The Natural Distribution of Tritium*

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The abundance of cosmic-ray-produced tritium has been measured in a variety of natural waters in the Mississippi Valley, the Chicago area, and in a few places elsewhere in the northern hemisphere. Contents ranging between 0.5 and 67 tritium atoms per 10^{18} hydrogen atoms have been found. These correspond to an average cosmic-ray production rate of about 0.12 tritium atoms per cm^2 per second if the total rate of transfer of tritium into the oceans by oceanic rain and snow and by rivers carrying continental water is taken as being equal to the total production rate. This is equivalent to assuming short land storage time in terms of eighteen years—the tritium average life. This production rate corresponds to an inventory of about 1800 g, with only about one percent of this in the atmosphere.

The tritium contents of vintage wines appear to agree with the time elapsed since bottling, indicating the tritium abundances over the last eighteen years to have been essentially equal to the present ones. Some of the possible applications of natural tritium to problems of hydrology and meteorology are discussed. The present production rate for tritium corresponds to an He^3 escape rate from the earth of about 5×10^7 years or less.

I. INTRODUCTION

THE probability of the occurrence of tritium in nature[1,2] as a disintegration product of the bombardment of the air by cosmic rays and as an explanation of the occurrence of helium-3 in the helium of the atmosphere at a higher abundance than in terrestrial or oil-well helium, the discovery of tritium in nature which resulted from testing Norwegian lake water[3] and atmospheric hydrogen,[4] as well as the potential usefulness of natural tritium[5] all have led to intensification of the study of natural tritium.

Since it seems clear that most of any tritium produced by the cosmic rays probably would soon be oxidized to form water, it follows that cosmic-ray tritium should be found in rain and snow. The dominance in magnitude of the cosmic-ray source as compared to the direct generation in the rocks and oceans is not obvious so we consider briefly the magnitude of the terrestrial ray sources. Since the helium in natural gas does contain helium-3 in an abundance of about 10 percent of that at which it occurs in atmospheric helium,[6,7] the production of tritium in the earth itself seems to be very likely, since helium-3 is the radioactive decay product. The production of tritium in rocks can occur by neutrons which are generated by the spontaneous fission of uranium and by the (α,n) reactions. The neutrons so generated then react with lithium traces in the rocks to form tritium, which decays with a half-life of 12.5 years[8] to form helium-3. The fission

reaction is probably a less important source than the bombardment of the rocks with the alpha particles from the uranium and thorium via the (α,n) reactions.[9,10] Using the cross sections for thermal neutrons[11] and the composition of igneous rock,[12] one can calculate the probability that a neutron liberated in igneous rock will form tritium. The result is about six percent. This together with the abundance of uranium and thorium allows a calculation of the ratio of the helium-3 to helium-4 production rates due to fission alone. The result is about 0.5×10^{-7}, which compares favorably with the values of about 1.7×10^{-7} actually found.[6,7] The variation in composition of rock is such that this must be taken only as an average figure and the tritium production in the earth's crust as a whole is difficult to estimate except as an order of magnitude. It does seem clear, however, from the theory outlined[9] that there is no essential mystery about the occurrence of helium-3 in terrestrial rock helium and that it must have been produced by the radioactive and fission disintegration of the uranium and thorium in the earth's surface via tritium. In terms of tritium production the terrestrial source is very small. In fact a layer of igneous rock one kilometer deep has a production rate of only 0.001 T atoms per cm^2 per second, whereas we shall see later that it is very likely that the cosmic ray production is 0.1 or higher. The production in sea water by a similar mechanism is completely negligible since the proton capture of the neutrons will prevent the absorption by lithium due to the great abundance of ordinary hydrogen in sea water. One concludes therefore that the production of tritium in the earth's crust constitutes a negligible source of tritium for natural waters. It is

[1] W. F. Libby, Phys. Rev. 69, 671 (1946).
[2] E. L. Fireman, Phys. Rev. 91, 922 (1953).
[3] Grosse, Johnston, Wolfgang, and Libby, Science 113, 1 (1951).
[4] V. Faltings and P. Harteck, Z. Naturforsch. 5A, 438 (1950).
[5] W. F. Libby, Proc. Nat. Acad. Sci. 39, 245 (1953).
[6] L. T. Aldridge and A. O. Nier, Phys. Rev. 74, 1590 (1948).
[7] J. H. Coon, Phys. Rev. 75, 1355 (1949).
[8] Jenks, Ghormley, and Sweeton, Phys. Rev. 75, 701 (1949).

[9] P. Morrison and D. B. Beard, Phys. Rev. 75, 1332 (1949).
[10] M. G. Inghram (private communication).
[11] *Nuclear Data*, National Bureau of Standards Circular No. 499 (U. S. Government Printing Office, Washington, D. C., 1950) and Supplements 1–3.
[12] K. Rankama and T. G. Sahama, *Geochemistry* (The University of Chicago Press, Chicago, 1950), pp. 39–40.

interesting that the consideration of natural spontaneous fission and (α,n) reactions[9,10] gives essentially quantitative explanation of the helium-3 content of well helium.

The half-life of tritium[8] fixes the time scale for the natural phenomena associated with the cosmic-ray tritium. For example, rain water bottled should lose its radioactivity at the rate of 50 percent every 12.5 years and one should expect therefore that natural products such as wine and other agricultural products which are fed essentially by rain water should be datable by their tritium content. Data reported in this paper seem to substantiate this. In addition it is clear that the terrestrial underground waters which have been out of atmospheric contact for several years should be distinguishable from rain water. This may well afford an opportunity to measure the flow of underground water and to determine storage time for underground reservoirs. Experiments checking these expectations are in progress, but no definitive results have been obtained as yet. In the field of meteorology it is clear that the tritium assay for a given storm depends not only on the cosmic ray intensity, but also on such meteorological factors as the trajectory of the air mass and its water content. Further studies of these factors reveal the potential usefulness of natural tritium for meteorology.

II. MEASUREMENT OF TECHNIQUE

A. Enrichment Process

The water sample to be assayed for tritium content is first distilled in a standard two gallon gas-fired still, mixed with sodium hydroxide to produce a 3 percent by weight solution, electrolyzed in an iron-nickel anode plant[13] to a final volume of about 1 cc or less, and the deuterium and tritium content of the final product determined. In addition it has been the custom to remove samples during the course of the enrichment to obtain confirmatory evidence as to the correctness of the assay and assurance of freedom from tritium contamination. The plant consists of 38 water-cooled steel cells of 3-liter capacity each operated in series at 100 amperes and 100 volts and arranged in three stages. A series of smaller cells constitute the final stages. The gases generated at each stage are collected by iron header pipes and conducted out of doors or simply allowed to escape into a lightly constructed drafty shed which houses the electrolytic plant. The cells are constructed of Shelby seamless steel tubing, four inches in diameter and eighteen inches in length. A bottom plate and a central tie-rod which secures the head are attached by arc welding. The head carries the gas outlet tube and the tube through which the cell is filled. The cell itself, insulated from the cooling water by paint and electrical tape, serves as the cathode. The anode consists of a perforated cylinder of sheet nickel, 3.5

inches in diameter and 5 inches high, attached by welding to the flat end of a $\frac{1}{2}$ inch nickel rod which passes through an inverted rubber stopper in the head part of the cell. The nickel cylinder is insulated from the cell wall by small pieces of hard rubber. The small cell which constitutes the fourth and final stage in the large plant is constructed on the same design, but the material is 2.5-inch iron pipe.

The water cooling is achieved by placing the cells in a trough through which the cooling water is circulated. The electrical insulation between ground potential water and the cell wall is achieved by painting the cells with three coats of Tygon paint, series TP, then wrapping with Scotch Electrical Tape (No. 33).

The source of electrical power is a 10-kw direct-current generator capable of delivering up to 125 amperes at 100 volts. The plant is located in a lightly constructed wooden shack next to the Jones Chemical Laboratory at the University of Chicago. In order to avoid freezing of the solutions including water during winter, a steam radiator has been installed. During the summer time the cooling water is cooled by a commercial refrigerating unit. During winter, tap water is sufficiently cold. Because of the possibility of explosion in the enclosure of the shack, the closure has purposely been made poor so a considerable air circulation takes place. The plant design is such that in case all the hydrogen and oxygen gas in the plant should explode at once it would do relatively little damage.

The thirty cells of the first stage are filled with three liters of a three percent sodium hydroxide solution made up of the water sample. The sodium hydroxide is a CP electrolytic grade and the water is distilled before use.

When the electrolysis has proceeded for about 72 hours, the initial charge, totaling 90 liters, is reduced to about $\frac{1}{6}$ of its original volume. It then is removed, neutralized and distilled, and transferred to the second stage. Similarly, the residue from the second stage is transferred to the third stage, etc. The whole plant is a direct reproduction of that constructed by Brown and Daggett[13] with the exception of a few minor changes such as the use of Tygon paint and electrical tape wrapping to insure the insulation between the cell wall and the cooling water.

The final stages of the enrichment are accomplished on laboratory bench cells made by the use of iron and nickel strips and glass containers. The current supply found to be most satisfactory for the laboratory cells has been commercial battery chargers. An important factor in the attainment of large fractionation has proved to be the cooling of the water. One notes that in the method of separation used in this work in which the hydrogen and oxygen gases are discarded without recirculation and no attempt is made to remove the water vapor from them the volume of electrolytic vapor is so large that a moderate vapor pressure of the liquid water makes the removal of water by volatiliza-

[13] W. G. Brown and A. F. Daggett, J. Chem. Phys. 3, 216 (1935).

tion appreciable relative to that removed by the electrolysis.

The deuterium assays have been used to measure the tritium separation actually obtained, it being assumed and confirmed experimentally that alterations in conditions which would change the deuterium enrichment would alter the tritium enrichment proportionately (see Table I). These assays were made by the falling drop technique.[14] It was found possible to determine deuterium contents as low as 0.1 percent with an accuracy of about 0.01 percent. The concentration range normally encountered was between 1 and 4 percent where the accuracy is about 0.02 percent. The more highly enriched water samples were diluted down to this concentration with ordinary water. This dilution also tends to reduce the error due to O^{18} accumulation to less than 1 percent in the deuterium content.

The equations governing electrolytic separation of the hydrogen isotopes are easily derived. The heavy isotopes are discharged at the cathode more slowly than protium. Labelling the number of moles of protium, deuterium, and tritium isotope as p, d, and t, respectively, we can write

$$d \ln p = \alpha d \ln d = \beta d \ln t, \tag{1}$$

where α and β are the separation factors for deuterium and tritium, respectively, with respect to protium. It was assumed that α is independent of the deuterium concentration, a fact for which experimental evidence exists,[15] and it was further assumed that β would also be independent of isotopic content. This allows Eq. (1) to be integrated to give

$$\ln(p/p_0) = \alpha \ln(d/d_0) = \beta \ln(t/t_0), \tag{2}$$

where the subscript indicates the initial condition. Since the mole volumes of H_2O and D_2O are almost identical, we can write

$$V = 18(p+d), \tag{3}$$

where V is the volume of solution in cc. At the start of the electrolysis the concentration of D_2O is only 0.015 percent for normal water.[16] For solutions low in deuterium, the enrichment equations are

$$V/V_0 = p/p_0 = (d/d_0)^\alpha = (t/t_0)^\beta. \tag{4}$$

If the concentration or specific activity of tritium is denoted by τ, the tritium enrichment is

$$\tau/\tau_0 = (t/t_0)(V_0/V) = (V_0/V)^{1-1/\beta}, \tag{5}$$

and

$$\tau/\tau_0 \cong V_0/V,$$

since β is nearly always larger than 10. If N denotes the

[14] I. Kirshenbaum, *Physical Properties and Analysis of Heavy Water* (McGraw-Hill Book Company, Inc., New York, 1951), National Nuclear Energy Series, Plutonium Project Record, Vol. III, Div. IVA, p. 324.
[15] A. Farkas, Trans. Faraday Soc. 33, 552 (1937).
[16] I. Kirshenbaum (see reference 14).

TABLE I. Experimental values of β/α (10°–25°C).

Standard	$\dfrac{V_0}{V}$	% D_2O	Sp. activity (counts min⁻¹ cm⁻¹)	α	β/α
No. 2	1	0.16	5.8		
	3.8	0.47	19.2	5.2 ±1.3	1.9 ±0.8
	14.5	1.32	59.6	4.4 ±0.6	1.5 ±0.4
No. 3	1	1.48	4.64		
	7.60	6.42	27.3	3.7 ±0.1	2.18±0.20
	47.2	28.0	138	5.9 ±0.2	1.75±0.16
	186	70.7	440	5.14±0.18	2.16±0.18
No. 4	1	1.94	10.03		
	8.01	10.85	67.7	6.1 ±0.3	2.08±0.19
	52.2	49.8	371	7.0 ±0.3	2.01±0.18
	239	96.5	1178	⋯	2.34±0.13
No. 5	1	1.89	11.65		
	6.55	9.75	71.2	8.2 ±1.4	3.5 ±1.4
	214	83.5	1268	3.9 ±0.1	2.20±0.11
No. 6	1	0.0148	0.002875		
	1070	5.18	1.93	6.3 ±0.2	2.4 ±0.3
	3420	12.4	5.05	6.0 ±0.2	2.10±0.15
	1650	11.20	3.15	9.7 ±0.6	1.91±0.19
	3170	20.3	6.29	10.0 ±0.6	2.22±0.25
	1300	10.40	2.70	12.0 ±0.5	1.86±0.19
	3060	17.1	5.63	8.4 ±0.3	2.18±0.15
	1190	7.60	2.15	8.5 ±0.3	1.81±0.18
	2650	15.3	5.23	8.5 ±0.3	2.45±0.25
Weighted average					2.10±0.10

mole fraction of deuterium, so that $N = d/18V$, an expression for the tritium enrichment valid at all deuterium concentrations is,

$$\frac{\tau}{\tau_0} = \frac{V_0}{V}\left(\frac{d}{d_0}\right)^{\alpha/\beta} = \frac{V_0}{V}\left(\frac{N \times V}{N_0 \times V_0}\right)^{\alpha/\beta}. \tag{6}$$

One previous measurement of β has been reported in the literature by Eidinoff.[17] Values of about 15 were obtained.

Using standard tritium solutions made by diluting tritium obtained from the U.S. Atomic Energy Commission and conducting electrolyses in the same way as for natural water samples, experimental values for α and β/α as shown in Table I were obtained.

It is clear from these data that the value of β/α is nearly constant while the value of α can fluctuate widely. This of course is to be expected since the effective separation depends on a variety of conditions which would hardly be expected to affect the relative separation factor, β/α. The data have been computed on the assumption that $\beta/\alpha = 2.1 \pm 0.10$.

B. Counting

The measurement of the tritium content of the enriched water samples consists in the conversion of water to hydrogen gas and its measurement in a low-level Geiger counter. The procedure has been described previously.[3,18] Further utilization of it has revealed no essential weaknesses. The technique for the conversion of water to gaseous hydrogen[3] consists of the use of finely divided zinc dust at about 500°C. The zinc dust

[17] M. L. Eidinoff, J. Am. Chem. Soc. 69, 977, 2507 (1947).
[18] R. L. Wolfgang and W. F. Libby, Phys. Rev. 85, 437 (1952).

is mixed with freshly dehydrated calcium oxide into which the water sample is distilled at room temperature. When this step has been completed, the mixture is heated in a Pyrex tube to about 500°C to cause the evolution of hydrogen gas. It has been found that the conversion is essentially quantitative by this technique and the isotopic fractionation therefore is of no consequence. The gaseous hydrogen is stored in a bulb and transferred to the vacuum line used for filling counters.

The counting technique consists in the use of an ordinary Geiger counter with flat ends in order that a known correction might be made for the end loss.[19] The gaseous mixture consisted of about 2.0-cm Hg pressure of ethylene gas, 3.0-cm Hg pressure of argon gas, and 0- to 20- or 30-cm pressure of hydrogen gas in which the tritium is contained. The counters used in our research were 2 in. in inside diameter and 18 inches in length. They were made of brass tubing with Lucite ends waxed in place. The center wire was No. 28 copper. The counter voltages depended a great deal on the pressure of hydrogen and ethylene, and ranged from 1500 to 3000 volts. An anticoincidence shield together with an 8-inch thick iron shield was customarily used.[20] The background for our counters in the iron shield with the anticoincidence shielding counters disconnected was 160 counts per minute. It was about 8 counts/min with these connected in the full shielding arrangement. We normally did not measure a sample with less than 1 count/min of radioactivity. In general, the activities were at least 5 to 10 counts per minute above background. Small corrections were made for the end losses to convert to absolute tritium contents. Normal measurements can be completed in about half an hour.

III. EXPERIMENTAL RESULTS

The experimental data are given in Tables II, III, and IV, and in Fig. 1. In Table II are given the detailed data and calculations of the tritium content for a series of samples, and in Table III are given the summarizing data for all the samples measured. The errors quoted
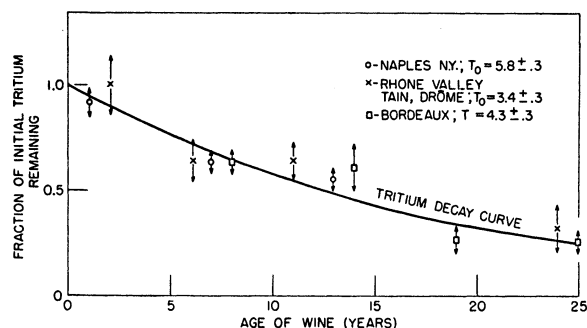

FIG. 1. Tritium content of vintage wines vs age.

[19] A. G. Engelkemeir and W. F. Libby, Rev. Sci. Instr. 21, 550 (1950).

[20] Anderson, Arnold, and Libby, Rev. Sci. Instr. 22, 225 (1951).

are standard deviations taken principally from the counting errors, that is, the errors in measurement of radioactivity. The error in the volume enrichment alone is about 3 percent. This relatively large error is due to the accumulation of small errors in the individual volume measurements. In addition other errors are present such as the variation in initial abundance of deuterium. In a few cases, as indicated in Table II, the initial deuterium abundances were measured directly, but in the other cases the abundance was taken as 0.015 percent, the average based on the careful study made several years ago.[16] An additional error lay in a failure to remove thoroughly all moisture from the hydrogen generation equipment in one or two instances. This introduced diluting nonradioactive hydrogen into the samples, as shown by a decrease in the deuterium content of the gases generated as compared to that of the water used in the generation. Correction was made for this whenever the effect was discovered; however, it may have been present in one or two undiscovered instances. It seems likely that the entire error is perhaps twice the error quoted.

The data in Fig. 1, taken from the wine data listed in Table III, have been computed by using the mean of the calculated initial assays for the wine as shown in the last column of Sec. E of Table III. This last column containing parenthetical figures consists of the calculated initial assays assuming that the tritium present has decayed at the 12.5-year half-life rate. Taking the weighted average, the weighting being done according to the inverse square of the counting errors as indicated, we deduce the average effective initial assays given in Table IV, and using these as the standard basis, the fraction of tritium remaining in the various wines is calculated and the data derived is shown in Fig. 1.

It appears that the data do agree with the curve within the rather large experimental errors. In spite of these errors, which are largely due to the fact that limited quantities of the wine were available for measurement, the agreement between the tritium content and the expected curve is quite satisfactory and we do find that we probably can date wine, agricultural products, and water in general, in the sense of measuring the time elapsed since the last precipitation as rain or snow, i.e., the last contact with atmospheric moisture.

IV. DISCUSSION

A. Tritium Production Rate $\bar{Q}$

It would seem reasonable that whatever the mechanism by which the cosmic rays produce tritium by bombarding the air—whether by the (n,t) reaction of fast secondary neutrons on nitrogen[1,2] or by direct production in cosmic ray "stars"[2,9]—the production rate should vary with latitude in a manner not too dissimilar from that in which the secondary neutrons

TABLE II. Typical experimental results.

No.	$\dfrac{V_0}{V}$	$\dfrac{\tau}{\tau_0}$	% D$_2$O	Sp. activity (counts min^{-1} cm^{-1})	α	$\left(\dfrac{T}{H}\right)\times 10^{18}$	Av.
5	1560	948	8.10	1.51 ±0.2	5.7±0.3	32 ±4	
	6250	3660	30.0	6.15 ±0.38	11 ±2	34 ±2	
	18 500	9300	64.5	15.3 ±0.2	7.1±1.3	33.5 ±3	33 ±2
14	1	1	0.0138				
	786	546	4.83	0.714±0.06	7.8±0.2	24 ±3	
	3420	2130	17.5	2.43 ±0.09	9.0±0.9	19.8 ±0.8	
	23 800	11 600	72.2	12.6 ±0.2	5.9±0.3	20.0 ±0.3	
	696	479	4.39	0.58 ±0.02	7.7±0.3	21 ±2	
	2240	1450	12.4	1.43 ±0.07	9.6±1.5	17.2 ±1.1	
	14 500	6860	43.7	8.03 ±0.18	3.8±0.3	21.3 ±0.5	20.4 ±0.7
16	2830	1875	17.6	4.45 ±0.17	9.4±0.4	41.1 ±1.7	
	21 000	11 500	72.3	21.7 ±1.1	5.3±0.7	35.0 ±2	37 ±3
17	1660	1150	11.3	4.08 ±0.23	9.7±0.6	65.0 ±2.5	
	12 800	7160	56.2	27.4 ±0.5	6.3±0.7	66.8 ±0.7	66.0 ±1.0
18	1	1	0.0147				
	1400	850	7.20	0.89 ±0.11	6.9±0.8	19.3 ±2.4	
	890	605	5.80	0.63 ±0.10	8.3±0.5	19.4 ±3.0	19.3 ±1.5
19	1	1	0.0132				
	1160	850	8.00	0.61 ±0.05	9.2±0.4	13.2 ±1.2	13.2 ±1.2
21	1	1	0.0129				
	1700	1170	10.0	0.48 ±0.03	7.5±0.2	7.1 ±0.5	7.1 ±0.5
22	1	1	0.0137				
	1600	1070	9.42	0.54 ±0.05	8.1±0.7	9.0 ±1.0	9.0 ±1.0
30	1	1	0.0148				
	1730	1130	10.4	0.33 ±0.05	8.4±0.3	5.0 ±0.7	5.0 ±0.7
33	1	1					
	2100	1760	18.7	1.14 ±0.09	16 ±2	10.8 ±1.0	11.9 ±1.0
34	1	1	0.0148				
	1860	1190	10.8	0.15 ±0.05	8.1±0.3	2.4 ±0.8	
	6800	3880	31.0	0.70 ±0.06	6.5±0.5	3.3 ±0.3	3.3 ±0.3
38	4290	2730	24.4	1.39 ±0.14	9.0±0.4	9.4 ±1.0	9.4 ±1.0
39	3190	1970	17.2	1.04 ±0.08	8.2±0.4	9.6 ±0.8	9.6 ±0.8
40	5050	3090	26.7	0.82 ±0.15	8.5±0.3	4.6 ±0.8	
	25 300	12 200	81.5	3.30 ±0.15	6.1±0.3	4.75±0.21	4.75±0.20

vary. Simpson[21] has published data for the variation of neutron intensity with latitude at 30 000-feet altitude (22.5-cm Hg pressure). Using these data we can calculate the ratio of the expected world-wide average production rate of tritium, $\bar{Q}$ (T atoms/cm^2 sec), to the local production rate Q to be 0.58 at Lake Mösvann, Norway, 0.64 at 48°N geomagnetic latitude, the approximate mean latitude of the Mississippi Valley, and 0.58 for Chicago.

If we suppose that the tritium produced is converted into water which is precipitated as rain or snow, equating the production rate to the rate of precipitation into the sea plus the rate of transport by rivers into the sea gives

$$\tfrac{1}{4}\bar{\rho}\bar{T}_l+\tfrac{3}{4}\bar{r}_s\bar{T}_s=4.7\bar{Q}. \tag{7}$$

In Eq. (7) $\bar{\rho}$ is the annual run-off from the world's land

[21] J. A. Simpson, Jr., Phys. Rev. 83, 1175 (1951).

areas in meters of water, $\bar{r}_s$ is the annual precipitation over the oceans in meters, $\bar{T}_l$ and $\bar{T}_s$ are the tritium contents of the run-off waters and ocean rain waters, respectively, in units of T atoms per 10^{18} H atoms, and $\bar{Q}$ is the world wide average tritium production rate in atoms per cm^2 per second. The factors $\tfrac{1}{4}$ and $\tfrac{3}{4}$ are the fractional land and ocean areas. The factor 4.7 is a numerical constant arising from the units selected. Equation (7) simply states that the tritium is transported into the oceans where it is absorbed and that this transport occurs in the first year or two before any appreciable decay into He^3 could occur. From the Norwegian Lake Mösvann datum (Table IV), which probably is typical of sea precipitation since it derives almost entirely from the sea saturated air masses which roll over the Norwegian coast, we can calculate $\bar{T}_s$ to be $(0.8\pm0.1)\times(0.58)\times(0.9/0.77)$ or 0.54 ± 0.07, where

TABLE III. Summary of data.

Sample No.	Description of sample	$(T/H) \times 10^{18}$
	A. Chicago rains and snows	
5	May 11, 1951. Collected from 1000 to 1200. Storm lasted from evening of 10th to afternoon of 11th. 3.81 in. rain.	33 ±2
14	October 14, 1952. Collected throughout storm. Storm lasted from 1700 to 2400. 0.70 in. rain.	20.4 ±0.7
16	November 17, 1952. Collected throughout storm. Storm lasted from 0030 to 0100; 0600 to 0630. 0.31 in. rain.	37 ±3
17	November 18, 1952. Collected throughout storm. Storm lasted from 2100 of 17th to 1200 of 18th. 0.70 in. rain.	66.0 ±1.0
18	November 22–24–25, 1952. Collected throughout storms. Rained afternoon of 22nd, evening of 24th, all day 25th. 1.13 in. rain.	19.3 ±1.5
19	December 2, 1952. Fell during night. 0.29 in. snow.	13.2 ±1.2
21	January 6, 1953. Fell during afternoon. 0.05 in. snow.	7.1 ±0.5
22	January 23, 1953. Collected from 1515 to 1530. Storm lasted from 1200 to 1900. 0.32 in. rain.	9.0 ±1.0
30	February 11, 1953. Collected from 0930 to 1245. Light rain all morning. 0.03 in. rain.	5.0 ±0.7
33	February 16, 1953. Collected 1030. Fell from 0300 to 1400. 0.19 in. snow.	10.8 ±1.0
34	February 20, 1953. Collected 1615. Storm lasted from 1530 to 1645. 0.94 in. rain.	3.3 ±0.3
38	March 3, 1953. Collected throughout storm. Rain, sleet and snow fell from 1300 to 2000. 0.38 in. rain.	9.4 ±1.0
39	March 7, 1953. Collected 1200. Fell from 0800 to 1500. 0.18 in. snow.	9.6 ±0.8
40	March 12, 1953. Collected 1030. Storm lasted from 0900 to 1700. 0.98 in. rain.	4.75±0.20
45	March 14, 1953. Collected throughout storm. Rained from 1000 to 1600; 2000 to 2200. 1.05 in. rain.	1.16±0.18
46	March 18, 1953. Collected throughout storm. Light rain from 1300 to 1700. 0.13 in. rain.	7.9 ±0.3
48	March 21–22, 1953. Collected throughout storms. Rained night of 21st, night of 22nd. 0.06 in. rain.	3.10±0.13
50	March 31, 1953. Collected from 1030 to 1100. Rained lightly from 1000 to 1200. 0.07 in. rain.	9.5 ±0.4
	Wtd. Ave. (December to March):	5.5
	B. Rains and snows from other areas	
42	Fayetteville, Arkansas, snow. January 23, 1953. 1.17 in. snow.	5.5 ±0.6
49	Honolulu, Hawaii, rain. March 26, 1953. Collected in morning. Trace rain.	0.61±0.10

the world wide average,[22] $\bar{r}_s$, of 0.77 is used to correct for the unusually high precipitation on the mountain plateau, Hardangervidda, east of Bergen which feeds Lake Mösvann. For the value of $\bar{T}_l$ we take the Mississippi Valley average of 5.2±0.2 (Table IV) and correct it for the latitudinal effect with the factor 0.64. Substituting in Eq. (7) and using a value[22] of 0.28 for $\bar{p}$, we find $\bar{Q}$ to be 0.12 T atoms per cm² per second, to an accuracy of about 30 percent.

B. Meteorology

Having evaluated the tritium production rate Q, we can calculate the expected value of T, the tritium concentration in water in an air mass, in terms of the amount of water w, (meters per cm²) and the time τ, in years, elapsed since the water evaporated from the oceans. For a given latitude we would write

$$Tw = 4.7Q\tau \qquad (8)$$

For example, if the water content of the average air mass traveling over the Hardangervidda is 3 g per cm², τ would be on the average 0.024 years, or about nine days.

The much larger values of the tritium concentration

[22] Reference 12, pp. 39–40.

found in the rain and run-off waters over the land masses (Table IV) as contrasted to sea rains and snows undoubtedly are due to longer exposure of these waters to atmospheric tritium. The average length of exposure is to be calculated from Eq. (8) in which the total water, atmospheric plus run-off is to be included as w. Estimating the surface and ground water in the Mississippi Valley to average about 7 g per cm² we estimate w to be 0.10 and τ is 0.9 year. In other words, the water flowing into the Gulf of Mexico at New Orleans left the ocean about eleven months earlier. More accurate values of w should be used to improve this calculation. This time, while somewhat surprisingly long, still does not violate our primary assumption that the tritium reaches the great depths of the oceans before decaying appreciably.

The data on the individual storms in the Chicago area for the past year reveal no obvious correlations of real importance. Averaging the rains from December 1, 1952 through March, 1953, and excluding the fall rains which followed an unusually dry summer and fall in the Northwest gives a value of 5.2—a value not only in good agreement with the Mississippi River waters collected over essentially the same period, but also with the Lake Michigan value of 7.7±0.3 which is an average for approximately the last 18 years calculated from the

TABLE III.—*Continued.*

Sample No.	Description of sample	$(T/H)\times10^{18}$
	C. Mississippi and other rivers	
24	Mississippi River, Rock Island, January 29, 1953.	2.5 ±0.3
27	Mississippi River, Rock Island, February 6, 1953.	3.7 ±0.4
37	Mississippi River, Rock Island, February 24, 1953.	4.4 ±0.2
23	Mississippi River, St. Louis, January 31, 1953.	5.6 ±0.6
26	Mississippi River, St. Louis, February 4, 1953.	4.5 ±0.6
31	Mississippi River, St. Louis, February 10, 1953.	6.0 ±0.9
36	Mississippi River, St. Louis, February 20, 1953.	6.4 ±0.5
28	Mississippi River, Memphis, February 4, 1953.	6.0 ±1.0
29	Mississippi River, New Orleans, February 8, 1953.	4.7 ±0.3
	Wtd. Ave. for St. Louis, Memphis, and New Orleans:	5.2 ±0.2
15	Sangamon River, Decatur, August 6, 1952.	1.15±0.08
52	Arkansas River, Conway, Arkansas, March 20, 1953.	3.12±0.10
	D. Lake Michigan	
8	Jones Laboratory, Tap water, July 7, 1952.	1.35±0.25
32	Jones Laboratory, Tap water, February 13–16, 1953.	1.73±0.06
13	Oak Park tap, hot water heater, *ca* 12 years old.	0.62±0.06 (1.2)
	E. Vintage wines	
55	Widmer's New York Riesling wine, Vintage 1940, Naples, New York.	3.2 ±0.2 (6.6±0.4)
62	Widmer's New York Riesling wine, Vintage 1946, Naples, New York.	3.63±0.16 (5.4±0.3)
54	Widmer's New York Riesling wine, Vintage 1952, Naples, New York.	5.3 ±0.3 (5.6±0.3)
63	Hermitage Rhone wine, Vintage 1929, Tain, Drôme, France.	1.13±0.38 (4.3±1.4)
64	Hermitage Rhone wine, Vintage 1942, Tain, Drôme, France.	2.15±0.21 (3.92±0.4)
65	Hermitage Rhone wine, Vintage 1947, Tain, Drôme, France.	2.15±0.28 (3.0±0.3)
66	Hermitage Rhone wine, Vintage 1951, Tain, Drôme, France.	3.4 ±0.4 (3.8±0.5)
69	Chateau Laujac Bordeaux wine, Vintage 1928, France.	1.16±0.16 (4.6±0.7)
70	Chateau Laujac Bordeaux wine, Vintage 1934, France.	1.16±0.30 (3.3±0.9)
71	Chateau Laujac Bordeaux wine, Vintage 1939, France.	2.6 ±0.4 (5.6±0.9)
72	Chateau Laujac Bordeaux wine, Vintage 1945, France.	2.70±0.18 (4.2±0.3)
	F. Miscellaneous	
9	Cistern, Decatur, collected August 6, 1952. Covered loosely about 29 years ago.	5.9 ±0.5
12	Cistern, Sullivan, Illinois, collected August 6, 1952. Covered with tight iron lid about 14 years ago.	2.9 ±0.2 (6.3±0.4)
20	Fire extinguisher, Skokie, Illinois. Filled June 5, 1936.	12.5 ±0.5 (32±1.2)
75	Pacific Ocean, Santa Monica, California, June 8, 1953.	0.54±0.02

1.7 assay of the lake water as explained in the next paragraph. In addition the Naples, New York, wine datum of 5.8±0.3 is in agreement.

The Lake Michigan rainfall value of 7.7 is calculated from the observed assay for the Lake of 1.7 (Table III) by use of the factor 4.5 for the storage and hydrologic effects. The factor of 4.5 is obtained as follows: The drainage area feeding Lake Michigan is 43 148 square miles, excluding lakes, and the annual run-off is 14.5 inches.[23] The annual rainfall over the lake itself is 31.3 inches, and the lake area is 22 336 square miles. The mean depth of the lake is 312.56 feet.[23] It is well known that the lake has complete vertical mixing each year, since the water inverts once each year as shown by the temperature gradient reversal. We therefore assume that the lake is perfectly mixed on the time scale of the lifetime of tritium. We further assume that the lake level is fixed and that the annual rainfall is exactly balanced by outflow and evaporation and that these processes do not fractionate the hydrogen isotopes appreciably. With these assumptions, we set up the equation for the steady condition that the rate of

[23] "Hydrology of the Great Lakes," Report of the Engineering Board of Review on the Sanitary District of Chicago for the year 1927, Horton.

introduction of tritium into Lake Michigan must equal that at which it leaves the lake both by overflow and evaporation, and the radioactive decay into helium-3. The resulting equation is

$$[(T_r)-(T_l)]\left(31.3+14.5\times\frac{43148}{22336}\right)$$

$$=(T_l)\frac{312.56\times12}{18}. \quad (8)$$

This equation gives the expected ratio of the tritium content of rain (T_r) to that of lake water (T_l) as 4.5.

TABLE IV. Average T content for precipitation in the northern hemisphere.

Location	Latitude (geomagnetic)	Precipitation (meters/ year)	T content (T atoms/ 10^{18} H's)
Lake Michigan	~54°N	0.80	7.7±0.3
Mississippi Basin	48°N	0.76 (0.19 run-off)	5.2±0.2
Naples, New York (wine)	~54°N	1.0	5.8±0.3
Rhone Valley, Tain, Drôme, France (wine)	~54°N	0.8	3.4±0.3
Bordeaux, France (wine)	~54°N	0.8	4.3±0.3
Lake Mösvann, Norway	55°N	0.9	0.8±0.1[a]

[a] See reference 3.

C. The Age of Waters and Agricultural Products and Hydrology

Clearly the data on vintage wines given in Tables III and IV and Fig. 1 show that the tritium content of rain waters probably disappears at the tritium decay rate and that waters more than a few decades old in the sense of exposure to contamination by atmospheric water will show an undetectably low tritium content. Therefore it appears likely that we can distinguish underground from surface run-off water. Similarly, deep lake waters in which the storage time is appreciable relative to the life time of tritium (eighteen years, average) will be distinguishable. Michigan is such a lake. The possibility of making such distinctions should have application to hydrology. In particular the storage times for underground reservoirs would appear to be measurable in this way.

D. Escape Time for He³ from the Earth; World Tritium Inventory

If $\bar{Q}$ be 0.12 ± 0.04, there must be $5.7\times10^8\times0.12$ T atoms per cm² to maintain a steady-state balance guaranteeing equality of the rates of production and radioactive decay of tritium. This corresponds to a total inventory of 1800 ± 600 grams of tritium in the world distributed about in the following way: 11 grams in the atmosphere ($w=0.03$) and 13 grams in the ground waters (10 grams per cm² of ground water assumed), with the remainder in the ocean depths.

Since the abundance of He³ in the atmosphere is known[6,7] to be 1.8×10^{14} atoms/cm², $\bar{Q}$ gives an upper limit to the rate at which He³ must escape from the earth. Being nonradioactive and chemically inert, physical escape is the only way in which the low atmospheric abundance can be maintained in view of the tritium production $\bar{Q}$. In fact the escape time τ (years) will be given by

$$\tau \leq \frac{1.8\times10^{14}}{0.12\times3.16\times10^7} \quad \text{or} \quad 4.7\times10^7\pm1.6\cdot10^7 \text{ years.}$$

Since it seems extremely likely that cosmic-ray stars may be involved in the production mechanism for tritium and it is difficult to imagine tritium being produced in the star mechanism method without helium-3 also being formed, we can expect that the true value of the escape time is less than 47 million years by perhaps thirty percent. Of course this assumes constant cosmic-ray intensity over this time, τ.