observed value of 29.2 T.U. for summer 1953—54, a period which included both the U.S.S.R. and the Castle tests, seems much too low considering that Ottawa precipitation averaged about 30 T.U. during the eight months before Castle, and about 1 000 T.U. for the four months from Castle to summer, 1954, and that the Castle tritium appeared in Chicago and Ottawa almost immediately. The seasonal distribution of precipitation at the location of the core is not known to us, but PETTERSSEN *et al.* (1956, Table 15) show that at Thule, about 80 % of the annual precipitation occurs from July through February. Taking the Ottawa levels as given above, weighted 80/20 for the two periods, we calculate an approximate mean value for this period as 200 T.U., which may be compared with the value 212 T.U. given by Begemann for the 1954—55 layer, a period in which no increases were observed in Chicago. We conclude that the dates shown in Figure 2 should be put back one year, and that the first observed increase, to 21.7 T.U., represents tritium from the Greenhouse test incorporated in a summer melt layer and showing up in the snow for 1951—52. The following layer with 29.2 T.U. would then contain the artificial tritium from Ivy. If our interpretation is not correct it is necessary to assume that Castle tritium arrived simultaneously and almost immediately at Chicago and Ottawa but took at least five months longer to get to Greenland, which seems improbable.

Table 1. Tritium assays (T.U.) of pre-Castle Chicago precipitation.

(Data from KAUFMAN and LIBBY, 1954, von BUTTLAR and LIBBY, 1955).

Period	Unweighted mean	Weighted mean
I. *1 January—1 August 1953*		
Summer rains...	7.3	7.3
Winter rains....	5.5	3.9
All rains.....	6.4	5.7
Snow.....	9.2	9.6
All precipitation	7.0	6.0
II. *3 August 1953—2 March 1954*	Unweighted mean	Ratio of means II/I, = increase factor
Rain.....	10.8	1.7
Snow.....	22.5	2.4
All precipitation	13.5	~2

tamination from the Russian tests. Humidity and total precipitation factors do not account for the difference; this point will be discussed elsewhere together with the details of the isotopic data.

The weighted mean of Chicago precipitation from 1 January to 1 August, 1953, is 6.0 T.U.; this should be a good annual average inasmuch as it includes both winter and summer precipitation covering almost the entire range of D/H variation (Figure 3). The extent of possible remnant contamination from Ivy can be answered approximately by comparison with data on two old samples of Illinois precipitation (K-L); water collected August, 1952 from a Decatur cistern gave 5.9 T.U., and water from a Sullivan cistern about 15 years old gave 6.3 T.U. extrapolated to time of origin. It seems likely therefore that the precipitation during this period was not significantly contaminated; we shall take the tritium content of average pre-thermonuclear era Chicago precipitation to be 6.0 T.U., and hereafter we refer to the period 1 January—1 August, 1953, as the "clean period".

The only other extensive set of precipitation data is that reported by GILETTI, BAZAN, and KULP (1958) for New York rains. Unfortunately all their pre-Castle samples were taken after October, 1953, during the period of contamination from the U.S.S.R. thermonuclear tests. In order to make an approximate estimate of the natural level in N.Y. rain it is necessary to apply a correction factor to their data. There are enough data on Chicago precipitation to insure that the contamination factor estimated in Table I is statistically significant, and we assume that an approximately similar factor applies to the N.Y. data. Deuterium concentrations are quite similar in waters from the two areas; average Chicago precipitation is about—5 ‰ relative to SMOW, while the following δD values have been obtained for N.Y. area waters:

Lake Erie (17 July, 1954)	− 5.3 ‰
Lake Ontario (19 Sept., 1948)	− 4.6 ‰
Lake Ontario (20 July, 1954)	− 5.0 ‰
Niagara River (12 March, 1954)	− 5.3 ‰
Hudson River (27 June 1954)	− 6.0 ‰

(H. CRAIG, paper in preparation). Considering the relationships shown in the isohydrogram, we conclude that the average moisture received by the two areas is similar enough in history that the Chicago correction can be applied to N.Y. data.

There are only three snow samples in the pre-Castle Lamont data and these analyses vary by a factor of three in T content, but there are eleven rain samples which fell between 25 October 1953 and 3 March 1954 with an unweighted average T content of 9.45 T.U. Dividing this by 1.68, the increase factor found in Chicago rain during this period, we obtain a value for the natural level of 5.6 T.U. which agrees well with the average of 5.9. T.U. obtained for three N.Y. wines (K-L), and therefore fixes an approximate figure for uncontaminated N.Y. precipitation.

In Table 2 we list all the available data for pre-thermonuclear era precipitation, including the approximately corrected N.Y. value and the average figure derived for Chicago precipitation during the clean period. The two Hawaiian samples listed are plotted in Figure 2 together with three other Hawaiian rains and one New Zealand rain taken during the period October—December, 1953. Two of the Hawaiian rains of this period contained 0.67 and 0.73 T.U. (VB-L) indicating that an average figure of 0.6 is not a bad average for the natural level in Hawaiian rain.

In our calculations of the natural tritium production rate we have not considered data from lakes, reservoirs, or wells, since the age

Table 2. Tritium levels in pre-thermonuclear precipitation.

Sample	Tritium content (T.U.)	
Greenland snow (1944—52)	12.4	Begemann (1959)
Chicago precipitation (clean period)	6.0	(K-L, VB-L)
New York rain (Lamont data, corrected)	5.6	Giletti *et al.* (1958)
Three New York wines (1940—52)	5.9	(K-L)
Arkansas snow (January, 1953)	5.5	(K-L)
Arkansas rain (February, 1953)	2.25	(VB-L)
Four French wines, Bordeaux (1928—45)	4.4	(K-L)
Four French wines, Rhone Valley (1929—51)	3.8	(K-L)
Three Spanish wines, Jerez de la Frontera (1942—51)	3.1	(VB-L)
Philippine Islands rain (June, 1953)	0.9	(VB-L)
Two Hawaiian rains	0.61	(VB-L)
(March and July, 1953)	0.59	

of such water at the time of collection is always in question. The only other data available refer to pre-Castle samples of surface ocean water. These data are shown in Table 3. It is obvious that not much can be said about the pre-Castle ocean from these measurements. For example, the analyses of GILETTI, BAZAN, and KULP (1958) are 1 T.U. higher for two samples, and 0.7 T.U. lower for a third, compared with measurements on identical samples by VB-L.[1]

Table 3. Pre-Castle oceanic mixed layer tritium analyses.

Sample	Tritium content (T.U.)		
Pacific, off California, 6/6/53	0.54 ± .02		(K-L)
Atlantic, Gulf Stream, 9/11/53	0.19 ± .05		(VB-L)
Atlantic, 300 miles from N.Y	0.55 ± .04		(VB-L)
Same sample	1.31		(GBK)[1]
Atlantic, Sargasso Sea 9/10/53	0.29 ± .02		(VB-L)
Same sample	1.34		(GBK)
Atlantic, Sargasso Sea, 9/7/53	1.6	± 0.1	(VB-L)
Same sample	0.92		(GBK)
Atlantic, 10/31/52	2.2	± .25	(B-L)
	1.8	± .25	
Atlantic, 10/22/52	1.3	± .1	(B-L)
Pacific, 10/28/52	1.05	± .1	(B-L)
	1.0	± .1	
Pacific, 11/26/52	1.5	± .2	(B-L)
Pacific, 11/18/52	10	± 1	(B-L)
Pacific, 12/19/52	16.3	± 1	(B-L)
Eleven Atlantic samples, 7/22 to 9/12/53	0.62 to 1.5		(GBK)

[1] Giletti, Bazan, and Kulp (1958)

The Lamont data are corrected for a blank of 0.3 T.U. found for dead water; Libby and his co-workers do not report any blanks. It is difficult to account for the generally high values found by B-L relative to the earlier data of VB-L and K-L except by assuming laboratory contamination due to the high atmospheric levels during the times of measurement. The average surface ocean water after Castle is about 2 T.U. as measured at Lamont and Chicago, and assuming that all of this is due to Castle production, we can estimate from Figure 1 that, considering atmospheric levels only, the Ivy and U.S.S.R. tests could not have produced more than about 10 % of the amount of T produced by Castle, which would therefore have raised the surface sea water level by possibly 0.2 T.U. as an upper limit. Of course this estimate does not include direct local introduction into the sea, and there is some evidence from the very high values obtained by B-L in the Pacific after Ivy that this may be significant, though one would still expect the effect to be considerably smaller than in the case of the Castle tests, and also that it would be completely diluted before reaching the Atlantic.

It is possible to calculate the rate of introduction of tritium into the troposphere by two basic methods (CRAIG, 1957). The first of these considers the balance in the oceanic mixed layer, assuming an oceanic mixing model with parameters given by radiocarbon data.[2] The introduction rate calculated by this method is a very sensitive function of the amount of tritium in the mixed layer. Considering the disparity between Lamont and Chicago

[1] Lamont sample numbers are given by VB—L, but GILETTI, BAZAN, and KULP do not list their sample numbers so that comparisons cannot be made from their paper. We have looked up the sample numbers and descriptions in their original reports.

[2] The calculation cannot be made for the global tropospheric balance without making an assumption about the rate of molecular exchange of H_2O between the atmosphere and the sea. See discussion by CRAIG (in press).

data on the same samples, and the scatter of data in Table 3, we do not believe a meaningful calculation can be made by this method. A high upper limit of about 0.65 T.U. for the mixed layer T concentration can be derived from the Hawaiian rain trajectory in the isohydrogram, assuming no T enters the troposphere (CRAIG, in press), but no good lower limit can be estimated. The second method is based on the precipitation data and water balance for the North American continent, using the data in Table 2; we make this calculation in the following section.

Tritium balance in the North American troposphere

We now calculate the net introduction rate of tritium into the North American continental troposphere by direct tropospheric cosmic ray production and by downward mixing from the stratosphere. The flux of tritium from these two sources is termed the *gradient flux* into the North American troposphere, ϕ_t^* (NA) (cf. discussion of the similar term for the global troposphere in the following section). The overall water balance for North America is known from the data of BENTON and ESTOQUE (1954) who measured the net transport of water vapor at a series of stations around the continental border in 1949 (Figure 4). We shall make the balance in the troposphere over the continent, rather than for the system troposphere + continent, because we do not have sufficient data to estimate accurately the tritium removed from the continent in runoff. The vapor transport, precipitation, and evaporation fluxes into and out of the continental atmosphere are given in the first column of Table 4. The equation for the atmospheric tritium balance is:

$$4.73\ \phi_t^*(\mathrm{NA}) = V_o T_o - V_i T_i + \\ + P T_p - E T_e + \lambda A T_a$$

in which the symbols are defined in Table 4, except for the last term which is the decay of tritium in the atmosphere, A being the standing water content and T_a its tritium content. This term can readily be shown to be of the order of 0.01 and can always be neglected. ϕ_t^* (NA) is the gradient flux of tritium into the North American troposphere by direct cosmic ray production and stratospheric

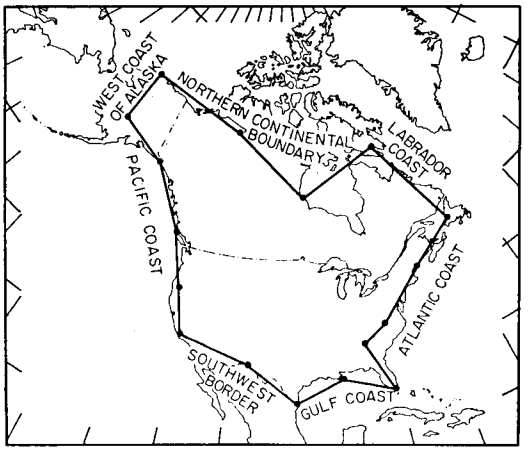

Fig. 4. North American continental boundaries used in the vapor transport study by Benton and Estoque (1954).

injection, and 4.73 meters of water/year = 10^{18} H atoms/cm^2 sec.

The tritium content of evaporating vapor on the continent can be obtained from the average precipitation value, as these concentrations must be quite similar (BOLIN, 1958). The exposed area of lakes and rivers is so small that they cannot contribute significantly to the large amount of evaporation and transpiration which takes place in the soil before the precipitation reaches these storage units. Moreover, this evaporation will take place so soon after the precipitation falls that no tritium can be lost by decay, and the only effect on the tritium content of the evaporating vapor will be isotopic fractionation. If a small amount of water evaporates the single stage factor will apply, so that T_e is about 0.91 T_p (SEPALL and MASON, 1960), whereas if it all evaporates $T_e = T_p$; moreover the effect in transpiration will be small if the plant transpires most of the water it takes in.[1] Therefore we may set $T_e = 0.95\ T_p$ as an average value for the continent.

Fortunately, it seems that Chicago and New York precipitation, the only extensive set of uncontaminated tritium data, should be a reasonably adequate approximation to the mean type of precipitation on the continent.

[1] The water in a tomato grown outside Chicago had $\delta D = -2.5$ %, about the same as mean Chicago rain. If we can extrapolate from tomatoes to grapes, this result indicates that the wine data in Table 2 have probably not been significantly affected by isotopic fractionation.

For example, the distribution of precipitation over the continent, as shown by REED (1941), and the trend of D and T concentrations in the isohydrogram, indicate that the precipitation received at Chicago should be an approximate average both with regard to amount of precipitation and absolute tritium content. The southeastern U.S. receives the most precipitation, but its area is small and the T content of the incoming vapor is low because of recent derivation from the ocean. δD values of waters in this area range from -1 to -2 %. The west and northwest sections of the continent receive less precipitation, but they make up more of the area. Rains along the U.S. Pacific coast show $\delta D = -4$ to -5 %, while inland waters from the Canadian border to the Beaufort Sea, in the western half of Canada and in Alaska, show δD uniformly about -12 to -16%, so that the T content of the precipitation will be correspondingly high (cf. our discussion of trajectories in the isohydrogram).

This pattern can be correlated roughly with Figure 5, taken from BENTON and ESTOQUE (1954), which shows the average integrated water vapor transport for the year 1949. In this figure one can see that Chicago and New York lie approximately on a sort of median convergence line between the major vapor trajectories into the continent across the Gulf coast and the Pacific coast. The large δD variations in Chicago, shown in Figure 3, which have a range equal to that found over the whole continent, and the associated T/H variations shown in Figure 2, are a measure of the sampling of northern and southern air during the seasonal migration of the polar front between Manitoba and Florida. Considering these variations, the fact that the U.S. gets slightly over half the continental precipitation with the highest rate in the southeast U.S., and the indication from Figure 2 that the Greenland snow probably represents a maximum value for any precipitation on the continent, we do not believe that the mean tritium content of North American precipitation could possibly have been greater than 8 T.U. or less than 4 T.U. in the prethermonuclear epoch. Accordingly we conclude that we can take the Chicago and New York averages in Table 2 as the continental average, and we set $T_p = 6 \pm 2$ T.U.

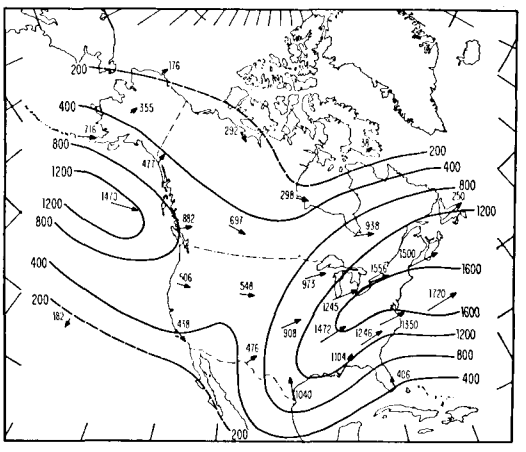

Fig. 5. The integrated water vapor transport (surface to 400 mb) for the North American continent, averaged for 1949. The figures are vapor transport in grams/cm sec (Benton and Estoque, 1954).

In order to estimate the amount of tritium transported by vapor, the liquid-vapor fractionation factor for HTO is needed. We have obtained this in the following way. The ratio between deuterium and oxygen 18 variations in worldwide precipitation samples is uniformly about 8, indicating an average temperature for precipitation-vapor equilibrium in the atmosphere of about $-10°\,C \pm 10°$ (H. CRAIG, 1961). Extrapolation of the data of SEPALL and MASON (1960) for minimum and maximum slopes shows that the liquid-vapor fractionation factor for HTO at —10° C may be taken as $\alpha = 1.1 \pm 0.1$. The actual relationship between the T/H ratios in mean vapor crossing a boundary and precipitation observed in storms will depend upon whether an open or closed system is assumed as a model, but in all cases the T/H ratio of mean vapor will vary between limits of the mean ratio in precipitation, or this ratio divided by α. Therefore α as given above, with the limits noted, can be taken as a mean value covering all possibilities.

According to BENTON and ESTOQUE (1954) about half the vapor entering the continent comes in along the Gulf coast and southwest border boundaries (Figure 4), and about half comes in along the Pacific coast, with a principal vector at about 50° of latitude (Figure 5). The precipitation characteristic of such vapor is estimated as follows. There is undoubtedly a latitude effect in the tritium content of marine vapor due to the occurrence of the

stratospheric injection site in high latitudes. For the Pacific coast vapor we use the French and Spanish wines in Table 2 (in which fractionation is probably not important; cf. our comment on the deuterium content of natural tomato juice) especially at Bordeaux, assuming an average of 4 T.U. for the characteristic precipitation. For the Gulf and southwest border, the Hawaiian and Philippine rains (Table 2) and our estimated upper limit for the mixed layer, indicate that average precipitation from such vapor will have about 1 T.U. Also, a measurement on a Puerto Rican river gave 1.1 T.U. (VB-L). Therefore we take the precipitation characteristic of the mean incoming vapor as about 2.5 T.U., and we assume for the incoming vapor $T_i = 2.3 \pm 0.5$ T.U.

About 32 % of the outgoing vapor leaves along the Labrador coast boundary, and about 68 % along the Atlantic coast border, according to the measurements of Benton and Estoque. The characteristic precipitation from Labrador coast vapor is taken as the mean of Greenland snow, and New York precipitation as estimated from rain and wine, or about 9.0 T.U. The Atlantic coast shows a fairly uniform outward flux (Figure 5); we have divided it in half, and taken New York precipitation as characteristic of the northern half, and the mean of New York and estimated Gulf coast precipitation for the southern half, for a mean Atlantic coast precipitation level of 4.75 T.U. Weighting these two means according to the proportions given by Benton and Estoque gives 6.1 T.U. for precipitation from outgoing vapor; and we take $T_o = 5.5 \pm 0.9$ T.U. for the outward vapor transport from the continent.

In Table 4 we summarize the water transport data, the estimated natural tritium concentrations, and the flux of T by each route. The limits of uncertainty indicated for the tritium flux data are those estimated from the tritium concentrations and the uncertainties in averaging and in α; these errors are believed to be much more important than the uncertainties in the Benton and Estoque transport values which probably tend, to some extent, to cancel each other, and which are, in any case, unknown. It should be remembered, however, that these values actually apply only to the year 1949. The removal of tritium by vapor transport is seen to be four times as great as removal by precipitation to the continent.

The net introduction of tritium into the North American troposphere, by tropospheric cosmic ray production and stratospheric mixing, is found to be ϕ_t^* (NA) $= 0.64 \pm .33$ atoms T/cm^2 sec, for the pre-thermonuclear epoch. We shall use this value to estimate the global tropospheric and total atmospheric production rates of natural tritium.

The gradient flux of tritium into the global troposphere

Prior to entrance into the sea, tritium is introduced into the troposphere by direct cosmic ray production and by stratospheric injection during the downward mixing of stratospheric air across the tropopause. We shall call the sum of these two introduction rates the *gradient flux*, ϕ_t^*, i.e. the mean

Table 4. Values of annual water transport, pre-thermonuclear titrium concentrations, and tritium flux, estimated for North American troposphere.

	Annual net flux H_2O (meters)[1]	Tritium content[2] (T.U.)	Tritium flux[2] (atmos T/cm^2 sec)
Vapor, sea to land	$V_i = 0.87$	$T_i = 2.3 \pm 0.5$	$+ 0.42 \pm .08$
Vapor, land to sea	$V_o = 0.72$	$T_o = 5.5 \pm 0.9$	$- 0.84 \pm .14$
Precipitation	$P = 0.68$	$T_p = 6 \pm 2$	$T_p(P - 0.95E) =$
Evaporation	$E = 0.53$	$T_e = 0.9\, T_p$	$- 0.22 \pm .07$
			ϕ^* (NA) $= 0.64 \pm .33$

[1] Data from BENTON and ESTOQUE (1954). Evaporation was calculated (a) as the difference between precipitation and estimated continental runoff, $E = 0.50$, and (b) from atmospheric transport data and estimated change of atmospheric reservoir, $E = 0.56$. We have taken the mean of these two values.

[2] Errors shown are calculated for $\alpha = 1.1$, except for the final value of the net T flux where the limits are the total range including the uncertainty in α.

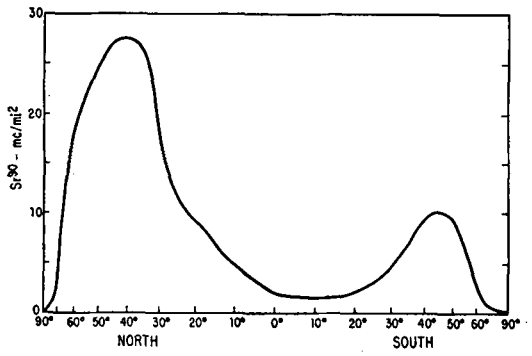

Fig. 6. Stratospheric Sr^{90} deposition through spring, 1958. From Machta and List (1959).

introduction rate exclusive of back mixing from reservoirs farther down the gradient (in this case the sea and the continental standing water).

The steady mixing fluxes of stable and radioactive isotopes from reservoir i to reservoir j are termed ϕ_{i-j} and ϕ^*_{i-j} respectively.

In order to calculate the global tritium production rate $\overline{Q}$, we first need to calculate the tropospheric gradient flux ϕ^*_t from the North American tropospheric gradient flux ϕ^*_t (NA) obtained in the previous section. To evaluate the ratio ϕ^*_t/ϕ^*_t (NA), the distribution of cosmic ray production between stratosphere and troposphere, and the distribution pattern of stratospheric injection into the troposphere, must be known.

In a later section of this paper we calculate $\overline{Q}$ directly from cosmic ray data. The relative production rates in the stratosphere and troposphere can be obtained from the relative star production ratios, independent of the normalization to absolute values, because the triton yield per star does not vary more than 15 % throughout the atmosphere. The tropospheric and total global triton production rates as a function of geomagnetic latitude, assuming constant triton/star ratio, are shown in Figure 9; the integrated fractions of total production in the troposphere and stratosphere are $\overline{Q}_t/\overline{Q} = 1/3$; $\overline{Q}_{st}/\overline{Q} = 2/3$.

The ratios of North American to global production rates are obtained by integrating the star production rates over the continent (30—65° latitude, using the area defined in Figure 4); this can be done with respect to latitude only, because the east-west continental dimension happens to be practically constant over the area considered.[1] The ratios of North American to global star production rates/cm² in the troposphere, stratosphere, and total atmosphere, are then found to be 0.97, 1.67, and 1.40 respectively. Thus the continental shape is such that the North American troposphere is almost a perfect average for global tropospheric production.

The general features of the distribution of stratospheric tritium can be evaluated from the studies on fission products injected into the stratosphere by nuclear weapons because the fission products are removed from the stratosphere by air circulation rather than by gravitational settling. Models for stratospheric-tropospheric mixing have been proposed by LIBBY (1959), MACHTA (MACHTA and LIST, 1959), and MARTELL (1959); a detailed discussion of these models and of the most recent data is given by Martell and reference is made to his paper for details. The minor differences between these models do not affect our discussion which is based on the following general characteristics:

1. The fallout pattern of stratospheric activity shows a pronounced peak at middle latitudes, regardless of the latitude of injection. Figure 6 from MACHTA and LIST (1959) shows the latitudinal distribution of Sr^{90} fallout; practically all of this material is of stratospheric origin (LIBBY, 1959; MARTELL, 1959).

2. The average residence time of material injected into the stratosphere is a function of the injection latitude. The residence time is of the order of 5 years for high altitude equatorial injection, but for middle and high latitude injection it is of the order of 6 months to a year (MARTELL, 1959).

From these observations, it is possible to calculate the approximate ratio of the global and North American tropospheric gradient fluxes for three limiting types of stratospheric tritium injection. For this purpose we may assume that there is no stratospheric decay (cf. the mean residence time derived in the next section) and we take the mean tropospheric production rate in North America as

[1] That is, we integrate $S(\Theta)\, d\Theta$, and compare with $S(\Theta) \cos \Theta\, d\Theta$, where S is the star production rate.

equal to $\overline{Q}_t$ as noted above. Then the tropospheric gradient flux ratio may be written:

$$\phi_t^*/\phi_t^*(\mathrm{NA}) = \overline{Q}/(\overline{Q}_t + F\overline{Q}_{st}) = 3/(1+2F)$$

where F is the ratio of the tritium flux from the stratosphere into the North American troposphere to $\overline{Q}_{st}$. The following limiting cases are readily derived from the parameters discussed above:

1. We assume all stratospheric tritium is injected into the troposphere between latitudes 30 and 90°. Then $F = 2$, and the gradient flux ratio as written above is 0.60.

2. We assume that stratospheric injection occurs at the tropopause at all latitudes with relative rates/cm² as given by the Sr^{90} stratospheric fallout curve in Figure 6. From this curve one can see that the mean fallout rate/cm² over North America is about three times the rate for the rest of the troposphere. Then $F = 1.5$ and the gradient flux ratio is 0.75.

3. We assume that only the tritium produced in the North American stratosphere is injected into the North American troposphere. Then, as given above, $F = 1.67$ and the gradient flux ratio is 0.69.

Case 1 is the most likely, but in order to have reasonable limits for $\overline{Q}$ we shall take a mean value of ϕ_t^*/ϕ_t^* (NA) = 0.68 ± 0.08. From the value obtained previously for ϕ_t^* (NA), we find the mean flux of tritium into the global troposphere from production and stratospheric injection to be $\phi_t^* = 0.44 \pm .27$ atoms T/cm².

Calculation of $\overline{Q}$ from the geochemical inventory

Using the terminology defined at the beginning of the previous section, the steady state tritium balance in the stratosphere is given by:

$$\overline{Q}_{st} + \phi_{t-st}^* = \phi_{st-t}^* + \lambda N_{st}^*$$

The back flux from the troposphere, ϕ_{t-st}^*, is completely negligible because of the very small amount of water in the stratosphere. If internal mixing in the stratosphere is rapid enough, relative to the decay constant λ, so that significant tritium gradients are not present, then we may write $\phi_{st-t}^* = N_{st}^* \phi_{st-t}/N_{st}$, where the * signifies the radioactive, low concentration, isotope and the unstarred terms refer to the stable species. We also write $N_{st}/\phi_{st-t} = \tau_{st}$, the residence time or average life of a water molecule in the stratosphere relative to exchange into the troposphere. The stratospheric balance equation may then be written:

$$\overline{Q}_{st} = \phi_{st-t}^*(1 + \lambda\tau_{st})$$

in which we have only assumed that tritium obeys first order kinetics because of its low concentration and rapid internal mixing. The gradient flux of tritium into the troposphere is the sum of the tropospheric production rate and the mixing rate from the stratosphere, and remembering the proportionality factors between total, tropospheric, and stratospheric cosmic ray production rates deduced earlier, we have, finally:

$$\frac{\phi_t^*}{\overline{Q}} = \frac{1}{3} + \frac{2}{3}\left[\frac{\tau_r}{\tau_r + \tau_{st}}\right]$$

where ϕ_t^* is the mean global tropospheric gradient flux calculated in the last section, and we have written λ^{-1} as τ_r, the mean radioactive life (18.0 years).

As discussed in the previous section, the fallout studies indicate a variation of the stratospheric residence time with the latitude of injection into the stratosphere (MARTELL, 1959). We have therefore assumed a graded series of stratospheric residence times over four latitude intervals, based on Martell's work, and we apply these factors to the relative fractions of stratospheric tritium produced by cosmic rays in these intervals, as evaluated from the latitudinal production curves given in Figure 9 in a following section. The assumed intervals, residence times, and stratospheric production fractions are as follows:

Latitude Interval	Residence time, τ_{st}	Fraction of total Stratospheric Production
0—20°	6 ± 2 years	8 %
20—30°	3 ± 1 years	7 %
30—45°	1.5 ± .5 years	20 %
> 45°	1.0 ± .3 years	65 %

The mean residence time for stratospheric tritium, relative to removal to the troposphere, is then found to be 1.6 ± 0.5 years, in which we have used the maximum limits given above. Therefore only 8 % of the tritium produced in the stratosphere decays in the stratosphere and 92 % is injected into the troposphere.

From the stratospheric balance equation and the mean residence time we then have $\overline{Q} = (1.06 \pm .02)\ \phi_t^*$, and with the gradient flux obtained in the last section we obtain: $\overline{Q} = 0.46^{+.34}_{-.26}$ atoms T/cm² sec as the mean global production rate calculated from the geochemical inventory. The errors assigned in the various stages have been kept as maximum deviations, rather than combined as statistical errors, and we take in round numbers $\overline{Q} = 0.5 \pm 0.3$.

The single most serious assumption in this calculation seems to us to be that the average North American precipitation tritium level can be taken as the Chicago and New York mean, plus or minus 2 T.U. Our study of the precipitation data and the isohydrogram leads us to believe these limits are justified.[1] We turn now to the calculation of $\overline{Q}$ from the cosmic ray and nuclear cross section data, independent of the inventory.

Calculation of $\overline{Q}$ from cosmic ray data

The cosmic ray production rate of tritium has been calculated directly by FIREMAN and ROWLAND (1955) and by CURRIE *et al.* (1956) who obtained values of 0.2 and 0.14 tritons/cm² sec. BENIOFF (1957) recalculated the tritium production rate using the theories of nucleonic cascade development in the atmosphere, and obtained a slightly higher value of 0.31 atoms/cm² sec. SIMPSON (1960) has estimated that the low energy (~ 100 Mev) solar protons incident at the polar regions following solar flares may produce about 3 times the global amount produced by cosmic rays. WILSON and FERGUSSON (1960) estimated the tritium production rate in the atmosphere from the observed T contents of stone meteorites, and also calculated the atmospheric production rate using the theoretical production rate of helium in iron meteorites (MARTIN, 1953) and nuclear evaporation theory. These calculations gave values of $.63^{+.40}_{-.20}$ and 1.3 ± 0.5 tritons/cm² sec. Their calculations require knowledge of several factors necessary to transform the production rate in a meteorite to that in the atmosphere; the choice of the parameters is quite arbitrary and with a reasonable set of numbers, one can easily obtain values smaller by a factor of five. A calculation of this type therefore turns out to be very inaccurate and not very meaningful.

Fireman and Rowland, and Currie *et al.* used the available cross sections for the formation of tritium in nitrogen and oxygen in bombardments by protons of 450 MeV and 2 Bev, and in nitrogen by fission neutrons above 4.4 Mev. Recently, tritium cross sections have become available for medium energy protons (HONDA and LAL, 1960) as well as for very high energy protons (CURRIE, 1959). These values combined with cosmic ray data, particularly the recently studied neutron energy spectrum in the atmosphere, suffice to make fairly reliable estimates of tritium production in the atmosphere.

Tritium production takes place principally in the nuclear disintegrations of atmospheric nitrogen and oxygen. The nuclear interactions can be produced by the nucleonic component (neutrons and protons) and by the weakly interacting component consisting of fast and slow mesons, and photons. The abundance of μ mesons and photons is known fairly well for atmospheric depths greater than 100 gm cm^{-2}. No cross sections for tritium production in their interactions have been measured as yet, but we can estimate reasonable values for the total rates of all interactions caused by these particles in the atmosphere. With conservative estimates of the yield of tritium in stars produced by μ mesons and photons, it is found that tritium production by these particles is smaller by two orders of magnitude than the amount produced by the nucleonic component; thus the inherent large uncertainties in these calculations are not serious and we need

[1] BEGEMANN (1959) has calculated $\overline{Q}$ from his Greenland snow data, assuming all tritium formed over Greenland in the troposphere precipitates there and none is carried in by vapor. It is impossible to estimate the reliability of this value since no vapor transport data are available and his samples are from only the northwest fringe of the continent. He has assumed τ_{st} = 10 years, and we only wish to point out that the use of the residence time we assume would make his value of Q become 0.5.

only consider the production by neutrons and protons.

Tritium production by the nuclear component

The rate of occurrence of nuclear disintegrations (stars) in the atmosphere has been calculated as a function of altitude and latitude by LAL *et al.* (1958) using only the experimentally determined cosmic ray data. The relative variations within the atmosphere are based on the extensive data on slow neutrons and stars. Absolute star production rates were obtained by normalization at the point 680 gm cm^{-2}, $\lambda = 50°$, where star production rates in a nitrogen and argon filled cloud chamber have been determined (BROWN, 1954). Measurements of the Be^7 production rate in oxygen at Echo Lake ($\lambda = 50°$, 685 gm cm^{-2}) and the excitation function of Be^7 in nitrogen and oxygen (HONDA and LAL, 1960) have now shown that the normalization value for stars as used by LAL *et al.* (1958) is correct within ± 20 %. We will use their calculated star production rate together with the tritium yield per star for different positions in the atmosphere. The star production rate refers primarily to nuclear disintegrations produced by nucleons of energy above 40 Mev. Appreciable tritium production also occurs by lower energy nucleons because the thresholds in nitrogen and oxygen are 4.4 Mev and 15 Mev respectively (CURRIE *et al.*, 1957). The tritium yield per star is calculated below using (a) the excitation function of tritium in air, and (b) the nucleon energy spectrum in the atmosphere.

The average cross sections, per atom, for tritium production in the bombardment of a mixture of nitrogen and oxygen having the composition of air are plotted in Figure 7. The errors in the cross sections are ~ 20 %. The cross section data are fairly well spaced above 225 MeV and permit a reasonable interpolation. Below 225 Mev the only available measurement is in nitrogen for fission neutrons above 4.4 Mev. The mean neutron energy is estimated to be 5.7 Mev (CURRIE *et al.*, 1957). At this energy the average cross section for air nuclei is obtained by multiplying the nitrogen cross section by 0.78 because tritium production does not occur in oxygen below 15 MeV.

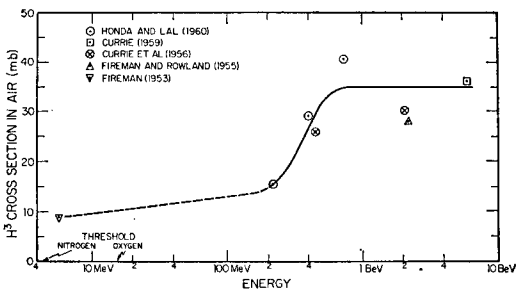

Fig. 7. Excitation function of tritium in air. Note: the value of Fireman and Rowland should be increased by about 20 % (to atomic values of 33 ± 4 mb for N and 39 ± 4 mb for O) because of recent revisions in the cross section for their monitor reaction Al^{27} $(p, 3pn)$ Na^{24} (Rowland, personal communication).

The dotted line in Figure 7 shows the interpolation made between 5.7 MeV and 225 MeV.

The differential energy spectrum of neutrons and protons has been measured at atmospheric depths greater than 200 gm cm^{-2}. Various measurements show that nucleons of energy below 500 MeV are in equilibrium for depths greater than 200 gm cm^{-2}; the shape of the energy spectrum below 500 MeV remains unaltered throughout the equilibrium region at all latitudes and altitudes. The relative variations in intensity can be obtained from the data on slow neutrons (SOBERMAN, 1956; HESS *et al.*, 1959). The nucleon flux for $\lambda = 50°$, 680 gm cm^{-2}, is plotted in Figure 8. The ordinate shows the integrated flux, J, of nucleons passing through a unit sphere (particles/cm^2 MeV sec), i.e.

$$J = 2\pi \int_0^{\pi/2} J_\theta \sin\theta \; d\theta$$

where J_θ represents the intensity (cm^{-2} sec^{-1} sterad^{-1} MeV^{-1}) at azimuth angle θ. The number of interactions per gram is then given by $JN\sigma$, where N is the number of atoms/gm and σ is the cross section for the interaction.

The results of the vertical proton flux determinations agree within the experimental errors (MYLROI and WILSON, 1951; FILTHUTH, 1955; PUPPI, 1956). The angular dependence of the flux is given by CONVERSI and ROTHWELL (1954). In the case of neutrons, the agreement between the various data is not as good. Curve I in Figure 8 shows the energy spectrum of neutrons from 1 MeV to 2 BeV as obtained

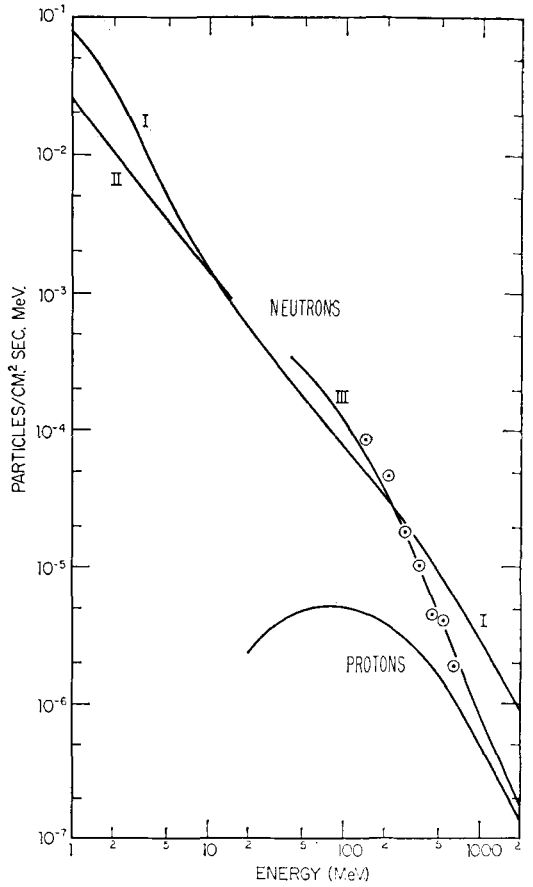

Fig. 8. Differential energy spectrum of nucleons in the atmosphere at $\lambda = 50°$, 680 gm cm^{-2}.

by HESS *et al.* (1959). These workers employed several calibrated detectors of varying sensitivity to neutron energies from thermal to few hundred MeV. The shape of the spectrum was determined by trial and error functions which matched the total counting rates of the detectors, and production rate of stars in nuclear emulsions. Curve II shows the neutron energy spectrum as measured by MIYAKE *et al.* (1957) using proton recoils in a high pressure hydrogen cloud chamber.

The circled points were obtained (LAL, 1958) using the proton energy spectrum and the relative frequency of neutron and proton induced stars of different sizes in nuclear emulsions (BROWN *et al.*, 1949; BARFORD and DAVIS, 1952). The average energy $\bar{E}$, of nucleons producing a star of N prongs was calculated using the empirical relation $\bar{E} = 37N + 4N^2$ (BROWN *et al.*, 1949). This relation holds for stars where the energy of no emitted particle exceeds 350 MeV. The solid curve III drawn through these points has been extended to 40 MeV using the data on the production spectrum of protons in stars (CAMERINI *et al.*, 1949; LAL, 1958). Curve III approaches the proton energy spectrum at $E > 1$ BeV, as anticipated, because the production spectra of neutrons and protons are expected to be identical for energies well above the coulomb barrier. Above 1 BeV absorption or loss of energy occurs only by nuclear interactions, while at the lower end of the spectrum neutrons are more abundant than protons as the latter are depleted by ionization losses. Curve I departs considerably from the expected behavior above 500 MeV.

The yield of tritium per star depends on the shape of the energy spectrum, and we have therefore calculated the tritium yields separately for these spectra in order to estimate the errors introduced. The average cross section for the formation of tritium in stars above 40 MeV was calculated by the relation:

$$\bar{\sigma}_T = \frac{\int_{40}^{\infty} \sigma_T(E) J(E)\, dE}{\int_{40}^{\infty} J(E)\, dE}$$

where $J(E)$ represents the differential energy spectrum of nucleons (particles/cm² sec MeV) as given in Figure 8. The total nucleon flux $J_{n+p}(>40)$, above 40 MeV and $\bar{\sigma}_T$ are tabulated separately for the neutron spectrum I and III in Table 5. In the same table, we also give the tritium yield in stars, Y_T, obtained by dividing $\bar{\sigma}_T$ by σ_S, the average cross section for star production. The value of σ_S in air is estimated[1] to be 225 ± 20 mb, by subtracting the cross sections for the nuclear reactions involving emission of neutrons only (which lead to zero pronged stars) from the total inelastic cross section in nitrogen and oxygen.

The ratio of the amounts of tritium produced

[1] Support for this value is obtained from the measurements of cross sections in C, N and O nuclei of emulsions by protons of energy 40 MeV—900 MeV (Lock and March, 1955, and references therein). The average cross sections for 45—100, 240, 600, and 950 MeV protons were found to be 170 ± 20, 230 ± 30, 222 ± 60 and 202 ± 50 mb respectively.

Table 5. Tritium production parameters (see text).

Neutron energy spectrum	$J_{p+n}(>40)$ (cm^{-2} sec^{-1})	$\bar{\sigma}_T$(mb)	$Y_T(>40)$	R	$Y_T(1+R)$
Curve I	27.6×10^{-3}*	21.3	9.5 %	0.52	14.4 %
Curve III	27.5×10^{-3}*	16.3	7.2 %	0.66	12 %
Average	27.5×10^{-3}	18.8 ± 2.5	8.4 ± 1.2	0.59 ± .07	13.2 ± 1.2 %

* Though the shape of the energy spectra I and III differ significantly, the total fluxes above 40 MeV agree very well. The star production rate at 680 gm cm^{-2}, $\lambda = 50°$, is found to be 2.5×10^{-4} stars/gm air sec, which should be compared with the value of $2.3\ 10^{-4}$ used in the calculations by Lal *et al.* (1958).

below and above 40 MeV, R, is given in the fifth column of Table 5. The spectrum used below 40 MeV for Curve III was obtained by extrapolating through the curves I and II. The total tritium production due to nucleons of $E > 5$ Mev, $Y_T(1+R)$, is found to be 13.2 % ± 1.2 % in stars (Table 5).

As mentioned earlier, these calculations apply for all latitudes and altitudes in the equilibrium region of the atmosphere. No measurements of nucleon energy spectrum are available for depths < 200 gm cm^{-2}. The energy spectrum is expected to be flatter near the top, and the tritium yield per star will consequently be higher. For this region we have calculated the total tritium yield per star under the following assumptions:

(a) The ratio of the neutron flux, $5 < E <$ 40 MeV to total remains constant throughout the atmosphere. The tritium cross section in this energy interval remains essentially constant and no error is introduced by using the same energy spectrum as in the equilibrium region.

(b) The shape of the energy spectrum in the non-equilibrium region can be obtained by comparing the star size distributions. Star size distributions at several latitudes and altitudes are available (Birnbaum *et al.*, 1952; Lal *et al.*, 1958).

We find that the total tritium produced per star at depths < 200 gm cm^{-2} is larger than the value for the equilibrium region of the atmosphere by 15 % and 7 % in low and medium latitudes respectively. Considering the absolute rates of star production in different regions of the atmosphere, the average tritium produced per star in the entire atmosphere is effectively 8 % higher than the calculated value for the equilibrium region.

The global star production rate in the atmosphere has been estimated to be 1.7 stars/cm^2 sec (Lal *et al.*, 1958). The corresponding rate of tritium production is therefore $1.7 \times 0.13 \times 1.08 = 0.24$. The uncertainty in this value[1] is probably less than ± 30 %, i.e. ± 0.07.

The approximate distribution between tropospheric and total atmospheric triton production as a function of geomagnetic latitude is shown in Figure 9, in which the T production

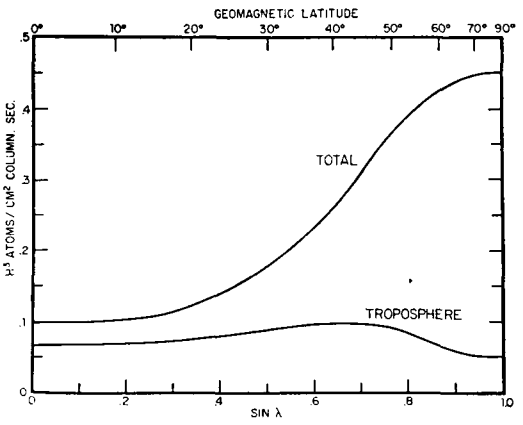

Fig. 9. Calculated tritium production rate in a cm^2 column to the top of the atmosphere ("total" curve) and up to the tropopause ("troposphere" curve), vs. geomagnetic latitude.

rates have been plotted by assuming constant proportionality to the star production rates. Integration of these curves shows that about $^2/_3$ of the total global tritium production

[1] It has so far been assumed that the star production rate obtained by Lal *et al.* (1958) refers to stars produced by nucleons above 40 MeV. The production rate of stars below 40 MeV is small since the star production cross section is expected to fall rapidly below 30—40 MeV. In order to estimate the uncertainty due to the cut off energy used in the calculation, we have made the unlikely extreme assumption that the star production cross section in air is 225 mb up to 25 MeV. This would lower the tritium per star value by 18 %.

Table 6. Comparison of $\bar{Q}$ values calculated from cosmic ray and nuclear data.

Energy Region (MeV)	Global production rate of T (atoms/cm² sec)			
	Present Work	Currie *et al.* (1956)	Fireman & Rowland (1955)	Benioff (1957)
< 10	0.04	0.05	0.1*	0.05**
10—40	0.05	0.01 (for 10—100 MeV)	0.1	0.26
> 40	0.15	0.082		
Total $\bar{Q}$	0.24 ± 0.07	$0.14^{0.22}_{0.09}$	0.2	$0.31^{0.45}_{0.15}$

* Fireman and Rowland estimated a value of 0.1 for slow neutrons without specifying the energy range considered. Part of this production belongs to neutrons of ~ 10 MeV.

** Benioff used the value of Currie *et al.* (1956) for < 10 MeV.

takes place in the stratosphere and $^1/_2$ in the troposphere. These data were used earlier to calculate $\bar{Q}$ from the gradient flux into the North American troposphere.

The value of $\bar{Q}$ obtained here is compared with previous calculations in Table 6. Within the calculation errors, the various estimates are seen to be in good agrement. The mean value of Currie *et al.* is the lowest and this can be ascribed to their underestimating the contribution to production by 10—100 MeV nucleons. Our calculations yield a value of 0.1 for this region compared to the value of 0.01 estimated by Currie *et al.* Taking this into account, their value becomes 0.23, in good agreement with ours.

Time variations in $\bar{Q}$, and the mean $\bar{Q}$ value over the solar cycle

The incident cosmic ray intensity varies with time due to solar modulations in space. The variation has been shown to be inversely correlated with the 11-year sunspot cycle. The changes brought about in the energy spectrum of primary cosmic rays, as well as those in the neutron counting rates at different depths in the atmosphere, have been studied fairly extensively between 1954 (sunspot minimum) and 1958 (sunspot maximum). The changes during 1956 and 1958 with respect to 1954, when cosmic ray intensity was maximum, are shown in Figure 10. For a detailed discussion see LAL and PETERS (1960).

The calculations of LAL *et al.* (1958) of the star production rate were based on the cosmic ray data obtained during 1948—1949, a period close to the maximum in a sunpot cycle. It can be seen from Figure 10 that during 1958 solar activity was unusually high and the cosmic ray intensity was therefore abnormally low. The mean yearly sunspot numbers in 1958 are in fact higher than observed in any year during the last 200 years for which

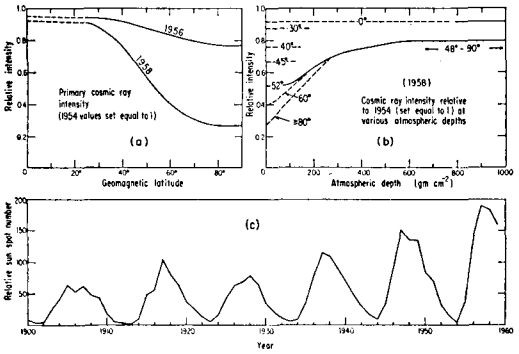

Fig. 10. (a) Primary cosmic ray intensity during 1956 and 1958, relative to 1954 values, vs. geomagnetic latitude. (b) Cosmic ray intensity during 1958 relative to 1954 values, plotted vs. atmospheric pressure for several latitudes. (c) Relative annual sunspot numbers from 1900—1959.

measurements are available. The sunspot activity during 1948—49 and 1956 is nearly the same, and we have therefore assumed that the primary cosmic ray spectrum during these years was nearly the same. The changes with time in total tritium production rate in a 1 cm² atmospheric column, ΔI, can be calculated from the corresponding change ΔP in the primary cosmic ray flux:

$$\Delta I = \frac{\left(\frac{\partial I}{\partial \lambda}\right)}{\left(\frac{\partial P}{\partial \lambda}\right)} \Delta P$$

The derivatives of the total tritium production rate and the primary cosmic ray intensity with respect to latitude, $\partial I/\partial\lambda$ and $\partial P/\partial\lambda$ are known (LAL *et al.*, 1958; MCDONALD, 1959). We find that the mean global production rates during 1958 and 1954 were respectively 22 % lower and 9 % higher than during 1948—49 (or 1956).

From the available solar data, we find that the maximum and minimum sunspot activities during a typical cycle are close to that observed during 1956 and 1954 respectively. Since we estimate that the global tritium production rate during 1954 was higher than in 1956 by 9 %, the average deviation amounts to $\pm$ 4.5 %. The calculated value of 0.24 for $\overline{Q}$ refers to 1948—1949 (or 1956) and the average value during a typical solar cycle becomes, $\overline{Q} = 0.24 \times 1.05 = 0.25 \pm 0.08$ T atoms/cm^2 sec.

Tritium production by solar protons

Recently it has been found that the occurrence of solar flares which give rise to a substantial flux of low energy protons is quite frequent. The number of such flares has been estimated to be about 20 for the period May 1957—July 1959, based on the measurements of cosmic radio noise absorption in the polar regions. The proton flux in some events is believed to have reached levels of 10^6 times the normal cosmic ray level for a few hours. The average numbers of protons incident at the poles (cm^{-2}, yr^{-1}) have been estimated to be 10^{10} and 10^8 respectively for protons above 30 and 100 MeV respectively (K. A. ANDERSON, private communication). The zone of incidence of protons depends on their energy. For conservative estimates of tritium production by solar protons we have taken the flux of protons above 30 MeV and assumed that they arrive down to 60° geomagnetic latitude where the cut-off under normal conditions is 400 MeV. (FREIER *et al.*, 1959, have reported that over short periods, particles of lower rigidities than the cut-off values were incident at Minnesota following a solar flare.) The average T cross section was taken to be 10 mb and the average range of protons was estimated to be 1.5 gm cm^{-2}, taking for the differential energy spectrum of protons a slope of 4.5 (ANDERSON *et al.*, 1959).

The calculated solar flare production rate of tritium in the polar region is found to be 0.20 atoms/cm^2 sec. This corresponds to an increase of 45 % in the tritium production rate in the polar region (see Figure 9). The corresponding change in the global value is only about 10 % because of the small area involved. The uncertainty in this calculation is very large due to very limited knowledge of particles accelerated in solar flares. Furthermore, the data are based on observations during unusually high solar activity. The solar proton flux should probably exhibit a positive correlation with the solar activity, in which case the present calculations would not be typical of normal conditions. A 10 % increase in $\overline{Q}$ during say 4 years at the peak of a sunspot cycle would amount to only a 3 % increase in the mean production rate averaged over the solar cycle.

Two independent arguments lead to the conclusion that solar flares do not produce appreciable changes in the average production rate of tritium:

(a) BEGEMANN (1959) has measured T contents of dated Greenland snows covering approximately one solar cycle period. Within the errors of measurements ($\pm$ 15 %) the tritium fall-out is found to be constant. A slight indication of negative correlation with the solar activity may be present.[1] The data at least rule out any large contributions by solar flares, in which case a positive correlation should be seen.

(b) The hypothesis of substantial tritium production by solar protons can be checked by studies of the C^{14} production rate, which must be affected more greatly. The polar flux of solar protons above 10 MeV has been estimated to be 10^{12}/cm^2 yr (K. A. ANDERSON, private communication). The production rate of C^{14} due to secondary neutrons produced

[1] BEGEMANN calculated a yearly production rate from the specific activities obtained from the thickness of each annual snow layer. However, PETTERSSEN, JACOBS, and HAYNES (1956) have pointed out that in general the snow cover in Greenland at any place and time bears no fixed relation to the actual amount of precipitation because of extensive drifting. Their tables 17 and 18 show large deviations at Thule, both positive and negative, between monthly snowfall and mean monthly snow cover. A somewhat different plot of Begemann's data is obtained if one assumes constant annual precipitation; four layers before the sunspot peak are rather uniformly higher than four layers after the peak. The true situation can only be determined by a large number of such analyses from different sites.

by protons can be estimated from the behavior of (p, n) cross sections in light nuclei. We find that the global production rate of C^{14} due to solar protons is about the same as that calculated from cosmic ray neutrons. This seems extremely unlikely since the C^{14} inventory checks closely with the estimated cosmic ray production rate (CRAIG and LAL, in press).

Our present conclusion is that the mean global production rate of tritium over an average cycle is not significantly increased by solar flare activity relative to the limits of uncertainty assigned to the value calculated from cosmic ray data.

Summary and conclusions

1. Deuterium and tritium analyses of precipitation from Chicago, Greenland, and Pacific islands, indicate a rather consistent general relationship between these isotopes in fresh precipitation, when no synthetic tritium from thermonuclear explosions is present. The general relationship reflects the balance between continuous injection of cosmic ray tritium, discontinuous preferential removal of the heavy isotopes in precipitation, and mixing.

2. The global mean production rate of natural tritium, calculated from the tritium and water balance in the North American troposphere, is $\overline{Q} = 0.5 \pm 0.3$ atoms T/cm^2 sec. The principal assumption is that the tritium content of the mean continental precipitation is given by the Chicago and New York means (excluding contaminated samples) of 6 ± 2 T.U. Within these limits the assumption seems justified.

3. The present value is three to four times lower than values obtained previously by similar calculations. This is due to the following factors:

a) Pre-Castle tritium data have previously been assumed to represent uncontaminated natural conditions. Our present analysis, based on both deuterium and tritium analyses, indicates that fallout of artificial tritium was already important in 1953 when most of the pre-Castle data were obtained. The available uncontaminated tritium data reduce to three sets of precipitation, from Chicago, Greenland, and Pacific islands, two samples of Arkansas precipitation, and vintage wines from New York, France and Spain, excluding data from lakes and reservoirs. Except for the Greenland snow, the precipitation samples are confined to the seven month "clean period" from 1 January to 1 August, 1953.

b) The residence time of stratospheric air has previously been taken as about 10 years based on early estimates from Sr^{90} fallout. Recent studies by Martell, Libby, and Machta, indicate significantly lower times which thus decrease the calculated decay of tritium in the atmosphere. The stratospheric residence time is a function of latitude; in this paper we consider the latitudinal variation in both residence time and stratospheric production rate of tritium, and conclude that the mean stratospheric tritium residence time is about 1.6 years.

c) The recent discovery of preferential concentration of stratospheric fallout at medium and high latitudes shows that the North American average influx rate must be significantly higher than the global average.

4. A detailed calculation of the cosmic ray production rate based on cosmic ray and nuclear cross section data gives a predicted mean global production rate of 0.25 ± 0.08 atoms T/cm^2 sec. The variation in the production rate over a mean solar cycle, due to the effect of the solar activity maxima on the cosmic ray flux, is found to be $\pm$ about 5 %.

5. The production rate calculated from the observed tritium concentrations agrees with that predicted from cosmic ray data within the limits of uncertainty in the calculations and the data. We thus conclude that there is no observational evidence for accretion of tritium from extraterrestrial sources.

Acknowledgements

We are deeply indebted to Dr. B. Peters for detailed discussions of most of the material in this paper. Dr. Peters had independently concluded that the pre-Castle tritium data included significant contamination from thermonuclear testing and that the tritium concentrations observed during the "clean period" are consistent with the production rate calculated from cosmic ray data. Drs. Libby, Kaufman, von Buttlar, and Begemann provided the precipitation samples which they

had analyzed for tritium content, and the senior author has had the benefit of many discussions with them. The research on deuterium variations was done in Dr. Harold C. Urey's laboratories at the University of Chicago and was supported by the National Science Foundation and the U.S. Atomic Energy Commission. We are grateful to Dr. A. Bainbridge and Dr. F. Begemann for criticism of the manuscript of this paper.

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