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Sources of

tritium

D.G. Jacobs

and its behavior upon release
to the environment

AEC CRITICAL REVIEW SERIES

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Health Physics Division
Nuclear Safety Information Center
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FOREWORD

This report is the first in the AEC Critical Review Series, a new series of state-of-the-art studies prepared for the Atomic Energy Commission. The author reviews published information on tritium production and the pertinent factors that affect the behavior of tritium in the environment. Because of the extremely large number of publications dealing with tritium, the review is not exhaustive; however, the most important aspects have been mentioned and extensive references are given. Estimates are made for production and accumulation of tritium in an expanding nuclear power economy, including the impact of an increased tritium production on local and worldwide populations.

This report was originally prepared for the Nuclear Safety Information Center, one of the USAEC's specialized information analysis centers. Established in 1963, the Nuclear Safety Information Center is a focal point for the collection, evaluation, storage, and dissemination of safety information on reactors and other nuclear facilities. Principal services include (1) preparation of state-of-the-art reports, (2) cooperation in the preparation of *Nuclear Safety*, (3) answering technical inquiries as time is available, (4) counsel and guidance on nuclear safety problems, and (5) operation of a program of Selective Dissemination of Information (SDI) which offers abstracts to individuals according to their particular interest. Services are available without charge to government agencies, research and educational institutions, and the nuclear industry. Inquiries are welcomed.

J. R. Buchanan, *Assistant Director*
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1 INTRODUCTION

Tritium is one of the three radionuclides, along with ^{59}Ni and ^{55}Fe , which have a maximum permissible body burden of 1 mc, the highest value listed in the recommendations of the International Commission on Radiological Protection (ICRP).^{1,2} Tritium does not constitute a significant external radiation hazard because the beta particle given off during its decay is of low energy and has very low penetrating power;^{2,3} however, tritiated water and its vapor can be taken into the body by skin penetration.¹ Retention of tritium is dependent on its chemical form when it enters the body; therefore the ICRP recommendations for the maximum permissible concentrations in air are at least a factor of 100 greater for tritium gas than for tritiated water vapor.² (Tritiated thymidine is an interesting example of the effect of the chemical form of tritium on its behavior in the body. Thymidine, a specific precursor of deoxyribonucleic acid (DNA), is incorporated preferentially in the nuclei of cells.³ Thus the probability of somatic and genetic damage from tritium exposure is enhanced when tritium is ingested in the form of tritiated thymidine. Tritiated thymidine is not a commonly expected form of tritium in the natural environment; however, a scan of *Nuclear Science Abstracts* indicates that tritiated thymidine is used considerably in biological research.)

In addition to the radiation emitted by tritium, which is absorbed by the body tissue in a very localized area, the transmutation of ^3H to ^3He may be of biological significance.¹ However, even greater detrimental effects may result from the relatively large mass differences that arise from the substitution of ^3H for ^1H in a cell. These mass effects would begin immediately rather than being initiated by decay of the tritium atom.¹ Because tritiated water vapor is taken into the body almost as fast by skin penetration as by inhalation,^{1,2} it presents a special hazard for personnel who must handle high concentrations of tritium.

Tritium is produced by numerous reactions (see Chap. 2) and is released in a number of different types of nuclear activities (see Chap. 3). At present most tritium problems are encountered at heavy-water reactors, where the tritium hazard is as important as all other radionuclide hazards combined under normal operating conditions,⁴ and at tritium production facilities. Large quantities of tritium are also produced and released to the environment during the detonation of thermonuclear devices.^{5,6} The rather recent discovery that tritium is a ternary fission product⁷ has evoked considerable interest in the management of tritium in fuel-reprocessing plants.^{8,9}

When tritium is released as a gas or as the oxide vapor, it can be concentrated by ordinary chemical separation of hydrogen and water vapor from air. However, when tritium is present as the oxide in aqueous solutions, it is not amenable to separation and concentration by conventional waste-treatment techniques.⁸ Isotopic separations are required, and these may be difficult. The more satisfactory procedures of isotopic separation are usually physical in nature because mass differences result in greater relative differences in physical properties than in chemical properties.¹⁰ As a result of the similarity of the properties of HTO and H₂O, tritium generally follows ordinary water in processing streams and in the environment.^{8,9}

The present levels of tritium released to the environment do not constitute a serious hazard. Production and release, however, are expected to increase in the next few decades as a nuclear power economy is developed,⁸ and, therefore, the question of tritium release deserves some consideration. There will be a strong economic incentive to increase the size of fuel-reprocessing plants as the nuclear industry expands.¹¹ A major fraction of the fission-product tritium will probably be released during fuel reprocessing at a limited number of sites. Therefore, in addition to the worldwide increase in tritium levels, tritium could constitute a local environmental problem in some areas. The amount of tritium produced in thermonuclear reactions is several orders of magnitude higher than the amount of tritium produced by an equivalent amount of fission energy. In a thermonuclear power economy, tritium management could be a much more significant problem. Large quantities of tritium have already been released to the atmosphere from the detonation of thermonuclear devices. This tritium has become widely dispersed in the environment, with about half of the deposition occurring in the region 30 to 50° north latitude.¹² Future testing or use of thermonuclear devices could add significantly to general tritium levels in the environment if venting is allowed.

This review surveys the published information on tritium production and the more pertinent factors that affect its behavior in the environment. Because of the extremely large number of publications dealing with tritium, this review is not exhaustive. The more important aspects, however, have at least been mentioned, and references are given. Chapter 7 presents a projection of tritium production in an expanding nuclear power economy. The material reviewed in Chaps. 2, 3, and 4 is used as a basis for estimating the impact of increased tritium production on local and worldwide populations.

REFERENCES

1. K. Z. Morgan, Radiation Hazards Associated with Tritium, pp. 1-3, in *Seminaire sur la Protection Contre les Dangers du Tritium*, Service Central de Protection Contre les Rayonnements Ionisants, le Vesinet, Avril 16-18, 1964 (CONF-640413).
2. Report of Committee II on Permissible Dose for Internal Radiation (195), *Health Physics*, 3: 1-380 (June 1960).
3. J. S. Handloser, Tritium Health Physics Considerations, pp. 201-204, in *Advances in Tracer Methodology*, Plenum Press, New York, 1962.
4. C. E. Holmquist, Hazards of Tritium Oxides Induced in Heavy Water Reactors, pp. 34-39, in *Seminaire sur la Protection Contre les Dangers du Tritium*, Service Central de Protection Contre les Rayonnements Ionisants, le Vesinet, Avril 16-18, 1964 (CONF-640413).
5. O. I. Leipunsky, *At. Energy (USSR)*, 3: 530 (1957); also Radiation Hazards from Clean Hydrogen Bomb and Fission Atomic Bomb Explosions, in *Fallout from Nuclear Weapons Tests*, Hearings Before the Special Subcommittee on Radiation of the Joint Committee on Atomic Energy, 86th Congress, May 1960, pp. 2423-2447, U. S. Government Printing Office, Washington, 1960.
6. F. W. Stead, Tritium Distribution in Groundwater Around Large Underground Fusion Explosions, *Science*, 142(3596): 1163-1165 (Nov. 29, 1963).
7. E. L. Albenesius, Tritium as a Product of Fission, *Phys. Rev. Lett.*, 3(6): 274-275 (Sept. 15, 1959).
8. J. O. Blomeke, *Management of Fission Product Tritium in Fuel Processing Wastes*, USAEC Report ORNL-TM-851, Oak Ridge National Laboratory, May 4, 1964.
9. W. A. Haney, Fission-Product Tritium in Fuel-Processing Waste, *Nucl. Safety*, 5(4): 399-402 (Summer 1964).
10. T. Moeller, *Inorganic Chemistry*, p. 39, John Wiley & Sons, Inc., New York, 1954.
11. F. L. Culler, *The Effect of Scale-Up on Fuel Cycle Costs for Enriched Fuel and Natural Uranium Fuel Systems*, USAEC Report ORNL-TM-564, Oak Ridge National Laboratory, Apr. 16, 1963.
12. W. F. Libby, Moratorium Tritium Geophysics, *J. Geophys. Res.*, 68: 4485-4494 (August 1963).

2 PROPERTIES OF TRITIUM AND TRITIUM COMPOUNDS

RADIOACTIVE AND NUCLEAR PROPERTIES

The radioactivity of tritium was established in 1939 by Alvarez and Cornog,¹ who found that the radiation is of very short range and that the half-life is long. Their first attempts at estimating the half-life of tritium decay gave erroneous results because of diffusional losses of the gas;^{2,3} their further studies³ showed a half-life in excess of 10 years. Subsequent work has established the half-life of tritium at 12.36 ± 0.03 years. Tritium decays by the emission of a beta particle with a maximum energy of 18 keV and an average energy of 5.7 keV (Table 2.1) to form ^3He . The beta decay spectrum has been of particular interest to physicists because the relatively simple structure of the tritium nucleus permits verification of the Fermi theory of beta decay and permits calculation of the mass of the neutrino.^{8,9,12} Early assays of the tritium content of natural surface waters indicated that there was about one tritium atom per 10^{18} atoms of hydrogen.²⁰

It became quite convenient to express tritium assays in relation to the number of hydrogen atoms in the sample. The term "tritium unit" (TU) is commonly used to denote the number of tritium atoms per 10^{18} atoms of hydrogen. Recently the International Commission on Radiological Units and Measurements raised an objection to the use of this term and suggested that it be replaced by the term "tritium ratio" (TR).²¹ A tritium ratio, then, is not a concentration unit but is a measure of specific activity. Table 2.2 compares tritium ratios and various concentration units for different media at 25°C.

Table 2.1
HISTORY OF THE DETERMINATION OF THE
DECAY CHARACTERISTICS OF TRITIUM

Date	Half-life, years	Maximum energy, kev	Average energy, kev	Ref.
1940	>10		10	3
1940	31 ± 8	15 ± 3		4
1941		14.5 ± 1	6.5	5
1947	10.7 ± 2.0			6
1947	12.1 ± 0.5			7
1948		16.9 ± 0.3	~5.5	8
1949		17.9 ± 0.3		9
1949	12.46 ± 0.2		5.69 ± 0.06	10
1949		17.0		11
1949		18.95 ± 0.5		12
1949		19.6 ± 0.2		13
1949		18.0 ± 0.5		14
1950	12.46 ± 0.1		5.69 ± 0.04	15
1951	12.41 ± 0.04			16
1955	12.262 ± 0.004			17
1963	12.355 ± 0.010			18
1963	12.361 ± 0.028			19

Table 2.2
EQUIVALENCE OF ONE TRITIUM RATIO
IN VARIOUS MEDIA AT 25°C*

Medium	Atoms/cm ³	Dis/sec/cm ³	μc/cm ³
Water	6.7 × 10 ⁴	1.2 × 10 ⁻⁴	3.20 × 10 ⁻⁹
Benzene	4.1 × 10 ⁴	7.2 × 10 ⁻⁵	1.95 × 10 ⁻⁹
Hydrogen	49	8.7 × 10 ⁻⁸	2.35 × 10 ⁻¹²
Ethane	149	2.65 × 10 ⁻⁷	7.17 × 10 ⁻¹²

*Note that 1.0 g of tritium is approximately equal to 9600 curies.

**PHYSICAL AND CHEMICAL
PROPERTIES OF TRITIUM**

The atomic weight of tritium is 3.016997 ± 0.000011 g, compared with the atomic weights for ^1H and ^2H of 1.008142 ± 0.000003 g and 2.014735 ± 0.000006 g, respectively (Ref. 22). Accurate calculations of the thermodynamic properties of tritium and tritium hydride were first presented by Jones.²³ At room temperature the combination of H_2 and T_2 to form HT is favored. Hammel²⁴ used de Boer's modified law of corresponding states to calculate the vapor pressure of tritium in a low-temperature range (12.2 to 33.9°K), critical constants, triple-point constants, and a number of molecular constants. Grilly²⁵ measured the vapor pressures of the hydrogen isotopes in similar temperature ranges and found that the measured vapor pressures of tritium exceeded those calculated by Hammel. His experimentally measured values for the boiling-point and triple-point temperatures were 24.92 and 20.27°K, respectively, compared with Hammel's calculated values of 25.57 and 21.65°K. Friedman, White, and Johnston²⁶ plotted critical constants, boiling points, and triple-point constants for the six isotopic hydrogen molecules vs. the reciprocal of the square roots of their masses and found that the plots were nearly straight lines. They concluded that this graphical method could be used to predict constants for the isotopes for which experimental data are not available. Table 2.3 shows a comparison of the values calculated by Hammel, the experimental values measured by Grilly, and the graphically predicted values of Friedman, White, and Johnston. Later studies by

Table 2.3
PROPERTIES OF TRITIUM

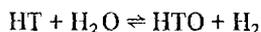
	Hammel ²⁴	Grilly ²⁵	Friedman, White, and Johnston ²⁶
Critical temperature, °K	43.7		40.6
Critical volume, cm ³ /mole	53.7		57.1
Critical pressure, atm	20.8		18.1
Triple-point temperature, °K	21.65	20.27	20.5
Triple-point pressure, mm Hg	188	157.4	157.4
Boiling point, °K	25.57	24.92	24.9

Rogers and Brickwedde²⁷ give an experimental critical-point temperature for T_2 of 40.0°K and a triple-point temperature of 20.62°K; Mittelhauser and Thodos²⁸ report a calculated value of 40.44°K for the critical-point temperature and an experimental value of 20.62°K for the triple-point temperature.

Other properties of tritium, such as the energy of dissociation of tritium gas (4.59 ev) and the ionization energy (13.55 ev), have been compiled by Brunner.²⁹

Properties of Tritiated Water

The mass action equilibrium coefficient for the reaction



is approximately 6 at 25°C; hence the formation of tritiated water is favored. Because of the predominance of this reaction, any discussion of the properties of tritium must necessarily include a discussion of tritiated water since this is the probable tritiated species in man's environment. Price³⁰ determined that, since in the range 25 to 80°C the vapor pressure of HTO is less than that of H₂O, a higher boiling point is indicated for HTO. These general conclusions have been supported by more recent studies³¹⁻³⁴ in which the measured values of the vapor pressure and boiling point of tritiated water have been refined. Jones³³ used Raman spectra and inelastic-neutron-scattering spectra for determining the parameters to be used with Bigeleisen's³⁵ formulation of isotope effects on vapor pressure. The properties of the oxides of the three hydrogen isotopes are listed in Table 2.4.

Table 2.4
THERMODYNAMIC PROPERTIES OF THE OXIDES
OF HYDROGEN ISOTOPES³³⁻³⁴

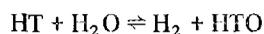
	H ₂ O	D ₂ O	T ₂ O	Ref.
Boiling point, °C	100.00	101.42	101.51	34
Triple-point temperature, °C	0.010	3.82	4.49	34
Triple-point pressure, mm Hg	4.58	5.02	4.87	34
Heat of vaporization at the boiling point, kcal/mole	9.72	9.9	10.1	33
Entropy at 298.16°K, eu	16.75	18.9	19.0	33

Wang, Robinson, and Edelman³⁶ measured the diffusion coefficient of HTO in ordinary water at 25°C and obtained a value of $2.44 \pm 0.057 \times 10^{-5}$ cm²/sec. Nakayama and Jackson³⁷ made measurements in dilute agar gel concentrations and obtained a value of $2.41 \pm 0.055 \times 10^{-5}$ cm²/sec by extrapolation to zero concentration of gel at 25°C.

The density of T₂O in the range from 5 to 54°C has been measured by Goldblatt.³⁸ The maximum density, 1.2150₂ g/cm³, occurred at 13.4°C, compared with the maximum density for D₂O of 1.10589 at 11.2°C and for H₂O of 0.999973 at 3.98°C (Refs. 22, 39). Other physical constants of the various isotopic varieties of water have been tabulated by Dirian⁴⁰ and by Kirshenbaum.⁴¹

Isotopic Exchange in Water

Tritium closely follows the reactions of ordinary hydrogen. However, the relatively large mass differences between the hydrogen isotopes make isotopic effects easily discernible. Because of the prevalence of water and its importance in the life processes, its isotopic exchange with tritium is of special concern. Libby^{42,43} calculated the equilibrium constants for a number of reactions involving the isotopic variants of hydrogen gases and their oxides. His calculations were based on the vibrational levels of the water molecule at temperatures ranging from 20 to 500°C. He assumed that only an atom of a different mass moving in the same force field affects the molecule. Black and Taylor⁴⁴ experimentally determined the equilibrium constants for the reaction



over the temperature range 16 to 303°C and found that they compared quite well with the theoretically derived values of Libby (Table 2.5); the experimental values were

Table 2.5
EQUILIBRIUM CONSTANTS FOR THE
REACTION $\text{HT} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \text{HTO}$

Temperature, °C	Experimental equilibrium constant ⁴⁵	Theoretical equilibrium constant ^{43,44}
16.0	6.75 ± 0.04	6.47
20.2	6.47 ± 0.02	6.24
25.0	6.25 ± 0.05	6.01
56.2	5.05 ± 0.05	4.84
79.6	4.37 ± 0.05	4.23
111.2	3.76 ± 0.04	3.64
158.4	3.10 ± 0.06	3.03
217.1	2.64 ± 0.04	2.54
302.9	2.17 ± 0.02	2.08

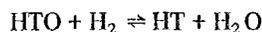
consistently higher, but they were within the predicted limits of accuracy estimated by Libby. The experimental values can be summarized by the equation

$$\log K = 0.292 \log T + (336.5/T) - 1.055$$

Roesch⁴⁵ estimated that tritium gas would be easily converted to tritiated water in the atmosphere in the presence of a suitable catalyst. He felt that it might be possible

to store tritium gas in the absence of a catalyst with little or no conversion to tritiated water since deuterium gas undergoes little exchange with water without a catalyst. Ionizing radiation can cause the exchange of hydrogen isotopes between their gases and water.⁴⁶⁻⁵⁰ Studies by Dorfman and Hemmer⁵⁰ showed that the beta radiation from tritium decay is sufficient to initiate a reaction between tritium and oxygen to form tritiated water. Yang and Gevantman⁴⁷ suggest that the conversion of tritium to tritiated water in the atmosphere by this process would amount to less than 1% per day.

Bond⁵¹ indicates that tritium produced by a nuclear explosion will be practically 100% converted to tritiated water and mixed with environmental water. He also finds that the reverse of the preceding reaction,



is catalyzed at 600°C by a number of oxygenated salts, calcium sulfate being especially effective. Even in the Gasbuggy experiment, conducted in a formation having 11% porosity filled with liquid water (59% of the volume) and short-chain hydrocarbons at 84 atm of pressure (41% of the volume), only about 5% of the tritium was found in the gas phase.^{52,53} The nongaseous tritium was assumed to be in the form of HTO.⁵³

Harteck⁵⁴ bases his discussion of the relative abundance of HT and HTO in the atmosphere on several reactions. When tritium atoms are formed by cosmic radiation, they initially have a high kinetic energy. He suggests that the most probable initial reaction for tritium at pressures below atmospheric pressure is a three-body collision with oxygen to form the rather stable radical TO_2 . Subsequent reactions of the TO_2 would be expected to yield HTO, but not HT, in the atmosphere. He suggests that repeated photochemical decomposition of TO_2 and reactions with ozone are necessary to account for the relative abundance of HT and HTO. A second possible initial reaction is the collision of tritium with an H_2 molecule with resulting isotopic exchange.

Altitude has a pronounced effect on the reactions that occur in the atmosphere. Below 5 km, TO_2 will be consumed to form HTO. In the region from 10 to 40 km, HT would be the predominant form, and above 40 km the concentrations are so small that the contribution of HT to the total tritium is negligible. Harteck also states that the tritium concentration in atmospheric hydrogen should remain rather stable, but the tritium concentration in rainwater may be expected to vary with locality, as shown by Libby.⁵⁵

Harteck⁵⁴ found the specific tritium activity of atmospheric methane to be several orders of magnitude higher than that of rainfall and somewhat less than that of atmospheric hydrogen and stratospheric water vapor. Martell⁵⁶ concludes that in thermonuclear clouds tritiated hydrogen is produced in the stratosphere by radiative dissociation of water under oxidizing conditions. The occurrence of tritiated methane is explained by the tropospheric exchange of methane with the tritiated hydrogen that has moved down from the stratosphere.

Isotopic Exchange in Organic Molecules

The exchange between deuterium gas and methanol or water is catalyzed by platinum and proceeds at a convenient rate at room temperature.^{5,7} This reaction is limited to the exchange of hydroxyl hydrogen. Eastham and Raen^{5,8} found an exchange between tritiated isopropyl alcohol and the active hydrogens of organic compounds. The number of active hydrogens determined by tritium exchange is in good agreement with the number expected. Lang and Mason^{5,9} used tritium exchange between the hydroxyl hydrogen of cellulose and water vapor to study accessibility. The incomplete reversibility indicated changes in accessibility which occurred during wetting and drying. For amylopectin, an apparent accessibility of 123% of the hydroxyl hydrogen was obtained, indicating that isotopic effects are operative. Two isotopic effects were concluded to be responsible—one in the exchange reaction and the second in the recovery of tritiated water.

Leach and Springell^{6,0} used tritiated water to study the exchangeable hydrogen atoms in proteins. They consider that although carbon tritiation in proteins is unlikely, it might have the best chance of occurring when racemization at asymmetric centers is possible or when specific activities due to tritiation at nitrogen and oxygen centers are so high that self-radiation induces labeling at adjacent carbon sites. Cha^{6,1} used tritium-exchange techniques for determining the alcoholic and carboxylic groups of polyethylene terephthalate.

When nuclear transformation occurs, the emission of a particle or gamma ray gives the resulting species a recoil momentum that is very large in chemical terms.^{6,2} Wolfgang and his associates^{6,2} suggested that recoil tritium (so-called "hot atoms") could be used for labeling organic compounds. In this case, tritium labeling is not restricted to the replacement of active hydrogens; the recoil momentum of the (³HeT)⁺ formed by beta decay is sufficient to break C-H bonds and allow substitution of tritium at any position occupied by a hydrogen atom. The proposed technique is limited since it does not lead to very high specific activities or to the labeling of specific positions obtainable by chemical synthesis. Wilzbach^{6,3} developed the recoil technique and found that exposure of organic compounds to tritium gas yields products of high activity without extensive radiation damage. Tritium is distributed throughout the product, but the distribution is not completely random. The advantages and limitations of tritium-recoil labeling have been discussed by Rowland and Wolfgang.^{6,4}

In addition to recoil labeling, organic compounds can be labeled by beta labeling^{6,5-7,3} and by beta radiolysis of T₂ (Ref. 68). Beta labeling is the term applied when the labeling reaction is initiated by electrons.^{6,5,7,4} The electrons can be supplied internally by the beta decay of one of the reactants, such as tritium, or they can be added from an external source. Formation of tritiated ethylene involves both recoil labeling and beta labeling,^{6,5} the rate is independent of temperature and is not affected by the presence of nitric oxide. Tritiated ethane, propane, and *n*-butane are formed exclusively by beta labeling. Their rate of formation is increased by decreasing the temperature, and nitric oxide reduces their production to nearly zero. The labeling

yield per beta decay for tritiated methane, ethane, and propane increases linearly with tritium concentration.⁶⁸ Yields decrease when T₂ is replaced by HT, but irradiation with an external gamma source increases yield.

In a study of exchange between tritium gas and methane, Pratt and Wolfgang⁶⁷ obtained kinetic data indicating the existence of all three mechanisms discussed in the preceding paragraph. The recoil-labeling reaction shows a first-order dependence on T₂ pressure and is insensitive to scavenging by xenon. Beta labeling gives an observed 3/2 power dependence on T₂ pressure and is inhibited by the presence of ion scavengers. The beta radiolysis of T₂ is felt to be the cause of a small square-power term in the kinetics.

Lee, Tang, and Rowland⁷⁰ substituted recoil tritium atoms on the carbon skeleton of numerous saturated hydrocarbons and halocarbons and found that significant yields of variously labeled olefins were produced, perhaps as the result of the replacement of a single group in the primary energetic process followed by the elimination of a small molecule from the excited labeled product. Shores and Moser⁷⁵ found that reacting tritium atoms of intermediate energy with unsaturated hydrocarbons resulted in both addition and substitution. With saturated hydrocarbons, substitution was the principal reaction.

Isotopic Effects in Tritium Reactions

Swain and Schaad⁷⁶ derived an equation to describe the relation between the isotope effects of tritium and deuterium based on quantum mechanics considerations:

$$\frac{k_H}{k_T} = \alpha \left(\frac{k_H}{k_D} \right)^{1.442}$$

where k_H , k_T , and k_D are molecular constants pertaining to hydrogen, tritium, and deuterium, respectively. The value of α has a low-temperature limit of 1.000 and a high-temperature limit of 1.050. From a consideration of the birational partition function, α can be expected to vary from 0.907 to 1.157. As an experimental test of the derived equation, Swain and Schaad measured the rate of racemization of α -phenylisocaprophenone and compared this rate with the rates of exchange of deuterium between α -phenylisocaprophenone- α -d and water or of tritium between α -phenylisocaprophenone- α -t and water. For these studies the deuterium isotope effect, k_H/k_D , was 5.02, from which the tritium isotope effect was calculated to have a maximum of 11.8, a high-temperature limit of 10.7, a low-temperature limit of 10.2, and a minimum of 9.7. The observed tritium effect, 10.2, was well within the predicted range and agreed most closely with the low-temperature limit.

Bigeleisen⁷⁷ developed the theory of relative tritium-hydrogen and deuterium-hydrogen isotope effects for both kinetic and equilibrium processes. He concluded that the lower limit of the ratio $\log \alpha_{T-H} / \log \alpha_{D-H}$ should be 1.33 and the upper limit 1.55. Small effects occur in systems where there is no significant change in the

chemical bonding of the labeled hydrogen atom in the net reaction. The largest kinetic and equilibrium effects arise when the labeled hydrogen is strongly bonded in the reactant and is loosely bonded in either the product or in a transition state. Abnormal ratios of tritium-to-deuterium isotope effects provide evidence of such phenomena as tunneling.

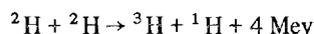
Bigeleisen⁷⁸ also found that kinetic isotope calculations yield exactly the same results as calculations of equilibrium isotope effects and that they are the same as those obtained from collision theory. The preexponential, or temperature independent, factor is the ratio of the square roots of the molecular weights of the reactants and the transition states. At high temperatures this ratio is exactly cancelled by the Boltzmann excitation terms.

Kinetics of the base-catalyzed exchange of acetone, deuterated acetone, and tritiated acetone indicate secondary isotope effects to the extent of 5 to 10% (Ref. 79). For the limited data, the values of the ratio of $\log(k_H/k_T)/\log(k_H/k_D)$ seem to be about 1.44, which is to be compared with Bigeleisen's limits of 1.33 and 1.55. However, the experimental values of k_H/k_T were considerably higher than those predicted by Swain's equation.

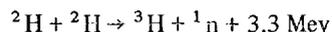
Varshavskii⁸⁰ calculated the distribution coefficient of tritium between various hydrogenous substances on the basis of statistical mechanics and estimated that values as high as 20 can be obtained for the hydrides of alkali metals. Kandel⁸¹ measured the rates of the forward and reverse reactions of CH_4 with T_2 to give successively CH_3T , CH_2T_2 , CHT_3 , and CT_4 . Equilibrium constants calculated from the steady-state concentrations were close to the high-temperature classical values.

TRITIUM-PRODUCING REACTIONS

Oliphant, Harteck, and Rutherford⁸² first detected tritium following deutron bombardment of compounds containing deuterium. The tritium was ascribed to the reaction



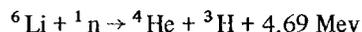
Dee⁸¹ confirmed this reaction and the reaction



by observations of tracks in a cloud chamber. Bonner⁸⁴ studied the energy distribution from this second reaction and concluded that ${}^3\text{H}$ might spontaneously disintegrate, with a long half-life, into ${}^3\text{He}$ by emission of an electron. Verzaux⁸⁵ has reviewed the details of these and other tritium-producing reactions. The cross section is 1.3×10^{-4} barn for incident deuterons of 15 kev and increases rapidly to 10^{-2} barn

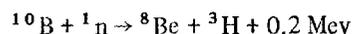
toward 60 kev and 0.052 barn at 300 kev. There is a maximum of 0.09 barn at 2 Mev, and this value is maintained up to 3.5 Mev. At 10 Mev the cross section is 0.073 barn.

Chadwick and Goldhaber⁸⁶ discovered that neutron irradiation of ${}^6\text{Li}$ produces tritium by the reaction

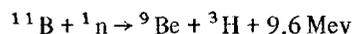


The singly charged particles had a maximum range of about 5.5 cm in air, whereas that of the doubly charged particles was less than 1.5 cm. For thermal and slow neutrons this is the principal reaction in the neutron irradiation of lithium.⁸⁷ For fast neutrons, ${}^7\text{Li}$ plays the principal role. For producing ${}^3\text{H}$ from lithium, the incident neutrons should be as slow as possible. Neutron irradiation of lithium metal or lithium salts is one of the predominant methods for the production of tritium.^{85,88} Lithium fluoride was found to be a good source of lithium since the fluorine has a low cross section and the tritium that is produced is easily liberated.⁸⁸

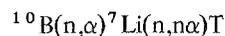
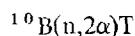
Chadwick and Goldhaber⁸⁶ also found that neutron irradiation of ${}^{10}\text{B}$ produces tritium. Cornog and Libby⁸⁹ suggested the reactions



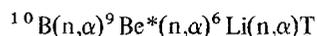
and



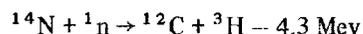
Other neutron reactions in boron which lead to the production of tritium are⁸⁶



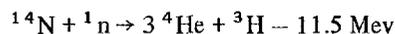
and



The last reaction probably does not lead to the production of tritium because the ${}^9\text{Be}^*$ is unstable and decays to a neutron and two alpha particles.⁸⁶ The first two reactions are time dependent and can contribute substantially to tritium production in reactors.⁹⁰ Cornog and Libby⁸⁹ found that neutron irradiation of nitrogen compounds forms tritium according to the reactions

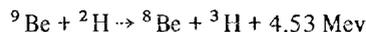


and

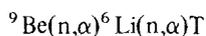


These reactions require a source of energetic neutrons.

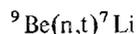
O'Neal and Goldhaber⁹¹ found that tritium is produced by deuteron bombardment of beryllium by the reaction



Tritium is also produced in beryllium through reaction chains⁹⁰



and



The (n,t) reaction, however, has a threshold above 10 Mev and can usually be ignored.⁹⁰ Tritium is also produced when copper, silver, or antimony is bombarded with deuterons.⁹² The (²H,³H) reaction also takes place with fluorine and with other elements.⁹³⁻⁹⁸

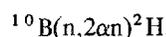
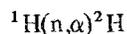
Coon and Nobles⁹⁷ determined that bombardment of ³He with thermal neutrons produces tritium with a cross section of about 5000 barns. King and Goldstein⁹⁸ found that for fast neutrons the cross section is inversely proportional to the velocity of the neutrons.

Proton bombardment^{96,99,100} and helium bombardment^{96,101,102} also produce tritium. Libby¹⁰³ had first suggested that tritium was produced from atmospheric nitrogen by bombardment with cosmic-ray neutrons and that most of the atmospheric helium results from the decay of tritium.¹⁰⁴ Later studies of tritium production by high-energy protons led to the conclusion that most of the naturally occurring tritium is produced by primary cosmic-ray reactions.¹⁰⁵ The rate of production was estimated to be 0.082 tritons/cm²/sec, compared with 0.05 for intermediate-energy-neutron reactions and 0.01 for low-energy-neutron reactions. Later estimates range as high as 2.0 tritons/cm²/sec for the total atmospheric production rate.¹⁰⁶⁻¹¹⁴ Some controversy arises regarding whether some of the tritium is accreted from extraterrestrial sources or whether it is all produced in the earth's atmosphere and in incoming meteors (Refs. 107, 109, 111, 114-118).

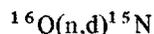
Albenesius^{119,120} was the first to establish that tritium is produced as a fission product at the rate of 1 atom per 1×10^4 to 2×10^4 fissions for three types of material, natural uranium, enriched uranium, and a mixture of transuranium nuclides. For natural uranium a fission-to-tritium ratio of $(1.05 \pm 0.09) \times 10^4$ was obtained.¹²⁰ Sloth and his associates¹²¹ obtained a ratio of $(1.25 \pm 0.15) \times 10^4$ for the fission of natural uranium. Watson¹²² obtained a ratio of 4500 ± 900 fissions per tritium atom for the spontaneous fission of ²⁵²Cf. This ratio was confirmed by studies of Wegner¹²³ and of Horrocks.¹²⁴

One of the major sources of tritium is the neutron irradiation of deuterium.⁸⁵ The cross section has been established as 5.7×10^{-4} barn by Kaplan and his associates.¹²⁵

In light-water reactors the natural concentration of deuterium is about 0.015%.⁹⁰ Deuterium can also be formed by the reactions



and



The production of deuterium from neutron capture by protium almost doubles the deuterium concentration during one year of irradiation.⁹⁰ The production of deuterium from the other two reactions is much smaller and can be disregarded.⁹⁰ Of course, in heavy-water reactors the supply of deuterium is orders of magnitude greater; so tritium production is much higher than in light-water reactors.

SUMMARY

Tritium closely follows the reactions of ordinary hydrogen. However, the relatively large mass differences between the hydrogen isotopes make isotopic effects easily discernible. At room temperature the reaction of tritium to form tritiated water is favored, and most of the earth's inventory of tritium exists in the form of water.

Tritium is produced by a number of nuclear reactions, including fission. Some of the more important sources are ternary fission and neutron irradiation of deuterium, lithium, and boron.

REFERENCES

1. L. W. Alvarez and R. Cornog, Helium and Hydrogen of Mass 3, *Phys. Rev.*, [2]56: 613 (Sept. 15, 1939).
2. L. W. Alvarez and R. Cornog, Radioactive Hydrogen, *Phys. Rev.*, [2]57: 248 (Feb. 1, 1940).
3. L. W. Alvarez and R. Cornog, Radioactive Hydrogen----A Correction, *Phys. Rev.*, [2]58: 197 (July 15, 1940).
4. R. D. O'Neal and M. Goldhaber, The Decay Constant of H^3 , *Phys. Rev.*, [2]58: 574-575 (Sept. 15, 1940).
5. C. E. Nielsen, The Energy Spectrum of H^3 Beta-Rays, *Phys. Rev.*, [2]60: 160 (July 15, 1941).
6. M. Goldblatt, E. S. Robinson, and R. W. Spence, The Half-Life of Tritium, *Phys. Rev.*, [2]72: 973 (Nov. 15, 1947).
7. A. Novick, Half-Life of Tritium, *Phys. Rev.*, [2]72: 972 (Nov. 15, 1947).

8. S. C. Curran, J. Angus, and A. L. Cockcroft, Beta Spectrum of Tritium, *Nature*, 162(4112): 302-303 (Aug. 21, 1948).
9. S. C. Curran, J. Angus, and A. L. Cockcroft, Investigations of Soft Radiations. II. The Beta Spectrum of Tritium, *Phil. Mag.*, 40(300): 53-60 (January 1949).
10. G. H. Jenks, J. A. Ghormley, and F. H. Sweeton, Measurement of the Half-Life and Average Energy of Tritium Decay, *Phys. Rev.*, [2] 75(4): 701-702 (Feb. 15, 1949).
11. W. T. Byatt, F. T. Rogers, Jr., and A. Waltner, On the Beta Particle Spectrum from the Decay of Tritium, *Phys. Rev.*, [2] 75(5): 909 (Mar. 1, 1949).
12. G. C. Hanna and B. Pontecorvo, The Beta-Spectrum of H^3 , *Phys. Rev.*, [2] 75(6): 983-984 (Mar. 15, 1949).
13. L. Slack, G. E. Owen, and H. Primakoff, On the Maximum Beta-Energy Release in Tritium, *Phys. Rev.*, [2] 75(9): 1448 (May 1, 1949).
14. E. R. Graves and D. I. Meyer, End Point of the Tritium Beta-Ray Spectrum, *Phys. Rev.*, [2] 76(1): 183 (July 1, 1949).
15. G. H. Jenks, F. H. Sweeton, and J. A. Ghormley, A Precise Determination of the Half-Life and Average Energy of Tritium Decay, *Phys. Rev.*, 80(6): 990-995 (Dec. 15, 1950).
16. W. M. Jones, The Half-Life of Tritium by Absolute Counting, *Phys. Rev.*, 83(3): 537-539 (Aug. 1, 1951).
17. W. M. Jones, Half-Life of Tritium, *Phys. Rev.*, 100(1): 124-125 (Oct. 1, 1955).
18. J. F. Eichelberger, G. R. Grove, and L. V. Jones, *Mound Laboratory Progress Report for June 1963*, USAEC Report MLM-1160, Mound Laboratory, June 28, 1963.
19. J. F. Eichelberger, G. R. Grove, and L. V. Jones, *Mound Laboratory Progress Report for September 1963*, USAEC Report MLM-1176, Mound Laboratory, Sept. 30, 1963.
20. A. V. Gross et al., Tritium in Nature, *Science*, 113: 1-2 (Jan. 5, 1951).
21. *Report of the International Commission on Radiological Units and Measurements, (ICRU) 1962*, National Bureau of Standards, Handbook 86, p. viii, Superintendent of Documents, U. S. Government Printing Office, Washington, 1963.
22. N. A. Lange and G. M. Forker (Comp. and Ed.), *Handbook of Chemistry*, 10th ed., McGraw-Hill Book Company, Inc., New York, 1961.
23. W. M. Jones, Thermodynamic Functions for Tritium and Tritium Hydride. The Equilibrium of Tritium and Hydrogen with Tritium Hydride. The Dissociation of Tritium and Tritium Hydride, *J. Chem. Phys.*, 16(11): 1077-1081 (November 1948).
24. E. F. Hammel, *Some Calculated Properties of Tritium*, USAEC Report AECU-647, Los Alamos Scientific Laboratory, 1949.
25. E. R. Grilly, *The Vapor Pressures of Hydrogen, Deuterium, and Tritium Up to Three Atmospheres*, USAEC Report AECU-928, Los Alamos Scientific Laboratory, Sept. 22, 1950.
26. A. S. Friedman, D. White, and H. L. Johnston, Critical Constants, Boiling Points, Triple Point Constants, and Vapor Pressures of the Six Isotopic Hydrogen Molecules, Based on a Simple Mass Relationship, *J. Chem. Phys.*, 19(1): 126-127 (January 1951).
27. J. D. Rogers and F. G. Brickwedde, Deuterium and Tritium Saturated-Liquid PVT According to Quantum Mechanical Principle of Corresponding States, *J. Chem. Phys.*, 42(8): 2822-2825 (Apr. 15, 1965).
28. H. M. Mittelhauser and G. Thodos, Vapour Pressure Relationships Up To the Critical Point of Hydrogen, Deuterium, and Tritium, and Their Diatomic Combinations, *Cryogenics*, 4(6): 368-373 (December 1964).
29. H. Brunner, Survey of Available Data of Tritium, pp. 10-16, in *Seminaire sur la Protection Contre les Dangers du Tritium*, Service Central de Protection Contre les Rayonnements Ionisants, le Vesinet, Avril 16-18, 1964 (CONF-640413).
30. A. H. Price, Vapour Pressure of Tritiated Water, *Nature*, 181(4604): 262 (Jan. 25, 1958).
31. O. Sepall and S. G. Mason, Vapor/Liquid Particles of Tritium in Tritiated Water, *Can. J. Chem.*, 38(7): 2024-2025 (July 1960).

32. M. M. Popov and F. P. Tazetdinov, The Vapour Pressure of T₂O, USAEC file No. NP-tr-534, translated from *At. Energ. (USSR)*, 8: 420-424 (1960), 1961.
33. W. M. Jones, *Vapor Pressures of Tritium Oxide and Deuterium Oxide. Interpretation of the Isotope Effect*, USAEC Report LADC-5905, Los Alamos Scientific Laboratory, 1963.
34. H. A. Smith and K. R. Fitch, Determination of the Separation Factor for the Vaporization of Mixtures of Protium and Tritium Oxides, *J. Phys. Chem.*, 67(4): 920-921 (Apr. 15, 1965).
35. J. Bigeleisen, Correlation of Tritium and Deuterium Isotope Effects, in *Tritium in the Physical and Biological Sciences*, Symposium Proceedings, Vienna, 1961, Vol. I, pp. 161-168, International Atomic Energy Agency, Vienna, 1962 (STI/PUB/39).
36. J. H. Wang, C. V. Robinson, and I. S. Edelman, Self-Diffusion and Structure of Liquid Water. III. Measurement of the Self-Diffusion of Liquid Water with H², H³, and O¹⁸ as Tracers, *J. Amer. Chem. Soc.*, 75(2): 466-470 (Jan. 20, 1953).
37. F. S. Nakayama and R. D. Jackson, Diffusion of Tritiated Water (H³H¹O¹⁶) in Agar Gel and Water, *J. Phys. Chem.*, 67(4): 932-933 (Apr. 15, 1963).
38. M. Goldblatt, The Density of Liquid T₂O¹, *J. Phys. Chem.*, 68(1): 147-151 (Jan. 15, 1964).
39. I. L. Chang and J. Y. Chien, Maximum Difference Between Densities of Ordinary and Heavy Water, *J. Amer. Chem. Soc.*, 63(6): 1709-1711 (June 6, 1941).
40. J. Dirian, Constantes Physiques des Variétés Isotopiques de l'Eau (¹⁷O-¹⁸O-D-T), French Report CEA-Bib-15, 1962.
41. I. Kirshenbaum, *Physical Properties and Analysis of Heavy Water*, National Nuclear Energy Series, Division III, Volume 4A, McGraw-Hill Book Company, Inc., New York, 1951.
42. W. F. Libby, Vibrational Frequencies of the Isotopic Water Molecules; Equilibria with the Isotopic Hydrogens, *J. Chem. Phys.*, 11(3): 101-109 (March 1943).
43. W. F. Libby, Errata: Vibrational Frequencies of the Isotopic Water Molecules; Equilibria with the Isotopic Hydrogens, *J. Chem. Phys.*, 15(5): 339 (May 1947).
44. J. F. Black and H. S. Taylor, Equilibrium in Hydrogen-Water Systems Containing Tritium, *J. Chem. Phys.*, 11(9): 395-402 (September 1943).
45. W. C. Roesch, *P-10 Chemical Equilibria*, USAEC Report HW-17318, Hanford Atomic Products Operation, Mar. 23, 1950.
46. S. O. Thompson and O. A. Schaeffer, Radiation Induced Equilibrium of Hydrogen-Deuterium Mixtures, *J. Chem. Phys.*, 23(4): 759-760 (April 1955).
47. J. Y. Yang and L. H. Gevantman, Tritium-β-Radiation-Induced Isotopic Exchange in the T₂-H₂O System, Report USNRDL-TR-471, Naval Radiological Defense Laboratory, Sept. 28, 1960.
48. G. J. Casaletto, L. H. Gevantman, and J. B. Nash, The Self-Radiation Oxidation of Tritium in Oxygen and Air, Report USNRDL-TR-565, Naval Radiological Defense Laboratory, May 8, 1962.
49. J. Y. Yang and L. H. Gevantman, Tritium Beta-Radiation-Induced Isotopic Exchange with Water Vapor, *J. Phys. Chem.*, 68(11): 3115-3119 (Nov. 16, 1964).
50. L. M. Dorfman and B. A. Hemmer, Ion Pair Yield of the Tritium-Oxygen Reaction, *J. Chem. Phys.*, 22(9): 1555-1558 (September 1954).
51. W. D. Bond, *Production of Tritium by Contained Nuclear Explosions in Salt: I. Laboratory Studies of Isotopic Exchange of Tritium in the Hydrogen-Water System*, USAEC Report ORNL-3334, Oak Ridge National Laboratory, Dec. 6, 1962.
52. H. Gevertz (Ed.), *Project Gasbuggy*, El Paso Natural Gas Company, El Paso, Texas, May 14, 1965.
53. J. A. Korver and D. E. Rawson, *Gasbuggy: Postshot Investigations in the GB-ER*, USAEC Report UCRL-50425, Lawrence Radiation Laboratory, University of California, April 19, 1968.
54. P. Harteck, The Relative Abundance of HT and HTO in the Atmosphere, *J. Chem. Phys.*, 22(10): 1746-1751 (October 1954).

55. W. F. Libby, Tritium in Nature, *Phys. Rev.*, **91**(2): 442 (July 15, 1953).
56. E. A. Martell, On the Inventory of Artificial Tritium and Its Occurrence in Atmospheric Methane, *J. Geophys. Res.*, **68**(13): 3759-3769 (July 1, 1963).
57. C. G. Swain and A. J. Kresge, Exchange Reactions Between Hydrogen Gas and Hydroxyl Groups. A Convenient Preparation of Tritium-Labeled Water, *J. Amer. Chem. Soc.*, **80**(19): 5281-5283 (Oct. 7, 1958).
58. J. F. Eastham and V. F. Raaen, Determination of Active Hydrogen in Organic Compounds by Exchange with Tritiated Isopropyl Alcohol, *Anal. Chem.*, **31**(4): 555-558 (April 1959).
59. A. R. G. Lang and S. G. Mason, Tritium Exchange Between Cellulose and Water. Accessibility Measurements and Effects of Cyclic Drying, *Can. J. Chem.*, **38**(3): 373-387 (March 1960).
60. S. J. Leach and P. H. Springell, Tritium-Hydrogen Exchange in Studies of Protein Structure, *Aust. J. Chem.*, **15**(2): 350-364 (May 1962).
61. C. Cha, Tritium Exchange Studies on Poly(ethylene) Terephthalate, *J. Polym. Sci., Part B*, **2**(11): 1069-1073 (November 1964).
62. R. Wolfgang et al., Production of Radioactive Compounds with Recoil Tritons, *Science*, **121**: 715-717 (May 20, 1955).
63. K. E. Wilzbach, Tritium Labeling by Exposure of Organic Compounds to Tritium Gas, *J. Amer. Chem. Soc.*, **79**(4): 1013 (Feb. 27, 1957).
64. F. S. Rowland and R. Wolfgang, Tritium-Recoil Labeling of Organic Compounds, *Nucleonics*, **14**(8): 58-61 (August 1956).
65. K. Yang and P. L. Gant, Reactions Initiated by Beta Decay of Tritium. II. The Tritium-Ethylene System, *J. Chem. Phys.*, **31**(6): 1589-1594 (December 1959).
66. P. L. Gant and K. Yang, Reactions Initiated by the Beta Decay of Tritium. III. The Tritium-Cyclopropane System, *J. Chem. Phys.*, **32**(6): 1757-1763 (June 1960).
67. T. H. Pratt and R. Wolfgang, The Self-Induced Exchange of Tritium Gas with Methane, *J. Amer. Chem. Soc.*, **83**(1): 10-17 (Jan. 16, 1961).
68. K. Yang and P. L. Gant, Reactions Initiated by Beta Decay of Tritium. IV. Decay and Beta Labeling, *J. Phys. Chem.*, **66**(9): 1619-1622 (Sept. 19, 1962).
69. A. Soklowska, Reactions of Tritium Recoil Atoms in Liquid Organic Mixtures, in *Chemical Effects of Nuclear Transformations*, Proceedings, Vienna, 1964, Vol. I, p. 255, International Atomic Energy Agency, Vienna, 1965 (STI/PUB/91).
70. E. K. C. Lee, Y. N. Tang, and F. S. Rowland, The Mechanism of Recoil Tritium Reactions: Formation of Labeled Alkenes from Saturated Hydrocarbons and Halocarbons, *J. Amer. Chem. Soc.*, **86**(22): 5038-5039 (Nov. 20, 1964).
71. E. K. C. Lee, G. Miller, and F. S. Rowland, Moderator Effects on Recoil Tritium Reaction: with Methyl and Methyl-d₃ Fluorides, *J. Amer. Chem. Soc.*, **87**(1): 190-199 (Jan. 5, 1965).
72. J. B. Nash, *The Production of Tritium-Labeled Methane and Ethane in the CH₄-T₂ System*, USAEC Report UCRL-16009, University of California at Berkeley, Apr. 12, 1965.
73. S. Wexler, On the Mechanism of the Isotopic Exchange of Tritium with Methane, *J. Amer. Chem. Soc.*, **85**(3): 272-277 (Feb. 19, 1963).
74. L. M. Dorfman and H. C. Matraw, The Exchange Reaction of Hydrogen and Tritium, *J. Phys. Chem.*, **57**(7): 723-725 (Oct. 28, 1953).
75. R. D. Shores and H. C. Moser, Reactions of Tritium Atoms with Frozen Hydrocarbons, *J. Phys. Chem.*, **65**: 570-571 (1961).
76. C. G. Swain and L. J. Schaad, *A Relation Between Protium-Tritium and Protium-Deuterium Isotope Effects*, USAEC Report AECU-3968, Massachusetts Institute of Technology, 1958.
77. J. Bigeleisen, Correlation of Tritium and Deuterium Isotope Effects, in *Tritium in the Physical and Biological Sciences*, Symposium Proceedings, Vienna, 1961, Vol. I, pp. 161-168, International Atomic Energy Agency, Vienna, 1962 (STI/PUB/39).
78. J. Bigeleisen, Correlation of Kinetic Isotope Effects with Chemical Bonding in Three-Centre Reactions, *Pure Appl. Chem.*, **8**: 217-223 (1964).

79. J. R. Jones, Rates of Abstraction of Hydrogen, Deuterium and Tritium from Acetone in Alkaline Media, *Trans. Faraday Soc.*, **61**: 95-99 (1965).
80. Y. M. Varshavskii, in *Tritium in the Physical and Biological Sciences*, Symposium Proceedings, Vienna, 1961, Vol. I, p. 170, International Atomic Energy Agency, Vienna, 1962 (STI/PUB/39).
81. R. J. Kandel, Methane-Tritium System. II. Kinetics of the Exchange Reaction, *J. Chem. Phys.*, **41**(8): 2435-2442 (Oct. 15, 1964).
82. M. L. Oliphant, P. Harteck, and Lord Rutherford, Transmutation Effects Observed with Heavy Hydrogen, *Nature*, **133**(3359): 413 (Mar. 17, 1934).
83. P. I. Dee, Disintegration of the Diplon, *Nature*, **133**(3363): 564 (Apr. 14, 1934).
84. T. W. Bonner, Formation of an Excited He^3 in the Disintegration of Deuterium by Deuterons, *Phys. Rev.*, **53**(8): 711-713 (May 1, 1938).
85. P. Verzaux, Tritium; Hydrogen Isotope of Mass 3, Bibliography and Review, *J. Phys. Radium*, **13**: 94-106 (February 1952).
86. J. Chadwick and M. Goldhaber, Disintegration by Slow Neutrons, *Nature*, **135**(3402): 65 (Jan. 12, 1935).
87. P. Verzaux, Investigation of the Collision Cross Section of Lithium for Neutrons, *J. Phys. Radium*, **13**: 21-27 (January 1952).
88. C. V. Cannon et al., *The Production and Purification of Tritium: Problem Assignment CXL-8*, USAEC Report MonC-35, Clinton Laboratories, Nov. 29, 1945.
89. R. Cornog and W. F. Libby, Production of Radioactive Hydrogen by Neutron Bombardment of Boron and Nitrogen, *Phys. Rev.*, **59**(12): 1046 (June 15, 1941).
90. J. W. Ray, R. O. Wooton, and R. H. Barnes, *Investigation of Tritium Generation and Release in PM Nuclear Power Plants*, USAEC Report BMI-1787, Battelle Memorial Institute, Oct. 31, 1966.
91. R. D. O'Neal and M. Goldhaber, Radioactive Hydrogen from the Transmutation of Beryllium by Deuterons, *Phys. Rev.*, **58**(11): 1086-1087 (June 1, 1940).
92. R. S. Krishnan and T. C. Banks, A New Type of Disintegration Produced by Deuterons, *Proc. Cambridge Phil. Soc.*, **37**: 317-323 (1941).
93. R. S. Krishnan, Deuteron-Tritium Reaction in Fluorine, *Nature*, **148**(3753): 407-408 (Oct. 4, 1941).
94. D. N. Kunda and M. L. Pool, H^3 Reaction in Cb and Ag, *Phys. Rev.*, **71**(2): 140 (Jan. 15, 1947).
95. R. L. Macklin and H. E. Banta, Tritium Production from Lithium by Deuteron Bombardment, *Phys. Rev.*, **97**(3): 753-757 (Feb. 1, 1955).
96. J. Gonzalez-Vidal and W. H. Wade, Survey of Tritium-Producing Nuclear Reactions, *Phys. Rev.*, **120**: 1354-1359 (1960).
97. J. H. Coon and R. A. Nobles, Disintegration of He^3 and N^{14} by Thermal Neutrons, *Phys. Rev.*, **75**(9): 1358-1361 (May 1, 1949).
98. L. D. P. King and L. Goldstein, The Total Cross Section of the He^3 Nucleus for Slow Neutrons, *Phys. Rev.*, **75**(9): 1366-1369 (May 1, 1949).
99. L. A. Currie, W. F. Libby, and R. L. Wolfgang, Tritium Production by High-Energy Protons, *Phys. Rev.*, **101**(5): 1557-1563 (Mar. 1, 1956).
100. L. A. Currie, Tritium Production by 6-Bev Protons, *Phys. Rev.*, **114**(3): 878-880 (May 1, 1959).
101. W. H. Wade et al., Spallation-Fission Competition in Heaviest Elements: Triton Production, *Phys. Rev.*, **107**(5): 1311-1315 (Sept. 1, 1957).
102. C. Brun, M. Lefort, and X. Tarrigo, Contribution to the Study of Double-Indirect Pickup: Measurement of Tritium Produced by 82- and 105-Mev Protons on Several Targets, *J. Phys. Radium*, **23**: 167-172 (March 1962).
103. W. F. Libby, Atmospheric Helium Three and Radiocarbon from Cosmic Radiation, *Phys. Rev.*, **69**(11 and 12): 671-672 (June 1 and 15, 1946).

104. A. V. Grosse et al., Tritium in Nature, *Science*, **113**: 1-2 (Jan. 5, 1951).
105. L. A. Currie, W. F. Libby, and R. L. Wolfgang, Tritium Production by High-Energy Protons, *Phys. Rev.*, **101**(5): 1557-1563 (Mar. 1, 1956).
106. F. Begemann and W. F. Libby, *Continental Water Balance, Ground Water Inventory and Storage Times, Surface Ocean Mixing Rates and World-Wide Water Circulation Patterns from Cosmic Ray and Bomb Tritium*, USAEC Report OSR-TN-56-561, Office of Scientific Research, Nov. 15, 1956.
107. H. Craig, Distribution, Production Rate, and Possible Solar Origin of Natural Tritium, *Phys. Rev.*, **105**(3): 1125-1127 (Feb. 1, 1957).
108. F. Hagemann et al., Stratospheric Carbon-14, Carbon Dioxide, and Tritium, *Science*, **130**: 542-552 (Sept. 4, 1959).
109. A. T. Wilson and G. J. Ferguson, Origin of Terrestrial Tritium, *Geochim. Cosmochim. Acta.*, **18**(314): 273-277 (1960).
110. F. Begemann, The Natural Tritium Economy of the Earth and the Question of Its Variation with Time, *Chimia (AARAU)*, **16**(1): 1-10 (January 1962).
111. E. Flamm et al., Tritium and Helium-3 in Solar Flares and Loss of Helium from the Earth's Atmosphere, *Science*, **138**(3536): 48-49 (Oct. 5, 1962).
112. V. Lujanas, On Production of Tritium in the Atmosphere, *Lietuvos TSR Mokslu Akad. Darbai*, [B] **1**(32): 21-28 (1963). (In Russian)
113. L. L. Newkirk, Calculation of Low-Energy Neutron Flux in the Atmosphere by the S_n Method, *J. Geophys. Res.*, **68**(7): 1825-1833 (Apr. 1, 1963).
114. D. Lal, G. Rajogopalan, and V. S. Venkatavaradan, Radioactivity Induced by Solar Particles, in *International Conference on Cosmic Rays*, Vol. I, pp. 99-136, Tata Institute of Fundamental Research, Bombay, 1964.
115. U. Karfunkel, *Measurement of Tritium; Methods and Interpretation*, USAEC Report TID-19994, Weizmann Institute of Science, July 1961.
116. M. A. Tamers, Low Concentration of Tritium in Iron Meteorites, *Nature*, **197**(4864): 276-277 (Jan. 19, 1963).
117. D. Tilles, J. DeFelice, and E. L. Fireman, Measurements of Tritium in Satellite and Rocket Material, 1960-1961, *Icarus*, **2**(3): 258-279 (October 1963).
118. R. H. Ide, *Production of Tritium and ^3He by Proton Bombardment of Metals; Solar Origin of Terrestrial Tritium*, USAEC Report UCRL-14346, University of California at Los Angeles, 1965.
119. E. L. Albenesius, Tritium as a Product of Fission, *Phys. Rev. Lett.*, **3**(6): 274-275 (Sept. 15, 1959).
120. E. L. Albenesius and R. S. Ondrejcin, Nuclear Fission Produces Tritium, *Nucleonics*, **18**(9): 100 (September 1960).
121. E. N. Sloth et al., Tritium in the Thermal Neutron of Uranium-235, *J. Inorg. Nucl. Chem.*, **24**: 337-341 (April 1962).
122. J. C. Watson, High-Energy Alpha Particles and Tritons from the Spontaneous Fission of Californium-252, *Phys. Rev.*, **121**(1): 230-231 (Jan. 1, 1961).
123. H. E. Wegner, Additional Long-Range Particles from the Spontaneous Fission of Cf^{252} , *Bull. Amer. Phys. Soc.*, **6**(3): 307 (Apr. 24, 1961).
124. D. L. Horrocks, Tritium Produced During Spontaneous Fission of Californium-252, *Phys. Rev.*, **134**(6B): B1219 (June 22, 1964).
125. L. Kaplan et al., Thermal Neutron Absorption Cross Section of Deuterium, *Phys. Rev.*, **87**(5): 785-786 (Sept. 1, 1952).

3 SOURCES OF TRITIUM PRODUCTION AND ITS RELEASE

REACTORS

Light-Water Reactors

Tritium can be produced in reactors by neutron bombardment of a number of elements and by fission of the reactor fuel.¹ Fast neutrons produce tritium from the ^{10}B of control rods or from the ^{14}N in residual air. These sources, however, are small compared with the thermal-neutron irradiation of the deuterium, ^3He , or ^6Li in the reactor coolant.² In light-water reactors, Bramati² estimates that the amount of tritium produced by the irradiation of deuterium and that by the irradiation of lithium impurities are about equal in magnitude, except in a special case where 0.5 ppm lithium was added to the primary circuit of the Shippingport pressurized-water reactor to provide monitoring of the neutron flux in the core. When lithium-based cation exchangers are used for cooling-water purification, tritium production may be quite high. For thermal and slow neutrons, the production of tritium from lithium is due to the ^6Li isotope; for fast neutrons, ^7Li plays the principal role.³ A changeover from natural LiOH resin to $^7\text{LiOH}$ resin in the Bettis pressurized-water reactor reduced the tritium concentration⁴ in the primary coolant by a factor of 100.

The yield of tritium produced as a fission product in reactors is 0.01%. Fission probably produces more tritium than all other sources in light-water-cooled reactors.^{5,6} However, significant quantities of tritium may be formed by fast-neutron reactions with soluble boron, which is frequently used in pressurized-water reactor coolants as a chemical shim. Early studies indicated that only a very small fraction of the fission-product tritium diffuses out of the fuel and cladding into the reactor

coolant.⁷ Much of the fission-product tritium (47 to 64%) at Hanford could be accounted for in the low-level waste streams associated with fuel reprocessing.⁸ Albenesius and Ondrejcin⁹ found that about 25% of the tritium was released in the gas phase during fuel dissolution. In hot-cell experiments at Oak Ridge National Laboratory, less than 1% of the tritium was evolved during dissolution of highly irradiated ThO₂-UO₂ fuel specimens.¹⁰ This latter value is more nearly the fraction of tritium found in condensed vapor from the operating Redox stack at Hanford.⁸

In contrast with these findings, Ray, Wooton, and Barnes⁶ suggest that as much as 80% of the fission-product tritium will recoil into the stainless-steel cladding of uranium oxide fuel elements and will be able to diffuse from the cladding into the primary-coolant stream. On the basis of their estimates of the rate of diffusion, they suggest that within about a day of start-up the tritium leakage rate is equal to the tritium production rate. Their theoretical calculations were in rather close agreement with operating experiences at the Portable Medium Power Plant (PM-3A) reactor. Correlations between calculated and observed tritium levels at other reactors were quite poor; the calculated values were considerably higher than the observed values.⁶ One plant operating with Zircaloy-clad fuel experienced no buildup of tritium in the primary coolant,⁶ which suggests that, owing to tritide formation, Zircaloy cladding may provide a barrier to tritium diffusion; but the evidence is not conclusive. Most of the tritium that diffuses into the coolant stream is expected to be converted to HTO. Smith¹¹ asserts that the diffusion of fission-product tritium into the reactor cooling water would be masked by the tritium formed from boron, if boron was in the water to control reactivity. In reactors with no boron or lithium present in the water, on the order of 1% of the fission-product tritium was estimated to have diffused through stainless-steel fuel cladding, in comparison with only about 0.1% that diffused through Zircaloy cladding.¹¹

Heavy-Water Reactors

Heavy water can be used as a moderator, a reflector, and a coolant in certain types of reactors.^{7,12-15} Tritium is formed in these reactors primarily by neutron bombardment of deuterium.⁷ Although some fission-product tritium can penetrate thin fuel-element claddings, this addition to the induced tritium activity of heavy water is negligible compared with the activity produced from deuterium.⁷ The concentration of tritium in the heavy water is a function of the reactor power level and the irradiation time. Losses of tritium from the heavy water are quite low.¹⁵

Three reactions play a role in the tritium chemistry in such a system: (1) the DTO formed by neutron irradiation can dissociate to form tritium radicals that further react with deuterium radicals to form DT, (2) D₂O can react with DT to form DTO and D₂, and (3) the probability of deuterium-radical formation in the radiolysis of DTO is about twice that of tritium-radical formation, so the hydrogen molecules formed will be depleted in tritium. The first process would lead to tritium discharge as a gas, and the last two processes would favor tritium retention. The tritium history of the RA

reactor at Vinca, Yugoslavia, calculated on the basis of the reactor power history,¹⁵ indicated that the retention of tritium was favored. When heavy water serves as a coolant as well as a moderator, the complex system of heat exchangers and lines provides opportunities for line breaks and occasional spills.^{7,13} The primary hazards are to operating personnel since tritium absorption through the skin is equal to absorption by respiratory processes.^{7,13,16}

External losses from heavy-water reactors are relatively small. At Chalk River about 3 curies of tritiated water vapor is released daily from the reactor stack,¹⁷ and the moderator contains about 4 curies of tritium per liter. Releases of tritium to surface water at the Savannah River Plant are due primarily to releases from heavy-water reactors. The concentration of tritium in the Savannah River ranges from 10^{-5} to 1.4×10^{-5} $\mu\text{c/ml}$, or about 0.3 to 0.4% of the maximum permissible concentration.^{18,19} However, tritium activity induced in a large heavy-water power reactor will be of the same radiological importance as all other isotopes together at a normally operating reactor station because, unlike the other radionuclides, T_2O is a constant hazard owing to its appreciable vapor pressure.^{7,20} In terms of total hazard potential, on the other hand, the tritium contained in a heavy-water reactor has a lesser hazard potential than does the fission-product activity of a single fuel rod.²¹ The preliminary hazards analysis of the Heavy Water Components Test Reactor (shutdown in 1964) suggested that primary-coolant leaks up to 4.5 gal/min might escape detection.¹⁶ Bergstrom, Devell, and Gebert²¹ considered the possibility of excessive tritium release from heavy-water power reactors of the Swedish type and concluded that (1) continuous leak rates cannot exceed more than about 30,000 curies per year, (2) environmental hazards due to tritium are nonexistent, and (3) normal reactor operation will not create tritium levels inside the plant that are difficult to cope with. Holmquist⁷ takes exception to these conclusions and suggests that leakages of heavy water could realistically average 2 or 3% of the inventory annually.⁷ He further suggests that, even if it could be safely stated that there is very little actual hazard to the public due to these continuous releases of tritium, extensive surveying is necessary to ensure that the tritium levels are well below acceptable values.⁷

TRITIUM-PRODUCTION PLANTS

Fusion reactions involving DT require much less severe conditions than those involving DD;²² hence, there is a demand for the production of large quantities of tritium for use as a thermonuclear fuel. In addition to this demand, there is a demand for tritium for use as a radioisotope. Tritium can be produced economically in a power reactor by irradiation of lithium metal, alloys, or salts.²²⁻²⁶

In a thermonuclear power economy based on DT reactors, efficient breeding of tritium in blankets around the machine would be required.²⁷ The ${}^6\text{Li}$ reaction offers the only real hope of attaining total tritium regeneration.²⁸ Tritium produced from lithium metal or LiD could be used directly as fuel, but tritium produced from other

lithium salts would require processing.²⁷ Lithium fluoride has been found to be a good source of lithium. The tritium produced can be liberated by heating the fluoride above 450°C (Refs. 28-32). Other suggested sources for lithium are fused LiNO_3 , from which tritium would be produced as T_2O in the gas phase;³² lithium metal;^{33,34} lithium-aluminum alloy;³⁵ and lithium-magnesium alloy.³⁶

The amount of tritium released to the environment from these sources would be small because the value of tritium as a fuel makes its recovery economically attractive. The tritium would be purified as T_2 gas, and releases to the environment would probably occur through releases of the free gas to stacks.

Thermonuclear Detonations

In a deuterium-tritium bomb, 10 single deuterium-tritium reactions release 180 Mev of energy, which is equivalent to the energy released by a single fission event, and 10 neutrons, in contrast to 1.5 neutrons in a fission device of the same energy.³⁷ In a pure thermonuclear detonation, Leipunsky³⁷ estimates that there is a residual of about 0.7 kg of ^3H per megaton-equivalent explosion.* In addition to this yield of tritium from the fusion reaction, the neutron irradiation of nitrogen³⁸ may yield an additional 0.15 kg of ^3H . Miskel³⁹ suggests that the residual tritium may range as high as 5.0 kg of ^3H per megaton equivalent.

The concentration levels of tritium in rain rose sharply after the Castle series of tests in the spring of 1954 (Refs. 40 and 41) and briefly reached peak concentrations two orders of magnitude above the natural level. The quantity of tritium deposited during these tests suggests a minimum production of 1.16 kg of ^3H per megaton-equivalent explosion.^{42,43} Most of the bomb tritium is apparently oxidized to water and removed from the troposphere by precipitation,⁴³ although the tritium-to-hydrogen ratio for atmospheric hydrogen gas and methane is much higher.⁴² The concentration of tritium in stratospheric water had risen from about 9 tritium units (TU) in rainwater prior to nuclear testing to a level of about 1 to 7.2×10^6 TU in 1960. Since early 1958 much of the tritium has been injected into the stratosphere where scavenging by precipitation is not so rapid as it was in the period following the Castle tests.⁴⁴

In underground fusion explosions the tritium would be expected to be present mostly as tritiated water and to move with the groundwater.⁴⁵ Partition of radioactive debris between the stratosphere and troposphere varies with the height of the shot, the latitude, and the yield.^{42,46} However, Bibron⁴⁶ generalizes that detonations at the ground surface inject into the stratosphere about 20% and those at a water surface about 80% of the radionuclides released to the atmosphere.

*A 1-megaton-equivalent explosion is a nuclear detonation that would release the same amount of energy as a million tons of TNT; 1 g of tritium is about 9600 curies.

Natural Tritium Production

In 1938 Sherr, Smith, and Bleakney⁴⁷ concluded that if tritium is present in ordinary water its concentration must be less than 1 tritium atom per 10^{12} hydrogen atoms. In 1947 Eidinoff⁴⁸ determined that the upper limit of the tritium content of ordinary water is less than 1 atom per 10^{17} hydrogen atoms. The natural tritium content has been estimated to be about 4×10^{-15} tritium atoms per hydrogen atom for atmospheric hydrogen and about 1×10^{-18} tritium atoms per hydrogen atom for surface water.⁴⁹⁻⁵⁵ The relative concentration of tritium in atmospheric hydrogen is about 10^3 to 10^4 times that in rainwater,^{50-52,54} but the quantity of hydrogen gas in the atmosphere is a factor of 10^4 less than the average quantity of water vapor.⁵⁶ Begemann⁵⁷ estimates that about 0.12% of the earth's total of tritium exists as hydrogen gas, another 0.1% as water vapor, and over 99% is in the hydrosphere, primarily in the sea. Kaufman and Libby⁵⁸ estimate an inventory of about 1800 g of tritium (17 megacuries) on the earth with 11 g (10^5 curies) occurring in the atmosphere, 13 g (1.25×10^5 curies) in groundwater, and the remainder in the sea. Bishop and his associates⁵⁹ indicated that in 1958 atmospheric tritium was distributed between free hydrogen (2×10^6 curies), atmospheric methane (2×10^5 curies), and rainwater (2×10^8 curies). Harteck⁵² suggests a total of 6000 g (58 megacuries) of tritium, with 2 g occurring as HT and the remainder as HTO. Begemann⁶⁰ later estimated the tritium distribution shown in Table 3.1.

Table 3.1
NATURAL TRITIUM DISTRIBUTION

	Tritium distribution, %	Tritium ratio
Hydrosphere	~90	$\lesssim 10$
Troposphere		
Water vapor	0.1	$\lesssim 80$
Molecular hydrogen	0.02 to 0.2	4×10^3 to 3.5×10^4
Methane	≤ 0.04	$\lesssim 10^3$
Stratosphere		
Water	~10	6×10^5
Molecular hydrogen	0.004 to 0.007	3×10^3 to 6×10^4

Natural tritium production is estimated to occur at a rate of about 0.12 to 2.0 tritium atoms/cm²/sec, with the most probable values near 0.5 to 1.0 tritium atoms/cm²/sec (Refs. 40, 57, 61-75). This estimate amounts to an annual production rate of about 4 to 8 megacuries and would give a steady-state tritium inventory of 70 to 140 megacuries of tritium. Reactions leading to natural tritium production have been discussed previously; calculated estimates of tritium production by cosmic rays in

the stratosphere are generally lower than the measured tritium accumulation, suggesting the possibility of extraterrestrial sources of tritium. Fireman^{7,6} suggests that the major tritium production processes are fast-neutron irradiation of nitrogen by cosmic rays and direct ejection of tritium by stars, which together total 0.4 to 0.9 triton/cm²/sec. The slow-neutron reaction on ⁶Li in the oceans yields less than 10⁻⁶ triton/cm²/sec; the neutron irradiation of deuterium gives less than 5 × 10⁻⁹ triton/cm²/sec; and the reactions of neutrons produced during spontaneous fission in terrestrial material give less than 10⁻¹¹ triton/cm²/sec.

FUEL-REPROCESSING PLANTS

Tritium is produced as a fission product in reactors with a yield of about 0.01% (Refs. 5, 8, 9, 77-80). Some of the tritium may penetrate thin fuel-element claddings and escape into the coolant,⁷ but most of it is retained until the fuel is reprocessed.^{7,9,81} There has been some concern regarding the possible diffusion of large fractions of fission-product tritium through fuel claddings,⁶ but this phenomenon has been seriously questioned after more recent inspection of operational data.¹¹ Because of the possible significance of fission-product tritium leaking from fuel elements into reactor coolant water, further studies of tritium levels in the coolant of operating reactors are warranted. During fuel reprocessing about 20% of the fission-product tritium appears in the dissolver offgas and is released through the stack in the gaseous phase.^{8,10} Most of the remaining tritium follows the aqueous phase and is released to the environment in low-level waste streams.^{8,82} With present solvent-extraction flow sheets, only 2 to 5% of the tritium is retained in high-level wastes.⁸¹ Therefore essentially all fission-product tritium can be considered released to the environment within a few years of its production. There is an economic incentive to increase the size of fuel-reprocessing plants since the net fuel-cycle costs are expected to decrease as the processing rate is increased.^{8,3} The release of tritium from large fuel-reprocessing plants may lead to local contamination problems.¹⁰

THERMONUCLEAR REACTORS

Although the development of thermonuclear reactors in the near future seems rather remote, production of residual tritium in the fusion reaction could lead to a very considerable tritium-management problem.^{84,85} Homeyer⁸⁶ indicates that for a thermonuclear reactor producing 312 Mw(e) a daily input of 228 g of tritium will be required, which equals about 2.2 × 10⁶ curies. About half this tritium will be produced in an Li₂BeF₄ blanket; the other half will be recovered from unburned tritium in the plasma. In both instances tritium-separation processes will be required. Injection of tritium and deuterium into the plasma will be required to offset losses to

the exhaust stream and to fusion.⁸⁶ Some of the tritium may be adsorbed on components and will not be discharged to the environment,^{85,86} but Homeyer⁸⁶ asserts that losses of tritium by diffusion through coolant ducts, heat-exchanger surfaces, and other parts of the fused-salt heat transfer loop external to the blanket could be serious, especially for heat exchangers that have large surface areas at elevated temperatures. A tritium breeding ratio of 1.15 would result in an increased tritium inventory of about 9% per year, or a doubling of the inventory in eight years.⁸⁵ This increased inventory would be used to counterbalance internal losses and to provide additional fuel. At this time there is only sufficient information to suggest the magnitude of the external releases of tritium from such a system.⁸⁷ However, the quantities of tritium handled will be considerably greater than those in fission-powered reactors and will require careful management.

SUMMARY

Tritium is produced by a number of different types of nuclear activity. Production at heavy-water reactors currently creates the most serious operational problems. As reactor-fuel reprocessing plants are established, the tritium produced by fission will eventually be released to the environment. The status of tritium in the coolant of light-water reactors is still not clear. The possibility of diffusion of fission-product tritium into the coolant has been mentioned, but the evidence is not decisive. If diffusion into the coolant is significant, tritium contamination problems might arise at reactor sites. In this event, the amount of tritium released during fuel reprocessing would be lowered by whatever fraction had been lost by diffusion. Further studies of the tritium released to the coolant in light-water reactors and of the tritium retained in the fuel and released during reprocessing will be required before quantitative evaluations of tritium releases are possible. Furthermore, it is quite likely that both the production and release of tritium in light-water reactors will depend on the type of fuel and cladding used and the energy spectrum of the neutron flux.

Production of residual tritium in thermonuclear weapons and reactors could present a very considerable source of release. However, the possibility of developing thermonuclear reactors in the near future seems rather remote. Also, the value of tritium as a fuel makes its recovery economically attractive; so little would be allowed to escape.

REFERENCES

1. R. Estournel, *Presence de tritium dans les Circuits de refroidissement des reacteurs G2 et G3*, French Report CEA-2205, 1962.
2. L. Bramati, Production of Tritium in Nuclear Reactors, pp. 28-38, in *Seminaire sur la Protection Contre les Dangers du Tritium*, Service Central de Protection Contre les Rayonnements Ionisants, le Vesinet, Avril 16-18, 1964 (CONF-640413).

3. P. Verzaux, Investigation of the Collision Cross-Section of Lithium for Neutrons, *J. Phys. Radium*, **31**: 21-27 (January 1952).
4. W. Lechnick, *Tritium Concentration in PWR Using Lithium⁷ Resin*, USAEC Report WAPD-PWR-TE-103, Westinghouse Electric Corporation, March 1962.
5. E. L. Albenesius, Tritium as a Product of Fission, *Phys. Rev. Lett.*, **3**(6): 274-275 (Sept. 15, 1959).
6. J. W. Ray, R. O. Wooton, and R. H. Barnes, *Investigation of Tritium Generation and Release in PM Nuclear Power Plants*, USAEC Report BMI-1787, Battelle Memorial Institute, Oct. 31, 1966.
7. C. E. Holmquist, Hazards of Tritium Oxides Induced in Large Heavy Water Reactor Stations, paper presented at the American Industrial Hygiene Conference, Houston, Texas, May 3-7, 1965 (CONF-650540-6).
8. W. A. Haney, D. J. Brown, and A. E. Reisenauer, *Fission Product Tritium in Separations Wastes and in the Ground Water*, USAEC Report HW-74536, Hanford Atomic Products Operation, Aug. 1, 1962.
9. E. L. Albenesius and R. S. Ondrejcin, Nuclear Fission Produces Tritium, *Nucleonics*, **18**(9): 100 (September 1960).
10. J. H. Goode, *Hot-Cell Evaluation of the Release of Tritium and ⁸⁵Kr During Processing of ThO₂-UO₂ Fuels*, USAEC Report ORNL-3956, Oak Ridge National Laboratory, June 1966.
11. J. M. Smith, Jr., The Significance of Tritium in Water Reactors, General Electric Company, unpublished, Sept. 19, 1967.
12. C. M. Patterson, Radiation Protection Considerations in a Heavy-Water-Moderated Reactor, in *Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958*, Vol. 23, pp. 295-301, United Nations, New York, 1958.
13. H. L. Butler, Tritium Hazards in Heavy-Water-Moderated Reactors, *Nucl. Safety*, **4**(3): 77-82 (March 1963).
14. R. F. Jackson, Experience of Operation and Use of the UK High-Flux Research Reactors, in *Proceedings of the Third International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1964*, Vol. 7, pp. 168-175, United Nations, New York, 1965.
15. Z. Matić-Vukmirović et al., Determination of the Tritium Buildup in a Heavy-Water-Moderated Reactor, in *Proceedings of the Third International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1964*, Vol. 3, pp. 407-413, United Nations, New York, 1965.
16. D. S. St. John et al., *Preliminary Hazards Evaluation of the Heavy Water Components Test Reactors (HWCTR)*, USAEC Report DP-383, Savannah River Laboratory, May 1959.
17. G. C. Butler and P. J. Barry, *Experience with Dilution Rate Factors from the AECL Reactor Stack*, Canadian Report AECL-1518, May 1962.
18. W. C. Reinig and E. L. Albenesius, *Control of Tritium Health Hazards at the Savannah River Plant*, USAEC Report DPSPU-62-30-5, Savannah River Laboratory, January 1962.
19. Savannah River Laboratory, *Effect of the Savannah River Plant on Environmental Radioactivity, Semiannual Report July through December 1964*, USAEC Report DPSPU-65-30-1, February 1965.
20. C. E. Holmquist, Hazards of Tritium Oxides Induced in Heavy Water Reactors, pp. 34-39, in *Seminaire sur la Protection Contre les Dangers du Tritium*, Service Central de Protection Contre les Rayonnements Ionisants, le Vesinet, Avril 16-18, 1964 (CONF-640413).
21. S. O. Bergstrom, L. Devell, and G. Gebert, Studies on Tritium Hazards at Swedish Reactors, pp. 40-52, in *Seminaire sur la Protection Contre les Dangers du Tritium*, Service Central de Protection Contre les Rayonnements Ionisants, le Vesinet, Avril 16-18, 1964 (CONF-640413).
22. E. F. Johnson, Thermonuclear Power Reactors, *Chem. Eng. Progr.*, **58**(8): 60-64 (August 1962).
23. H. Seligman, Die Gewinnung von Radioaktiven Isotopen in der Pile, *Angew. Chem.*, **66**(4): 95-99 (February 1954).

24. General Nuclear Engineering Corp., *A Study of Reactor Systems for the Production of Tritium and Radioactive Cobalt*, USAEC Report GNEC-98, June 8, 1959.
25. Radioisotope Production in Power Reactors, *Nucl. Energy*, **14**(9): 437-438 (September 1960).
26. C. B. Magee, J. E. Fulenwider, G. J. Rotariu, and R. P. Petersen, *A Study of the Feasibility and Economics of Radioisotope Production in Power Reactors, Final Report*, USAEC Report AECU-4355, Booz-Allen Applied Research, Inc., February 1960.
27. M. T. Robinson, *On the Chemistry of Thermonuclear Reactor Breeder Blankets*, USAEC Report CF-57-12-39 (Rev.), Oak Ridge National Laboratory, Feb. 7, 1958.
28. W. G. Homeyer and A. J. Impink, Jr., Materials and Energy Recovery in Proposed Fusion Power Reactors, *Trans. Amer. Nucl. Soc.*, **5**(1): 100 (June 1962).
29. C. V. Cannon et al., *The Production and Purification of Tritium: Problem Assignment CXI-8*, USAEC Report MonC-35, Clinton Laboratories, Nov. 29, 1945.
30. N. Chellew, J. McGuire, W. Olsen, and A. H. Barnes, *Tritium Production Process*, USAEC Report ANL-4159, Argonne National Laboratory, May 25, 1948.
31. G. H. Jenks, E. M. Shapiro, N. Elliott, and C. V. Cannon, Production of Tritium, U. S. Patent No. 3,079,317, to U. S. Atomic Energy Commission, Feb. 26, 1963.
32. H. Cohen and W. S. Diethorn, A Laboratory Source of Tritium with Applications in Neutron Dosimetry and Li^6 Analysis, *Int. J. Appl. Radiat. Isotop.*, **15**(9): 553 (1964).
33. J. G. Linhart, Improvements Relating to Thermonuclear Reactors, British Patent No. 855,857, to British Thomson-Houston Co., Ltd., Dec. 7, 1960.
34. J. G. Linhart, Improvements Relating to Thermonuclear Reactors, British Patent No. 855,858, to British Thomson-Houston Co., Ltd., Dec. 7, 1960.
35. B. M. Abraham, Tritium Production by Neutron Irradiation of Aluminum-Lithium Alloy, U. S. Patent No. 3,100,184, to U. S. Atomic Energy Commission, Aug. 6, 1963.
36. M. B. Neiman and K. M. Sadilenko, Thermonuclear Weapons, USAEC Report AEC-tr-6533, translated from *Termoyadernoe Oruzhie* (Russian), 1958.
37. O. I. Leipunsky, *At. Energy (USSR)*, **3**: 530 (1957); also Radiation Hazards from Clean Hydrogen Bomb and Fission Atomic Bomb Explosions, in *Fallout from Nuclear Weapons Tests, Hearings Before the Joint Committee on Atomic Energy, 86th Congress, May 5-8, 1959*, pp. 2423-2447, U. S. Government Printing Office, Washington, D. C.
38. E. Eriksson, An Account of the Major Pulses of Tritium and Their Effects in the Atmosphere, *Tellus*, **17**(1): 118-130 (February 1965).
39. J. A. Miskel, Characteristics of Radioactivity Produced by Nuclear Explosives, in *Engineering with Nuclear Explosives, Proceedings of the Third Plowshare Symposium, Livermore, California, April 21-23, 1964*, pp. 153-160, (TID-7695), 1964.
40. H. von Buttlar and W. F. Libby, Natural Distribution of Cosmic-Ray Produced Tritium, Part II, *J. Inorg. Nucl. Chem.*, **1**(1): 75-91 (1955).
41. F. Begemann and W. F. Libby, Continental Water Balance, Ground Water Inventory and Storage Times, Surface Ocean Mixing Rates and World-Wide Water Circulation Patterns from Cosmic-Ray and Bomb Tritium, *Geochim. Cosmochim. Acta*, **12**(4): 277-296 (1957).
42. E. A. Martell, On the Inventory of Artificial Tritium and Its Occurrence in Atmospheric Methane, *J. Geophys. Res.*, **68**(13): 3759-3769 (July 1, 1963).
43. E. A. Martell, GRD Res. Notes No. 19, *Artificial Radioactivity from Nuclear Tests up to November 1958*, Report AFERN-TN-59-444, Air Force Cambridge Research Laboratories, September 1959.
44. A. K. Stebbins III, *Technical Analysis Report, Second Special Report on the High Altitude Sampling Program (HASP)*, Report DASA539B: 111-117, Defense Atomic Support Agency, August 1961.
45. F. W. Stead, Tritium Distribution in Ground Water Around Large Underground Fusion Explosions, *Science*, **142**(3596): 1163-1165 (Nov. 29, 1963).
46. R. Bignon, *Detection of Atmospheric Tritium by Scintillation: Variations in Its Concentration in France*, French Report CEA-R-2629, 1965.

47. R. Sherr, L. G. Smith, and W. Bleakney, On the Existence of H^2 , *Phys. Rev.*, **54**(5): 388 (Sept. 1, 1938).
48. M. L. Eidinoff, Upper Limit to the Tritium Content of Ordinary Water, *J. Chem. Phys.*, **15**(6): 416 (June 1947).
49. V. F. Faltings and P. Harteck, Der Tritiumgehalt der Atmosphäre, *Z. Naturforsch., A*, **5**(8): 438-439 (August 1950).
50. P. Harteck and V. F. Faltings, The Helium-3 Problem of the Atmosphere, *Nature*, **166**(4235): 1109 (Dec. 30, 1950).
51. A. V. Grosse et al., The Natural Tritium Content of Atmospheric Hydrogen, *Phys. Rev.*, **93**(1): 250 (Jan. 1, 1954).
52. P. Harteck, The Relative Abundance of HT and HTO in the Atmosphere, *J. Chem. Phys.*, **22**(10): 1746-1751 (October 1954).
53. E. L. Fireman and F. S. Rowland, An Additional Measurement of the Tritium Content of Atmospheric Hydrogen of 1949, *J. Geophys. Res.*, **66**(12): 4321 (December 1961).
54. R. Bibron et al., Physique De L'Atmosphère, *Compt. Rend.*, **256**: 4951-4954 (June 1963).
55. A. V. Grosse et al., Tritium in Nature, *Science*, **113**: 1-2 (Jan. 5, 1951).
56. F. Verniani, Total Mass of the Earth's Atmosphere, *J. Geophys. Res.*, **71**: 385 (1966).
57. F. Begemann, The Natural Tritium Economy of the Earth and the Question of Its Variation with Time, *Chimia (AARAU)*, **16**(1): 1-10 (January 1962).
58. S. Kaufman and W. F. Libby, The Natural Distribution of Tritium, *Phys. Rev.*, **93**(6): 1337-1344 (Mar. 15, 1954).
59. K. F. Bishop et al., in *Tritium in the Physical and Biological Sciences*, Symposium Proceedings, Vienna, May 3-10, 1961, Vol. 1, pp. 55-67, International Atomic Energy Agency, Vienna, 1962 (STI/PUB/39).
60. F. Begemann, *Earth Science and Meteorites*, pp. 169-187, North Holland Publishing Co., Amsterdam, 1963.
61. L. A. Currie, Tritium Production by 6-Bev Protons, *Phys. Rev.*, **114**(3): 878-880 (May 1, 1959).
62. L. A. Currie, W. F. Libby, and R. L. Wolfgang, Tritium Production by High-Energy Protons, *Phys. Rev.*, **101**(5): 1557-1563 (Mar. 1, 1956).
63. F. Begemann and W. F. Libby, Continental Water Balance, Ground Water Inventory and Storage Times, Surface Ocean Mixing Rates and World-Wide Water Circulation Patterns From Cosmic Ray and Bomb Tritium, *Geochim. Cosmochim. Acta.*, **12**(4): 277-296 (1957).
64. H. Craig, Distribution, Production Rate, and Possible Solar Origin of Natural Tritium, *Phys. Rev.*, **105**(3): 1125-1127 (Feb. 1, 1957).
65. F. Hagemann et al., Stratospheric Carbon-14, Carbon Dioxide, and Tritium, *Science*, **130**: 542-552 (Sept. 4, 1959).
66. A. T. Wilson and G. J. Ferguson, Origin of Terrestrial Tritium, *Geochim. Cosmochim. Acta.*, **18**(314): 273-277 (1960).
67. E. Flamm et al., Tritium and Helium-3 in Solar Flares and Loss of Helium from the Earth's Atmosphere, *Science*, **138**(3536): 48-49 (Oct. 5, 1962).
68. V. Lujanas, On Production of Tritium in the Atmosphere, *Liet. TSR Mokslu Akad. Darbai*, [B] **1**(32): 21-28 (1963). (Russian).
69. L. L. Newkirk, Calculation of Low-Energy Neutron Flux in the Atmosphere by the S_n Method, *J. Geophys. Res.*, **68**(7): 1825-1833 (Apr. 1, 1963).
70. W. F. Libby, *Natural Tritium Assay, Routine Method for Absolute Assay of Beta Radioactivity, and the Reactions of Negative π Mesons with Elementary Bromine: Final Report*, USAEC file No. NP-4654, Dec. 1, 1952.
71. B. Bolin, On the Use of Tritium as a Tracer for Water in Nature, in *Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958*, Vol. 18, pp. 336-343, United Nations, New York, 1958.

72. F. Begemann, New Measurements on the World-Wide Distribution of Natural and Artificially Produced Tritium, in *Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958*, Vol. 18, pp. 545-550, United Nations, New York, 1958.
73. H. Craig and D. Lal, The Production Rate of Natural Tritium, *Tellus*, **13**(1): 85-105 (February 1961).
74. Tritium from Nuclear Tests, A/AC.82/R.105/Add. 1, Secretariat, United Nations, July 13, 1960.
75. H. von Buttlar, Stratospheric Tritium, *Geochim. Cosmochim. Acta*, **27**(7): 741-751 (July 1963).
76. E. L. Fireman, Measurement of the (n, H^3) Cross Section in Nitrogen and its Relationship to the Tritium Produced in the Atmosphere, *Phys. Rev.*, **91**(4): 922-926 (Aug. 15, 1953).
77. E. N. Sloth et al., Tritium in the Thermal Neutron of Uranium-235, *J. Inorg. Nucl. Chem.*, **24**: 337-341 (April 1962).
78. J. C. Watson, High-Energy Alpha Particles and Tritons from the Spontaneous Fission of Californium-252, *Phys. Rev.*, **121**(1): 230-231 (Jan. 1, 1961).
79. H. E. Wegner, Additional Long-Range Particles from the Spontaneous Fission of Cf^{252} , *Bull. Am. Phys. Soc.*, **6**(3): 307 (Apr. 24, 1961).
80. D. L. Horrocks, Tritium Produced During Spontaneous Fission of Californium-252, *Phys. Rev.*, **134**(6B): B1219 (June 22, 1964).
81. J. O. Blomeke, *Management of Fission Product Tritium in Fuel Processing Wastes*, USAEC Report ORNL-TM-851, Oak Ridge National Laboratory, May 4, 1964.
82. J. H. Horton and D. I. Ross, Use of Tritium from Spent Uranium Fuel Elements as a Ground-Water Tracer, *Soil Sci.*, **90**(5): 267-271 (November 1960).
83. F. L. Culler, *The Effect of Scale-Up on Fuel Cycle Costs for Enriched Fuel and Natural Uranium Fuel Systems*, USAEC Report ORNL-TM-564, Oak Ridge National Laboratory, Apr. 16, 1963.
84. F. L. Parker, Radioactive Wastes from Fusion Reactors, *Science*, **159**(3810): 83-84 (Jan. 5, 1968).
85. F. L. Parker and D. J. Rose, Wastes from Fusion Reactors, *Science*, **159**(3821): 1376 (Mar. 22, 1968).
86. W. G. Homeyer, *Thermal and Chemical Aspects of the Thermonuclear Blanket Problem*, USAEC Report RLE-TR-435, Massachusetts Institute of Technology, Mar. 31, 1965.
87. A. P. Fraas, *A Diffusion Process for Removing Tritium from the Blanket of a Thermonuclear Reactor*, USAEC Report ORNL-TM-2358, Oak Ridge National Laboratory, December 1968.

4 PROCEDURES FOR TRITIUM ENRICHMENT

The natural concentration of tritium in the environment is so low that it cannot be measured directly.^{1,2} Even with the increase in tritium levels due to thermonuclear testing, the concentration of environmental tritium remains so low that its direct measurement is only rarely possible.^{3,4} Several methods have been developed, particularly since 1939, which permit the separation, or at least the concentration, of many isotopes.⁵ Most of the procedures are physical in character because mass differences produce greater differences in physical properties than in chemical properties.⁵ The most commonly used technique for the enrichment of tritium for analytical purposes is electrolysis.⁴

In addition to the need for concentrating tritium in environmental samples prior to counting, there may be a need for separating tritium to reduce the quantities released to the environment. This separation would be especially necessary in the event of large-scale use of thermonuclear reactors because large quantities of tritium remain unburned during the fusion process and must be recovered from the plasma for reinjection as fuel. Also, additional tritium must be formed in the blanket and recovered for reinjection to make up for losses in the system. In these cases the separation or enrichment method must be adaptable to relatively large-scale operations.

ELECTROLYSIS

According to Moeller,⁵ electrolysis was first suggested as a means of isotope separation by J. Kendall and E. D. Crittenden in 1923 but was not confirmed until 1932 when E. W. Washburn and H. C. Urey observed that the concentration of deuterium in residual electrolytic hydrogen cells was greater than that in ordinary water. In determining the tritium content of hydrogen in the atmosphere, Faltings and Harteck¹ separated hydrogen from the helium–neon fraction obtained during the production of liquid air, oxidized it into water over CuO, and increased the tritium concentration 20-fold by electrolysis.

A good description of the apparatus and procedures used in a single-cell electrolytic enrichment of tritiated water is given by Oestlund and Weiner,⁶ who describe a cell similar to the one used by Brown and Grummitt.⁷ In this system large electrode surfaces are used with iron as the cathode and nickel as the electrode. From a 250-ml sample, 50 ml is introduced into the electrolysis cell, and approximately 0.6 g of sodium hydroxide is added. When the volume has been reduced to 25 ml, after about 24 hr, an additional 25 ml of solution is introduced, and electrolysis is continued. During this time a constant current of 3.0 amp is supplied. After the last increment of solution has been added and the volume has been reduced to 15 to 25 ml, the current is reduced to 0.4 amp, and electrolysis is continued until the size of the remaining sample is about 2.5 g. Following electrolytic enrichment, the sodium hydroxide is neutralized with sodium carbonate, and the sample is distilled. This procedure provides tritium enrichment ranging from about 6- to 20-fold.

For greater enrichment electrolysis must be carried out in several stages, with distillation of the sample between stages to keep the concentration of the hydroxide in the optimum range.⁷⁻¹⁰ With five stages of electrolysis, the tritium concentration can be increased⁷ by factors of 2,000 to 20,000.

Libby¹¹ used electrolysis to enrich tritium in natural waters. He estimated the enrichment of tritium by measuring the enrichment of deuterium and assuming that the ratio of tritium to deuterium enrichment is 2.0. Samples were distilled, brought to 3 wt.% NaOH, and electrolyzed in three stages to less than 1 cm³ using an iron cathode and nickel anode at 10 to 25°C. He and Kaufman¹² studied the electrolytic enrichment of both tritium and deuterium and found that, although the individual enrichment factors varied from run to run, the weighted average of the ratio was 2.1 ± 0.1 . This factor was widely used for estimating the relative tritium enrichment^{3,7} until Bigeleisen¹³ showed, theoretically, that the ratio of the logarithm of the tritium enrichment factor, β , to the logarithm of the deuterium enrichment factor, α , should be 1.40 ± 0.01 . Calculation of the ratio $\log \beta / \log \alpha$ from the data of Kaufman and Libby¹² yields an average value of 1.40 ± 0.09 , which is in good agreement with Bigeleisen's theoretical value. Foster, Purcell, and Wheat¹⁴ measured the average instantaneous electrolytic separation for hydrogen isotopes and obtained values of $\alpha = 5.6$, $\beta = 10.4$, and $\beta/\alpha = 1.9$. They used nickel electrodes, Na₂CO₃ as the electrolyte, and performed the electrolysis at 0°C. When expressed as values of log

$\beta/\log \alpha$, an average of 1.36 ± 0.07 was obtained. Bibron¹⁵ compared the results of his own measurements, those of Oestlund and Weiner,⁶ and those of Kaufman and Libby¹² and found that all were in good agreement with Bigeleisen's theory over a wide range of isotopic separation factors.

If the electrolytic enrichment process is carried out at a conveniently fast rate, water is lost from the electrolysis cell by entrainment and by evaporation.¹⁶ The entrained water has the same isotopic composition as the electrolyte solution, but, owing to differences in vapor pressures, there is some enrichment of the lighter hydrogen isotopes in the evaporated water vapor.¹⁶ In most experiments these losses are too small to affect the electrolytic separation, or there may be no need to measure the enrichment so accurately.¹⁶ Oestlund and Weiner⁶ made corrections of their data for both types of losses. They concluded that losses by entrainment or spraying were not significant, but, when corrections for vapor losses were made, the ratio of $\log \beta/\log \alpha$ ranged from 1.35 to 1.41 when α_0 ranged from 4 to 12 compared with an uncorrected ratio of 1.337 ± 0.007 for a conventional batch electrolysis.

Although electrolysis is a relatively simple technique, consistent and reliable results for high degrees of enrichment require careful attention to the efficiency of cooling, the temperature of the coolant, current density, and electrolyte concentration.⁴ The process is satisfactory, however, for enrichment factors on the order of 10 where small volumes suffice. It is not economically feasible to run water-electrolysis facilities solely for the purpose of heavy-water pre-enrichment; the technique is only possible when the electrolysis costs can be borne by other industrial processes, such as the production of ammonia.^{17,18} Hence, electrolysis would not be a suitable process for near-quantitative removal of tritium from water.

THERMAL DIFFUSION

The partial demixing of gases due to a temperature gradient is called thermal diffusion: the heavier isotope moves toward the cooler region.⁵ The existence of thermal diffusion was first suggested by W. Feddersen in 1873, but its theoretical derivation was developed independently by D. Enskog (1911--1917) and by S. Chapman (1916--1917).¹⁹ The doctoral dissertation presented by Enskog in 1917 consisted of a rigorous derivation of various gas coefficients, including those of thermal diffusion.²⁰ The first experimental verification was made in 1917 by Chapman and F. W. Dootson.^{5,19,21} The degree of separation that can be attained by thermal diffusion is not large,^{19,22} but K. Clusius and G. Dickel discovered that separation could be greatly enhanced when combined with convection.¹⁹

A theoretical discussion of parameters that must be considered in designing and operating thermal-diffusion columns is given by Jones and Furry²⁰ and by London.²¹ In a single column where the absolute temperature of the hot wall is twice that of the cold wall, relaxation times may be on the order of one year.²¹ (Relaxation time is

defined as the time in which a fraction $1/e$ of equilibrium is attained.) This time can be reduced to an acceptable value simply by using a two-stage column.

A two-stage thermal-diffusion column for tritium enrichment has been described by Verhagen and Sellschop.^{2,3} The first stage consists of a 7.2-m-long column of concentric tubes. The inner tube has a radius of 6.30 cm and is heated to 600°K; the outer tube has a radius of 8.76 cm and is held at 300°K. Tritium is enriched at the cold outer wall and is carried downward by convective currents because the cold gas enriched in tritium has a higher density than the hot gas that has been depleted of tritium. The second stage consists of a hot-wire column of much smaller capacity. This column is 2.75 m long with a 0.02-cm-radius wire heated to 1200°K inside a 1.50-cm-radius tube maintained at 300°K. With this laboratory-scale apparatus, tritium enrichments of 100 were obtained after 9 hr and 800 after 30 hr of operation.^{4,2,3} Because of the concentration gradient that is established, remixing sets in and limits the enrichment that can be attained.⁴

Although thermal diffusion is considered a complicated technique, it provides the advantages of good reproducibility, short-running times, and a relatively high yield.^{4,2,3,2,4} Impurity concentrations in the separation of tritium from hydrogen should be kept low because the impurities, which have a higher mass than that of tritium, are even more easily enriched.^{2,3} Thermal diffusion has an added advantage in that columns can be simply constructed to provide automatic and continuous separations^{5,2,5} that yield several liters of tritium per day with a purity exceeding 99%.

DISTILLATION

In 1919 F. A. Lindeman presented theoretical arguments indicating that isotopes could be enriched by distillation since the rates of escape of atoms or molecules from a liquid surface are generally inversely proportional to the square roots of their masses.⁵ Preliminary concentration of heavy water has been made using the distillation technique.^{5,1,7} The method is also of interest for intermediate and final enrichment of heavy water where simplicity and operational safety are more important than economic considerations.

When enrichment of tritiated water is begun, the species to be separated are primarily HTO and H₂O. Data on the relative vapor pressures of the two species are plotted in Fig. 4.1. The separation factor is rather small; so multistage distillation techniques are necessary for satisfactory enrichments.^{1,7,3,2,3,3} There is also a marked decrease in the degree of separation as the temperature is increased; the separation factor is only about 1.036 at 100°C. More efficient separations can be achieved by using rectification methods (vacuum distillation).^{1,7,3,2,3,3} Zel'venskii and his associates^{3,2} suggest that the optimum fractionation of tritium with respect to water, for identical times of distillation, is achieved at a pressure of 100 to 120 mm Hg. In this pressure range water boils at 52 to 55°C.

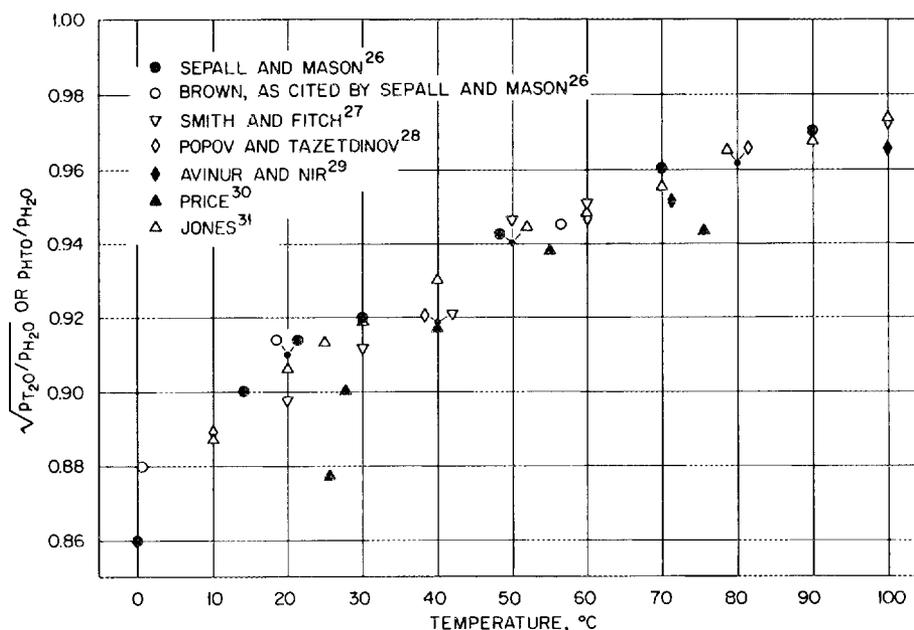


Fig. 4.1 Relative vapor pressures of HTO and H₂O. Note that $P_{\text{HTO}}/P_{\text{H}_2\text{O}}$ is the reciprocal of the separation factor.

The major drawbacks to distillation as an enrichment process are the relatively long times required for enrichment,^{4,23} the poor reproducibility,³³ and the modest enrichment factors attained.^{4,33} Following concentration by distillation, further re-concentration and volume reduction would be required for counting low-activity tritium samples.³³

Thermodynamically hydrogen gas distillation is much more attractive than water distillation.^{17,34} The separation factors are considerably greater, but the low boiling point of liquid hydrogen requires use of special techniques and handling.¹⁷

GAS CHROMATOGRAPHY

Uranium reacts with hydrogen isotopes to yield hydrides with a maximum uranium-to-hydrogen atomic ratio³⁵ of 1:3. Evans and Wilson³⁶ have used the differences in the vapor pressure of dissociation of the hydride and the tritide to effect an enrichment of tritium in a mixture of tritium and hydrogen gases. The vapor pressure of the tritide dissociation is lower than that of the hydride, and the tritium is enriched in the initial fractions.

Haag and Heumann³⁷ separated tritium from helium by sorbing tritium on palladium and then evolving the tritium gas at 160°C. Recovery of tritium ranged from 91 to 98%. Glueckauf and Kitt³⁸ found that a 20-g column of palladium could separate about 1 liter of a 1:1 mixture of deuterium and hydrogen. The factor for separating tritium from hydrogen is about 40% larger than that for separating deuterium from hydrogen: so even more effective separation should be possible.³⁸

Hoy³⁹ developed a palladium chromatograph that can be used to detect fewer than 10 atoms of tritium per 10^{18} atoms of hydrogen. The system is simpler and faster than the electrolytic or thermal-diffusion techniques normally used. Columns operated at ambient temperature have a 70-liter hydrogen capacity and provide 60% recovery in the first 500 cm³ of gas evolved. The technique is specific for tritium and is unaffected by trace amounts of other radioactive isotopes. Recovery and enrichment are low if any trace of oxygen remains in the system, and all leaks must be eliminated. Two and a half hours are required for the tritium to evolve from the column. Approximately 3% of the tritium remains in the hydrogen generator and may contaminate subsequent samples if they are significantly lower in tritium. This contamination can be avoided, however, by baking the generator at 80°C for 2 hr before reuse.

Extremely pure fractions of the hydrogen isotopes can be obtained, but the method is not suitable for large-scale separation because of the large quantities of palladium that would be required and because of the discontinuous mode of operation.³⁸ Chadwick⁴⁰ used this method for the separation of 99+% pure tritium from 2-liter batches of 16% tritium-hydrogen mixtures with an estimated recovery of 99%.

Gant and Yang⁴¹ used a molecular-sieve column at -160°C to separate hydrogen isotopes. The hydrogen was also separated into orthoisomers and paraisomers. Basmadjian⁴² found that in all cases deuterium was adsorbed to a greater extent than protium on charcoal, silica gel, and Linde molecular sieves. Separation factors as high as 2.54 were found for 4A molecular sieves at 75°K and 750 mm Hg. His results suggest that the differences in adsorption are due to the difference in the chemical composition of the adsorber rather than pore size, surface area, or origin of the material.⁴² Duncombe⁴³ looked at the sorption of hydrogen on 4A molecular sieves and concluded that, although isotopic fractionation is possible during adsorption, the major fractionation occurs mainly during desorption. Crespi and Perschke⁴⁴ used small molecular-sieve columns to obtain an enrichment factor of 17 for a 200-ml sample of tritiated hydrogen. Charcoal has also been used as a filler for chromatographic columns.^{42,45} Jones and Hutcheson⁴⁵ found that the isotope effect arises principally because of changes in the monolayer volume rather than in the adsorption-desorption energetics.

Smith and Carter⁴⁶ tested the separation of tritium from hydrogen with a number of column materials. They achieved no separation on columns filled with palladium on silica. Separation with a silica column was good when hydrogen was the carrier gas, but helium failed to elute the isotopes. The best separation was obtained on a column filled with activated alumina. King⁴⁷ found that D₂ and HT were separable on a

column of alumina and ferric hydroxide. This finding indicated that differences in the total mass are not primarily responsible for the separations. King hypothesizes that the separations are caused by electrostatic interactions between the polarized isotopes and the oxygen atoms of the Al_2O_3 lattice. West and Marston⁴⁸ studied the gas chromatographic separation of hydrogen isotopes having a high tritium concentration by using ferric-coated alumina. The separation factors obtained were essentially the same as those found by Carter and Smith⁴⁹ and by King,⁴⁷ which indicated that the tritium radiation level had no significant effect on the separation factor.

Isotopic methanes can also be separated by gas chromatography.⁵⁰ As King⁴⁷ found for the isotopic forms of hydrogen gas, the separation of isotopic methanes is not due to differences in total mass but is consistent with changes in polarizability that accompany substitutions.⁵⁰

The processing times for gas chromatography are comparable to those for electrolysis.⁵¹ The method is rather complex, but a high degree of enrichment can be attained with nearly complete recovery and with high reproducibility.⁵¹ The major disadvantage is that for aqueous samples large quantities of water must be converted to hydrogen gas without fractionation.

OTHER METHODS FOR ENRICHMENT

Numerous other methods are available for separating isotopes. Gaseous diffusion⁵¹ has been used to prepare tritium in excess of 99.9%, but this process is time consuming.⁴³ Chemical exchange is used in the production of heavy water and could presumably be used for the enrichment of tritium.^{17,53,54}

SUMMARY

Electrolysis is a relatively simple procedure for modest enrichments of tritiated water where small volumes are sufficient. For large-scale continuous separations, thermal diffusion seems to have an advantage, especially if the tritium exists as the gas. Gas chromatography appears to have considerable promise as a laboratory procedure for enrichment for tritium analysis. Although gas chromatography is a complex method, the recovery and the degree of enrichment are quite high. Furthermore, tritiated isotopes of simple molecules other than the gas can be separated.

REFERENCES

1. V. F. Faltings and P. Harteck, Der Tritium gehalt der Atmosphäre, *Z. Naturforsch., A*, **5**(8): 438-439 (August 1950).
2. A. V. Grosse et al., Tritium in Nature, *Science*, **113**: 1-2 (Jan. 5, 1961).
3. H. von Buttlar and I. Wendt, Groundwater Studies in New Mexico Using Tritium as a Tracer, in *Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958*, Vol. 18, pp. 591-597, United Nations, New York, 1958.
4. B. Th. Verhagen and J. P. F. Sellschop, Enrichment and Assay of Naturally Occurring Tritium, in *National Conference on Nuclear Energy; Application of Isotopes and Radiation*, pp. 109-119, Pelindaba, South Africa, Atomic Energy Board, 1963.
5. T. Moeller, *Inorganic Chemistry*, pp. 38-52, John Wiley & Sons, Inc., New York, 1954.
6. H. G. Oestlund and E. Weiner, The Electrolytic Enrichment of Tritium and Deuterium for Natural Tritium Measurements, in *Tritium in the Physical and Biological Sciences*, Symposium Proceedings, Vienna, May 3-10, 1961, Vol. 1, pp. 95-105, International Atomic Energy Agency, Vienna, 1962 (STI/PUB/39).
7. R. M. Brown and W. E. Grummitt, The Determination of Tritium in Natural Waters, *Can. J. Chem.*, **34**: 220-226 (March 1956).
8. B. S. Johnson, Jr., J. T. Grace, D. G. Karraker, L. H. Meyer, and C. K. Nicholson, *Isotopic Purification of Tritium by Electrolysis*, USAEC Report DP-261, Savannah River Laboratory, May 1958.
9. C. B. Taylor, H. A. Polach, and T. A. Rafter, *Tritium Measurements in Nature, A Review of the Work of the Tritium Laboratory Institute of Nuclear Sciences, New Zealand*, New Zealand Report INS-R-24, July 1963.
10. C. B. Taylor, *Accuracy in the Determination of the Tritium Contents of Natural Waters in the South Pacific Ocean Area, 1959-63, at the Tritium Laboratory, Institute of Nuclear Sciences, Lower Hutt, New Zealand*, New Zealand Report INS-R-27, August 1963.
11. W. F. Libby, Natural Tritium Assay, Routine Method for Absolute Assay of Beta Radioactivity, and the Reactions of Negative π Mesons with Elementary Bromine: Final Report USAEC file No. NP-4654, Dec. 1, 1952.
12. S. Kaufman and W. F. Libby, The Natural Distribution of Tritium, *Phys. Rev.*, **93**(6): 1337-1344 (Mar. 15, 1954).
13. J. Bigeleisen, *Correlation of Tritium and Deuterium Isotopes Effects*, in *Tritium in the Physical and Biological Sciences*, Symposium Proceedings, Vienna, 1961, Vol. 1, pp. 161-168, International Atomic Energy Agency, Vienna, 1962 (STI/PUB/39).
14. R. R. Foster, D. H. Purcell, and J. A. Wheat, *Electrolytic Separation Factors for Hydrogen Isotopes*, USAEC Report DP-558, Savannah River Laboratory, April 1961.
15. R. Bibron, *Detection of Atmospheric Tritium by Scintillation, Variations in Its Concentrations in France*, French Report CEA-R-2629, 1965.
16. A. E. Bainbridge, *Corrections To Be Applied to the Electrolytic Enrichment Factor of Deuterium and Tritium When Water Is Being Lost from the Cell by Entrainment and by Evaporation*, New Zealand Report NS-1, New Zealand Department of Scientific and Industrial Research, Division of Nuclear Sciences, Jan. 30, 1959.
17. E. W. Becker, *Heavy Water Production*, Review Series, No. 21, International Atomic Energy Agency, Vienna, 1962 (STI/PUB/15/21).
18. P. T. Walker, Electrolysis, in *Separation of Isotopes*, H. London (Ed.), pp. 411-415, George Newnes Books Ltd., London, 1961.

19. W. Jost, *Diffusion in Solids, Liquids, Gases*, pp. 489-532, Academic Press Inc., New York, 1960.
20. R. C. Jones and W. H. Furry, The Separation of Isotopes by Thermal Diffusion, *Rev. Mod. Phys.*, **18**: 151-224 (1946).
21. H. London (Ed.), *Separation of Isotopes*, pp. 295-331, George Newnes Books Ltd., London, 1961.
22. S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases*, pp. 252-258, Cambridge University Press, Cambridge, 1952.
23. B. Th. Verhagen and J. P. F. Sellschop, Enrichment of Low-Level Tritium by Thermal Diffusion for Hydrological Applications, in *Proceedings of the Third International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1964*, Vol. 12, pp. 398-405, United Nations, New York, 1965.
24. E. Almqvist, K. W. Allen, and J. H. Sanders, Thermal Diffusion Column for Concentrating Tritium in Tritium-Hydrogen Mixtures, *Rev. Sci. Instr.*, **26**: 649-654 (July 1955).
25. E. S. Robinson, A. C. Briesmeister, B. B. McInteer, and R. M. Potter, Separation of Tritium from Hydrogen by Thermal Diffusion, in *Radioisotopes in the Physical Sciences and Industry, Symposium Proceedings, Copenhagen, 1960*, Vol. 2, pp. 431-438, International Atomic Energy Agency, Vienna, 1962 (STI/PUB/20).
26. O. Sepall and S. G. Mason, Vapor/Liquid Partition of Tritium in Tritiated Water, *Can. J. Chem.*, **38**: 2024-2025 (October 1960).
27. H. A. Smith and K. R. Fitch, Determination of the Separation Factor for the Vaporization of Mixtures of Protium and Tritium Oxides, *J. Phys. Chem.*, **67**: 920-921 (April 1963).
28. M. M. Popov and F. I. Tazetdinov, The Vapor Pressure of T₂O, *At. Energ. (USSR)*, **8**: 420-424 (May 1960).
29. P. Avinur and A. Nir, Separation Factor of Tritiated Water In Fractional Distillation, *Nature*, **188**: 652 (Nov. 19, 1960).
30. A. H. Price, Vapor Pressure of Tritiated Water, *Nature*, **181**: 262 (Jan. 25, 1958).
31. W. M. Jones, *Vapor Pressures of Tritium Oxide and Deuterium Oxide. Interpretation of the Isotope Effect*, USAEC Report LADC-5905, Los Alamos Scientific Laboratory, 1963.
32. Y. D. Zel'venskii, D. A. Nikolaev, V. S. Tatarinskii, and V. A. Shalygin, Concentration of Water Samples for the Determination of the Tritium Content, *Soviet At. Energ. (USSR)*, **18**(4): 366-372 (April 1965).
33. D. B. Smith and D. S. Rawson, The Reconcentration of Tritium by Distillation, in *Tritium in the Physical and Biological Sciences, Symposium Proceedings, Vienna, May 3-10, 1961*, Vol. 1, pp. 105-120, International Atomic Energy Agency, Vienna, 1962 (STI/PUB/39).
34. T. F. Johns, Fractional Distillation and Solvent Extraction, *Separation of Isotopes*, H. London (Ed.), pp. 41-94, George Newnes Books Ltd., London, 1961.
35. T. Moeller, *Inorganic Chemistry*, p. 415, John Wiley & Sons, Inc., New York, 1954.
36. C. Evans and E. J. Wilson, *The Concentration of Tritium in Mixtures of Tritium and Hydrogen Using Pyrophoric Uranium*, British Report AERE-I/M-31, Mar. 10, 1954.
37. R. M. Haag and F. K. Heumann, *Separation of Tritium from Helium by Sorption on Palladium*, USAEC Report KAPL-1098(Del.), Knolls Atomic Power Laboratory, Dec. 20, 1960.
38. E. Glueckauf and G. P. Kitt, *Gas Chromatographic Separation of Hydrogen Isotopes*, British Report AERE-C/R-1847, Feb. 9, 1956.
39. J. E. Hoy, Tritium Enrichment by Gas-Solid Chromatography: Technique for Low-Level Analysis, *Science*, **161**(3840): 464-465 (Aug. 2, 1968).
40. J. Chadwick, *A Palladium Column for Concentrating Tritium from 2-Litre Mixtures of Tritium and Hydrogen*, British Report AERE-I/M-47, October 1957.
41. P. L. Gant and K. Yang, Separation of Hydrogen Isotopes by Gas-Solid Chromatography, *Science*, **129**: 1548-1549 (June 5, 1959).
42. D. Basmadjian, Adsorption Equilibria of Hydrogen, Deuterium, and Their Mixtures. Part I, *Can. J. Chem.*, **28**: 141-148 (January 1960).

43. W. G. Duncombe, The Adsorption of Hydrogen in a Molecular Sieve at -196°C and the Observation of an Isotope Effect, in *Radioisotopes in the Physical Sciences and Industry*, Symposium Proceedings, Copenhagen, 1960, Vol. 3, pp. 379-385, International Atomic Energy Agency, Vienna, 1962 (STI/PUB/20).
44. M. B. A. Crespi and H. Perschke, Application of Solid-Gas Chromatography to the Enrichment of Low-Level Tritium Samples, *Int. J. Appl. Radiat. Isotop.*, **15**: 569-578 (October 1964).
45. P. M. S. Jones and G. G. Hutcheson, Adsorption of the Three Hydrogen Isotopes on Charcoal, *Nature*, **213**: 490-491 (Feb. 11, 1967).
46. H. A. Smith and E. H. Carter, Jr., The Separation of Hydrogen, Tritium, and Tritium Hydride by Gas Chromatography, in *Tritium in the Physical and Biological Sciences*, Symposium Proceedings, Vienna, 1961, Vol. 1, pp. 121-133, International Atomic Energy Agency, Vienna, 1962 (STI/PUB/39).
47. J. King, The Chromatographic Separation of the Hydrogen Isotopes, Including Tritium, *J. Phys. Chem.*, **67**: 1397 (1963).
48. D. L. West and A. L. Marston, Gas Chromatographic Separation of the Hydrogen Isotopes, *J. Amer. Chem. Soc.*, **86**: 4731 (Nov. 5, 1964).
49. E. H. Carter, Jr., and H. A. Smith, The Separation of Hydrogen, Hydrogen Deuteride, Tritium Hydride, Deuterium, Tritium Deuteride, and Tritium Mixtures by Gas Chromatography, *J. Phys. Chem.*, **67**: 1512-1516 (July 1963).
50. P. L. Gant and K. Yang, Chromatographic Separation of Isotopic Methanes, *J. Amer. Chem. Soc.*, **86**: 5063-5064 (Dec. 5, 1964).
51. J. L. Borowitz and J. R. Gat, Evaluation of Elution Gas Chromatography as a Method for the Pre-Enrichment of Tritium for Low-Level Counting, *Int. J. Appl. Radiat. Isotop.*, **15**: 401-406 (July 1964).
52. F. J. Dunn, J. R. Mosley, and R. M. Potter, A Separation of Mixtures of Tritium and Hydrogen Using Hertz Pumps, *Anal. Chem.*, **27**: 63-64 (January 1955).
53. D. A. Brown, *Tritium Separation Factor in the Calcium-Water Reaction*, USAEC Report DP-217, Savannah River Laboratory, May 1957.
54. H. K. Rae, *Chemical Exchange Processes for Heavy Water*, Canadian Report AECL-2555, May 1966.

5 MONITORING PRACTICES AND INSTRUMENTS FOR THE DETECTION AND ASSAY OF TRITIUM

The primary objective of the routine monitoring is to ensure that plant releases of radioactivity comply with relevant national requirements¹ and that local populations are not receiving excessive exposure to ionizing radiation. Many factors affect the design of routine monitoring programs. Since radionuclides can move in many paths in the environment, the International Commission on Radiological Protection (ICRP) suggests that only exposure via critical pathways needs routine examination.¹ For control purposes the source of radioactivity in the environment should be identified and the trend of concentration should be predicted.

The low energy of tritium beta emission complicates monitoring and requires assay by internal counting systems. The instruments used in the monitoring of tritium are primarily adaptations of the ion chamber, internal gas counters, and the liquid-scintillation counter.

MONITORING FOR TRITIUM AT SPECIFIC SITES

Savannah River Plant

The Savannah River Plant is the center of tritium production in the United States.² Significant quantities of tritium are formed and released in three processes:

neutron irradiation of lithium for the scheduled production of tritium, neutron irradiation of deuterium in the heavy-water moderators of reactors, and release of fission-product tritium during the reprocessing of reactor fuels. Both area and environmental monitoring and analytical procedures used at the Savannah River Plant are discussed in Refs. 2 and 3.

Ventilation air from process areas is released to the environment through tall stacks that are monitored continuously with Kanne chambers.² A Kanne chamber is a simple, sturdy, and stable monitoring device consisting of a large ionization chamber through which air is drawn; the current produced within the chamber by ionization is measured by a micromicroammeter.⁴ Except when tritium concentrations are very high, there is no problem with internal contamination. Spurious ions produced from any source are detected by the device; therefore, external penetrating radiation must be either compensated for or eliminated. This instrument is capable of monitoring tritium concentrations in air ranging from 10^{-5} to $60 \mu\text{C}/\text{cm}^3$ (Refs. 2, 5).

At the tritium separations facility of the Savannah River Plant, 50 continuous air monitors, equipped with Kanne chambers, are used to monitor air pumped at a rate of about 150 liters/min from 125 sampling locations.⁵ The Kanne chambers are located in shielded rooms where the background gamma radiation is low and the output is sent to a panel board adjacent to the Health Physics office.⁵

A portable tritium monitor has been developed for measuring tritium concentrations in air in areas having an external gamma-radiation field. It is based on the air-sampling principle of the Los Alamos 101 sniffer^{6,7} and the Tracerlab tritium-flow monitor⁸ but has an additional gamma-compensating chamber.⁹ In a uniform gamma field of 10 mr/hr, there is an error of approximately $10^{-5} \mu\text{C}$ of $^3\text{H}/\text{cm}^3$ (Ref. 9). For accurate results, the gamma field, if present, must be uniform.³ The effective tritium air concentration range that can be measured is 4×10^{-5} to $2.5 \times 10^{-2} \mu\text{C}/\text{cm}^3$ (Ref. 2).

If nonuniform gamma fields are likely, the tritium concentration in air is monitored with a 1-liter ionization chamber and a vibrating-reed electrometer.² The chamber is evacuated and air is admitted at the sampling point. The chambers are then removed to a counting area where they are coupled to an electrometer. With this combination of instruments, tritium concentrations in air ranging from 1.4×10^{-6} to $1.4 \times 10^{-2} \mu\text{C}/\text{cm}^3$ can be measured.

An ion-chamber instrument has been developed for use as a leak detector to ensure the integrity of storage bottles containing concentrated tritium gas.^{3,10} This instrument can detect tritium leaking at a rate of $10^{-13} \text{ cm}^3/\text{sec}$ over a gas-collecting period of 16 hr (this corresponds to a total tritium leakage of $0.015 \mu\text{C}$); an additional time of 10 min is required for analysis.¹⁰

Air and rainwater samples are collected continuously at 15 monitoring stations spaced on two concentric circles: the inner circle is within a few miles of the plant boundary, and the outer circle extends 25 miles from the center of the plant.¹¹ Four additional stations are located on quadrants about 100 miles from the plant. Horton¹² discusses the basis for this geometrical pattern of sampling stations. Sampling stations are spaced on concentric circles so that the angles between locations are equal to the

minimum horizontal dispersion angle as determined from equations of atmospheric dispersion. This pattern provides a high probability of detecting any significant release of radioactivity regardless of the prevailing wind direction. The zone of maximum air concentration from stack releases occurs well within the plant boundary and is not monitored continuously because the area is not occupied regularly.¹³ Instead, the working areas are monitored. The stations near the plant boundary provide information regarding the maximum concentrations likely off-site, and the sampling stations at greater distances from the point of release provide base-line data to permit differentiation between plant releases and fallout from weapons testing. Air is pulled through a silica-gel column at a continuous rate of 100 cm³/min by an aquarium aerator pump. The columns are replaced weekly, and the water is distilled from the silica gel and counted by liquid-scintillation counting. The concentration of tritium oxide in air is then estimated from the tritium content of the sampled moisture and the absolute humidity of the atmosphere. Sampling of stack gases with silica-gel columns shows that only a small amount of tritium oxide is released by this route.¹⁴

Most of the tritium oxide is released to seepage basins, and the remainder is stored with high-level wastes in underground storage tanks.¹⁴ Tritium released with aqueous wastes to seepage pits has been monitored by intercepting the leading edge of the tritium front before it reaches a flowing surface stream or by correlating fluctuations in its concentration in seepage basins with those in the groundwater.¹⁴⁻¹⁶

Spent-fuel elements are transferred routinely into cooling basins and carry with them some of the tritium-contaminated heavy-water moderator. Effluent from the cooling-water basin and water in the Savannah River are sampled continuously by proportional samplers at 10 locations.^{3,11} The river samples show the impact of tritium seeping from the seepage basins. The concentration of tritium in the water of the Savannah River has averaged about 0.3 to 0.4% of the maximum permissible concentration of 0.003 $\mu\text{C}/\text{ml}$.^{11,17,18} In addition to these water samples, milk from three local dairies and two farms is analyzed for tritium each week. The maximum average concentration of tritium in milk has been 0.35% of the maximum permissible concentration suggested by the ICRP for the drinking water of large populations.^{11,17,18}

Liquid-scintillation counting, which is rapid and sensitive, is used to determine tritium in aqueous samples. For special samples requiring a detection limit of 5×10^{-7} $\mu\text{C}/\text{ml}$, 300 ml of the sample is concentrated to 10 ml by electrolysis.³ A concentration factor of 12 is achieved by a current flow of 25 amp for 48 hr (Ref. 3).

Pacific Northwest Laboratory

McConnon¹⁹ recently reviewed the present methods used for tritium monitoring at the Plutonium Recycle Test Reactor (PRTR) at the Pacific Northwest Laboratory. The two tritium monitoring systems installed at the PRTR have been developed on experience gained from handling tritium since about 1950.

The first system employs a single 16.3-liter Kanne chamber and continuously

draws, in sequence, samples from six operating areas of the containment vessel by means of a manifold and solenoid valve arrangement. The results are spurious owing to fission-product gases and nonradioactive ions in the air; so this system is used only to indicate the possible presence of airborne tritium. The instrument readout is displayed on a multipoint recorder in the control room.

The second system continuously monitors the tritium concentration in the exhaust-air duct by drawing a small sample through a commercial tritium monitor. The first sampling system tested to supplement the Kanne chamber system consisted of 1-liter ionization chambers which were evacuated and then used to sample air from a work area. This system proved unsatisfactory because the results were affected by the presence of gaseous fission products. A second system was tried in which sampling cartridges of silica gel were used. The silica gel was effective in discriminating against nontritium airborne contamination but was time consuming and required heating and vapor-condensing equipment. Finally, a satisfactory method was developed in which air is bubbled at a known rate through a gas wash bottle filled with a known volume of distilled water. The tritium concentration in the water is determined by liquid-scintillation counting and the air concentration is calculated. The method has proved to be both sensitive and reliable.

Some of the samples of the water vapor in the exhaust-stack air, which are routinely collected in a freeze trap to determine heavy-water loss from the stack, are also analyzed for tritium.¹⁹

Gaseous wastes at Pacific Northwest are released to the atmosphere through 200-ft stacks.²⁰ Iodine-131 is the radionuclide of principal interest in the offgases. Routine analysis for other specific nuclides in the gaseous effluents was discontinued in 1963 in favor of gross-activity measurements because previous analyses had shown that releases other than ¹³¹I were normally insignificant. As mentioned earlier, the ICRP recommends that only exposure via critical pathways be routinely monitored.¹ If it can be shown that releases of radionuclides from the installation result in a trivial radiation dose to man, then the release of these materials may be measured and controlled without making any environmental measurements.¹ Likewise, the relative abundance of tritium in reactor cooling water is considered to be on a trace level and of no serious consequence.²⁰

Following the discovery that tritium is a fission product, Haney, Brown, and Reisenauer²¹ analyzed the separations-plant waste streams and local groundwater for this radionuclide.^{22,23} About 47 to 64% of the theoretical quantity of fission-product tritium is discharged to the ground in process waste streams.^{21,22} Most of the remaining tritium is believed to be released to the atmosphere as a gas or stored with high-level liquid wastes in underground tanks.^{21,22} Tritium concentrations of over 10^{-3} $\mu\text{c}/\text{cm}^3$ were found in groundwater-monitoring wells located up to six miles from the disposal site.²¹⁻²³ The preferential direction of flow is toward the Columbia River, with local variations in flow patterns that are in agreement with the anticipated movement based on previous hydrologic and geologic studies.²¹ Some of this tritium may be entering the Columbia River, but the concentrations are too small to be detected.²⁰

National Reactor Testing Station

Most of the tritium released at the National Reactor Testing Station (NRTS) originates from the dissolution of fuel elements during reprocessing and is released as waste.^{2,4,25} The tritium was formed by ternary fission and by neutron irradiation of ⁶Li, which was used as a brazing flux in old-style reactor fuel elements.^{2,4,26} Approximately 18,000 curies of tritium has been released to the ground at NRTS.^{2,4}

The concentration of tritium in the wastes streams released to the ground is higher than the concentration of all other radionuclides combined but is still less than the radioconcentration guide (RCG = 3×10^{-3} $\mu\text{C/ml}$).^{2,4,26} Tritium has been detected in groundwater downgrade from the disposal well over an area of about 75 square miles.^{2,4-26} At the detectable perimeter of the contaminated groundwater, the concentrations have been diluted to less than 3×10^{-6} $\mu\text{C/ml}$ and thus do not constitute any potential for contamination of the drinking water.^{2,4} Sampling of 22 on-site production wells that supply water for human consumption showed an average tritium concentration of 0.02% of the maximum permissible concentration.^{2,7} Although these releases are not considered critical by the ICRP recommendation, knowledge of the behavior, in addition to other hydrologic and geochemical information, provides a basis for predicting the movement of other more hazardous radionuclides in that particular environment.

In addition to the discharges to the ground, a quantity of tritium estimated to be between 15,000 and 140,000 curies has been discharged to the atmosphere through a stack.^{2,4} On-site samples of precipitation are in good agreement with those obtained in the Salt Lake City area, and it is concluded that operations at NRTS have no obvious effect on the tritium contamination of local precipitation.^{2,4}

Chalk River

Tritium is produced at Chalk River when heavy water is irradiated in a reactor.²⁸⁻³⁰ Methods have been developed for detecting tritium in air in the presence of significant background gamma radiation.^{29,31-33} An instrument described by Cowper and Simpson³¹ employs a pair of compensated ion chambers to achieve satisfactory operation in a fluctuating background of several milliroentgen per hour of gamma radiation without shielding. One ion chamber responds to background gamma radiation plus gaseous radioactivity; the other chamber is sealed and responds only to the background gamma radiation. The two chambers have opposite polarization; so the d-c amplifier measures only the net ionization contribution from the gaseous radioactivity. Tritium concentrations of 2.5×10^{-5} $\mu\text{C/cm}^3$ can be detected.³¹

Osborne and Cowper³³ found that much better compensation for the external gamma field could be obtained when one ionization chamber was placed within the other rather than having the chambers placed adjacent to one another. The adjacent placement of the chamber caused the compensation to be dependent on the gamma-field direction. Also, the ionization chamber volume was increased from 4 to

40 liters for use as an area monitor, and a 1.2-liter chamber model was devised for use as a portable monitor.³³

Sannes and Banville³² developed a monitor that uses a spiral plastic scintillator for detecting tritium. This arrangement has an advantage over an ionization-chamber detector since it is possible to select only those pulses that correspond to the energies of tritium beta particles. The scintillations are detected by two photomultiplier tubes, and a coincidence circuit is used to screen out noise. An electronic circuit has also been incorporated to make the instrument less sensitive to gamma radiation. Under ideal conditions the instrument can detect 10^{-6} μc of $^3\text{H}/\text{cm}^3$. As the external gamma field increases, the sensitivity to tritium is reduced by 1.5×10^{-6} $\mu\text{c}/\text{cm}^3$ per 1 r/hr gamma field.

In addition to the use of tritium monitors for health physics applications, these instruments have also been useful in discovering leaks in heavy-water systems.²⁹ Bayly, Booth, and Stevens³⁴ developed an instrument to analyze liquids by automatically measuring their infrared absorption at two or more wavelengths. The instrument was specifically developed for monitoring the isotopic purity of heavy water. When heavy water contains a known concentration of tritium, the instrument can monitor tritium without being influenced by other radioactive contaminants in the air.³⁴

About 3 curies of tritiated water vapor is released daily from the reactor stack at Chalk River.³⁵ The total deposition for a 4-month period was measured by taking samples of snow in March 1962. The samples were distilled, and the tritium was measured with an anticoincidence liquid-scintillation counter. Elevated tritium concentrations were found in the snow in the vicinity of the Atomic Energy of Canada Ltd. Project area, especially near the NRU reactor, probably due to the escape of tritium oxide vapor from the reactor building.³² The concentrations decreased regularly with distance from the stack.

Low-level radioactive wastes discharged into the ground at Chalk River contain fission products as well as tritium produced by the irradiation of heavy water.²⁸ The tritium migrates through the ground at roughly the same rate as the groundwater and has become dispersed over a much more extensive area than other radionuclides. Parsons²⁸ made an intensive survey of the movement and dispersion of the tritium that has been released and correlated the movement of tritium with the hydrology of the disposal area. The movement of the tritium is toward Perch Lake; from Perch Lake the water moves through Perch Creek into the Ottawa River.

One of the more interesting aspects of the tritium-monitoring program at Chalk River was the reconstruction of environmental dispersion of tritiated water by analyzing cellulose from the annual growth rings of a tree grown in the liquid-waste disposal area.²⁹ Water with high tritium content had penetrated to the 1945 ring and beyond, but no tritium was observed in the separated cellulose predating 1958. From concentrations in the cellulose, it was determined that tritium first appeared in 1958 and reached a peak in 1962. This technique enables an investigator to determine the historical increases of tritium in groundwater after they have occurred.

OTHER INSTRUMENTS FOR MONITORING TRITIUM IN AIR

Because of the extremely low penetrating power of tritium beta particles, ordinary beta-sensitive devices are not adequate for tritium air monitoring.^{3,6} Other instruments than those described in the preceding section have been developed which use various modifications of internal counting.

Ionization-Chamber Instruments

Ionization chambers enable the measurement of tritium in external gamma-radiation fields. Pittendrigh and Vousden³⁷ developed a differential ionization-chamber instrument that can operate with no significant error in a uniform gamma field. Gamma compensation was achieved by using two ionization chambers with a common central electrode but with the outer electrodes equally and oppositely polarized. Kowalsky³⁸ patented an instrument that compensates for background radiation by using oppositely polarized ionization chambers and removing tritium from the air that enters one of the chambers.

Geiger-Counter Instruments

Gutman³⁹ devised a Geiger-counter instrument for detecting traces of tritium oxide in air. Tritium steam is thermally decomposed over heated tungsten or magnesium to liberate tritium gas, which is separated from other gases by diffusion over a nickel or palladium tube. Ballard and Ely^{40,41} also developed a tritium oxide monitoring instrument with a Geiger counter as a detector. They extracted water vapor from the air with a dehumidifier and counted the water vapor directly in a heated flow counter using a Geiger mixture of helium or helium and isobutane along with water vapor. Because the water is condensed from the air, the sensitivity is dependent on the moisture content.

Monitors with Scintillation Detectors

Sannes and Banville,³² as mentioned before, developed a monitor with a spiral plastic scintillator for the direct detection of tritium in air. Gibson and Burt⁴² also used a scintillation detector for the continuous measurement of tritium oxide in air. In their method water is condensed continuously from the air by a condenser cooled to +1°C. The condensed liquid is then drawn through a spiral cell filled with anthracene crystals, and the scintillations are detected by a photomultiplier.

Where continuous monitoring of tritium levels in air is not necessary, moisture can be removed from the air with a cold trap and the collected water sample can be analyzed for tritium with a laboratory counter.⁴³ Another technique is to remove tritiated water vapor by bubbling the gas through water and adsorbing the water vapor on an anhydrous drying column.^{44,45} The carbon dioxide in the dried gas is then absorbed into potassium hydroxide, and the tritium in the dry gas is oxidized by mixing the gas with oxygen and passing it over heated copper oxide. The tritiated water vapor formed is then removed from the dried gas as described above. The tritiated water can be assayed in the laboratory by standard tritium counting techniques.

COUNTERS FOR DETECTING TRITIUM

The classical detectors for radiation are the ionization chamber, the proportional counter, and the G-M tube. They are widely used, but no outstanding improvements in them have been made recently.⁴⁶ Scintillation detectors have been developed more recently and are now standard equipment. Reliable methods for counting tritium require internal counting, generally by using one of the classical detection methods in a gas phase or by using liquid-scintillation counting in a condensed phase.⁴⁷ Numerous reviews, articles, and books have been written on counting techniques. The following discussion, however, is restricted to a summary of some of the more important advantages and limitations of the various methods that have been used for tritium counting.

Gas Counters

Several methods have been used to measure tritium activity in the gaseous phase.⁴⁸ Robinson⁴⁸ gives a bibliography and an outline of the methods used for converting tritium to the form in which it is counted.

Tritium is detected by introducing the gaseous sample into a G-M tube, a proportional counter, or an ionization chamber with a vibrating-reed electrometer.⁴⁸

The ionization chamber may be a very simple and rugged measuring device.⁴⁹ Tolbert lists numerous advantages that ionization chambers offer for the assay of radioactive gases. The most important advantages he lists are: (1) they can be used with any gas or mixture of gases, (2) they can be used in flowing-gas systems, (3) the operating temperature is limited only by the materials of construction, (4) alpha-particle discrimination is possible at low activity levels, (5) the ionization chambers are inexpensive, (6) they are easy to decontaminate, and (7) the sample size is essentially unlimited. In comparing ionization chambers with liquid-scintillation methods for the assay of tritium, Guinn and Wagner⁵⁰ found that for small samples of

tritiated organics the two methods have nearly the same sensitivity but for larger samples the liquid-scintillation method can be much more sensitive. For small samples of tritiated water, the ion chamber is more sensitive; for larger samples the reverse is true. The sensitivities for aqueous samples are within about a factor of 2 for the entire range of sample size considered.

Geiger counters have been used for counting tritium by introducing the tritiated gas into the counters.^{4,8} Proportional counting is preferred, however, because the pulses produced are not so large that they induce appreciable dead times. Hence proportional counters combine the advantages of simplicity, maximum sensitivity, and applicability to a very wide range of counting rates.^{5,1} For accurate measurements the samples must be counted in a gaseous state.^{5,1} The gas proportional counter is about an order of magnitude more sensitive than the liquid-scintillation instruments.^{5,2} The sample can be counted as hydrogen gas or can be converted to a hydrocarbon.^{4,8,5,2,5,3}

Liquid-Scintillation Counters

The technique of liquid-scintillation counting was reviewed by Davidson and Feigelson^{5,4} in 1957, and an updated review was prepared in 1964 by Rapkin.^{5,5} In 1958 the proceedings of a conference on liquid-scintillation counting held at Northwestern University in August 1957 were published.^{5,6}

Liquid-scintillation counting of tritium permits rapid analysis of aqueous samples, especially since sample changers can be used conveniently.^{5,5} Although the sensitivity that is attained is quite satisfactory, it is not competitive with that of the proportional counter.^{5,2} One of the more serious limitations of liquid-scintillation counting has been the difficulty of incorporating aqueous samples into scintillator solvents at the temperatures required for good counting efficiency.^{5,7} A partial solution to this problem can be achieved by preparing emulsions having a rather high water content.^{5,8} The background can be reduced substantially by using glass vials low in potassium or by using polyethylene vials.^{5,5}

Quenching is another substantial disadvantage to liquid-scintillation counting.^{5,4,5,5} Quenching is reduced when emulsions are used.^{5,8} Corrections for quenching can be made by using internal or external standards, by adding increments of sample to the counting vial and extrapolating to zero sample weight, or by applying corrections on the basis of a spectral shift when a dual-channel instrument is used.^{5,5} If quenching is due to the color of the sample, it can be overcome by decolorization by charcoal filters, distillation, or chemical bleaching.^{5,5}

Tamers and his associates^{5,9,6,0} found that the tritium activity in rain could be measured without isotopic enrichment by converting the water to benzene. The major disadvantage of this method is the low chemical yield of benzene compared with the high efficiency of water enrichment by electrolysis; hence, large initial samples of water are required. The advantage is that a large quantity of tritium can be exposed to the counter.

Although this discussion may imply that liquid-scintillation counters have several disadvantages, the rapidity, simplicity, and sensitivity of such counters often offer the best assay system for tritium.^{4,5} Recent improvements in the design of electronic components have resulted in much less cross contribution of spectra when double-label counting is being used. By using solid, suspended scintillators, such as anthracene or a mixture of anthracene and liquid scintillator, continuous measurements of chromatographic column effluents can be made. The flexibility afforded by liquid-scintillation counting makes it one of the fastest growing instrumental methods for the measurement of low-energy beta activity.^{5,5}

SUMMARY

For routine monitoring of tritium in air, the ionization chamber with gamma compensation offers the advantage of simplicity and ruggedness. When highly precise results are required for low-activity samples, some pre-enrichment method (preferably electrolysis) coupled with internal gas counting seems to be the preferred system of analysis. Liquid-scintillation counting offers a fast, convenient means for measuring tritium activity in moderately active solutions.

REFERENCES

1. *Principles of Environmental Monitoring Related to the Handling of Radioactive Materials*, International Commission on Radiological Protection Publication 7, Pergamon Press, Inc., London, Sept. 13, 1965.
2. W. C. Reinig and E. L. Albenesius, *Control of Tritium Health Hazards at the Savannah River Plant*, USAEC Report DPSPU-62-30-5, Savannah River Laboratory, January 1962.
3. E. L. Albenesius and L. H. Meyer, *Analytical Techniques for the Use and Control of Tritium at Savannah River*, USAEC Report DP-771, Savannah River Laboratory, September 1962.
4. J. E. Hoy, Operational Experience with Kanne Ionization Chambers, *Health Phys.*, 6: 203 (1961).
5. D. C. Nichols, *Radiological Protection in a Tritium Separations Facility*, USAEC Report DPSPU-65-30-31, Savannah River Laboratory, January 1966.
6. B. C. Eutsler, G. L. Evans, R. D. Hiebert, R. N. Mitchell, C. Robbins, and R. J. Watts, *Instruments for the Monitoring of Tritium in the Atmosphere*, USAEC Report LA-1909, Los Alamos Scientific Laboratory, April 1955.
7. B. C. Eutsler et al., Instrument for Monitoring Tritium in the Atmosphere, *Nucleonics*, 14(9): 114-117 (September 1956).
8. J. Brinkerhof et al., Continuous Air Monitor for H³, *Nucleonics*, 17(2): 76 (February 1959).
9. J. D. Anthony, Portable Tritium Monitor Has Gamma Compensation, *Nucleonics*, 17(4): 110 (April 1959).
10. D. W. Colvin, *A Simple Leak Detector for Tritium*, USAEC Report DP-198, Savannah River Laboratory, January 1957.

11. W. C. Reinig and E. L. Albenesius, Control of Tritium Health Hazards at the Savannah River Plant, *Amer. Ind. Hyg. Ass. J.*, 24(3): 276-283 (May-June 1963).
12. J. H. Horton, Jr., *Design of a Regional Survey Program*, USAEC Report DP-253, Savannah River Laboratory, November 1957.
13. J. H. Horton, Jr., Savannah River Laboratory, personal communication, Feb. 7, 1968.
14. J. H. Horton, *Fission Product Tritium at the Savannah River Plant*, USAEC Report DPSPU-63-30-38B, Savannah River Laboratory, October 1963.
15. J. H. Horton, Jr., and D. I. Ross, Use of Tritium from Spent Uranium Fuel Elements as a Ground-Water Tracer, *Soil Sci.*, 90(5): 267-271 (November 1960).
16. S. O. Reichert, Radionuclides in Groundwater at the Savannah River Plant Waste Disposal Facilities, *J. Geophys. Res.*, 67: 4363-4374 (October 1962).
17. Savannah River Laboratory, *Effect of the Savannah River Plant on Environmental Radioactivity, Semiannual Report, July-December 1964*, USAEC Report DPSPU-65-30-1, February 1965.
18. Savannah River Laboratory, *Effect of the Savannah River Plant on Environmental Radioactivity, Semiannual Report, July-December 1965*, USAEC Report DPST-66-30-1, February 1966.
19. D. McConnon, *Tritium Experience at Pacific Northwest Laboratory*, USAEC Report BNWL-SA-1026, Battelle Memorial Institute, Pacific Northwest Laboratory, Jan. 15, 1967.
20. R. H. Wilson (Ed.), *Evaluation of Radiological Conditions in the Vicinity of Hanford for 1963*, USAEC Report HW-80991, Hanford Atomic Products Operation, Feb. 24, 1964.
21. W. A. Haney, D. J. Brown, and A. E. Reisenauer, *Fission Product Tritium in Separations Wastes and in the Ground Water*, USAEC Report HW-74536, Hanford Atomic Products Operation, Aug. 1, 1962.
22. W. A. Haney, Fission-Product Tritium in Fuel-Reprocessing Waste, *Nucl. Safety*, 5(4): 399-403 (1964).
23. D. J. Brown, *Chemical Effluents Technology Waste Disposal Investigations, January-December 1964*, USAEC Report HW-84549, Hanford Atomic Products Operation, 1964.
24. D. B. Hawkins and B. L. Schmalz, *Environmental Tritium Studies at the National Reactor Testing Station*, USAEC Report IDO-12043, Idaho Operations Office, August 1965.
25. B. L. Schmalz and W. S. Keys, Retention and Migration of Radioactive Isotopes in the Lithosphere at the National Reactor Testing Station—Idaho, *Retention and Migration of Radioactive Ions in Soils*, pp. 243-256, University Press of France, Paris, 1963.
26. D. A. Morris et al., *Hydrology of Waste Disposal, National Reactor Testing Station, Idaho. Annual Progress Report, 1962*, USAEC Report IDO-22044, Idaho Operations Office, April 1963.
27. A. O. Dodd (Ed.), *Health and Safety Division Annual Progress Report, 1963*, USAEC Report IDO-12037, pp. 36-37, Idaho Operations Office, August 1964.
28. P. J. Parsons, *The Movement of Tritium from the Chalk River Liquid Disposal Area*, Canadian Report AECL-1739, April 1963.
29. A. M. Marko et al., *Activities of AECL in the Fields of Biology, Health Physics and Medicine*, Canadian Report AECL-2107, November 1964.
30. W. R. Bush, *Tritium Hazards*, Canadian Report AECL-2594, June 1966.
31. G. Cowper and S. D. Simpson, *A Monitor for Airborne Tritium*, Canadian Report AECL-1049, July 1960.
32. F. Sannes and B. Banville, *A Portable Tritium-in-Air Monitor*, Canadian Report AECL-2283, July 1965.
33. R. V. Osborne and G. Cowper, *Detection of Tritium in Air with Ionization Chambers*, Canadian Report AECL-2604, October 1966.
34. J. G. Bayly, R. J. Booth, and W. H. Stevens, *An Improved Infra-Red Method of Monitoring Heavy Water*, Canadian Report CRRP-1099, July 1962.

35. G. C. Butler and P. J. Barry, *Experience with Dilution Rate Factors from the AECL Reactor Stack*, Canadian Report AECL-1518, May 1962.
36. J. E. Dummer, Jr. (Ed.), *General Handbook for Radiation Monitoring*, USAEC Report LA-1835(3rd ed.), Los Alamos Scientific Laboratory, November 1958.
37. L. W. D. Pittendrigh and J. E. Vousden, *A Differential Ionisation Chamber Method for Continuous Flow Monitoring of Tritium in Air in the Presence of a Significant Gamma Background and with Occasional Traces of Radon in the Sampled Air*, British Report AERE-Hp/R-1585, Dec. 6, 1954.
38. E. Kowalsky, Method and Arrangement for the Continuous Detection of Small Tritium Concentrations in the Air, German Patent 1,153,550, Aug. 29, 1963; from *Nucl. Sci. Abstr.*, 18(6): 1121, No. 8318 (Mar. 31, 1964).
39. W. Gutman, The Continuous Detection of Low Tritium Traces in Air and in Other Reactor Gases, German Patent DAS 1,074,880; *Keintechnik*, 3: 552 (December 1961).
40. L. F. Ballard and R. L. Ely, Jr., *A Sensitive Tritium Monitor*, USAEC Report ORO-491, Oak Ridge Operations Office, May 31, 1963.
41. L. F. Ballard and R. L. Ely, Jr., A Sensitive Tritium Monitor, *Trans. Amer. Nucl. Soc.*, 6(2): 400-401 (November 1963).
42. J. A. B. Gibson and A. K. Burt, A Method for the Continuous Measurement of Tritiated Water in Air, *J. Nucl. Energy, Parts A & B*, 20(3): 185-190 (March 1966).
43. T. S. Iyengar et al., A Cold Strip Apparatus for Sampling Tritium in Air, *Health Phys.*, 11(4): 313-314 (April 1965).
44. *Analytical Method for the Determination of (A) Tritiated Water and (B) Tritium and Tritiated Hydrocarbons in Reactor Coolant Gas*, British PG-Report-469 (Rev.), 1965.
45. R. V. Osborne, *Studies and Techniques in Tritium Health Physics at CRNL*, Canadian Report AECL-2699, November 1967.
46. W. A. Higginbotham, Recent Advances in Instrumentation, in *Advances in Tracer Methodology*, Vol. 1, pp. 195-200, Plenum Press, New York, 1963.
47. J. R. Arnold, Liquid Scintillation Counting of Tritium, in *Advances in Tracer Methodology*, Vol. 1, pp. 69-75, Plenum Press, New York, 1963.
48. C. V. Robinson, Gas Counting of Tritium, in *Advances in Tracer Methodology*, Vol. 1, pp. 178-182, Plenum Press, New York, 1963.
49. B. M. Tolbert, Tritium Measurement Using Ionization Chambers, in *Advances in Tracer Methodology*, Vol. 1, pp. 167-177, Plenum Press, New York, 1963.
50. V. P. Guinn and C. D. Wagner, A Comparison of Ionization-Chamber and Liquid-Scintillation Methods for Measurement of Beta Emitters, in *Advances in Tracer Methodology*, Vol. 1, pp. 160-166, Plenum Press, New York, 1963.
51. R. L. Wolfgang, Vapor Phase Proportional Counting, in *Advances in Tracer Methodology*, Vol. 1, pp. 183-184, Plenum Press, New York, 1963.
52. D. Lal and R. N. Athavale, The Measurement of Tritium Activity in Natural Waters, Part I. Techniques, *Proc. Indian Acad. Sci., Sect. A*, 63(3): 166-183 (March 1966).
53. A. E. Bainbridge, Determination of Natural Tritium, *Rev. Sci. Instrum.*, 36(12): 1779-1782 (December 1965).
54. J. D. Davidson and P. Feigelson, Practical Aspects of Internal Liquid-Scintillation Counting, *Int. J. Appl. Radiat. Isotop.*, 2(1): 1-18 (January 1957).
55. E. Rapkin, Liquid-Scintillation Counting 1957-1963: A Review, *Int. J. Appl. Radiat. Isotop.*, 15(2): 69-87 (February 1964).
56. C. G. Bell, Jr., and F. N. Hayes (Eds.), *Liquid Scintillation Counting*, Pergamon Press, Inc., London, 1958.
57. J. A. Baxter, L. E. Fanning, and H. A. Swartz, Liquid Scintillation Solvent Systems: Water Content and Related Counting Efficiencies, *Int. J. Appl. Radiat. Isotop.*, 15(7): 415-418 (July 1964).

58. M. S. Patterson and R. C. Greene, Measurements of Low Energy Beta-Emitters in Aqueous Solution by Liquid Scintillation Counting of Emulsions, *Anal. Chem.*, **37**(7): 854-857 (June 1965).
59. M. Tamers et al., A New Method for Measuring Low-Level Tritium Using A Benzene Liquid Scintillator, in *Tritium in the Physical and Biological Sciences, Symposium Proceedings*, Vienna, 1961, Vol. 1, pp. 303-312, International Atomic Energy Agency, Vienna, 1962 (STI/PUB/39).
60. M. A. Tamers and R. Bibron, Benzene Method Measures Tritium in Rain Without Isotope Enrichment, *Nucleonics*, **21**(6): 90 (June 1963).

6 MOVEMENT IN THE ENVIRONMENT

RELEASE TO THE STRATOSPHERE

Natural tritium is produced primarily in the atmosphere; production at the earth's surface is quite low. About two-thirds of the natural tritium is produced in the stratosphere.¹ Thermonuclear explosions at high altitudes in tropical regions introduce tritium directly into the stratosphere,^{2,3} where mixing processes are very slow. However, with low-altitude detonations in tropical regions, a sizable fraction of the water vapor of the environmental atmosphere is entrained by the ascending air current created by the explosion; the tropopause acts like a cold trap and prevents most of the water vapor from penetrating into the stratosphere.³ The ice particles formed at the tropopause fall back rapidly into the troposphere. In the polar regions the natural water-vapor content of the air is relatively low, and much of the tritium from detonations in polar regions penetrates into the stratosphere and moves to lower latitudes before moving into the troposphere.³

In the atmosphere tritium is distributed in various chemical forms,⁴ as indicated in Chap. 3. The tritium produced by nuclear detonations is distributed in roughly the same manner as natural tritium,⁵ with HTO being the predominant species. Under the oxidizing conditions of the thermonuclear fireball, tritiated water is formed rapidly.^{6,7} Wolfgang⁸ hypothesized that a reducing medium in the center of the fireball accounts for the production of highly tritiated hydrogen and methane.

Stratospheric tritium is slowly released into the troposphere, where the flushing action of rainfall causes a much more rapid removal of tritium as water vapor. The

mean residence time of tritium in the stratosphere has been estimated to range from a little over 1 year to as long as 10 years (Refs. 1, 2, and 9-14). Seasonal changes in the tritium content of rain indicate that the movement of material across the tropopause cannot be treated on the basis of a simple two-compartment model and that the residence time is strongly time and space dependent (Refs. 7, 11, 12, and 14). Bishop and his associates⁶ found that the distribution of tritium is consistent with the Dobson-Brewer model of global stratospheric circulation. According to this model, upward diffusion from the troposphere in the temperate latitudes is prevented by the slow sinking of air in the lower stratosphere which has penetrated the tropopause near the equator and spread toward the polar regions. There have been objections to this model because meteorological observations indicate that the tropopause seems stable in the equatorial zone.³

Bibron³ reviewed a more satisfactory model, which suggests that the transport of masses of air and debris from the stratosphere to the troposphere arises from the action of turbulent diffusion caused by currents of horizontal circulation. Extremely fast jet currents, especially in subtropical breaches, can initiate relatively important exchanges. These jet currents have their maximum intensity at the end of winter and in the spring, which explains the observed seasonal variations in fallout.

North-south mixing in the stratosphere is thought to be quite rapid.² The excess tritium from the Castle test series was distributed rather homogeneously over the northern hemisphere.¹⁵ Any tritium retained for long periods in the stratosphere and subjected to stratospheric mixing processes should be expected to enter the troposphere preferentially in the mid-latitudes, with a maximum in spring.^{16,17} Libby⁵ showed that about one-half of the tritium from the explosion of thermonuclear devices falls in the zone between 30° and 50° north latitude.

After tritium crosses the tropopause, vertical mixing becomes quite pronounced, and the residence time in the troposphere is short compared with the mean residence time in the stratosphere. Material in the troposphere is flushed out by rains within about a month of its entry.² Estimates of the mean residence time of tritium in the troposphere range from 21 to 40 days (Refs. 2, 12, and 18-22). If the tropopause is assumed to be located at about 12 to 15 km,^{2,3} the deposition velocity of tritium is estimated to be between 0.4 and 0.8 cm/sec. On the basis of diffusion, the concentration velocity of tritium has been estimated to be less than 0.4 cm/sec, but the effective value depends almost entirely on air motion.²⁴ Eriksson¹⁴ estimated the eddy diffusion velocity of tritium over ocean areas to be about 1 cm/sec, on the basis of the rate of evaporation and the relative humidity of the air.

Another estimate of the deposition velocity for tritium can be made from the concentration and deposition rate of natural tritium. Harteck²³ estimates 0.6 mole of HT in the atmosphere and gives a value for the ratio of tritium to hydrogen in water of $(3.5 \pm 0.7) \times 10^{-18}$. Verniani²⁵ estimates the average water-vapor content of the atmosphere to be 9.4×10^{17} moles. Another 3.3 moles of tritium is present in the atmosphere as HTO. If tritium is distributed similarly to the rest of the mass of the atmosphere,^{25,26} the surface concentration of tritium would be about 0.48 atom/cm³. Bainbridge²⁷ gives an average of 0.39 ± 0.15 atom/cm²/sec for the

deposition rate of natural tritium integrated for all latitudes, which yields a mean deposition velocity of 0.8 cm/sec, in close agreement with the values estimated in other ways.

Tritium may also be transferred by vapor exchange between the air and the earth's surface. Eriksson¹⁴ estimates that transfer of tritium by vapor exchange over the oceans may account for about two-thirds of the tritium removal into the oceans. This transfer may explain the discrepancy between Libby's⁵ estimate of rainfall of 2.5 m/year over oceans and measured values of about 0.9 to 1.1 m/year.^{2,8,29}

Bolin³⁰ suggests that in light rains the tritium concentration is representative of the moisture at lower levels, whereas in moderate or heavy rains the exchange at lower levels is insignificant. Chamberlain and Eggleton³¹ considered the exchange of tritium between rain drops and water vapor on the basis of a film-diffusion-controlled process. Their findings that the specific activity of drops reaching the ground after passage through a plume contaminated with tritium is very dependent on drop size supports Bolin's suggestions. Chamberlain and Eggleton further estimate that the washout coefficient for the plume of tritiated water vapor should be on the order of 10^{-4} /sec.

When the atmospheric concentration of tritium is uniform, rainfall over continental areas will be higher in tritium content than rainfall over oceans.^{14,32,33} Precipitation falling on land has only a small probability of dilution owing to mixing. Hence, reevaporated water has nearly the same tritium content as the original precipitation. Conversely, precipitation falling on the ocean and other deep bodies of water is rather rapidly mixed within a zone of about 75 m, and the concentration of tritium in evaporated water is reduced.^{2,7} Brown³³ tried to correlate temporal fluctuations of tritium concentration in Canadian precipitation with meteorological factors, such as type of storm, radar height of precipitation formation, rainfall duration and intensity, and type and origin of the associated air mass. Only air-mass considerations led to any significant correlation: the deeper the air mass traversed by precipitation, the higher the tritium concentration. Also, air-mass trajectories from the north and west yielded precipitation of high tritium concentration, but those originating in the south and east resulted in low tritium concentration. This phenomenon was probably due primarily to transfer rates from the stratosphere.

RELEASE TO THE TROPOSPHERE

As already mentioned, the residence time for tritium in the troposphere is only a matter of a few weeks rather than a few months to a few years, as in the stratosphere. Consequently, the fallout of tritium released to the troposphere is limited to the general latitude of release.² Some lateral mixing occurs, and some possibility of lateral tropospheric mixing exists, even across the equator,¹⁶ but, in general, the concern with tropospheric releases is limited to local areas of discharge.

Three general conditions of tropospheric release must be considered for evaluation of the consequences:³⁴ (1) emergency (short-term) releases from a stack, (2) emergency (short-term) releases at ground level, and (3) routine (continuous) releases from a stack. For short-term releases the most severely limiting meteorological conditions are ordinarily considered. In an accident all releases may not be made through a stack; this possibility imposes another severe limit since the minimum dilution factor is likely to be less for ground releases than for stack releases.³⁴ For continuous releases an average dilution factor can be used. Since the average dilution factor is time integrated, these values show the influence of changing meteorological conditions, such as wind speed, stability, and direction. Obviously the mean dilution factor is always greater than the minimum, often by several orders of magnitude.

The release of tritium is usually expected to be in the form of water vapor. If the release is in the form of tritiated hydrogen gas, the permissible concentration or quantity of release is considerably higher, but allowances must be made for oxidation of the tritium to water vapor. Doury³⁵ considered this complication in regard to establishing limits of tritium releases for both continuous and single-discharge situations. He estimated that 75 curies of tritiated water vapor or 3900 curies of tritiated hydrogen gas discharged daily from a 30-m stack would be permissible under the most unfavorable meteorological conditions.

Chamberlain and Eggleton³¹ estimated a permissible continuous emission rate for tritium based on the specific activity of water vapor in the air at a point where the plume from a stack release reaches the ground. A harmonic mean wind speed of 2 m/sec and an absolute humidity of 8.6 g/cm³ were used to estimate working curves based on a uniform swing of wind direction through a 360° arc. Finally, a factor of 2.5 was used as an estimate of the frequency by which the prevailing wind exceeds the mean. On the basis of these estimates, they indicate that an emission rate of 200 curies/day of tritiated water vapor would be permissible from a 30-m stack and that the rate could be increased to 1000 curies/day for a 60-m stack. Barry³⁴ reviewed average dilution factors for various stack heights ranging from 300 to 600 ft at a number of locations and concluded that continuous releases of 2000 curies/day of tritiated water vapor could be tolerated. Blomeke³⁶ estimated that 1200 curies/day could be released from a 100-m stack under "extremely unstable" meteorological conditions and a mean wind speed of 3 miles/hr (1.3 m/sec). For single-discharge incidents, Doury³⁵ suggests limits of 68,000 curies of HTO and 8 × 10⁶ curies of HT; Barry³⁴ estimates that a stack release of 4 × 10⁶ curies or a ground-level release of 4 × 10⁵ curies of HTO could be tolerated.

These authors have not considered the impact of releases of this magnitude on worldwide tritium distribution, but continuous releases of 1000 curies/day would be about an order of magnitude lower than the estimated 10,000 to 20,000 curies/day of natural tritium production. In a nuclear power economy, there may be several plants releasing tritium to the environment and release of fission-product tritium from all plants would constitute a significant fraction of the total production.

DEPOSITION ON
THE GROUND SURFACE

Even when tritium is rather uniformly distributed throughout the stratosphere of the northern hemisphere, it is preferentially deposited in the mid-latitudes.^{5,14} This zone contains some of the most highly industrialized regions of the world, including most of the United States and Europe. Hence, this region must be considered of prime importance regarding the potential exposure of general populations to environmental tritium. When the releases of tritium are restricted to the troposphere, there is much less chance for lateral mixing, and deposition is limited to the general latitude of the release.² Of course, when the releases are made directly to the ground surface, the area affected by the release is even smaller.

In addition to latitudinal variations, deposition of tritium over continental areas differs markedly from deposition over oceanic areas.¹⁴ First, the annual precipitation over the oceans is greater than over the continents.²⁹ Eriksson¹⁴ suggests that deposition of tritium over the oceans is considerably greater than that estimated from precipitation, owing to direct exchange of water vapor between air and seawater.

Practically all the continental deposition of tritium occurs from precipitation.² In local situations, however, where tritium is released through a stack, the downward diffusion of the released plume will probably cause the plume to reach the ground surface before washout by rain occurs.³¹ Once deposited the tritium can undergo one of several fates³⁷ as illustrated in Fig. 6.1. The most rapid loss of tritium can occur by surface runoff during and immediately following a rain and by direct evaporation from the surfaces of vegetation, standing pools of water, and the soil surface. Water that infiltrates the soil is cycled more slowly. Movement may occur both laterally and vertically with losses due to transpiration, evaporation, recharge of surface streams, and direct groundwater flow into oceans. Some of the water that recharges the groundwater moves so slowly that the tritium associated with this fraction of the precipitation is effectively lost from circulation.

The annual rainfall over continental areas of the world is about 0.66 m/year.³⁸ Of this amount, about 0.25 m/year, or 37%, is lost by runoff and underground flow; the remaining 63% is lost to the atmosphere by evaporation and transpiration.³⁹ For the continental United States, the annual rainfall is about 0.76 m, of which about 28% is lost by runoff and underground flow, with the remainder lost by evapotranspiration.⁴⁰ In the Clinch River watershed, the runoff and underground flow amount to about 40% of the rainfall.⁴¹

Begemann and Libby¹⁸ summarized in detail the water balance in the Mississippi River valley following the Castle operation in the spring of 1954. There is a precipitation of about 0.77 m/year, of which about two-thirds is water evaporated from the ocean and about one-third is reevaporated groundwater. The Mississippi River annually returns about 0.28 m of water to the ocean by runoff; the remaining

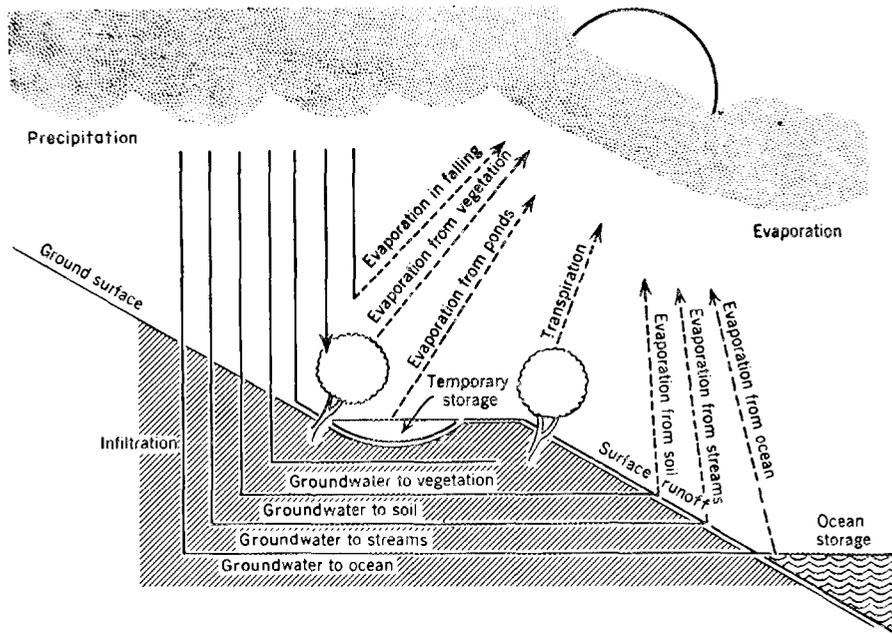


Fig. 6.1. The hydrologic cycle. (From L. D. Baver, *Soil Physics*, John Wiley & Sons, Inc., New York, 1956; reprinted with permission of publisher.)

0.49 m/year is evaporated, with about 0.24 m/year of the evaporated water being returned to the ocean. They estimate that about 8 m of groundwater is available for mixing and that this groundwater has a storage time of about 10 years. Considering radioactive decay, they estimate that tritium has a residence half-life of 5.7 years on the North American continent.

In the Ottawa River drainage basin of 24,000 square miles, the mean residence time for tritium has been estimated to be 3.7 years, with an effective storage reservoir⁴² of 2.1 m. About $55 \pm 10\%$ of the reevaporated water is made up of fresh precipitation. There is a fast-drainage component that cannot be adequately accounted for by a simple one-compartment model, assuming complete mixing with a single turnover time.⁴³ Eriksson⁴⁴ made a detailed analysis of Brown's data,⁴³ along with later data, and determined the runoff of water as a function of storage time. The results are in good agreement with the physiography and geology of the basin. An amount of tritium equivalent to about that deposited during two years precipitation stays in the basin less than eight years. The peaks in the runoff vs. storage-time curves occur at about three years, with an indication of an earlier peak occurring after about one year. Eriksson⁴⁴ suggests that the early peak is due to surface runoff and near-surface groundwater flow into streams and rivers that discharge rather directly

into the Ottawa River. The second peak he attributes to holdup in the system of lakes in the upper Ottawa River valley.

Carlston⁴⁵ reported results of hydrologic studies conducted by the U. S. Geological Survey on two small stream basins, the Black Earth Creek Basin (46 square miles) in Wisconsin and McDonalds Branch Basin (2.3 square miles) in New Jersey. Both basins are quite permeable, and it is estimated that about 30% of the rainfall goes into groundwater storage. At the Wisconsin site only about 1% of the rainfall was lost by surface runoff, but in New Jersey the surface runoff amounted to about 10%. The mean residence time for groundwater recharge in the two basins was 45 and 30 days, respectively.

In general, tritiated water is expected to behave the same as ordinary water in the ground, except for the slight difference in vapor pressure. However, the water associated with minerals in the ground may have various degrees of mobility, depending on the nature of the association. In a water-saturated formation the bulk of the water will be ordinary liquid water that occupies the interparticle pores. This water may be considered freely mobile, although its velocity of movement will vary depending on the pore size. In addition to this water, loosely bound water of hydration is on the mineral surfaces. Joergensen and Rosenqvist⁴⁶ studied the bonding of hydrogen in micas and found that the water of hydration is in equilibrium with its environment at room temperature after a very short time. This water can be removed at temperatures below 400°C. A second phase of adsorbed water requires much longer for equilibration and is vaporized in the 200 to 500°C temperature range. Finally, a third phase requires very long times or hydrothermal alterations for exchange. This water can be removed in the 500 to 1150°C temperature range. This phase is thought to consist primarily of structural hydroxyl groups.

The impact of these adsorbed phases of water on tritium behavior in the ground is dependent primarily on two factors: (1) the relative amounts of these phases compared with the free water in the macropores and (2) the conditions under which the adsorption and desorption reactions occur. The relative amounts of these phases increase markedly as the moisture content decreases. Hence, tritiated water would be expected to move relatively more slowly through a very dry soil than through a moist soil. If the tritiated water is initially deposited under conditions involving a very high temperature, i.e., in the high-temperature region of a nuclear detonation, exchange with the structural hydroxyl groups may occur. Since an activation energy must be exceeded to initiate the exchange reaction, the subsequent replacement of this fraction of the tritium would be expected to be very slow. Koranda⁴⁷ found that in the Pacific Proving Ground, the mineral-bound water of the soil is high in tritium. The "soil" consists almost entirely of CaCO₃ and Ca(OH)₂. The free water in the soil had a concentration of 60 tritium units; the bound water had a concentration of 3.7×10^5 tritium units. In a saturated formation nearly all the tritiated water will be free water in macropores, and its velocity of movement will vary due to the dispersive characteristics of the formation.⁴⁸ Nakayama and Jackson⁴⁹ report that the apparent diffusion coefficient for tritiated water in soils was nearly constant for volumetric water contents between 10 and 40%. Below 10% the apparent diffusion coefficient

increased rapidly with a maximum at 4% water content, indicating gaseous diffusion of water vapor through large pores. Below 4% water content, the apparent diffusion coefficient decreased rapidly and suggested an influence of absorbed phases.

Lang and Mason⁵⁰ report that the exchange of tritium between cellulose and water vapor is not completely reversible. Bolin³⁰ suggested that the history of tritium concentration in the groundwater could be reconstructed by analyzing the specific activity of the cellulose in tree rings. At about the same time in the early sixties, workers in Japan presented data on the tritium content of tree rings to estimate the tritium content of rainwater.^{51,52} This technique has also been extensively developed in Canada,⁵³ where no exchange has been shown between ambient tritiated water and the C-H bonds of cellulose within a five-year period. Woods and O'Neal⁵⁴ showed that most of the water withdrawn by small trees comes from the first foot of the soil.

RELEASE OF TRITIUM TO SURFACE WATERS

Tritium can reach surface waters by a variety of pathways: directly through precipitation, through molecular exchange with the atmosphere, by release of tritiated water from nuclear plants, and indirectly from runoff or by influx to streams from groundwater. Surface waters, which contain over 99% of the total water, constitute the greatest reservoirs of water on earth.^{55,56}

Behavior of Tritium in Rivers

Water in stream channels is always moving rapidly into oceans and seas. In the Clinch River the measured flow velocities range from about 0.2 to 2.3 ft/sec (0.14 to 1.6 mph), depending on the discharge;^{57,58} the mean velocity is about 0.7 ft/sec (0.5 mph)⁵⁹ compared with a geometric mean wind speed of about 5 mph.³¹ In other streams the flow velocity may differ considerably, reflecting the hydraulics of the system.^{60,61}

At a steady discharge of 7990 cu ft/sec, tracer introduced into the Clinch River at the mouth of White Oak Creek at Clinch River Mile (CRM) 20.8 was completely mixed laterally⁶² by the time it reached CRM 17.5. In general, full vertical and transverse mixing occurs within 4 to 6 miles downstream from the mouth of White Oak Creek.⁶³ In the Ottawa River lateral mixing was complete after 2.8 miles of flow.⁶⁴ Therefore in most cases the full dilution capacity of a river may be reasonably assumed available for continuous discharges. The downstream concentration would be expected to vary with the rate of tritium release into the surface stream and with the discharge of the stream. Thus, the Clinch River, which has a mean discharge of 4600 cu ft/sec above

White Oak Creek, could accommodate a daily discharge of 1.1×10^4 curies of tritium without exceeding an average concentration of 10^{-3} $\mu\text{C}/\text{ml}$.

With a slug discharge of tritium, the duration and intensity of the tritium peak reaching downstream users would depend on the diffusion encountered in the river, the flow velocity, and the discharge.⁶⁵ Although doses may be averaged over a one-year period,⁶⁶ the concentration of tritium should be held to as low a level as possible, and the water contaminated to peak concentrations should not be used. Parker and his associates⁶⁵ have shown that downstream concentrations can be predicted if the dispersion characteristics of the stream are known. The concentration due to a slug discharge⁶⁷ is

$$C = \frac{W}{2A(\pi Dt)^{1/2}} e^{-(x-\mu t)^2/4Dt}$$

where

W = mass of the activity

A = cross-sectional area

t = time

x = downstream distance

μ = mean linear flow velocity

D = diffusion coefficient in the x direction

This equation has been derived for the simplified case in which the cross-sectional area remains uniform. In most actual situations the cross-sectional area of a stream increases downstream and varies with changes in discharge. The diffusion coefficient and flow velocity also vary with the discharge rate. Furthermore, the equation yields only the average concentration of the cross section. This approximation is valid provided the measurements are made far enough downstream that complete lateral mixing is achieved; at shorter distances corrections would be required for diffusion in the remaining two directions. Other hydraulic phenomena, such as thermal stratification, may also have a pronounced effect on the concentration profile.

If the parameters

$$Q = 4600 \text{ cu ft/sec}$$

$$D = 40 \text{ sq ft/sec}$$

$$A = 6800 \text{ sq ft}$$

$$\mu = 0.67 \text{ ft/sec}$$

$$\bar{t} = 28,800 \text{ sec}$$

where Q = mean discharge, are assumed representative for the Clinch River at the water intake to the Oak Ridge Gaseous Diffusion Plant at CRM 14.5, it is estimated that the maximum concentration at CRM 14.5 can be held to less than 10^{-3} $\mu\text{C}/\text{ml}$ of tritium for a point discharge of 970 curies.

Behavior of Tritium in Oceans and Seas

In contrast to rivers, the oceans and seas represent a vast reservoir for storing water.^{54,55} Tritium deposited into the oceans and seas, therefore, is greatly diluted by mixing processes (Refs. 14, 27, 33, and 68-70). Bainbridge^{27,68} estimated that on the basis of a simple one-compartment model, the mixing time for tritium in the ocean surface is about 3.5 years. If precipitation is the only source of tritium, the effective depth of mixing is about 40 m. If the mixing depth is assumed to be 75 m, precipitation can be considered only half of the input. Eriksson¹⁴ criticizes Bainbridge's estimate of tritium fallout over the North Pacific because it emphasizes data from continental stations. He feels that Bainbridge overestimates the amount of fallout and thus underestimates the turnover time of the mixed layer. Eriksson estimates that for a mixing depth of 75 m a 22-year turnover time would be required to give a best fit to the data. However, he acknowledges that the mixing depth and turnover time are interdependent and cannot be resolved with precision. Begemann and Libby¹⁸ estimate that the mixing time for water above the thermocline, which is at an average depth of about 100 m, is somewhat greater than one year but may be as short as five years. Movement into the ocean depths is apparently quite slow;¹⁸ however, Bowen and Sugihara⁷¹ indicate that there is about three to four times as much ⁹⁰Sr below 100 m as above. If the same ratio holds for tritium, a sizable tritium reservoir could exist in the ocean depths.

Releases of tritium in a waste-management program are likely to reach the ocean through the discharge of a river or by direct release through a pipeline to coastal waters. Direct release to coastal waters is practiced by the British.⁷² An extensive study of the mass balance of radionuclides in the Clinch River indicates that nearly all the activity moves with the water or suspended sediments;⁶⁵ in fact, only ¹³⁷Cs, which is very strongly adsorbed, is primarily associated with the suspended sediment. Nearly all the tritium released to surface streams would be expected eventually to enter oceans and seas.

Prior to the discharge of full levels of wastes into coastal waters, the British perform a series of careful analyses to determine the impact of the proposed releases.^{73,74} Amphlett⁷⁴ summarizes these stages:

- (1) Sea trials under inactive conditions are performed to determine the degree and pattern of dilution in the locality and their dependence on tides, wind, and distance of the discharge point from the shore. Although existing hydrological data can be used, further work is usually required to obtain precise figures.
- (2) Studies of biological concentration factors are made to determine their effect upon the initial dilution pattern, particularly for species used as food.
- (3) Maximum safe discharge levels are calculated on the basis of the results of (1) and (2) and the accepted maximum permissible concentrations. The latter will be less restrictive for oceans than for river disposal since oceans, except in special cases, are not concerned with drinking-water tolerances but rather with contact and exposure to radiation.

- (4) Active trial discharges at a fraction of the permitted discharge level are observed over a long period to confirm the results predicted and if possible to obtain more precise data for calculating safe discharge limits.

In contrast to oceans, Lake Michigan has complete vertical mixing each year.⁷⁵ McMahon⁷⁶ found that complete mixing occurs in Perch Lake, a small lake at the Chalk River site; a low tritium concentration near one of the shore lines is considered to be due to the presence of a subterranean spring.

As mentioned in the quotation from C. B. Amphlett, releases into freshwater are more restrictive because this water may be used directly for drinking, whereas ocean waters, especially those moderately contaminated by localized releases, will probably not be widely used for direct human consumption. Ships at sea often evaporate seawater to supply drinking water, but the feedwater is not likely to be contaminated to the same extent as that water in the immediate vicinity of a liquid release near the seashore.

RELEASE TO GROUNDWATER

At present a large fraction of the tritium produced on the North American continent is released into the ground.⁷⁷⁻⁸⁰ These releases of tritium have not resulted in any hazards, but they serve as tracers for predicting the migration of other more hazardous radionuclides. At Hanford approximately one-half to two-thirds of the theoretical production of fission-product tritium is released to the ground.⁷⁷ The tritium content of the groundwater shows preferential directional movement toward the Columbia River, and the general behavior of movement is in agreement with the movement expected on the basis of the hydrology and geology of the site. Concentrations of 10^{-3} $\mu\text{c}/\text{ml}$, the recommended maximum concentration in drinking water for continuous nonoccupational exposure, have been observed in monitoring wells located up to six miles from the disposal area. However, these waters are on the Hanford reservation and are not exploited, and no significant contamination of off-site water supplies is anticipated from current practices.

At Savannah River nearly all the tritiated water from the aqueous stream used in fuel reprocessing is discharged to open seepage pits, and most of this tritium enters the ground.⁷⁸ The tritium must move a distance ranging from 500 to 2000 ft before entering surface waterways.⁸¹ Movement of the groundwater is irregular; most of the movement has been through sandy strata or sand-filled clastic dikes.⁸¹⁻⁸²

At Chalk River a detailed study has been made of the movement of tritium from the liquid disposal area toward Perch Lake.⁷⁹ On the basis of the rate of movement of groundwater, about four to six years would be required for the tritium front to reach

Perch Lake. Owing to dispersion in the formation, however, a breakthrough of 10% of the concentration of the major breakthrough occurred about two years before the predicted arrival of the major front.

Approximately 18,000 curies of tritium was released to the ground at the National Reactor Testing Station⁸⁰ between 1953 and 1965. Tritium has been detected in groundwater over an area of about 75 square miles downgrade from the disposal well. An attempt was made to determine longitudinal and lateral dispersion coefficients, but the direction of flow could not be adequately described to get a good fit of the limited amount of data to a theoretical dispersion equation.

Tritium was also released to waste seepage pits at the Oak Ridge National Laboratory during the period 1952 to March 1966, but only cursory results on movement have been obtained.⁸³ Tracer studies⁸⁴ with injections of tritiated water in the seepage-pit area indicate that the median groundwater velocity in the area is about 0.5 ft/day.

Tritium is released directly to the ground by the underground detonation of nuclear devices, especially fusion devices.^{85,86} Essentially all the released tritium is assumed to form water, either by oxidation or exchange.⁸⁵ If the exchange of tritium between the tritiated water and the rock matrix is negligible, it is estimated that the tritium concentration would be about 3 $\mu\text{c}/\text{ml}$ in the crushed zone; outside this zone the concentration of tritium could be reduced only by dilution and dispersion in nearby groundwaters. The actual tritium concentrations that would be attained would, of course, be dependent on the extent of the crushed zone, the water content of the formation, and the amount of venting of tritium that occurred. In addition, any high-temperature reaction between tritium and the minerals of the formation would be expected to reduce the quantity of tritium available for contamination of the groundwater.

In general, the velocity of groundwater flow ranges from about 5 ft/year to about 5 ft/day, though in highly permeable aquifers the velocity may be several hundred feet per day.⁸⁷⁻⁹¹ Thus the storage time for groundwater is usually on the order of a few years. In deep subsurface strata, flow velocities may be on the order of a few inches per year,⁸⁷ and the storage time³⁹ may be greater than 50 years. In fact, residence times for the deep formations may be on the order of tens of thousands of years.^{39,92}

The age or storage time of groundwater cannot be determined exactly by assuming simple exponential decay of tritium from its time of entry into the ground because the mixing from hydrodynamic dispersion and diffusion influences the concentration.⁴⁷ The magnitude of this dispersion in the field is much greater than that measured in the laboratory and could result in significant spreading of a contaminant.⁹³ According to Theis,^{93,94} a wide range of permeabilities exists in any suite of sedimentary beds that is approximately exponential in character. Part of these effects is reflected in a more or less statistical variation of flow velocities over a wide range, but some variations may be due to the presence of lenses that are so extensive that they cannot be treated statistically.^{93,94} Thus, owing to dispersive phenomena, the magnitude of spreading that is likely to occur in a formation is almost impossible to predict a priori. The

geology and general hydrology of an area should be well defined before tracer tests are interpreted for determining the rates of movement and the degree of dispersion.

Where tritiated water is released to the ground near the surface, hydrologic studies would need to be undertaken to determine the transit times to surface waters. Tracer studies could be employed to estimate the magnitude of the dispersion that would likely occur. This information could then be used to estimate the loss of tritium by radioactive decay during its movement from the point of injection to its entry into surface water. Storage time would need to be on the order of a few half-lives of tritium, (a storage time of a few decades) however, to achieve any significant advantage over direct release to surface streams. Storage times of this magnitude, and longer, would be much easier to attain if deep permeable formations were used for disposal. Tritium could then be isolated from man's environment until it had decayed to innocuous levels.^{8,7,9,5}

Blomeke^{3,6} suggests that the total aqueous effluent from a fuel-reprocessing plant with a Purex process flow sheet may be as much as 10^6 gal/ton of fuel processed. Although the fission-product tritium would be concentrated in a smaller volume of process water, this larger amount of water would be available for dilution of the tritium prior to its release from the plant. If the production^{3,6} of tritium amounts to 200 curies/ton, the concentration of tritium in the aqueous effluent would be about $0.05 \mu\text{c/ml}$, or about 50 times the recommended maximum concentration in drinking water for continuous nonoccupational exposure. A containment time of 70 years would be required for decay to permissible concentrations.

Blomeke^{3,6} also indicates that if process waters are recirculated, except for the concentrated raffinate, concentrations would reach about 33 times the initial values. The tritium removed from the system would be stored with high-level wastes until subjected to further treatment. Total recycle is technically possible, but it could be rather complex since other fission products would tend to build up activity levels in various streams.

SUMMARY

Tritium released to the environment is usually converted to the oxide form quite rapidly and is dispersed like ordinary water. The relatively large mass difference between ordinary water and tritiated water has some influence on its properties. For example, the vapor pressure of T_2O is lower than that of ordinary water;^{9,6} hence, tritium would tend to become enriched in the condensed phase. In general, the circulation of tritium would be expected to closely parallel the circulation of water.

REFERENCES

1. F. Begemann, The Natural Tritium Economy of the Earth and the Question of Its Variation with Time, *Chimia*, **16**(1): 1-10 (January 1962).
2. W. F. Libby, Radioactive Fallout, *Proc. Nat. Acad. Sci. U. S.*, **44**: 800-820 (August 1958).
3. R. Bibron, *Detection of Atmospheric Tritium by Scintillation. Variations in Its Concentration in France*, French Report CEA-R-2629, 1965.
4. F. Begemann, *Earth Science and Meteorites*, pp. 169-187, North Holland Publishing Co., Amsterdam, 1963.
5. W. F. Libby, Moratorium Tritium Geophysics, *J. Geophys. Res.*, **68**: 4485-4494 (August 1963).
6. K. F. Bishop et al., The Tritium Content of Atmospheric Methane, in *Tritium in the Physical and Biological Sciences*, Symposium Proceedings, Vienna, 1961, Vol. 1, pp. 55-67, International Atomic Energy Agency, Vienna, 1962 (STI/PUB/39).
7. R. Bibron et al., Physique De L'Atmosphere, Evolution de la Concentration du Tritium dans les eaux de Precipitation en France, *Compt. Rend.*, **256**: 4951-4954 (June 5, 1963).
8. R. Wolfgang, Origin of High Tritium Content of Atmospheric Methane, Hydrogen, and Stratospheric Water, *Nature*, **192**: 1279-1280 (Dec. 30, 1961).
9. F. Hagemann et al., Stratospheric Carbon-14, Carbon Dioxide, and Tritium, *Science*, **130**: 542-552 (Sept. 4, 1959).
10. J. R. Gat, U. Karfunkel, and A. Nir, Tritium Content of Rainwater from the Eastern Mediterranean Area, in *Tritium in the Physical and Biological Sciences*, Symposium Proceedings, Vienna, 1961, Vol. 1, pp. 41-54, International Atomic Energy Agency, Vienna, 1962 (STI/PUB/39).
11. A. K. Stebbins III, *Technical Analysis Report, Second Special Report on the High Altitude Sampling Program (HASP)*, Report DASA539B, Defense Atomic Support Agency, August 1961.
12. E. W. Barrett and L. Huebner, *Atmospheric Tritium Analysis. Technical Progress Report No. 3*, USAEC Report TID-14425, University of Chicago, Nov. 27, 1961.
13. E. A. Martell, On the Inventory of Artificial Tritium and Its Occurrence in Atmospheric Methane, *J. Geophys. Res.*, **68**(13): 3759-3769 (July 1, 1963).
14. E. Eriksson, An Account of the Major Pulses of Tritium and Their Effects in the Atmosphere, *Tellus*, **17**(1): 118-130 (February 1965).
15. F. Begemann, New Measurements on the World-Wide Distribution of Natural and Artificially Produced Tritium, in *Proceedings of the Second United Nations International Conference on Peaceful Uses of Atomic Energy, Geneva, 1958*, Vol. 18, pp. 545-550, United Nations, New York, 1958.
16. C. B. Taylor, *Tritium in Southern Hemisphere Precipitation, 1953-1964*, New Zealand Report INS-R-32, August 1964.
17. C. B. Taylor, H. A. Polach, and T. A. Rafter, *Tritium Measurements in Nature. A Review of the Work of the Tritium Laboratory Institute of Nuclear Sciences, New Zealand*, New Zealand Report INS-R-24, July 1963.
18. F. Begemann and W. F. Libby, Continental Water Balance, Ground Water Inventory and Storage Times, Surface Ocean Mixing Rates and World-Wide Water Circulation Patterns from Cosmic-Ray and Bomb Tritium, *Geochim. Cosmochim. Acta*, **12**(4): 277-296 (1957).
19. A. Walton, E. L. Fisher, and P. W. Krey, *Studies of Nuclear Debris in Precipitation*, USAEC Report NYO-9532, New York Operations Office, May 31, 1962.
20. E. W. Barrett and L. Huebner, *Atmospheric Tritium Analysis, Technical Progress Report No. 2*, USAEC Report AECU-4739, University of Chicago, Feb. 16, 1960.
21. R. M. Brown and W. E. Grummitt, The Determination of Tritium in Natural Waters, *Can. J. Chem.*, **34**: 220-226 (March 1956).

22. B. Bolin, *Research in Geophysics*, Vol. 2, pp. 479-508, The M.I.T. Press, Cambridge, Mass., 1964.
23. P. Harteck, The Relative Abundance of HT and HTO in the Atmosphere, *J. Chem. Phys.*, 22(10): 1746-1751 (October 1954).
24. M. J. Engelke and E. A. Bemis, Jr., *A Study of the Diffusion and Mixing of Tritium Gas in Air*, USAEC Report LA-2671, Los Alamos Scientific Laboratory, January 1962.
25. F. Verniani, The Total Mass of the Earth's Atmosphere, *J. Geophys. Res.*, 71: 385-391 (Jan. 15, 1966).
26. N. A. Lange and G. M. Forker (Comps. and Eds.), *Handbook of Chemistry*, p. 169, McGraw-Hill Book Company, Inc., New York, 1961.
27. A. E. Bainbridge, Tritium in Surface Waters of the North Pacific, in *Nuclear Geophysics*, pp. 129-137, National Academy of Sciences, National Research Council, Washington, D. C., 1963.
28. G. Wust, Gesetzmässige Wechselbeziehungen Zwischen Ozean und Atmosphäre in den zonalen Verteilungen von Oberflächensalzgehalt, Verdunstung und Niederschlag, *Arch. Meteorol. Geophys. Bioklimatol., Ser. A*, 7: 305-329 (1954); as referenced by Eriksson (Ref. 14).
29. W. Gorczymski, *Comparison of Climate of US and Europe*, Polish Institute of Arts and Science in America, New York, 1945; p. 71 as referenced in E. L. Fireman, Measurement of the (n, H^3) Cross Section in Nitrogen and Its Relationship to the Tritium Produced in the Atmosphere, *Phys. Rev.*, 91(4): 922-926 (Aug. 15, 1953).
30. B. Bolin, *An Investigation of Tritium in Atmospheric Moisture. Rainwater and the Sea in the European Area*, USAEC Report TID-13376, July 1, 1961.
31. A. C. Chamberlain and A. E. J. Eggleton, Washout of Tritiated Water Vapour by Rain, *Int. J. Air Water Pollut.*, 8: 135-149 (February 1964).
32. G. Israel et al., Seasonal Variations of Bomb-Produced Tritium in Rain, *J. Geophys. Res.*, 68: 3771-3773 (July 1, 1963).
33. R. M. Brown, Tritium in Precipitation at Canadian Sites, 1953-1963, in *Tritium and Other Environmental Isotopes in the Hydrological Cycle*, Technical Report Series, No. 73, International Atomic Energy Agency, Vienna, 1964 (STI/DOC/10/73).
34. P. J. Barry, *Maximum Permissible Concentrations of Radioactive Nuclides in Airborne Effluents from Nuclear Reactors*, Canadian Report CRER-1098, October 1962.
35. A. Doury, Risks Presented by the Diffusion of Large Quantities of Tritium in the Atmosphere, in *Seminaire sur la Protection Contre les Dangers du Tritium*, Service Central de Protection Contre des Rayonnements Ionisants, pp. 17-26, le Vesinet, Avril 16-18, 1964.
36. J. O. Blomeke, *Management of Fission Product Tritium in Fuel Processing Wastes*, USAEC Report ORNL-TM-851, Oak Ridge National Laboratory, May 4, 1964.
37. L. D. Baver, *Soil Physics*, John Wiley & Sons, Inc., New York, 1956.
38. K. Rankama and T. G. Sahama, *Geochemistry*, pp. 316-318, The University of Chicago Press, Chicago, 1949.
39. C. W. Carlston, Use of Tritium in Hydrologic Research—Problems and Limitations, *Bull. Int. Ass. Sci. Hydrology*, (3): 38-42 (September 1964).
40. J. P. Griffiths, *Applied Climatology*, p. 99, Oxford University Press, Amer. House, London, 1966.
41. R. J. Morton (Ed.), *Status Report No. 1 on Clinch River Study*, USAEC Report ORNL-3119, Oak Ridge National Laboratory, Aug. 4, 1961.
42. R. M. Brown, Hydrology of Tritium in the Ottawa Valley, *Geochim. Cosmochim. Acta*, 21: 199-216 (January 1961).
43. R. M. Brown, Tritium in the Ottawa River, in *Progress Report, Biology and Health Physics Division, October 1 to December 31, 1964*, Canadian Report PR-B-64, pp. 18-19, October–December 1964.
44. E. Eriksson, Atmospheric Tritium as a Tool for the Study of Certain Hydrologic Aspects of River Basins, *Tellus*, 15: 303-308 (August 1963).

45. C. W. Carlston, Tritium-Hydrologic Research: Some Results of the U. S. Geological Survey Research Program, *Science*, **143**: 804-806 (Feb. 21, 1964).
46. P. Joergensen and I. Rosenqvist, Replacement and Bonding Conditions for Alkali Ions and Hydrogen in Dioctahedral and Trioctahedral Micas, *Norsk Geol. Tidsskr.*, **43**: 497-536 (December 1963).
47. J. J. Koranda, Preliminary Studies of the Persistence of Tritium and ^{14}C in the Pacific Proving Ground, *Health Phys.*, **11**: 1445-1457 (December 1965).
48. A. Nir, On the Interpretation of Tritium "Age" Measurements of Groundwater, *J. Geophys. Res.*, **69**: 2589-2595 (June 15, 1964).
49. F. S. Nakayama and R. D. Jackson, Diffusion of Tritiated Water in Soils, *Soil Sci. Soc. Amer. Proc.*, **27**(3): 255-258 (May-June 1963).
50. A. R. G. Lang and S. G. Mason, Tritium Exchange Between Cellulose and Water: Accessibility Measurements and Effects of Cyclic Drying, *Can. J. Chem.*, **38**: 373-387 (March 1960).
51. K. Kigoshi, *Natural Concentration of Krypton-85, Carbon-14, and Tritium in Recent Years*, Report A/AC.82/G/L.693, August 1961.
52. K. Kigoshi and Y. Tomikura, Tritium and Carbon-14 in the Tree Rings, *Bull. Chem. Soc. Jap.*, **34**: 1738-1739 (November 1961).
53. R. M. Brown, *Activities of AECL in the Fields of Biology, Health Physics and Medicine*, p. 11, Canadian Report AECL-2107, November 1964.
54. F. W. Woods and D. O'Neal, Tritiated Water as a Tool for Ecological Field Studies, *Science*, **147**: 148-149 (Jan. 8, 1965).
55. R. L. Nace, Water Management, Agriculture, and Groundwater Supplies, in *Water and Agriculture*, edited by R. D. Hockensmith, pp. 43-61, The Horn Shafer Company, Baltimore, 1960.
56. H. V. Sverdup et al., *The Oceans—Their Physics, Chemistry and General Biology*, pp. 8-46, Prentice-Hall, Inc., Englewood Cliffs, N. J., 1942.
57. R. J. Morton (Ed.), *Status Report No. 2 on Clinch River Study*, USAEC Report ORNL-3202, Oak Ridge National Laboratory, Apr. 13, 1962.
58. F. L. Parker, Movement of Radionuclides in the Clinch River, in *Proceedings of the Third Sanitary Engineering Conference, Nashville, Tennessee, May 25, 1964*, pp. 78-87, 1964 (CONF-772).
59. R. J. Morton (Ed.), *Status Report No. 4 on Clinch River Study*, USAEC Report ORNL-3409, Oak Ridge National Laboratory, Sept. 25, 1963.
60. M. Kato et al., A Study in River Engineering Based on the Results of Field Measurements of Flow Velocities with Radioisotopes in the Sorachi River, Japan, in *Radioisotopes in Hydrology*, Symposium Proceedings, Tokyo, 1963, pp. 89-110, International Atomic Energy Agency, Vienna, 1963 (STI/PUB/71).
61. C. G. Clayton and D. B. Smith, A Comparison of Radioisotope Methods for River Flow Measurements, in *Radioisotopes in Hydrology*, Symposium Proceedings, Tokyo, 1963, pp. 1-24, International Atomic Energy Agency, Vienna, 1963 (STI/PUB/71).
62. R. J. Morton (Ed.), *Status Report No. 3 on Clinch River Study*, USAEC Report ORNL-3370, Oak Ridge National Laboratory, Dec. 6, 1962.
63. E. G. Struxness et al., *Comprehensive Report of the Clinch River Study*, USAEC Report ORNL-4035, Oak Ridge National Laboratory, April 1967.
64. R. M. Brown, Possible NPD Tritium in the Ottawa River, in *Progress Report, Biology and Health Physics Division, July 1 to September 30, 1963*, Canadian Report PR-B-59, pp. 16-17, July-September, 1963.
65. F. L. Parker et al., Dilution, Dispersion and Mass Transport of Radionuclides in the Clinch and Tennessee Rivers, in *Disposal of Radioactive Wastes into Seas, Oceans, and Surface Waters*, Symposium Proceedings, Vienna, May 16-20, 1966, pp. 33-55, International Atomic Energy Agency, Vienna, 1966 (STI/PUB/126).

66. International Commission on Radiological Protection, Recommendations of the ICRP, International Commission on Radiological Protection Publication No. 6, Pergamon Press, Inc., New York, 1964.
67. F. L. Parker, Radioactive Tracers in Hydrologic Studies, *Trans. Amer. Geophys. Union*, 39: 434-439 (June 1958).
68. A. E. Bainbridge, Tritium in the North Pacific Surface Water, *J. Geophys. Res.*, 68: 3785-3789 (July 1, 1963).
69. H. von Buttlar and W. F. Libby, Natural Distribution of Cosmic-Ray Produced Tritium II, *J. Inorg. Nucl. Chem.*, 1(1): 75-91 (1955).
70. L. L. Thatcher and C. M. Hoffman, Tritium Fallout over North America from the Soviet Tests in 1961, *J. Geophys. Res.*, 68: 5899-5901 (Oct. 15, 1963).
71. V. T. Bowen and T. T. Sugihara, Strontium-90 in the Mixed Layer of the Atlantic Ocean, *Nature*, 186(4718): 71-72 (April-June 1960).
72. H. J. Dunster and L. F. U. Wix, The Practice of Waste Disposal in the United Kingdom Atomic Energy Authority, in *Disposal of Radioactive Wastes*, Symposium Proceedings, Monaco, 1959, Vol. I, pp. 403-409, International Atomic Energy Agency, Vienna, 1960 (STI/PUB/18).
73. F. Morgan, Fisheries Radiobiology and the Discharge of Radioactive Wastes, in *Disposal of Radioactive Wastes*, Symposium Proceedings, Monaco, 1959, Vol. II, pp. 17-24, International Atomic Energy Agency, Vienna, 1960 (STI/PUB/18).
74. C. B. Amphlett, *Treatment and Disposal of Radioactive Wastes*, pp. 222-230, Pergamon Press, Inc., New York, 1961.
75. S. Kaufman and W. F. Libby, The Natural Distribution of Tritium, *Phys. Rev.*, 93(6): 1337-1344 (Mar. 15, 1954).
76. J. W. McMahon, *The Dispersion of Tritium in Perch Lake*, Canadian Report AECL-1889, January 1964.
77. W. A. Haney, D. J. Brown, and A. E. Reisenauer, *Fission Product Tritium in Separations Wastes and in the Groundwater*, USAEC Report HW-74536, Hanford Atomic Products Operation, Aug. 1, 1962.
78. J. H. Horton, *Fission Product Tritium at the Savannah River Plant*, USAEC Report DPSPU-63-30-38B, Savannah River Laboratory, October 1963.
79. P. J. Parsons, *The Movement of Tritium from the Chalk River Liquid Disposal Area*, Canadian Report CRER-1146, April 1963.
80. D. B. Hawkins and B. L. Schmalz, *Environment Tritium Studies at the National Reactor Testing Station*, USAEC Report IDO-12043, Idaho Operations Office, August 1965.
81. S. O. Reichert, Radionuclides in Groundwater at the Savannah River Plant Waste Disposal Facilities, *J. Geophys. Res.*, 67: 4363-4374 (October 1962).
82. J. H. Horton and D. I. Ross, Use of Tritium from Spent Uranium Fuel Elements as a Groundwater Tracer, *Soil Sci.*, 90(5): 267-271 (November 1960).
83. W. de Laguna, Oak Ridge National Laboratory, unpublished, July 31, 1964.
84. T. F. Lomenick, D. G. Jacobs, and E. G. Struxness, The Behavior of Strontium-90 and Cesium-137 in Seepage Pits at ORNL, *Health Phys.*, 13(8): 897-906 (August 1967).
85. F. W. Stead, Tritium Distribution in Groundwater Around Large Underground Fusion Explosions, *Science*, 142(3596): 1163-1165 (Nov. 29, 1963).
86. F. L. Culler et al., Cane Program, in *Chemical Technology Division Annual Progress Report for Period Ending June 30, 1962*, pp. 207-208, USAEC Report ORNL-3314, Oak Ridge National Laboratory, Sept. 21, 1962.
87. J. E. Galley, Geologic Basin Studies as Related to Deep-Well Disposal, in *Second Ground Disposal of Radioactive Wastes Conference, Held at Atomic Energy of Canada Limited, Chalk River, Canada, Sept. 26--29, 1961*, USAEC Report TID-7628, pp. 347-355, March 1962.
88. A. Clebsch, Jr., and J. A. Lieberman, The Possibility of Groundwater Contamination by Fallout, in *Radioactive Fallout from Nuclear Weapons Tests, Proceedings of a Conference held*

- in *Germtantown, Maryland, November 15-17, 1961*, pp. 306-311, USAEC Report TID-7632, February 1962.
89. H. von Buttlar, Investigating Groundwater by Analysis of Atmospheric Tritium, *J. Amer. Water Works Ass.*, **50**: 1533-1538 (November 1958).
90. W. F. Merritt, Routine Measurements of Groundwater Velocity Using ^{35}S , *Health Phys.*, **8**: 185-189 (March-April 1962).
91. B. Blavoux, Hydrodynamics and Content of Tritium in the Waters of the Evian Basin (France), *Compt. Rend.*, **259**: 4323-4326 (December 1964).
92. J. C. Vogel and D. Ehhalt, The Use of Carbon Isotopes in Groundwater Studies, in *Radioisotopes in Hydrology*, Symposium Proceedings, Tokyo, 1963, pp. 383-395, International Atomic Energy Agency, Vienna, 1963 (STI/PUB/71).
93. C. V. Theis, Hydrologic Phenomena Affecting the Use of Tracers in Timing Groundwater Flow, in *Radioisotopes in Hydrology*, Symposium Proceedings, Tokyo, 1963, pp. 193-206, International Atomic Energy Agency, Vienna, 1963 (STI/PUB/71).
94. C. V. Theis, Notes on Dispersion in Fluid Flow by Geologic Features, in *Second Ground Disposal of Radioactive Wastes Conference, Held at Atomic Energy of Canada Limited, Chalk River, Canada, Sept. 26-29, 1961*, USAEC Report TID-7628, pp. 166-178, March 1962.
95. The American Association of Petroleum Geologists, *Radioactive Waste-Disposal Potentials in Selected Geologic Basins-A Reconnaissance Study*, USAEC Report SAN-413-2, June 24, 1964.
96. M. M. Popov and F. I. Tazetdinov, The Vapor Pressure of T_2O , USAEC File No. NP-tr-534, translated from *At. Energ. USSR*, **8**: 420-424 (1960), 1961.

7 PROJECTED TRITIUM PRODUCTION IN A NUCLEAR POWER ECONOMY AND ITS IMPACT ON LOCAL AND WORLDWIDE POPULATIONS

Although tritium is produced by a number of reactions, the amount of tritium produced by fission probably exceeds the amount produced from all other sources in light-water-cooled reactors. Fission-product tritium^{1,2} is produced with a yield of about 0.01%. Some tritium may penetrate fuel-element cladding and escape into the coolant,³ but most of it is apparently retained until the fuel is reprocessed.^{2,4,5} Other possible major sources of tritium include heavy-water reactor stations, thermonuclear detonations, and, perhaps, thermonuclear reactors.

PROJECTED RELEASES OF TRITIUM

Approximations of projected civilian nuclear power production in the free world, based on Atomic Energy Commission reports to the President,^{6,7} were used to estimate the annual production rate of fission-product tritium (Table 7.1).⁸ These projections were based on data from light-water-cooled reactors having a thermal

Table 7.1

**PRODUCTION OF FISSION-PRODUCT TRITIUM IN
FREE-WORLD NUCLEAR POWER ECONOMY**

Year	Power production		Tritium production rate, 10 ⁶ curies/year	Accumulated tritium, 10 ⁶ curies
	10 ³ Mw(e)*	10 ³ Mw(th)†		
1965	1.9	6.2	0.03	0.03
1970	9.6	31	0.1	0.3
1975	46	150	0.7	2
1980	120	390	2	6
1985	240‡	780	3	16
1990	430‡	1300	6	32
1995	670‡	2200	10	58
2000	1030	3320	15	96
Steady state	1030	3320	15	260§

*Assumed load factor of 0.80 to 1980 and 0.70 at 2000.

†Assumed thermal efficiency of 0.31.

‡Interpolated values.

§Based on a continued production rate at the level predicted for the year 2000.

efficiency of 0.31 with load factors of 0.8 until 1980 which decreased to 0.07 at the year 2000. The total capacity of the free world was assumed to be double the projected capacity of the United States. The yield of tritium was assumed to be 10^{-4} atom/fission, and a half-life of 12.36 years (reported by Eichelberger, Grove, and Jones⁹) was used to estimate the accumulation of tritium. Accumulation was calculated by allowing the tritium produced during a given 5-year period to decay for an effective time of 2.5 years and then adding this value to the previously accumulated quantity corrected for decay during an effective time of 5 years. Under current technology, practically all the tritium produced by fission is released to the environment with waste streams during fuel reprocessing.^{4,5}

Holmquist,¹⁰ after reviewing the operating experiences of heavy-water reactors, concluded that no reactor can be assumed to have a leakage rate lower than 2 to 3% per year of the heavy-water inventory. Bergstrom, Devell, and Gebert¹¹ indicate that the pressurized heavy-water reactor being designed for India will have a power rating of 350 Mw(e), a heavy-water inventory of 1.5×10^5 kg, a tritium concentration of 11 curies/kg of D₂O after 10 years of operation, and an equilibrium tritium concentration of 22 curies/kg of D₂O. Assuming that an annual loss of 3% of the D₂O coolant at a tritium concentration of 11 curies/kg of D₂O will be representative for tritium releases from heavy-water reactors, we can estimate that tritium releases from such reactors

will be a factor of 10 higher than the release of fission-product tritium from a fuel-reprocessing plant servicing reactors producing an equivalent amount of electric power. Thus, if heavy-water reactors comprise 10% of the electric-power-producing capacity in a nuclear economy, the production and accumulation rates for tritium will be double the values given in Table 7.1. Holmquist¹⁰ states that in the normal operation of heavy-water reactors tritium is as important as all the other radionuclides combined because of its appreciable vapor pressure.

Thermonuclear power is currently being developed.¹² Fusion reactors involving deuterium-tritium reactions require much less severe conditions than those involving deuterium-deuterium reactions,¹³ and hence there is a demand for the production of larger quantities of tritium for use as thermonuclear fuel. One of the advantages often mentioned for thermonuclear reactors is that they produce little radioactive waste.¹³ Homeyer¹² gives a schematic diagram for a thermonuclear reactor designed to produce 312 Mw(e) by deuterium-tritium reactions. The reactor would require 228 g of tritium/day, half of which is recovered from unburned fuel. This amount means an annual tritium requirement of 2.6×10^6 curies for each megawatt of electrical production capacity. Assuming that 10% excess tritium is produced,¹⁴ the excess tritium would amount to nearly 2×10^4 times the production of fission-product tritium for an equivalent fission-reactor power plant. Because of the large quantities of tritium that must be handled, efficient recovery will be essential.¹⁴

As indicated in Chap. 3, the most probable value of natural tritium production ranged from 0.5 to 1.0 atom/cm²/sec. This value would amount to an annual production of about 4 to 8 megacuries and would give rise to a steady-state tritium inventory of 70 to 140 megacuries. On the basis of these projections, the rate of production of fission-product tritium would begin to exceed the rate of natural tritium production by about 1990.

IMPACT OF TRITIUM RELEASED TO THE ENVIRONMENT

As previously mentioned, under current technology practically all fission-product tritium is released to the environment during the reprocessing of reactor fuels.^{2,4,5} Releases are made to the atmosphere through stacks and to the ground or to surface waters in low-level liquid wastes. Only 2 to 5% of the total fission-product tritium is retained in tanks with high-level raffinates.⁵ There is considerable discrepancy concerning the relative amounts of tritium released via stacks. Albenesius and Ondrejcin² found that about 25% of the fission-product tritium is released in a gaseous phase during fuel dissolution. Haney, Brown, and Reisenauer⁴ indicate that 47 to 64% of the tritium from fuel reprocessing is discharged in liquid-waste streams and that most of the remaining 36 to 53% of the tritium is considered to be released in a gaseous phase or retained with high-level wastes. Goode,¹⁵ however, measured the

release of tritium during the dissolution of oxide fuels and found that it equaled only about 0.2% of the amount produced by fission. The reasons for these discrepancies are not certain; discrepancies may result from differences in the type of fuel processed or from the procedures used in processing.

Some of the tritium may be released as HT gas through the stacks. Albenesius and Ondrejcin² and Haney, Brown, and Reisenauer⁴ indicate that about 25% of the tritium discharged through stacks was gaseous HT, the remainder being discharged in the HTO vapor phase. The tritium released as HT gas would be expected to oxidize at a rate ranging from 0.2 to 3% per day.¹⁶ Once tritium has been converted to the oxide form, it will be dispersed in much the same manner as ordinary water. However, the rather large mass difference between ordinary water and tritiated water has some influence on relative properties; for example, the vapor pressure of T₂O is lower than that of ordinary water.¹⁷ As a result, after tritium is condensed to liquid, it reevaporates less than ordinary water.

WORLDWIDE DISTRIBUTION OF TRITIUM

As indicated in Chap. 3, most of the naturally produced tritium is found in the hydrosphere; the oceans and seas are the largest reservoirs. The total quantity of water available for diluting tritium was estimated by assuming that tritium is mixed in oceans and seas¹⁸⁻²⁰ to a depth of 75 m, that all the water in stream channels and in the atmosphere is in circulation, and that only the portion of the groundwater in the root zone is available for mixing. The volumes of these various reservoirs of water were obtained from Nace²¹ and from Sverdup and his associates²² and are tabulated in Table 7.2.

Table 7.2
VOLUMES OF CIRCULATING WATER

	Volume of water, m ³	
	Total	North latitude (30 to 50°)
Oceans and seas (surface to a depth of 75 m)	2.70×10^{16}	2.68×10^{15}
Stream channels (av.)	1.17×10^{13}	2.51×10^{12}
Atmospheric moisture (av.)	1.29×10^{14}	1.72×10^{13}
Surface water in the root zone	2.50×10^{14}	5.38×10^{13}
Total circulating water	2.74×10^{16}	2.75×10^{15}

If the differences in vapor pressure between T_2O and H_2O are disregarded and complete isotopic dilution with all the circulating water is assumed, the concentration of tritium in the hydrosphere at various times can be estimated. For example, in the year 2000, 96 megacuries of fission-product tritium will have accumulated in the world. If this amount is diluted in the total volume of circulating water, $2.74 \times 10^{16} m^3$, the resulting increase in tritium concentration will be $3.5 \times 10^{-9} \mu c/ml$. Similarly, an average of 0.47% of the water is present as atmospheric water vapor within the first 10 km of the earth's surface²³ or in about $5.1 \times 10^{18} m^3$, and the average increase in the concentration of tritium in the air would be $8.6 \times 10^{-14} \mu c/cm^3$. These increased concentrations of tritium would annually increase the average doses to body tissue of standard man by 5.6×10^{-4} mrem from drinking water and 2.6×10^{-4} mrem from inhalation and absorption of water vapor through the skin. A submersion dose of 0.1×10^{-4} mrem would be restricted to the skin owing to the low penetrating power of the emitted beta particle. The average total increase in dose to the world population as a function of time for these modes of exposure is shown in Fig. 7.1. This estimate of the dose increase from release of fission-product tritium to the environment does not include additional ingestion of tritium in the form of solids, although it does include the fluids consumed in forms other than drinking water.

Libby²⁴ indicates that half the tritium released from detonations of thermonuclear devices has fallen between 30 and 50° north latitude. If this area remains the same for releases of fission-product tritium from fuel-reprocessing plants, approximately 10% of the earth's surface will receive half the total tritium. Hence, in this important region, which covers most of the United States and much of Europe, the average concentrations may be about five times the world average.

Tritium is not likely to be distributed uniformly among the reservoirs cited because only a small fraction of the total volume of water circulates annually.²⁵ Precipitation falling on land surfaces has only a small probability of mixing; so the groundwater nearest the surface has the highest concentration of tritium. Therefore water reevaporated over land areas has nearly the same concentration as the original precipitation.^{20,26,27} On the other hand, precipitation falling on the ocean and other deep bodies of water is rather rapidly mixed to the thermocline, and the concentration of tritium is markedly reduced.¹⁸ Concentrations in the various reservoirs are expected to approach steady-state values that reflect the turnover time of the reservoir. Because of their long turnover times, the oceans and seas will have lower tritium concentrations than such reservoirs as the lower atmosphere where turnover times are much more rapid.

If nuclear power production beyond the year 2000 is maintained at the level predicted for that year, a steady-state quantity of 260 megacuries of fission-product tritium will be accumulated by about 2060. This quantity will give radiation dose levels about three times those estimated for the year 2000. Even when allowances are made for nonuniform global distribution, it appears that the worldwide dose increase due to tritium will be quite small in comparison with the 100 mrad/year received from background radiation.²⁸

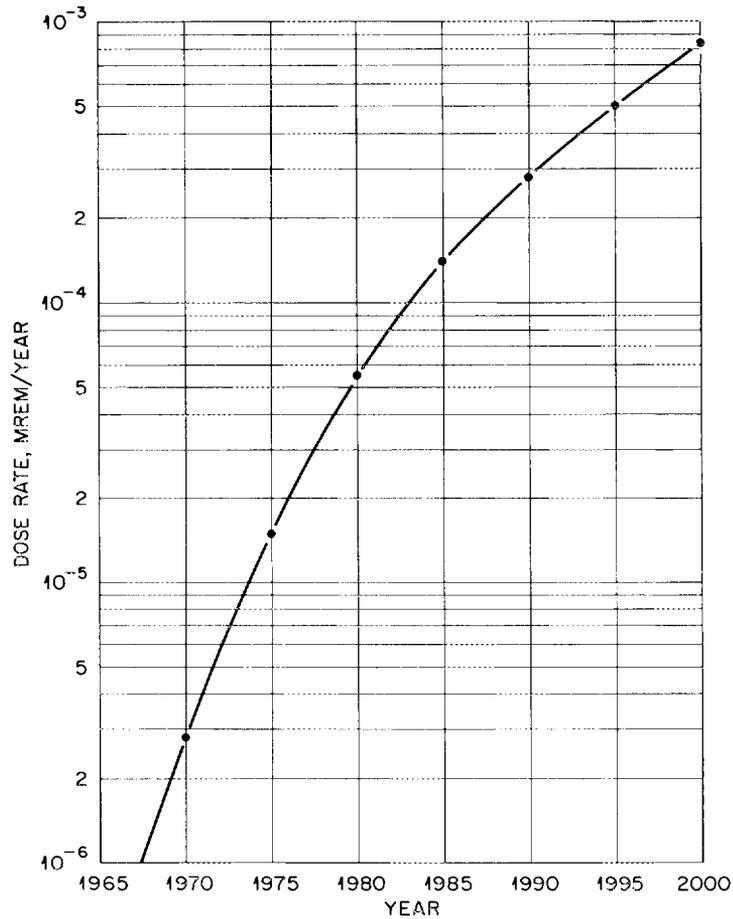


Fig. 7.1 Dose rate to body tissue of the worldwide population from tritium as a result of ingestion of drinking water and of inhalation and skin absorption of water vapor.

LOCAL DISPERSION AND DILUTION OF TRITIUM

The highest environmental concentration of tritium would be expected to exist in the area immediately surrounding the point of release. It is unlikely that all nuclear fuels will be processed at one plant, but there is an economic incentive for building large processing plants.²⁹ It is interesting to speculate as to whether environmental safety considerations will limit the size of fuel-processing plants. For didactic

purposes, we will consider the size limitations based on tritium releases for a fuel-reprocessing plant on the Oak Ridge Reservation. We must keep in mind, however, that in an actual case the probable releases of all radionuclides that make a substantial contribution to the total hazard must be considered.

Release to Surface Waters

Most of the fission-product tritium released during fuel processing has been released to the environment as water.⁵ Some of the water vapor released through stacks precipitates locally and enters surface waterways, and even a small portion of the tritium released as HT is deposited locally. Because of the uncertainty in our projected tritium-production figures, we will assume as a limiting case that all fission-product tritium will be released into surface streams.

For the Oak Ridge Reservation, the average flow of the Clinch River is 4560 cu ft/sec or 4.1×10^{12} liters/year at the confluence with White Oak Creek. The production of 100,000 Mw(th) of power would be accompanied by the production of about 440,000 curies of tritium. Annual release of this quantity of tritium into the Clinch River would produce a tritium concentration of 1.1×10^{-4} $\mu\text{c/ml}$. The annual dose to the total body from using this as the only source of drinking water would be about 11 mrem/year and would give an exposure of 0.3 rem in 30 years. Below the confluence of White Oak Creek, however, the Clinch River provides drinking water only for occupational workers at the K-25 plant. Since these workers would not use this water as their only source of fluid intake, the anticipated annual total body dose to workers at the K-25 plant would be about 4 mrem/year.

These dose levels are well below limits recommended by various agencies for the public³⁰ (see Table 7.3). These recognized authorities define a genetic dose relevant to the genetic risk imposed upon the whole population on the basis of assumptions of "no threshold" and on a "linear hypothesis."³⁰ Specifically, the authorities recommend that the genetic dose to the general population from all radiation sources, other than natural background and medical sources, should not exceed 5 rems in the interval from conception to the mean age of childbearing (30 years). Any determination of the annual genetically significant dose requires information on the number of individuals exposed as well as on the dose received by individual members. No specific recommendations are made regarding a permissible, somatically significant dose, but the limitation imposed by the genetic dose from external radiation reduces the dose to internal organs to or below the annual levels listed in Table 7.3. The same principle applies to internal exposure resulting from radionuclides contributing to the gonadal dose of a population.

Release of tritiated water to seepage pits at ORNL would not be advantageous since the holdup time for water is only about 1 year, and the decay occurring in this time would amount to only about 5%. At other sites where the holdup time in groundwater is considerably longer, ground disposal would be beneficial. Disposal into

Table 7.3
ANNUAL INDIVIDUAL DOSE LEVELS FOR THE PUBLIC³⁰

Organ or tissue	Dose, rem			
	NCRP*	FRC†	ICRP	IAEA
Gonads, red bone marrow	0.5	0.5‡	0.5	0.5
Total body	0.5	0.5‡	0.5	0.5
Lenses of eyes	0.5		0.5	0.5
Other single organs	1.5		1.5	1.5
Skin, bone, thyroid	3	1.5§	3¶	3
Hands, forearms, feet, ankles	7.5		7.5	7.5

*These levels are based on the National Commission for Radiation Protection (NCRP) recommendation that the permissible dose to members of the population at large be reduced to not more than one-tenth of the occupational values.

†The Federal Radiation Council (FRC) does not recommend radiation protection guides (RPG) for individual organ doses to the population other than gonads and whole body.

‡The FRC specifies that the RPG for gonads shall be 5 rems in 30 years for average population groups on the assumption that the majority of individuals do not vary from the average by a factor greater than 3; thus, the permissible annual dose to gonads and whole body for average population groups would be 0.17 rem.

§The FRC recommends an RPG for the thyroid of 1.5 rem/year for individual and 0.5 rem/year to be applied to the average of suitable samples of an exposed group in the population.

¶The International Commission on Radiological Protection (ICRP) recommends 1.5 rem/year to the thyroid of children up to 16 years of age.

deep, permeable formations would be advantageous, provided the formation did not supply local drinking or irrigation water.

As Blomeke⁵ stated, release of tritium to surface waters has limited applicability. Such releases would be restricted to sites that border rivers with average flows high enough to provide useful ranges of dilution.

Discharge Through Stacks

An alternative to the release of tritiated water to surface streams is the evaporation of water and discharge through stacks.³¹ Much greater environmental dispersion is

provided for atmospheric releases than for releases to surface waters because the flow lines are not so severely restricted, the velocities are much greater, and the dispersion coefficients are greater. Obviously, however, the dispersal is not uniform, and the air concentrations are highest near the point of release. Because of the variability in wind direction, speed, and the stability conditions of the atmosphere, accurate predictions of air and ground concentrations are difficult to make from a single set of conditions. An excellent review of meteorological factors requiring consideration in releases of radioactivity from stacks is given in *Meteorology and Atomic Energy—1968*.³² This reference also provides appropriate equations, nomographs, and graphical tabular displays of information for application to particular situations. Photographs and diagrams are used to enhance the effectiveness of descriptive presentations.

Atmospheric dispersion and downwind concentrations of gaseous effluents for discharge at the Oak Ridge Reservation were made by Blanco and his associates³³ with techniques and data developed by Culkowski³⁴ and Hilsmeier.³⁵ Estimates of ground concentrations were made for a source strength of 1 curie/sec from stack heights of 50 and 100 m based on meteorological data from the Tower Shielding Facility. The calculations were performed by integrating the Gaussian plume formula over crosswind directions and distributing the resultant concentration uniformly over the arc considered. The variables in the expression—wind speed and direction, frequency of occurrence, vertical diffusion coefficient, and stack height—were obtained from historical data. The concentrations resulting from continuous release through a 100-m stack are shown in Fig. 7.2.

From Fig. 7.2 the critical exposure zones appear to be the Y-12 plant, where occupational workers would be exposed, and the southwestern half of the city of Oak Ridge, where nonoccupational populations would be exposed. At the Y-12 plant, a steady-state ground-level air concentration of about $4 \times 10^{-7} \mu\text{c}/\text{cm}^3$ would result from the continuous release of 1 curie/sec through a 100-m stack. At the rate of release of tritium from the processing of fuel for 100,000 Mw(th) production, 1.4×10^{-2} curie/sec, the resulting concentration would be about $6 \times 10^{-9} \mu\text{c}/\text{cm}^3$. If the stack release occurred as HTO, the average annual dose to the total body through inhalation and skin absorption of HTO for a 40-hr exposure per week would be about 4 mrem/year.

At the edge of the city of Oak Ridge, the steady-state ground-level air concentration would reach $1.1 \times 10^{-9} \mu\text{c}/\text{cm}^3$. The exposure in this area would be effective 168 hr a week, and the average annual total body dose through inhalation and skin absorption of HTO would be about 7 mrem/year.

These estimates do not consider the effect of washout or deposition on the deflection of the cloud. Cowser and his associates³⁶ have considered these phenomena and concluded that the ground-level air concentrations would not be reduced significantly by washout. Deposition of HTO is difficult to assess because of the complications arising from the reevaporation of water from the land surface. Thus the land surface can act as either a source or a sink, depending on the direction and magnitude of water movement.

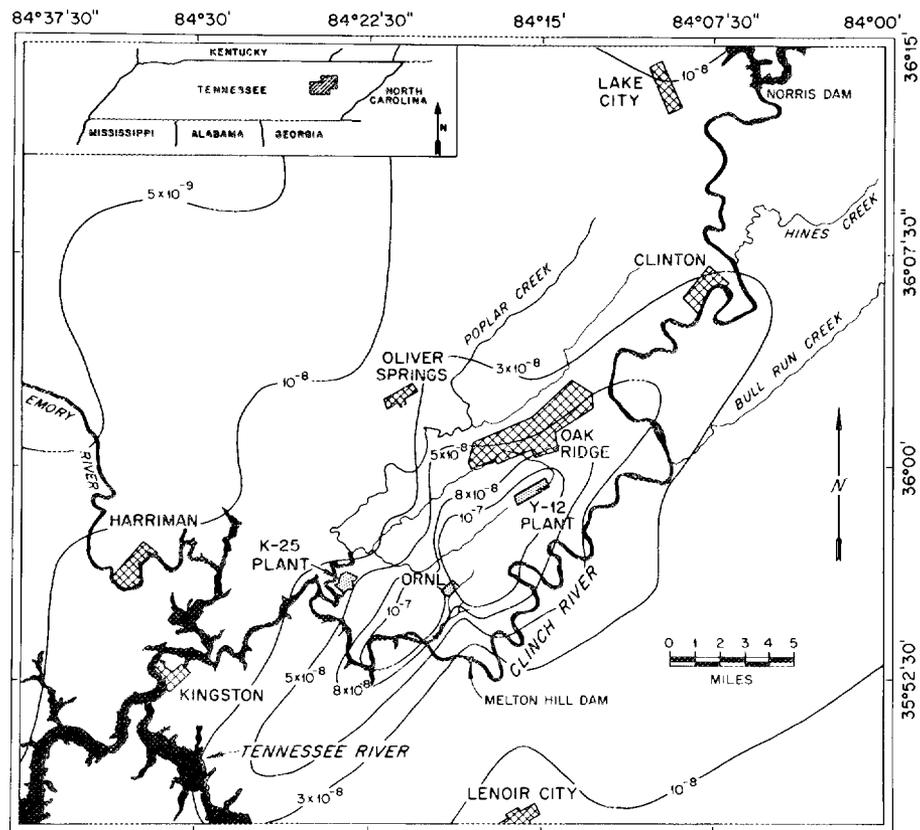


Fig. 7.2 Average annual air concentrations³² at ground surface ($\mu\text{C}/\text{cm}^3$) for source height of 100 m and source strength of 1 curie/sec.

Releases in the form of HT would present a less serious problem because of the decreased likelihood of retention of the tritium in the body. Locally this would provide some benefit because the tritium would have moved some distance before appreciable oxidation to HTO had occurred.

SUMMARY

A cursory look at the potential environmental hazards that are likely to be caused by increasing releases of tritium resulting from the growth of a nuclear power economy based on light-water reactors suggests that the general increase in the worldwide concentration of tritium is not likely to result in a significant increase in hazards. Local environmental contamination problems may be significant, but they appear to be of a lower order of magnitude^{33,36} than those arising from the release of ⁸⁵Kr. The magnitude of the local contamination problem will depend on the nature, mode, and quantity of the releases, as well as on local environmental conditions.

REFERENCES

1. E. L. Albenesius, Tritium as a Product of Fission, *Phys. Rev. Lett.*, **3**(6): 274-275 (Sept. 15, 1959).
2. E. L. Albenesius and R. S. Ondrejcin, Nuclear Fission Produces Tritium, *Nucleonics*, **18**(9): 100 (September 1960).
3. C. E. Holmquist, Hazards of Tritium Oxides Induced in Large Heavy Water Reactor Stations, paper presented at the American Industrial Hygiene Conference, Houston, Texas, May 3-7, 1965 (CONF-650540-6).
4. W. A. Haney, D. J. Brown, and A. E. Reisenauer, *Fission Product Tritium in Separations Wastes and in the Ground Water*, USAEC Report HW-74536, Hanford Atomic Products Operation, Aug. 1, 1962.
5. J. O. Blomeke, *Management of Fission Product Tritium in Fuel Reprocessing Wastes*, USAEC Report ORNL-TM-851, Oak Ridge National Laboratory, May 4, 1964.
6. *Civilian Nuclear Power*, Appendices to *A Report to the President--1962*, U. S. Atomic Energy Commission, 1962.
7. U. S. Atomic Energy Commission, *Estimated Growth of Civilian Nuclear Power*, USAEC Report WASH-1055, March 1965.
8. K. E. Cowser, W. J. Boegly, Jr., and D. G. Jacobs, ⁸⁵Kr and Tritium in an Expanding World Nuclear Power Industry, pp. 35-37, in *Health Physics Division Annual Progress Report for Period Ending July 31, 1966*, USAEC Report ORNL-4007, Oak Ridge National Laboratory.
9. J. F. Eichelberger, G. R. Grove, and L. V. Jones, *Mound Laboratory Progress Report for September 1963*, USAEC Report MLM-1176, Sept. 30, 1963.
10. C. E. Holmquist, Hazards of Tritium Oxides Induced in Heavy Water Reactors, pp. 34-39, in *Seminaire sur la Protection Contre les Dangers du Tritium*, Service Central de Protection Contre les Rayonnements Ionisants, le Vesinet, April 16-18, 1964 (CONF-640413).

11. S. O. Bergstrom, L. Devell, and G. Gebert, Studies on Tritium Hazards at Swedish Reactors, pp. 40-52, in *Seminaire sur la Protection Contre les Dangers du Tritium*, Service Central de Protection Contre les Rayonnements Ionisants, le Vesinet, April 16-18, 1964 (CONF-640413).
12. W. G. Homeyer, *Thermal and Chemical Aspects of the Thermonuclear Blanket Problem*, USAEC Report RLE-TR-435, Massachusetts Institute of Technology, Mar. 31, 1965.
13. E. F. Johnson, Thermo-Nuclear Power Reactors, *Chem. Eng. Prog.*, 58(8): 60-64 (August 1962).
14. R. A. Strehlow and D. M. Richardson, Chemistry of Tritium in Controlled Fusion Devices, pp. 111-116, *Thermonuclear Division Semiannual Progress Report for Period Ending April 30, 1965*, USAEC Report ORNL-3836, Oak Ridge National Laboratory, September 1965.
15. J. H. Goode, *Hot-Cell Evaluation of the Release of Tritium and ⁸⁵Kr During Processing of ThO₂-UO₂ Fuels*, USAEC Report ORNL-3956, Oak Ridge National Laboratory, June 1966.
16. A. Doury, Risks Presented by the Diffusion of Large Quantities of Tritium in the Atmosphere, pp. 17-26, in *Seminaire sur la Protection Contre les Dangers du Tritium*, Service Central de Protection Contre les Rayonnements Ionisants, le Vesinet, April 16-18, 1964 (CONF-640413).
17. M. M. Popov and F. P. Tazetdinov, *The Vapor Pressure of T₂O*, USAEC file number NP-tr-534, 1961 [translated from *Atom. Energ.*, 8: 420-424 (1960)].
18. A. E. Bainbridge, Tritium in Surface Waters of the North Pacific, pp. 129-137, in *Nuclear Geophysics*, National Academy of Sciences, National Research Council, Washington, D.C., 1963.
19. A. E. Bainbridge, Tritium in the North Pacific Surface Water, *J. Geophys. Res.*, 68(13): 3785-3789 (July 1, 1963).
20. E. Eriksson, An Account of the Major Pulses of Tritium and Their Effects in the Atmosphere, *Tellus*, 17(1): 118-130 (February 1965).
21. R. L. Nace, Water Management, Agriculture, and Ground Water Supplies, pp. 43-61, in *Water and Agriculture*, edited by R. D. Hockensmith, American Association for the Advancement of Science, The Horn-Shafer Company, Baltimore, 1960.
22. H. V. Sverdup et al., *The Oceans—Their Physics, Chemistry and General Biology*, pp. 8-46, Prentice-Hall, Inc., Englewood Cliffs, N. J., 1942.
23. E. E. Foster, *Rainfall and Runoff*, The Macmillan Company, New York, 1948.
24. W. F. Libby, Moratorium Tritium Geophysics, *J. Geophys. Res.*, 68(15): 4485-4494 (Aug. 1, 1963).
25. R. Revelle, Water, *Sci. Amer.*, 209(3): 93 (September 1963).
26. G. Israel et al., Seasonal Variations of Bomb-Produced Tritium in Rain, *J. Geophys. Res.*, 68: 3771-3773 (July 1, 1963).
27. R. M. Brown, Tritium Precipitation at Canadian Sites, 1953-1963, pp. 71-75, in *Tritium and Other Environmental Isotopes in the Hydrological Cycle*, Technical Report Series, No. 73, International Atomic Energy Agency, Vienna, 1967 (STI/DOC/10/73).
28. Sir John Cockcroft (Chairman), *The Assessment of the Possible Radiation Risks to the Population from Environmental Contamination*, Medical Research Council, Her Majesty's Stationery Office, London, 1966 (USAEC file No. NP-16119).
29. F. L. Culler, *The Effect of Scale-Up on Fuel Cycle Costs for Enriched Fuel and Natural Uranium Fuel Systems*, USAEC Report ORNL-IM-564, Oak Ridge National Laboratory, Apr. 16, 1963.
30. K. E. Cowser, S. V. Kaye, P. S. Rohwer, W. S. Snyder, and E. G. Struxness, *Dose-Estimation Studies Related to Proposed Construction of an Atlantic-Pacific Interoceanic Canal with Nuclear Explosives: Phase I*, USAEC Report ORNL-4101, Oak Ridge National Laboratory, March 1967.
31. W. H. Farrow, Jr., *Radiochemical Separations Plant Study. Part II. Design and Cost Estimates*, Appendix II, USAEC Report DP-566, Savannah River Laboratory, March 1961.
32. D. H. Slade (Ed.), *Meteorology and Atomic Energy—1968*, USAEC Report TID-24190, Environmental Science Services Administration, Air Resources Laboratories, July 1968.

33. R. E. Blanco et al., *Survey of a Site for a Nuclear Fuel Processing Plant and Waste Disposal Area at Oak Ridge*, USAEC Report ORNL-TM-1748, Oak Ridge National Laboratory, Jan. 13, 1967.
34. W. M. Culkowski, Estimates of Accumulated Exposures and Environmental Build-up of Radioactivity, pp. 89-99, in *Sixth Air Cleaning Conference July 7-9, 1959*, USAEC Report TID-7593, October 1960.
35. W. F. Hilsmeier, Supplementary Meteorological Data for Oak Ridge, USAEC Report ORO-199, Mar. 15, 1963.
36. K. E. Cowser et al., Evaluation of Environmental Hazards from Release of ^{85}Kr and ^3H in an Expanding Nuclear Fuel Reprocessing Industry, paper presented at the Health Physics Society Annual Meeting, Washington, D. C., June 18-22, 1967.

8 SUMMARY AND CONCLUSIONS

In the preceding chapters an attempt has been made to summarize some of the important properties of tritium and to use these properties in predicting the impact of diverse releases of tritium on local and worldwide populations. Such applications cannot be made with a high degree of precision because of several factors. First, an extremely large number of combinations of environmental conditions can exist, which limits calculations to consideration of a few specific cases, usually to mean conditions, modal conditions, and perhaps a few extreme conditions. In addition, the behavior of tritium in the environment is not completely understood. Of course, as a first approximation, HTO behaves like ordinary water, but this behavior is not always the case. Fluxes of HTO do not have to be proportional to fluxes of ordinary water. In fact, fluxes can be in opposite directions. For example, there could be a downward flux of tritiated water into the ocean depths or into the groundwater at the same time that a net evaporation of water was occurring.

Despite the inadequacies of some of the present information on the behavior of tritium, we can draw some general conclusions. In a nuclear power economy based on fission reactors, tritium poses no severe worldwide population exposure problems. However, tritium will continue to pose handling problems and local problems of environmental contamination. Estimates of projected releases of activity from fuel-processing plants suggest that tritium will not be as critical a factor in limiting the size of plants as will ^{85}Kr . This does not mean that tritium should be released promiscuously from such a plant; protective action is always warranted when such action can result in a significant reduction of personnel or population exposure at a reasonable cost.

Adequate approximations can be made for the capacity of a given local environment for accepting tritium, and estimates can be made for a number of conditions or, better yet, for a time-averaged condition that has been actually observed. More precise knowledge of rainout factors, deposition velocities, and washout coefficients will improve the estimates of local environmental contamination. Although we might reasonably assume that dry deposition over land areas will be small compared with removal of tritium during rainfall, the significance that bodies of surface water have as sinks for the removal of tritium that reaches their surfaces through dry deposition would be of considerable interest.

Estimates of the capacities of surface waters for tritium acceptance can be made with less error because the paths of movement are more restricted and changes in transport characteristics are more amenable to quantitative measurement. Movement of tritium can be assumed to be the same as the movement of water in such a system. However, movement of tritiated water in the ground is a bit more complex. The paths of movement are not so readily observed as in surface waters, and the paths and rates of movement may change considerably with changes in the moisture of the ground. Furthermore, any specific reactions of tritium with the soil particles will be accentuated as the ratio of soil to water increases; that is, as the moisture content decreases. Specific interactions are thought to occur, but they have not been very well documented to date.

In my opinion, a much more serious gap of information exists in the knowledge of the behavior of fission-product tritium within a light-water power reactor. On the basis of present information, some fission-product tritium can apparently diffuse out of oxide fuels clad with aluminum or stainless steel. Diffusion out of metal fuels or out of fuels clad with zirconium seems to be much less. Obviously, if the fission-product tritium diffuses out of the fuel element while it is still in the reactor, release at the reactor site will be increased. However, the quantities of water used for cooling appear to be adequate for dilution of tritium from this source as well as of tritium produced by activation of lithium, boron, and deuterium in the coolant system. In the situation where the tritium diffuses out of the fuel element, the tritium remaining in the fuel element to be released at the fuel-reprocessing plant would be reduced. Conversely, if little fission-product tritium escapes from the fuel during reactor operation, the tritium-release problem is limited to the fuel-reprocessing plant site. Much more operating data would be beneficial, especially data on the tritium concentrations of various aqueous and gaseous streams at fuel-reprocessing plants. The fission yield of tritium also needs to be determined more accurately under a wide variety of conditions prevailing in a nuclear power industry; e.g., as a function of the energy spectrum of the neutron flux, the type of fuel used, and the enrichment of the fuel.

Technologically tritium can be enriched, either as the gas or as the oxide. Enrichment may be essential in a power economy based on fusion reactors because of the extremely large quantities of tritium that will be needed. Although the costs may be rather high, the losses of tritium will have to be limited. Various methods will have to be evaluated, both on the basis of technological feasibility and on the basis of economics.

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