ATMOSPHERIC ACTIVITIES AND DATING PROCEDURES

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I. Radioactive Components of the Atmosphere

A variety of radioactive substances is found in the atmosphere; some present as gases, the remainder suspended as, or absorbed on, aerosols. These species are generally short-lived by comparison with the age of the earth and must therefore be replenished continuously by natural processes unless they owe their existence to human activities.

The naturally generated species are conveniently divided into two groups. The first comprises the emanations of the three natural radioactive series, together with their decay products. These substances are of terrestrial origin. A small part of the gaseous emanations formed by the decay of the uranium and thorium in the lithosphere and hydrosphere diffuses into the atmosphere; a further quantity is contained in the subterranean gases reaching the atmosphere through fumaroles or by other volcanic activity. A second group finds its origin in the cosmic radiation. It includes radioactive isotopes of a number of the lighter elements. Although the primary cosmic radiation includes nuclei of elements at least as heavy as calcium, it is generally considered unlikely that these include radioactive isotopes because the atoms are probably too old for such species to have survived. Tritium may be exceptional. It is more likely that these activities are one result of the interaction of the incident radiation with the constituents of the atmosphere.

Finally, human activities during the last twelve years have contributed several new radioactive species to the atmosphere. These are either released during the processing of nuclear fuels, or are produced and disseminated by the explosion of nuclear weapons. They include the fission products and a variety of isotopes of the heaviest elements as well as species duplicating some of those generated by the cosmic radiation.

II. Radioactive Species of Terrestrial Origin

A. NATURE

For many years it has been known that the atmosphere contains variable amounts of the emanations in the three naturally occurring series, together with the decay products from these gases. The relevant species are shown in Table I.

Although more than a dozen papers dealing with radon and thoron in the atmosphere have appeared every year for several years, as a result of the intensive study of the cosmic-ray generated activities and of those arising from human operations, radon and thoron and their decay products are now the least thoroughly understood radioactive components of the atmosphere. They are continuously supplied to the atmosphere as the gaseous emanations from the lithosphere and hydrosphere, which contain the long-lived parents thorium and uranium. Clearly, the amounts reaching the atmosphere will be determined not only by the concentrations of the parent elements in the generating magma, but also by the half-lives of the emanations. The chance of the short-lived thoron or actinon atoms reaching the atmosphere before decay is much less than for the comparatively long-lived radon. Since the primary production ratios for the radon and actinon are fixed by the isotopic composition of uranium, unless geochemical segregation of ionium, radium, or actinium has disturbed this ratio, the actinon decay products will only be present in the atmosphere at very much lower concentrations than the radon decay products. The similarity of the half-lives of some of the actinon and radon decay products further complicates the estimation of the actinon and its decay products (*48*). Thus no new observations on the actinon series in the atmosphere appear to have been reported in the last fifteen years. Earlier measurements of

TABLE I[a]

NATURAL RADON ISOTOPES AND THEIR DECAY PRODUCTS

4n			4n + 2			4n + 3		
Species		Half-life	Species		Half-life	Species		Half-life
Thoron	Em^{220}	51.5 sec	Radon	Em^{222}	3.83 day	Actinon	Em^{219}	3.92 sec
ThA	Po^{216}	0.16 sec	RaA	Po^{218}	3.05 min	AcA	Po^{215}	$1.8 \cdot 10^{-3}$ sec
ThB	Pb^{212}	10.6 hr	RaB	Pb^{214}	26.8 min	AcB	Pb^{211}	36.1 min
ThC	Bi^{212}	60.5 min	RaC	Bi^{214}	19.7 min	AcC	Bi^{211}	2.15 min
ThC′	Po^{212}	$3 \cdot 10^{-7}$ sec	RaC′	Po^{214}	$1.6 \cdot 10^{-4}$ sec	AcC′	Po^{211m}	0.52 sec
ThC″	Tl^{208}	3.1 min	RaC″	Tl^{210}	1.32 min	AcC″	Tl^{207}	4.79 min
			RaD	Pb^{210}	19.4 yr			
			RaE	Bi^{210m}	5.01 day			
			RaF	Po^{210}	138 day			

[a] *m* denotes nuclear isomer.

these radioactive components of the atmosphere have been summarized by von Benndorf and Hess (*270*) and more recently by Israël-Kohler (*141*).

B. MEASUREMENT

One reason for the unsatisfactory state of our knowledge of these constituents of the atmosphere is the difficulty of making reliable measurements. The primary species, the emanation isotopes, are true gases; the decay products are atoms of the metalloids and metals, polonium, bismuth, lead, and thallium. Once formed, they presumably suffer rapid oxidation to involatile products that soon adsorb onto dust particles and form a radioactive aerosol (*212, 213, 145, 241, 271*). One of the most popular methods for the determination of the radon and thoron in the atmosphere has been to remove the decay products by filtration of the air and to analyze the decay curves of the activity collected on the filter (*59, 132*). Either the alpha or beta activity of the final sample may be determined, but appropriate corrections to give absolute activities must be made. This method assumes that the emanations and their decay products are in radioactive equilibrium in the air that is analyzed. This assumption will not be valid, for instance, shortly after a shower of rain (*253*) and there is at present insufficient experimental evidence to establish its domain of validity, although Damon and Kuroda have investigated the disturbance of the equilibrium by measuring the RaA, B, and C activities of rain water (*65, 152*). Hurley has suggested that an inaccuracy of a factor of 2 might occasionally arise from this lack of radioactive equilibrium (*132*). Another factor that must be considered is the adsorption of radon and thoron themselves onto the aerosol particles. Jech has shown such adsorption does occur, and for 1–10μ particles is proportional to their surface area (*139. 144, 189, 190*). Such an effect will make the thoron content reported for the sample too high. However, under most conditions it should not necessitate a very large correction.

Probably more important is the often unknown and frequently low efficiency of the filters used to separate the decay products (*8*). Hurley found that the Whatman No. 41 filter papers generally used, varied from 8 to 66% in their retention of the decay products when sampling the air in a room containing a known concentration of radon (*132*). Crosthwait reported 50% collection of the aerosols. The efficiency depends on the nature and amount of the dust (*59*). Anderson, Mayneord, and Turner found much lower efficiencies, from 2 to 3%, when comparing filtration results with measurements of the radon content of the air by means of a large ionization chamber (*8*). It seems clear that the efficiency of the method depends on the particle size and distribution of the dust particles in the region of the atmosphere under investigation (*25*). Measurements by the filtration method are probably satisfactory for comparison purposes under more or less constant dust conditions, but are probably unsatisfactory for absolute measurements. Other methods of collection of the decay products include electrostatic precipitation and collection on a negatively charged wire. Wilkening has shown that the variable efficiency of the latter method can easily lead to spurious conclusions, in a study of the variation of the radon content of the atmosphere with the altitude (*272–274*).

The alternative and more reliable methods of radon estimation have the disadvantage of requiring less portable and compact apparatus (*31*, *70*, *116*, *135*). The use of a large ionization chamber has already been mentioned. It is also possible to use a scintillation counter (*186*, *230*). In either case, some concentration of the radon, for instance, using the gas analysis techniques developed by Paneth and collaborators, is an advantage; but this is not possible if it is intended to measure the thoron as well. Autoradiographic methods have also been tried (*212*, *213*).

C. FACTORS INFLUENCING THE EMANATION CONTENT OF THE ATMOSPHERE

Notwithstanding the probably low absolute accuracy of most of the published data on the radon and thoron content of the atmosphere, it is clear that there are large variations in these quantities and even their ratio, not only from place to place, but even from time to time at the same place.

1. Meteorological Factors

Reiter has made an interesting study of the relative radon and thoron contents of the atmosphere at a station at an elevation of 2,300 meters in the Northern Alps. He finds that the emanation content of the atmosphere depends on the direction of the wind, varying with the uranium and thorium content of the rocks up wind (*237*, *238*). The variation in the radon, thoron, and actinon concentrations in the atmosphere with the altitude is also critically dependent on the wind and temperature gradient (*2*, *44*, *109*, *110*, *140*). Old evidence indicates that the actinon and its products reach only about 20 meters above ground and thoron up to 100 meters; in the latter case, however, thorium B, probably no longer in equilibrium with thoron, must extend much further up (*212*). It is already established that a thermal inversion reduces the leakage of these gases, and their decay products, into the higher atmosphere, and thereby increases their concentration below the inversion level. Very sharp changes in the radon and thoron values are often found to be accompanied by changes in the temperature and humidity. Fog also reduces the diffusion and increases the radon and thoron concentrations in the atmosphere (*8*, *68*, *252*). A diurnal variation in the concentrations of these species has been reported by a number of investigators (*44*, *252*). Gale and Peaple observed (*107*) that it follows the potential temperature gradient in the region 32–108 ft. The average diurnal variation is by a factor of between 1 and 2.5 times the minimum value (*184*).

2. Geological Factors

As might be expected, different kinds of soil and different kinds of drift material have a considerable influence on the diffusion of the emanation isotopes into the atmosphere (*3*, *106–108*, *221*, *237*, *238*). The supply of radon to the atmosphere by the weathering of soil was discussed at the second Geneva Atoms for Peace Conference by Delwiche (*71*), who points out that soils tend to a common radium content independent of their rock origin. Special apparatus for the determination of the radon content of soil gases has been described. Reiter found that the prevailing Ra/Th ratio at his station was related to the U/Th ratio in the rocks and soil in the direction from which the wind was blowing. Substantial amounts of the emanation isotopes reach the atmosphere through fumaroles, in volcanic and spring gases (*143*, *149*, *150*). Indeed, the activities reaching the atmosphere in this way may reach as high a concentration as 10^{-7} c/liter. Generally, the lowest radon and thoron concentrations have been recorded over the sea and in the Arctic and Antarctic (*184*). It must be noted, however, that observations made by the filtration method are likely to be especially untrustworthy in the two polar areas because the low dust content of the atmosphere in these regions will probably lead to a lower particle size distribution in the aerosol and even less efficient collection by the paper than usual, with correspondingly low results.

Recent studies of radon in wind over the sea have shown that there is a radon excess in the sea and a current of radon into the atmosphere from the seabed, which concentrates ionium and therefore grows radium and thence radon. This current amounts to $0.5 \cdot 10^{-18}$ c/cm_e^2 sec (cm_e^2 = square centimeters of earth's surface). The air-sea interface acts as a barrier across which there is a transfer coefficient (equivalent to a diffusion coefficient) of 200 cm^2/day (*142*). Confirmation and extension of this result are desirable.

Another possibly important contribution to the radon in the atmosphere of industrial areas is the combustion of coal, both directly and through the intermediary of gas production. Anderson, Mayneord and Turner find a radon content of 1.10^{-12} c/liter for London coal gas (*8*). The atmospheres of confined and inadequately ventilated buildings often show an abnormally high value, and in a few cases, where the building materials themselves contained an unusually high uranium content, quite disturbingly high radon concentrations have been recorded (*68*, *105*, *220*). The continuous deposition of minute traces of short-lived alpha active substances is noticed by all who have had to construct low-background ionization chambers or alpha counters. Exposure of the parts of such a chamber or counter to the atmosphere of even a clean laboratory nearly always leads to a temporary increase in the background of the device, caused by this continuous deposition of radon decay products.

3. Recent Values for the Radon and Thoron Concentrations

Some recent values are shown in Table II. It will be observed that most of these were obtained by means of a filtration technique.

TABLE II
Some Recent Values for Radon and Thoron Concentrations

Place	Radon $\times 10^{-15}$ c/liter	Thoron $\times 10^{-15}$ c/liter	Method of measurement	Ref.[a]
New York	54		Ion chamber	*135*
London	2–3000		Filtration, β	*68*
Rochester, New York	RaA 130	ThB 5.2		*204*
Wellington, New Zealand	34, max. 110 34, min. 2.6		Filtration, α	*59*
Wellington, New Zealand	37		Filtration, α, and electrostatic ppn.	*44*
Harwell, England	64, max. 386		Filtration, β	*107*
Washington, D.C.	172	2.3	Filtration, β	*184*
Yohasaka, Japan	54	0.48	Filtration, β	*184*
Kodiak, Alaska	7.3	0.04	Filtration, β	*184*
Antarctica	1.5	0.01	Filtration, β	*184*
Kjeller, Norway	300, max. 1100 300, min. 30		Filtration, β	*252*

[a] See also references *28*, *29*, *30*.

It seems quite possible that the accumulation of more accurate and extensive data on the concentration distributions of radon and thoron might lead to valuable methods of investigation of low-level meterological changes.

III. Activities Generated by the Cosmic Radiation

A. Mode of Formation

The primary cosmic radiation is believed to consist largely of energetic protons, together with perhaps 10% of heavier nuclei (*63*, *125*, *218*, *259*). The earth's magnetic field cuts off the less energetic protons so that the intensity falls sharply below about 1.5 bev in the region of the geomagnetic equator. It has already been observed that unless the heavier nuclei are partly or entirely of solar origin their age will preclude the presence of an appreciable proportion of short-lived radioactive species. The radioactive products must therefore be generated by the interaction of the primary radiation with the atmosphere. These reactions can be divided roughly into two categories. The first includes the very energetic reactions of the primary radiations with the atmospheric gas nuclei. It includes a high proportion of the very disruptive star reactions, which lead to several particulate products. The products will include, in varying yields, all nuclei of lower mass than the target atoms. Since the primary proton radiation has such a high average energy, the secondaries from the star reactions are often capable of initiating similar events; all these will be included in the first category.

The second category comprises the reactions of the neutrons produced as a by-product in the first kind of reaction, when these neutrons have been moderated to energies that exclude the first type of reaction, that is to say, below a few million electron volts.

Finally, small quantities of radioactive species produced by the cosmic rays are introduced into the atmosphere by the volatilization and erosion of meteoritic material swept up by the earth. The radioactive species have been generated in the meteorites by cosmic ray bombardment in space, and they include a wider range of unstable nuclei than is generated directly in the atmosphere in appreciable amounts (*86–88, 101, 154, 245*).

1. *Products of the Energetic Reactions*

The principal products of these reactions are given in Table III.

The *a priori* calculation of the average rates of production of such species by these processes is a problem of considerable difficulty, and a probable

TABLE III

PRINCIPAL PRODUCTS OF THE ENERGETIC REACTIONS

Nucleus	Half-life	Nucleus	Half-life
A^{39}	265 yr[a,b]	Si^{32}	~700 yr
A^{37}	34 day[b]	Al^{26}	~10^6 yr[b]
Cl^{39}	55 min	Na^{22}	2.6 yr
Cl^{38}	37 min	C^{14}	5600 yr[a]
Cl^{36}	3×10^5 yr[b]	Be^{10}	2.5×10^6 yr
S^{35}	87 day	Be^7	53.6 day
P^{33}	24.4 day	T	12,3 yr[a]
P^{32}	14.4 day		

[a] Also produced by the second category of reaction.

[b] So far only reported in meteorites.

error of ±50% is all that can be expected at present. The calculation requires data on the variation of the intensity of the neutron and proton fluxes in the cosmic radiation with the energy of the particles and with the altitude and latitude, as well as the variation of the cross sections for the reactions resulting in the desired product as a function of the energy of incident proton or neutron. The production of Be^7 has been treated in this way by Benioff (*26*), who separated the flux calculation into two parts, $E \geqslant 500$ Mev and $40 \leqslant E < 500$ Mev. In the high-energy region he used Messel's treatment (*206*) of the nucleon cascades following the primary protons by diffusion equations to obtain the vertical neutron and proton intensities as a function of altitude and geomagnetic latitude. From this relative directional intensity he calculated the relative total intensity and normalized this to absolute values by means of one value for the total flux of primary cosmic nucleons at the top of the atmosphere at one latitude. In the lower energy region a more approximate treatment had to be adopted and a procedure developed by Rossi was used (*242*). Finally, he used cross sections averaged over the appropriate energy ranges so that only the total neutron and proton fluxes were required and not the detailed spectra. Even these cross sections had to be extrapolated to nitrogen from data referring to carbon (*62, 80, 97–99 198*).

It is seen, therefore, that at present such calculations must be liable to large errors; nonetheless, it seems that they may be valid within ±50% and, indeed, still lead to valuable conclusions. The primary production of radioactive species by these reactions must clearly show the same variation with the geomagnetic latitude (*247*, *248*, *285*) and altitude (*27*, *67*, *248*, *256*, *257*, *285*) as the more energetic cosmic radiation. The latter variation is such that the larger part of these products must be generated in the stratosphere. The former leads to the production rate rising from the geomagnetic equator to about three times the rate at geomagnetic latitudes of 60° or greater. Thus, Benioff's calculations show that the Be^7 production in the stratosphere amounts to 5.0 atom/cm_e^2/min and 1.3 atom/cm_e^2/min in the troposphere averaged over all latitudes.

2. Products of Neutron Capture

Once the neutrons formed by the incident proton radiation are moderated by elastic collisions to energies of a few million electron volts, or alternatively react with nuclei to release neutrons in this energy region, the most probable nuclear reactions become the $(n,2n)$, (n,p), (n,t), (n,γ), and (n,α) reactions, the second and fourth reactions claiming most of those neutrons that reach thermal or epithermal energies. Of the principal stable nuclei present in air, H, D, C^{12}, C^{13}, N^{14}, N^{15}, O^{16}, O^{17}, O^{18}, A^{40}, only the last gives a moderately long-lived $(n,2n)$ product and A^{39} has not yet been detected in the atmosphere. The threshold for the reaction is 9.8 Mev (*131, 188*) and the A^{40} concentration is low, so that the A^{39} will confer a very low specific activity on natural argon. The same group of stable isotopes all show quite low radiative capture cross sections for thermal neutrons and the products are all either stable or short-lived and have not been detected. In fact, a very small proportion of the atmospheric neutrons participate in either of these reactions.

The most abundant atmospheric nucleus, N^{14}, however, participates in both the (n,t) (*47*) and (n,p) (*40*), the latter reaction having a very appreciable cross section, even at thermal energies (*146*). The (n,t) reaction shows a threshold of 4.3 Mev (*47*). It is considered further in Section V.

$$\begin{array}{l} N^{14} + n \rightarrow C^{14} + p \\ N^{14} + n \rightarrow C^{12} + t \\ \qquad\quad\;\; \searrow \\ \qquad\qquad\;\; 3\alpha + t \end{array}$$

Most of the neutrons reaching thermal energies are absorbed by the first of these reactions.

a. Distribution of the atmospheric neutrons. The quantity and initial distribution of these neutron-generated radioactive components of the atmosphere are determined by the distribution and rate of formation of the neutrons themselves. Fortunately sufficient experimental data on the cosmic ray neutrons are available to permit calculation of the resultant activities. For reasons which will be given, however, the probable accuracy of such calculations is not very great.

The absence of a strong diurnal variation in the atmospheric neutron intensity precludes a solar origin (*102, 251*) and the short half-life of the neutron (*240*) excludes an extrasolar origin, so that it is clear that the cosmic ray neutrons must be secondary products of the interaction of the primary radiation with the atmosphere. As suggested by this conclusion, the neutron intensity at first increases with decreasing altitude, then passes a maximum value, and finally, over the region from 200–700 millibars, falls exponentially with increasing depth in the atmosphere (*1, 103, 165, 246, 248, 249, 256, 257, 282–284, 286*), near the ground the intensity falls more sharply (*250*). Careful measurements of this change have been made by airplane and balloon flights, carrying boron trifluoride-filled neutron counters. Spurious counts arising from other nuclear interactions in the gas filling the counter can be avoided by the ingenious expedient of comparing the counts recorded by two identical counters filled to the same pressure with two samples of boron trifluoride of different isotopic composition (*165*). In such circumstances the spurious count rate is the same in each counter, but the neutron count is proportional to the B^{10} content of the counter.

Experiments with photographic plates and proton recoil counters show that the neutrons vary in energy from thermal values up to the same order of magnitude as the primary radiation (*27, 67, 155, 168, 210*). The neutrons show a variation with geomagnetic latitude similar to that of the primary radiation; the altitude for the maximum intensity is also dependent on latitude (*255*). For a given altitude, between 200 and 700 millibars, the neutron density is about 4.2 times as high at the magnetic poles as at the equator, and most of the change takes place between 15° and 50°. These altitude and latitude effects are shown equally by the fast and slow neutrons.

Together these observations indicate that over the portion of the atmosphere lying between 200 and 700 millibars, the cosmic ray neutron creation process is in equilibrium with the neutron consumption by the atmospheric gas nuclei (*27, 67, 165, 247–249, 256, 257, 285*). The absorption mean free path in this equilibrium region varies from about 164 gm/cm^2 to about 220 gm/cm^2, increasing with the geomagnetic latitude (*153, 246, 248*). The neutron spectrum is practically independent of the altitude and latitude. Thus most neutrons are captured within a kilometer of their birth place in the atmosphere. The initial distribution of the radioactive products of the absorption reactions must therefore resemble that of the neutron-generating events in their variation with latitude and, to a smaller extent, with altitude.

b. Production rate of the atmospheric neutrons. In principle, the calculation of the rate of formation of, say, the C^{14} formed by the atmospheric neutrons demands knowledge of the intensity-energy spectrum of the neutrons at all points in the atmosphere, together with the variation of the cross sections with the neutron energy of all nuclear reactions generating C^{14}. The rate of production of neutrons can be calculated from the same data with the addition of information on the cross sections as a function of neutron energy for all the neutron-consuming reactions in the atmosphere. In practice it is convenient to separate the problem into two parts; the neutrons whose energy reaches or exceeds the resonance capture region for N^{14}(n,p)C^{14}, 0.5 Mev, a proportion of which can participate in a variety of other energetic reactions, and the less energetic neutrons, almost all of which are absorbed in the N^{14}(n,p)C^{14} reaction under conditions such that the cross section for the reaction varies inversely with the neutron energy. The latter fraction of the neutrons can be determined rather accurately (*254*), the former much less satisfactorily.

The low-energy population of neutrons can be calculated from the boron chamber intensity-altitude data at different latitudes since both the cross sections of the boron fission reaction and the (n,p) reaction in the nitrogen are inversely proportional to the neutron velocity in this energy region. A calculation on this basis leads to an average neutron production, $\bar{Q}$, for the whole earth, of $1.1/\text{cm}_e^2$ sec (*254*). Another method utilizes data on the ratio of the count recorded by the boron counters with and without a covering of cadmium foil, the foil absorbing effectively all neutrons of energy less than 0.4 ev (*156, 164, 229*). The theory of the moderation of neutrons then permits the calculation of the neutron production up to some higher energy limit, provided the scattering and absorption cross sections of the nuclei of the atmospheric gases are known over this energy range (*27, 67, 172*). The second method introduces the possibility of errors in these cross sections as well as some inaccuracy in the theory of the neutron moderation arising from inelastic collisions of the neutrons of energies comparable with chemical bond energies.

Because of the relatively high ratio of the neutron capture to scattering cross sections in air, the neutrons do not reach as nearly a thermal velocity distribution as in, for example, a hydrogenous medium. The varying water content of the atmosphere might be expected to influence the energy distribution of the neutrons, but the effect is very small (*27*). The result obtained using the first and more direct method of determination ($1.1/\text{cm}_e^2$ sec) was much lower than the values obtained by various investigators using the second method (for example, $2.23/\text{cm}_e^2$ sec).

To this figure must be added the neutrons absorbed by the various nuclear reactions in which they can participate before reaching 0.4 Mev. This quantity amounting to nearly 10% of the total neutron production is more difficult to estimate. Knowledge of the primary energy spectra of the neutrons and the values and variation with neutron energy of the cross sections of all the reactions by which the neutrons can be absorbed is needed.

The estimates of the total neutron production made in this way vary from about $1.2–2.4/\text{cm}_e^2$ sec—a wider range of values than estimates of the probable error in the calculations would suggest.

The order of magnitude of these figures is confirmed by an entirely different mode of calculation. The primary rate of production of the neutrons has been estimated by measuring the average number of neutrons produced in the energetic interactions involving the primary radiations, and then integrating the incidence of these reactions as a function of altitude and latitude. The values obtained are still less precise, but compatible with the above values (*26, 111, 210, 223*). Measurements have also been made recently of the energy distribution and intensity of the more energetic atmospheric neutrons (>50 Mev) (*210*).

Once $\bar{Q}$, the average rate of production of neutrons in the atmosphere, is known, a fairly good estimate of the rate of production of C^{14} in the atmosphere is available, since virtually all the neutrons moderated to an energy of 0.4 Mev or less are ultimately absorbed with C^{14} production, and only a very small correction need be made for competing reactions for these neutrons. For the more energetic neutrons, however, several nuclear reactions have comparable probabilities, so that only a fraction of these neutrons is absorbed with C^{14} production; others, for example, produce T and other products. Even the correction for these losses is not very great, so that to a reasonable approximation $\bar{Q}$ is also the mean rate of production of C^{14}/cm_e^2 sec.

The calculation of the tritium and other fast neutron reaction products is more difficult (see Section V,D).

3. Other Sources of Natural Atmospheric Activities

Two other sources clearly contribute radioactive components to the atmosphere. Very small quantities of the gaseous fission products must be released by diffusion and the weathering of rocks where they have accumulated by spontaneous fission of the natural heavy elements. The present levels of artificially introduced radioactive contaminants in the atmosphere make the detection of the natural products virtually impossible.

Another possibly more important source of radioactive material is the meteoritic dust reaching the atmosphere. During their sojourn in space, meteorites are subjected to bombardment by the primary source radiation, and radioactive products are formed by reactions similar to the star reactions already described (see Section III,A,*1*). However, the meteorites, in particular the iron meteorites, contain target atoms up to nuclear mass number 60, so that a wider range of products can be formed (*86–88*). Comparison of the nature and distribution of these products as a function of the depth below the surface of an iron meteorite and an iron target bombarded with energetic protons has shown that the primary cosmic radiation has an effect equivalent to 6 bev protons (*101*). The smaller meteorites are generally volatilized on passing through the atmosphere, and this contributes their radioactive contents to the atmosphere. These include radioactive isotopes of argon (see Table III), of iron and manganese, and of course tritium. As yet, no radioactive species have been identified in the atmosphere that must necessarily arise from this source and artificially introduced species have complicated the problem of their detection. However, there is some possibility that a significant contribution to the tritium content of the atmosphere finds its origin in this mechanism.

B. DETECTION AND APPLICATION OF COSMIC RAY PRODUCTS

The C^{14} and T are of such importance that they will be discussed in separate sections. Here the more fragmentary data referring to the other species will be collected.

1. *Beryllium Isotopes*

Both Be^7 and Be^{10} have been detected (*10, 12, 61, 121, 219, 227*). They are found predominantly in the stratosphere, and measurements of the rate of deposition of Be^7 together with calculations of the probable rate of formation (see Section III,A,*1*) comprised some of the earliest data that the time of mixing of the stratosphere and the troposphere must be long compared with the half-life of the Be^7. Benioff's calculation giving 5.0 atom $Be^7/cm_e^2/min$ for the stratosphere and 1.3 atom $Be^7/cm_e^2/min$ for the troposphere has already been discussed (*26*). The experimental data indicated that very little of the stratospheric material reached the earth before decay (*61*). The studies on Be^7 provide a good example of the use of these short-lived natural products to explore the rates of natural processes. Study of the variation of Be^7 with meteorological conditions shows that it is largely removed from the atmosphere by washing out with rain, the half-life for the process being about three weeks (*61*). On the other hand, the mixing of the stratosphere and troposphere is a much slower process and must, on the Be^7 data, have a half-life of a few years (*26, 268*).

The long-lived Be^{10} has found another application. After being washed from the atmosphere into the sea, the beryllium oxide or hydroxide molecules attach themselves to colloidal material and eventually become incorporated in the sediment where they remain to provide yet another means of dating deep sea sediment cores. The Be^{10} production has been estimated to amount to 3–6 atom/cm_e^2/min. The time elapsing between creation of the Be^{10} and its incorporation in the sediment is small compared with the half-life of Be^{10}, so that measurement of the Be^{10} activity of a sediment core is suitable both for absolute dating or for comparison of the ages of different depths in the core (*122, 205, 228*).

2. *Other Activities*

A number of other activities have been reported in rain water that may reasonably be products of the energetic reactions of the cosmic radiation. Both P^{32} and P^{33} have been detected (*167, 196*), the total phosphorus activity amounting to about 1.5 dis/min/liter of rain.

Sulfur 35 has also been detected in rain water (*120*), the activity amounting to about 2 dis/min/liter of rain. An extremely small amount of Na^{22} has been reported, but since it amounts to only 0.02 dis/min/liter of rain confirmation of the observations would be desirable (*197*).

Natural Si^{32}, formed in the atmosphere by star reactions in the argon, has been detected in sea water. The silicon was separated and the daughter P^{32} milked off to determine the Si^{32}. About 8 dis/min/kg of silicon was found, equivalent to about 2.6 × 10^{-5} dis/min/liter of sea water, or about 2 × 10^{-4} atoms/cm_e^2/sec over the earth (*166*).

3. Chlorine Isotopes

The long-lived Cl^{36} has been detected in the superficial parts of chlorine-containing rocks, where it has presumably been formed by radiative capture of cosmic ray generated neutrons (*66*, *163*, *244*). It has been suggested that it might provide a chronological technique for the study of the weathering of such deposits (*66*.) Small amounts of the same species may also be produced in the atmosphere, but Cl^{36} has not yet been detected in the atmosphere.

On the other hand, the surprisingly high activity of 50 dis/min/liter of rain of the short-lived isotope Cl^{39} has been reported (*279*, *280*). Winsberg, who discovered this activity, has suggested a novel mode of formation involving the cosmic ray μ mesons:

$$A^{40} + \mu^- \rightarrow Cl^{39} + n + \nu$$

IV. Radiocarbon

A. METHODS OF MEASUREMENT

The low energy and weak intensity of radiation make the counting of natural radiocarbon by external end-window methods impracticable. It is, therefore, necessary to include the carbon inside the counting device in such a way that the disintegrations may be detected with the utmost efficiency.

1. Solid Carbon Counting

Libby and his associates solved this problem in the most direct way by introducing the sample as elementary carbon into a specially constructed screen wall Geiger counter (*172*). The carbon was spread evenly over the inner surface of a brass cylinder surrounding the gauze cathode.

The sample was burnt in a stream of oxygen and the carbon dioxide was then precipitated as calcium carbonate to remove radon. Carbon dioxide was re-evolved by the addition of hydrochloric acid and was reduced to elementary carbon by passing over heated magnesium powder at 600°C. Excess magnesium and its oxide were leached away with hydrochloric acid and the residual carbon was filtered, dried, and made into a slurry with distilled water. The cylinder was coated with the slurry to a depth which was effectively an infinite thickness of carbon, greater than the range of the carbon β-particles. In practice 20 mg/cm^2 fulfills this requirement. The cylinder was placed inside the counter, and the end sealed in place with de Khotinsky wax. After evacuation the counter was filled with 10 cm Hg argon and 0.5 cm Hg ethylene and operated in the Geiger region.

The unshielded background counting rate of Libby's screen wall counter was 500 counts/min, which was reduced to 100 counts/min by surrounding with 8 in. of iron in all directions. Further reduction to 5 counts/min was achieved by a ring of Geiger counters arranged in anticoincidence with the screen wall counter.

The count rate above background due to the activity of the carbon obtained from modern organic material was about 6.7 counts/min. Since the total amount of carbon introduced into the counter was in the region of 8 gm, the low count rate obtained represents an efficiency of hardly more than 5%. This sample requirement is in practice frequently difficult to obtain, and itself imposes a limitation on the method, apart from the low accuracy. Furthermore, a source of error which soon became sufficiently large to cause abandonment of solid carbon counting was the liability to atmospheric contamination from naturally occurring radon and fission products from nuclear weapon tests. The specific surface area of finely divided carbon is exceedingly large, exceeding 200 square meters of surface area per gram, and the samples readily absorb these activities. Nevertheless, solid carbon counting made an invaluable contribution in establishing the radiocarbon dating method (*5, 15, 19, 161, 173, 175, 176, 182*), but the need for higher accuracy with smaller sample requirements, and freedom from the ever increasing fall out problems, led to the examination of other counting methods.

Different methods of counting are most readily compared by the fraction c^2/b, where c is the count from a contemporary carbon sample and b is the background (*81*). The value for the screen wall counter is about 10.

2. Gas Counting

The counting of radiocarbon in the gas phase allows many of the disadvantages of the solid carbon to be overcome. In particular, it offers the advantages of high efficiency, demands smaller samples, and gives almost complete freedom from contamination problems.

The choice of gas which is to be used as the counting medium will be influenced by the following factors.

1. The ease of synthesis from the raw sample.
2. The counting characteristics of the gas.
3. The amount of carbon in the gas.

Crane (*56*) reported the use of a mixture of carbon disulfide and carbon dioxide at relatively low pressures, and operated the counter in the Geiger region. Although reliable, the efficiency of this method is, however, somewhat low, since the operating pressure is limited.

More generally, gases are used at higher pressures and the counters operated in the proportional region. Carbon dioxide (*32, 96, 118, 214, 222, 224, 233, 77, 78*), methane (*41, 81*), acetylene (*21, 58, 262*), and ethylene (*92*) have all been used successfully as counting gases for natural radiocarbon measurement.

Carbon dioxide is by far the easiest gas to synthesize, but for reliable counting characteristics, its purity requirements are stringent. It had long been held that it was impossible to use carbon dioxide as a counting medium, but by rigorous purification of all electronegative species it has been demonstrated to be extremely reliable. Fergusson (*96*) has estimated that one part of chlorine in ten million parts of carbon dioxide is sufficient to affect the counting characteristics appreciably. The crude carbon dioxide produced by the combustion of the sample is washed with permanganate solution and then absorbed in barium hydroxide solution (*275*). The precipitated barium carbonate is separated and the carbon dioxide regenerated by treatment with phosphoric acid. The carbon dioxide is then absorbed on calcium oxide at 700°. After pumping off volatile impurities at 400° the temperature of the calcium oxide is raised to 900°, when the carbon dioxide is given off again. It is finally passed through a furnace containing hot copper and silver gauze and then distilled into the counter through a trap at $-80°$. The calcium oxide used must be specially selected for freedom from radium since the presence of this element could lead to a high contamination of the carbon dioxide by the alpha active radon.

Methane (*41, 81*) is far more tolerant to impurities and therefore satisfies the second condition above very well. Its synthesis from carbon dioxide, however, requires two or three steps and since both carbon dioxide and methane are monatomic in carbon, methane offers few advantages over carbon dioxide. At liquid nitrogen temperatures, moreover, methane has a vapor pressure of 10 mm and is consequently a less convenient gas to handle in a conventional vacuum line. It does, however, have the desirable property of requiring a low operating voltage, and consequently it might allow high gas pressures in the counter such that with carbon dioxide, the pressures would necessitate an operating voltage high enough to make insulation and corona discharge problems too acute.

Both acetylene and ethylene are diatomic in carbon, and thus possess the immediate advantage of introducing twice as much carbon into the counter at a given pressure. Syntheses are again more complex, although acetylene in particular has been used successfully by Suess (*262*) and Barker (*21, 57*) for routine dating. Its synthesis requires the reaction of carbon

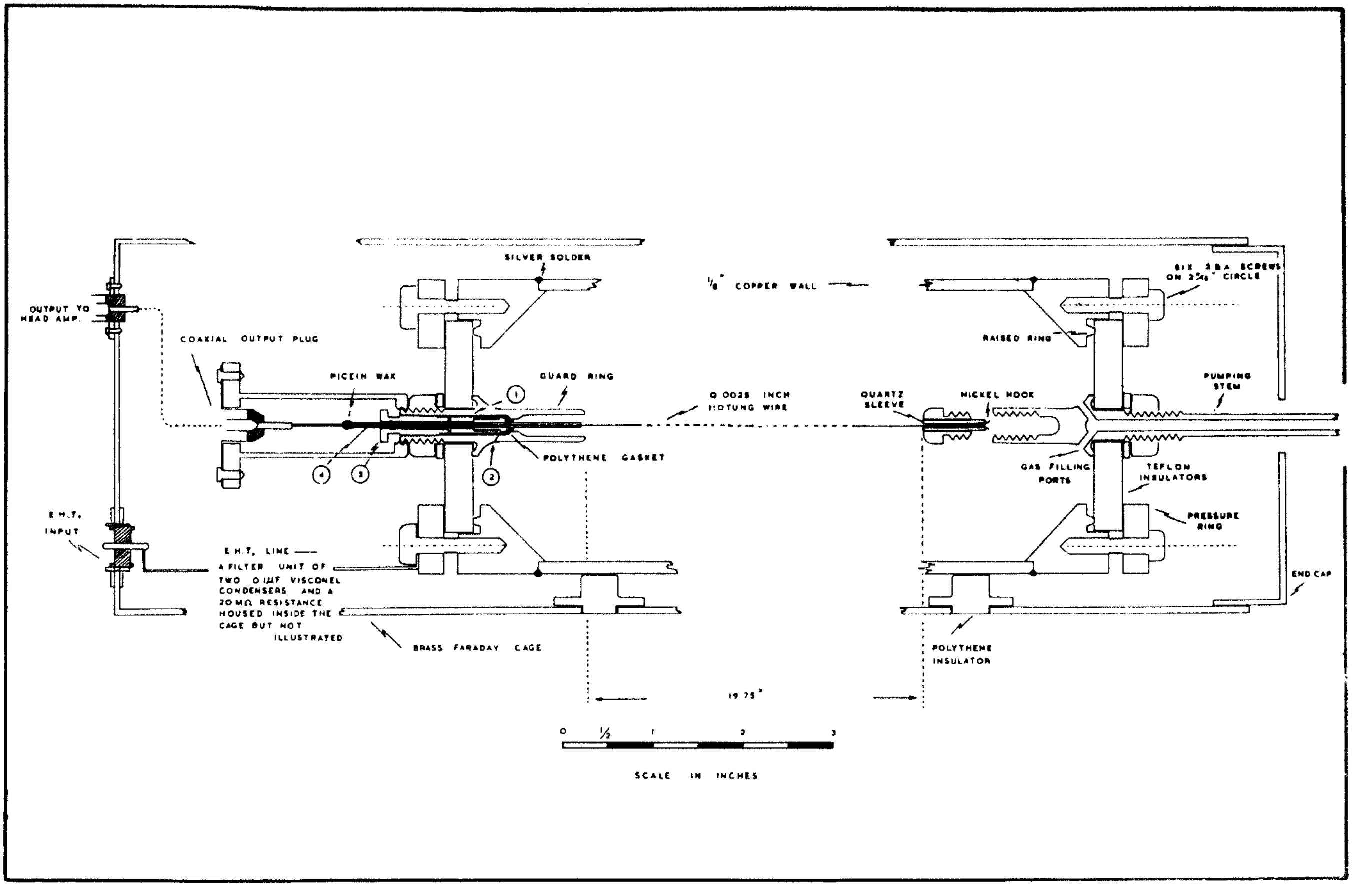

FIG. 1. Proportional counter for dating. 1. Perspex insulator. 2. Brass collar on needle. 3. Pressure screw. 4. Hypodermic needle. From Willis (*275*).

dioxide with molten lithium at a dull red heat, producing lithium carbide. Acetylene is evolved by the action of water on the cold carbide.

At present, one of the world's most sensitive installations, built by Fergusson (*96*) and his collaborators, operates with a carbon dioxide filled gas counter operating in the proportional region. The value of c^2/b is 760. Other similar installations have values between 80 and 300.

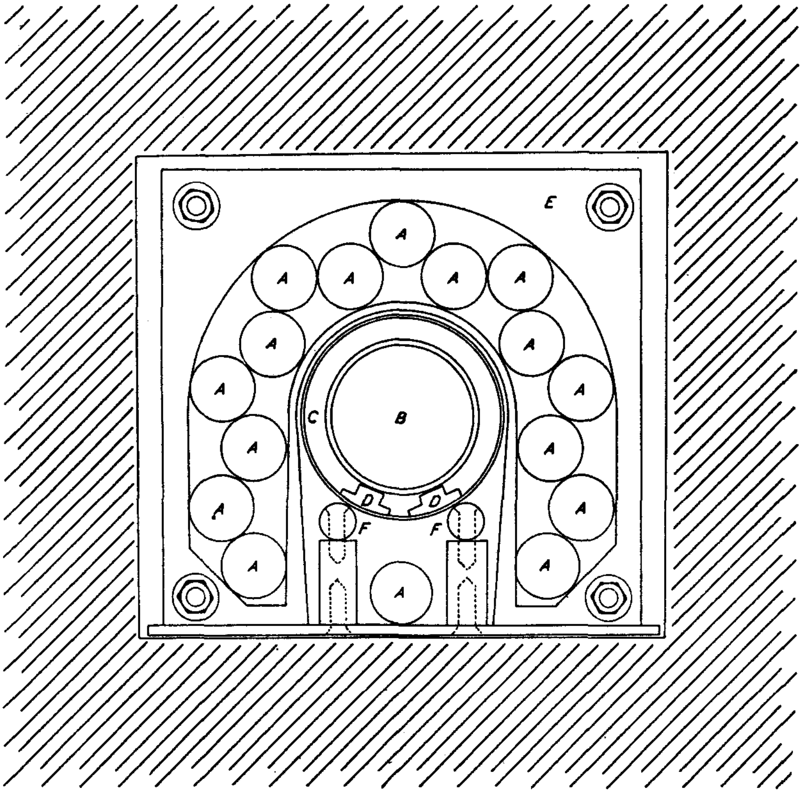

FIG. 2. Transverse section of the counter assembly within the zinc shield. *A*, cosmic ray Geiger counters; *B*, proportional counter; *C*, Faraday cage; *D*, Polythene insulators; *E*, support for Geiger assembly; *F*, supports for porportional counter.

De Vries (*79*) has recently been able to extend the range of age determination to 70,000 yr by means of isotopic enrichment in thermal diffusion columns.

A spectacularly low background of 2.2 counts/min with a 5.6-liter counter has also been achieved using a coincidence ring integral with the central counter with thin wire walls (*211*). A very successful design of counter for proportional counting with carbon dioxide up to 5 atm pressure is shown in Fig. 1. The anticoincidence assembly is shown in Fig. 2.

3. *Scintillation Counting*

Scintillation counting offers the attractive possibility of introducing a much larger quantity of carbon into the counting system that is possible with either of the two previous methods, supposing sufficient sample is available. The background count rate is also often high, but this can be considerably reduced by pulse height discrimination, which is a more effective practice with scintillation counting. Coincident pairs of photomultiplier tubes can also be used.

Audric and Long (*16–18*) reduced complex syntheses to a minimum by dissolving acetylene in toluene at −78°C, and used paraterphenyl as a phosphor. Pringle, Turchinetz, and Funt (*231*) synthesized toluene from carbon dioxide by adding the carbon to the side chain via benzoic acid and benzyl alcohol. The same workers also synthesized methanol.

Arnold (*9*) has used ethanol and a heptane-toluene mixture as counting media, while Hayes and Anderson (*4*) have measured the activity of natural *para*-cymene.

Routine measurements of natural radiocarbon have been successfully made by McAulay (*187*) at Trinity College, Dublin, using methanol. Specially selected photomultiplier tubes must be used in order to reach a sufficiently low background. In principle very large values of c^2/b are possible, for instance, Anderson reports a value of 1274. For routine operation, however, many of the foregoing possibilities must be excluded because of the length of time required for the preparation of these samples.

4. *Bubble Chamber Techniques*

An entirely novel method of measuring natural radiocarbon has been put forward by Dodd (*83*). For boiling in a liquid to be initiated, conditions must be such that a bubble of microscopic size formed within the liquid can increase in size continuously. Its internal pressure must therefore exceed the sum of the hydrostatic pressure and the surface tension pressure, both of which tend to collapse the bubble. Boiling is immediate if a solid nucleus is present on which a bubble of finite size can form. In a clean liquid in a smooth container, boiling will be delayed until thermal fluctuations produce a bubble whose internal pressure is great enough to enable it to grow to visible size. At low degrees of superheating, the probability of this occurring is so low that an appreciable delay occurs before the liquid begins to boil.

Should the bubble acquire an electric charge in the same way on its formation, an extra growth promoting factor exists, and this pressure increase varies inversely as the fourth power of the radius of the bubble. A bubble which would normally collapse, will grow.

Dodd postulated that an electron from a carbon disintegration might allow a bubble to acquire such a charge, and tested the hypothesis on diethyl ether. Ether containing no C^{14} was obtained from petroleum products, and "contemporary" ether was obtained from fermentation alcohol. Dodd found that the mean time for the "dead" ether to boil was appreciably longer than for the "contemporary." Moreover, mixtures of the two ethers gave intermediate boiling times. If it is possible to achieve an easy synthesis of ether from a sample submitted for dating, then it should be possible to establish its age by the delay in boiling with reference to the two standard samples.

5. *Origin of the Residual Background in Anticoincidence-Shielded Counters*

Although it is generally most important to increase the counting rate, c, rather than to reduce the background, b, in maximizing c^2/b, the possibility of fluctuations in b during the long counting periods involved makes too large a value of b very undesirable.

a. Natural activation. Part of the residual background arises from the natural activity of the screening materials and the components of the central and anticoincidence counters. The former can trigger the central counter, without the anticoincident ring generally by the interaction of photons with the wall material of the central counter. This effect can be reduced by: (i) a mercury screen round the central counter, which absorbs the photons (*160*); (ii) making the wall of the central counter of as light construction as possible. Thus a metallized silica counter may prove superior to a copper walled counter (*73*). Another solution that has been tried has been to use a metallized plastic film or even a grill of wires for the "walls" of the central counter (*138*). The natural contamination of the materials should preferably be estimated by radiochemical methods before use. The whole body scintillation counters used in radiobiological study are also valuable for this purpose. The alpha pulses in the background can also be identified by pulse analysis and may provide an indication of the components of the natural contamination, but it is well to remember that artificial radioactive substances are now so common that purely β or β-γ active contaminants often occur.

b. The neutron background. There is considerable evidence that part of the background finds its origin in the cosmic ray neutrons (*74*). The background generally changes with the atmospheric pressure but the relation is not a simple one. Solar flares may produce exceptional changes. Naturally, counters with hydrogeneous fillings, such as methane, are more sensitive to these effects than carbon dioxide filled systems. For the hydrogenous counters a screen of borated paraffin may be advantageous. If the background is not determined during the measurement, the observation should be corrected according to the difference in the total counting in the coincident ring during the two sets of observations.

B. VALIDITY OF THE FUNDAMENTAL ASSUMPTIONS

1. *The Fundamental Assumptions*

Libby (*172*), in postulating the idea that the cosmic ray produced radiocarbon might provide a valuable means of age determination, supposed that the C^{14} atoms would be readily oxidized to carbon dioxide and would mix freely with the atmospheric carbon dioxide. As a consequence of the rapid turnover of the earth's atmosphere, radiocarbon-labeled carbon dioxide would achieve a uniform global distribution, and might be expected to be taken up in the same proportion by all plant life during the process of photosynthesis. All animal life, derived directly or indirectly from plant material would also be expected to contain the same universal specific activity. Sea life would be similarly affected, since the carbon dioxide of the atmosphere is in exchange equilibrium with the oceans which in turn reach equilibrium with the atmospheric carbon dioxide. He argued that these equilibria are reached quickly compared with the half-life of C^{14}. Upon the death of an organism, further uptake or exchange of radiocarbon would cease, leaving the trapped radiocarbon to decay exponentially with time.

If the specific activity of organic material has been constant over many thousands of years, then ancient organic material would have exhibited the same specific activity at the time of its death as organic material at the present time. If, then, it were possible to measure the activity of such an ancient sample and compare it with the activity of a modern sample, it would be possible, knowing the half-life of radiocarbon, to calculate the time that has elapsed since the ancient sample was in isotopic exchange equilibrium with the carbon reservoir.

The time T since the death of the organism would be given by

$$T = \frac{1}{\lambda} \log \frac{I_0}{I},$$

where λ is the decay constant of radiocarbon; I is the measured activity of the ancient sample; and I_0 is the measured activity of modern organic material.

It was on this basis that Libby developed his radiocarbon dating method. It has proved an invaluable tool in the solution of geological, climatological, oceanographic, and archaeological problems.

From time to time criticisms of the method have been made (*60, 208*), on the ground that one or another of the fundamental assumptions is either not valid, or required serious modification (*90*). The more controversial assumptions are:

1. that the specific activity of living organic material has been constant over a very long period, and further that the contemporary assay is universal;
2. that the biological materials which are to be assayed have retained their true original composition and ceased exchanging with reservoir carbon at the time of death;
3. that the half-life of radiocarbon is accurately established.

It is, therefore, pertinent to examine the validity of these assumptions, and to see under what circumstances it is necessary to modify them to avoid serious errors in the estimation of the age of an ancient sample.

2. The Constancy of the Contemporary Specific Activity

The specific activity of contemporary plant carbon will depend upon the concentration of radiocarbon in the atmosphere and also the extent of any isotopic fractionation which occurs during photosynthesis, and subsequent metabolism. The constancy of the atmospheric activity will depend in turn on the constancy of radiocarbon production and the rates of isotopic equilibration within the components of the carbon reservoir.

To the first approximation the dates obtained using the method have been shown to be empirically correct. Nevertheless, with the refinement of the technique, de Vries (*75*) has shown that variations of the order of ±1% have occurred since 1500 A.D. This conclusion was reached by measuring the initial activity of carefully dated tree rings taking into account the radioactive decay. Following a similar technique, Willis, Münnich, and Tauber (*278*), conducting parallel measurements on the same sequoia tree in three separate laboratories, extended the pattern of variations back to 600 A.D. with good agreement (Fig. 3), and observed the order of variations described by de Vries. Such variations would lead to errors, independent of the error due to counting statistics, of ±100 yr. Thus it could be that materials of one, three, or even five, finite ages could exhibit the same radiocarbon activity and then be ascribed to one common radiocarbon date. The implications are particularly troublesome for the archaeologist, who often requires a more precise age for his samples (*217*).

The variation in the specific activity might imply that the production rate of atmospheric radiocarbon and thus the cosmic ray flux, have varied, or, that in some way the equilibrium of the carbon reservoir has been disturbed.

a. Equilibration between the parts of the reservoir. Craig (*51, 53*), Broecker (*35*), and others (*11, 13, 239*) have postulated a dynamic model to describe the equilibrium of the radiocarbon reservoir. This model represents a considerable simplification of the natural processes, but nevertheless affords an assessment to be made of the turnover times of the various phases of the reservoir.

The reservoir is continually being replenished by the radiocarbon production from cosmic radiation, and depleted by radioactive decay and sedimentation in the oceans. If the system has reached isotopic equilibrium, the rate of loss will equal the replenishment. The phases are represented by the atmosphere, the biosphere, the upper ocean, above the thermocline, and the deep sea. A certain amount of radiocarbon will leak out of the exchange reservoir by becoming entombed in the ocean sediment. This description is known as the chain model. A refinement of this interpretation, known as the cyclic model, has been made to include the direct exchange between deep ocean water and the atmosphere when the former rises to the surface in polar regions. De Vries (*75*) has described an electrical analogy of Craig's (*53*) model by considering the phases to constitute an interconnected network of condensers with parallel resistance leak paths.

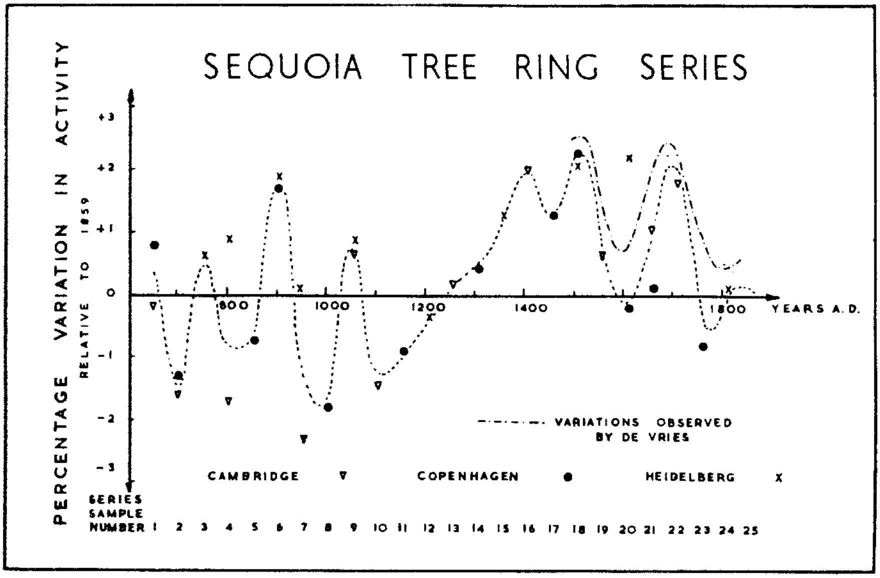

FIG. 3. The initial activities of each of the 25 samples taken at 50-year intervals from a giant sequoia, represented as a percentage variation from the activity of the wood from the 1859 tree ring. The dotted curve is intended as a visual aid only. The Copenhagen and Heidelberg measurements are both corrected for C^{13}/C^{12} variations, and the authors are greatly indebted to Dr. W. Dansgaard of Copenhagen and Dr. J. C. Vogel of Heidelberg for the measurements of these ratios (from Willis, Münnich and Tauber *278*).

The specific activity of the contemporary carbon in the different phases will depend largely on the mean residence time of a radiocarbon atom in each phase. Since the exchange between growing plant life and the atmosphere is rapid, the contemporary activity of the biosphere will reflect the activity of atmosphere almost exactly (*14*). The two activities will not, however, be identical since an isotopic enrichment in C^{12} is observed during the process of photosynthesis (*234*) The mean age of a radiocarbon atom in the surface ocean layers will be much larger than in the atmosphere, since it may have exchanged once or twice with the deep sea. This will mean that the specific activity of the upper ocean would be lower than the atmosphere if there were no isotopic fractionation. Because the latter effect enriches the ocean in radiocarbon, the activity is in fact nearly the same as that found in modern wood.

Similarly, the deep sea will exhibit a specific activity of an even lower value, since its large bulk means that the mean time spent by a radiocarbon atom in this phase is relatively large. The corrections for the isotopic fractionation between different carbonaceous materials can be calculated from data obtained by mass spectrometry recording the corresponding, but smaller, fractionation of C^{13}. Fractionation factors of this kind have been determined by Craig for a number of the common materials (*49*).

b. The fossil fuel effect. These natural processes are further complicated by the large amounts of fossil fuel (*263*), containing no residual radiocarbon, which have been burned during the past century. This addition to the carbon reservoir has diluted the atmosphere with C^{12}. A corresponding lowering of the specific activity of modern wood has been observed, but much of the effect has been buffered by exchange with the sea; there, however, the effect will as yet be moderately small (*225*).

The accuracy of the solid carbon method for the contemporary assay was $\pm 2\%$ (*172*). Kulp (*160*) found that in practice even this accuracy was difficult to obtain. The effects of isotopic fractionation, which had been demonstrated for several natural processes by Craig (*49*) for C^{13}, and predicted by extrapolation for C^{14}, were masked by this large error in the assay. The increased efficiency of gas proportional counting has led to the quantitative detection of these effects, especially by Süess (*263*), Rafter (*234*), and Brannon *et al.* (*33*).

Craig (*49*) had already shown by mass spectrometric measurements that the atmospheric carbon dioxide showed an enrichment of C^{13} with respect to modern wood of 1.84%. On this basis Craig predicted that the C^{14} enrichment would be twice this value, namely 3.6%. Rafter (*234*) has measured the specific activity of air from Makaia, New Zealand, and obtained results in good agreement with the predicted figure of Craig. Brannon *et al.* have confirmed this figure, which seems well established.

For dating purposes, this fractionation causes no appreciable error if samples submitted for dating are all derived from plant material. The effect of the fossil fuel dilution does, however, influence dating considerably, since samples older than 100 yr would exhibit a greater contemporary specific activity than 1950 wood. Moreover, the effect could conceivably be greater in some industrial areas, and dates published by different laboratories may be based on significantly different values for the specific contemporary activity. Before the recognition of this effect, such variations did in fact exist and the need for ammending date lists was recognized by de Vries.

Brannon *et al.* (*33*) have estimated a total combustion of 3.3 × 10^{17} gm of fossil fuel since 1860, from Putnam's (*232*) figures for world coal production, cumulative petroleum production, and natural gas from the ratio of gas to oil production. This sum is equivalent to 14% of the total amount of carbon dioxide in the atmosphere, which would have exhibited a similar percentage increase in C^{12} in the absence of exchange with the other phases. In fact, as has been shown, this exchange does exist, and the observed dilution is only about 3%.

c. Weapon testing effects. Since the introduction of extensive programs of nuclear weapon tests, radiocarbon has been added to the atmosphere to such an extent that the dilution effect of the fossil fuel has been far more than compensated (*36, 45, 76, 194, 215, 235, 236, 266, 276*). Figure 4 illustrates the progressive rise of the tropospheric radiocarbon activity since 1953 as indicated by measurements upon annual crops of oats grown at Cambridge, England (*276*). These levels are generally representative of the Northern Hemisphere, in which all the major detonations have taken place. The Southern Hemisphere on the other hand appears to have shown a slower rise.

The cessation of weapon testing after the conclusion of a very intense series by all three interested nations allowed the fate of a relatively large stratospheric injection of radiocarbon to be observed by samples taken over wide areas. The immediate response was a sharp rise in the Spring of 1959 corresponding to the annual flushing of stratospheric air through the tropopause gap. This effect had been demonstrated in previous years by Münnich and Vogel (*216*) for radiocarbon and by other workers for other fallout products. The rise of 1959 came to a peak at Midsummer with a level of about 32% above 1953 values. In 1960, a continuous sampling programme at Cambridge (*277*) showed no pronounced seasonal variation, and the midsummer level had dropped to 22% above 1953 values. At the same time, the tropospheric activity of the Southern Hemisphere rose to near equilibrium with the Northern Hemisphere. This near equilibrium has been reached quicker than might have been supposed which would indicate

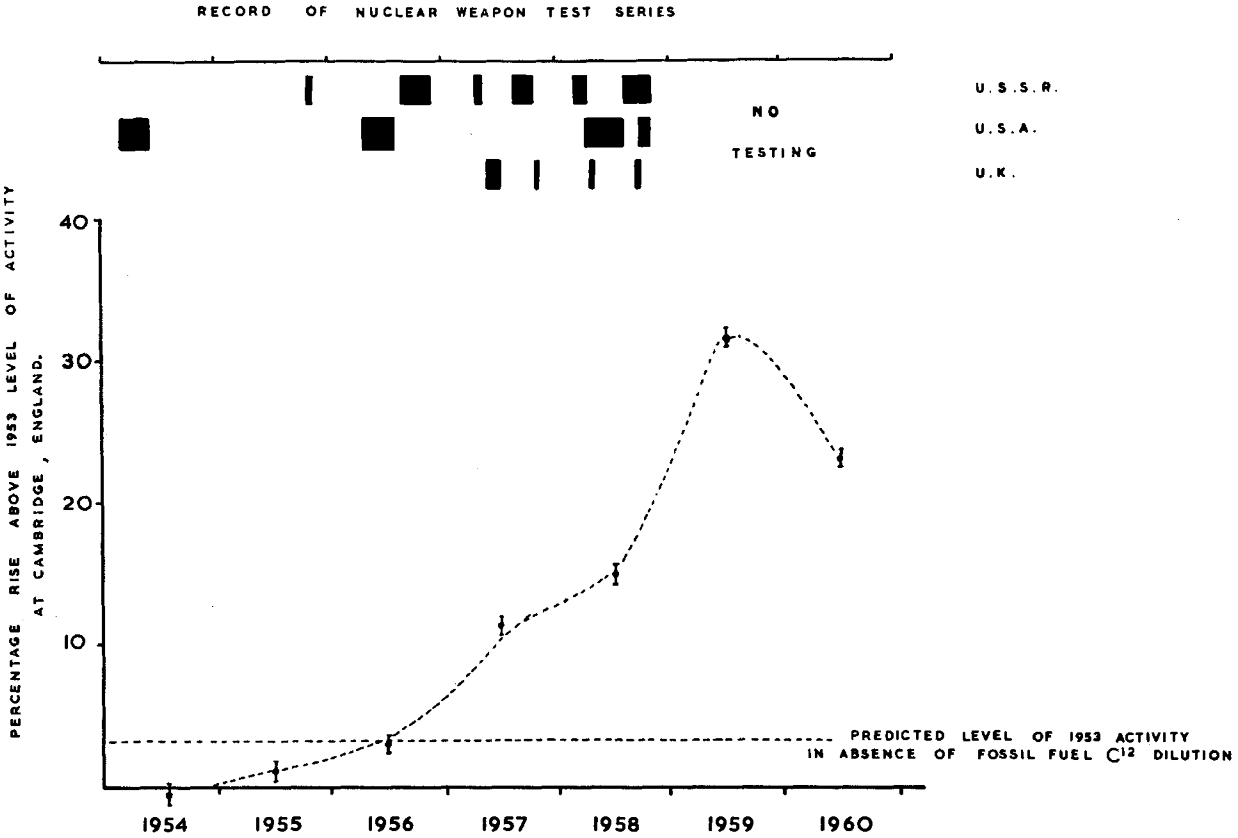

FIG. 4. The rise in tropospheric radiocarbon activity since 1953 as a result of Nuclear Weapon testing, showing the response to the cessation of testing after the fall of 1958. Record of Nuclear Weapon Tests adapted from Hagemann *et al.* (*130*).

a turnover time between the northern and southern tropospheres over only a year or so. Since there is very little seasonal effect observed in 1960, the same may be true of the stratosphere–troposphere interchange. Tauber (*267*) has suggested that because of the stratospheric annual flushing into the troposphere, a radiocarbon activity gradient might exist under natural conditions, and this could provide an explanation for observed anomalies in the radiocarbon assay from organic material from different locations on earth. It might also be that because of the predominance of water surface in the Southern Hemisphere, a greater aggregate radiocarbon exchange with the surface ocean water might produce a natural lower activity in that Hemisphere.

The question might also be posed as to how long it takes for a newly created radiocarbon atom to become carbon dioxide, or indeed if all of it does in fact become carbon dioxide. It might be possible for the carbon to form other compounds than carbon dioxide, such as formic acid, hydrogen cyanide, hydrogen cyanate, and carbon monoxide, which might remain in the stratosphere for a long time at high specific activity, although present at very small chemical concentration.

The effects of recent additions of both active and inactive carbon to the reservoir can largely be overcome for dating purposes by using a piece of wood over 100 yr old as a standard for the contemporary activity, and this procedure is now common practice. To offset any possible variation in the activity of contemporary samples used by different dating laboratories, the National Bureau of Standards, Washington, D.C., now holds a batch of oxalic acid which is available as a universal reference sample against which laboratory standards may be checked.

3. The Half-life of Radiocarbon

The half-life of radiocarbon has been variously determined at values ranging from 7,200 to 4,700 yr. The evaluation of this quantity is essential to the method if radiocarbon ages are to be truly identified with solar years. The present internationally accepted half-life is 5568 ± 30 yr (*172*), and is derived from the weighted average of three determinations. They are 5580 ± 45 yr (Engelkemeir, Hamill, Inghram, and Libby, *91*) 5589 ± 75 yr (Jones, *147*), and 5513 ± 165 yr (Miller, Ballentine, Bernstein, Friedman, Nier, and Evans, *207*). Each of these three values was derived from absolute gas counting methods and considerable trouble was taken to evaluate the efficiency of the counters used (*172*). In all three cases, mass spectrometric methods were used for the isotopic composition of the sample.

Later values (Caswell *et al.*, *43*, Manov and Curtiss, *195*) gave 5900 ±

250 and 5370 ± 210 yr, respectively, although the higher probable error signifies the lower accuracy of the measurements.

Since the three estimations from which the weighted average was taken were made on three different sets of apparatus, it seems probable that the accepted value for the half-life has a real error greater than the ±30 yr quoted, which is based on statistics. Historically dated samples have shown that the accepted value is empirically correct, and that the deviation from this figure must be small.

4. The Activity of Marine Biological Material

Craig's figures (*50*) show that the ocean bicarbonate is enriched in C^{13} with respect to modern wood by 2.32%, and that theoretically a C^{14} enrichment of 4.64% should be expected. This value is not in practice realized; indeed, the observed value for the contemporary specific activity of modern shell shows more nearly the same activity as modern wood. This would imply that since the mean time a radiocarbon atom spends in the ocean is larger than the mean time spent in the atmosphere, the true specific activity of the sea shell is really depleted by about 4.5% with respect to modern wood. This corresponds to an apparent age of contemporary ocean shell of about 400 yr. The experiments of Libby and von Buttlar (*42*) indicate that the turnover time for the atmosphere into the surface layers of the ocean is of the order of 10 yr. Arnold and Anderson (*13*) give a value of 7 ± 3 yr which is in good agreement. It thus follows from this consideration, and also the fossil fuel inventory, that some of this apparent age is due to the addition of C^{12} to this phase of the exchange reservoir. Relatively little of this fossil fuel carbon will have yet found its way into the deep ocean layers, whichever model is considered. Since the model is inevitably oversimplified, it is not surprising that some wide discrepancies appear in marine shell assay. Rafter (*234*) obtained a value for the specific activity of the bicarbonate in sea water, and by considering the isotopic enrichment between this and the carbonate, predicted a figure for the latter which agrees with the observed carbonate assay of other workers who found little difference from the activity of modern wood. Nevertheless, the carbonate from *paua* shells measured by Rafter showed an average enrichment of 2.2% above modern wood, but an average depletion of *paua* flesh of −1.24%, giving a total depletion of 3.46% for the activity of *paua* flesh with respect to the shell. This figure agrees with Craig's estimations of C^{12}/C^{13} ratios in marine carbonate and flesh.

Conversely, marine shells which might grow in water which is constantly upwelling from the deep sea, perhaps in higher latitudes as indicated by Broecker (*35*), might be expected to yield lower specific activities.

It appears likely therefore that dating of marine shell cannot be as unambiguous as the dating of terrestial life, whose exchange system is less complicated and more rapid.

5. *Absence of Exchange: The Retention by Biological Materials of Their Original Compositions*

Barghorn (*20*) has shown that under anaerobic conditions, there are no known bacteria which will attack lignin. The cellulose fraction of plant material, however, can be the subject of degradative processes. Unfortunately, the more resistant lignin fraction is appreciably soluble and material of similar chemical composition may migrate and be redeposited in another place (*117*). Since the more chemically stable cellulose fraction is depleted by degradation processes, the situation can easily arise where redeposited material forms a major source of contamination (*119*). Where such a contamination is suspected, the intrusive colloidal material may be extracted with alkali, and this material when assayed invariably yields a much younger age than the reservoir (*183*).

The intrusion of secondary material into a sample can be seen readily in many stratigraphic sections where growing roots have penetrated many feet below the contemporary horizon. Where such intrusion is recognized by fresh rootlets, these can be largely mechanically removed, but perhaps the case is more serious where the secondary intrusion has itself been humified and is indistinguishable from the primary material. Errors of this nature have the greater significance the greater the age of the deposit, and may prove to be one of the limiting factors of the method. The extent of the error which would result from 5% intrusion of modern carbon into the deposits of different ages can be seen in Table IV.

TABLE IV
ERRORS RESULTING FROM INTRUSION OF 5% OF MODERN CARBON

Time age (yr)	Apparent age with 5% modern intrusion
5,568	4,800
11,120	9,700
16,700	14,000
22,250	17,600
27,810	20,200
33,400	21,850

Intrusions do not necessarily have to be of younger origin. In areas such as Britain where there are large outcrops of Palaeozoic or Mesozoic coal, the boulder clays can be shown to contain much comminuted material derived from them, and lake deposits, such as are often employed in dating the Late Glacial Period, may contain enough inactive carbon from this source to increase the true dates appreciably (*119*).

It has been clearly shown by Deevey *et al.* (*69*) and Münnich (*215*) that when the prime source of organic lake mud is by the photosynthesis of submerged plants in hard water, the ancient carbon brought into lakes from limestone formations as soluble bicarbonate may be incorporated into the carbohydrates made by green plants. If this were the only source of carbon for the photosynthetic fixation of submerged aquatic plants in hard water lakes, the dating of their remains might be expected to yield a spurious activity of one half-life of radiocarbon, namely, about 5,000 yr. In practice, however, this figure is rarely realized since there is a constant exchange of carbon dioxide in the lake with the atmosphere, especially if it is shallow; this exchange will tend to restore a fraction of the C^{14} deficit.

V. Tritium

Next to natural radiocarbon, tritium has yielded the most interesting information on the time scale of natural processes, as well as posing an intriguing question of the origin of the greater part of the observed activity.

A. DISCOVERY

Libby (*170*) observed just after the end of World War II, that some tritium must be produced in the atmosphere by the cosmic radiation. Successful detection of the tritium activity was finally reported almost simultaneously in the autumn of 1950 by groups working in Germany (*93*) and the United States (*171*).

The former group used molecular hydrogen separated from the He–Ne fraction in an air liquefaction plant. The hydrogen was burned to water and the tritium further concentrated by electrolysis of the water to one-fortieth of its initial volume. Finally the water was converted to ethane and the activity of this gas measured by mixing it with the gas filling a Geiger counter (*134*).

Libby and his collaborators in the United States on the other hand made their first measurements on a sample of hydrogen prepared from a recently concentrated sample of heavy water (*128*). About 3 liters of the heavy water, which contained 99.74% D_2O, were electrolyzed to 15 cm^3; and some of the hydrogen, released from this water by decomposition by hot zinc, was introduced into a Geiger counter together with argon and ethylene, and the activity was recorded.

Similar measurements were made on an old sample (1935) of heavy water, similar to that used years before in the search for tritium, before the question of the relative stability of T and He^3 had been settled (*243*). An appropriately lower specific activity was observed, consistent with the decay of the tritium since concentration of the heavy water. The chemical identity of the activity was thoroughly established.

B. MEASUREMENT

The very low specific activities involved and the exceptionally soft radiation from tritium make the measurement of natural tritium activities a difficult problem. The radiation, β-rays with a maximum energy of only 18 kev is so soft that the hydrogen sample, or compound containing this hydrogen, must be introduced into the counter itself (*38*, *162*). In addition, despite the application of low background counting techniques, some isotopic concentration of the tritium is almost invariably made before measurement, since direct measurement is limited to a minimum tritium concentration of 1 in 10^{16}.

1. Isotopic Enrichment

Electrolytic methods are always employed and the sample is electrolyzed until the volume of water is reduced by a factor of 10^{-2} to 10^{-4}. About half the initial tritium is lost with the electrolytic gas in this process (*38*). The tritium enrichment is then calculated after measuring the initial and final deuterium content of the water (*162*). The ratio of the tritium to the deuterium enrichments can either be estimated theoretically or determined in a separate experiment with a sample spiked with a known tritium concentration.

2. Measurement of Activity

Earlier measurements were made by Geiger counting after incorporating the hydrogen in the counter filling either as molecular hydrogen or after conversion to ethane (*128*, *134*). More recently, proportional counting with much higher gas pressures has been used. Thus Kulp and collaborators used a 2-liter copper counter with a filling of 0.9 atm of the hydrogen sample, to which is added 0.1 atm of purified tank methane to improve the proportional characteristics of the filling. With such a counter a background of 9.5 ± 0.3 counts/min was obtained so that the over-all sensitivity was equivalent to 1 T in 10^{19} of hydrogen (*112*, *162*).

3. Other Methods of Measurement

The majority of measurements have been made using the method described in the previous sections. However natural tritium can be detected by means of a cloud chamber, and this method was used to show that old glacier water was free from tritium (*100*).

4. Units and Half-life of Tritium

The activities observed can, of course, be expressed as specific activities but for many reasons the tritium-hydrogen ratio is more interesting. For rain water this proves to be about 5×10^{-18}, so that Libby has suggested a convenient unit, the tritium unit or TU corresponding to a T/H ratio of 10^{-18} (*42*).

The presently accepted value of the half-life of tritium used in these studies is 12.3 yr. (*148*). The probably error is certainly less than for the C^{14} half-life and is believed to be $\pm 2\%$.

5. Isotopic Fractionation Effects

The equilibrium differences in isotopic composition between the hydrogen in different chemical compounds will, of course, be even larger than for the carbon isotopes. For most purposes, however, they can be calculated from the measured differences in deuterium concentration in the different compounds. It will be seen, however, that these isotope effects are not as yet important to the study of the tritium distribution.

C. SUMMARY OF RESULTS

The observations on natural tritium are sharply divided into two periods—the measurements over the three years preceding 1954 when, apparently, no substantial amount of tritium was introduced into the atmosphere by human agencies and the subsequent period up to the present day. It will be observed, incidentally, that neither the first American nor Russian thermonuclear warfare tests, reputedly in 1952 and 1953, respectively, released substantial amounts of tritium into the atmosphere, whereas the Castle series of tests in 1954 produced a profound effect. (Rain water tritium concentrations have not been published for the whole of 1953.)

1. Pre-1954 Data

A selection of data is shown in Table V. Most of the other observations are due to Libby and his collaborators (*24*, *42*, *52*, *112*, *129*, *174*).

2. Post-1954 Data

The 1954 thermonuclear weapon tests provided a remarkable opportunity to observe the effect of the introduction into the atmosphere of a quantity of tritium considerably in excess of the instantaneous tritium content of the atmosphere. Fortunately frequent measurements of the tritium content of the rain falling at a station in the United States were made throughout the relevant period and these measurements have supplied some very valuable information on some atmospheric processes (*24, 55*).

These results show that following the relatively local release of the tritium, the tritium content of the rain rose to a maximum, some hundred times the normal value, in a few days, indicating fairly rapid mixing within the troposphere. The tritium activity of the rain then gradually decreased to a new steady value with a half-life for this equilibration process of about 35 days (*174*). This period is characteristic of the washout time necessary for the rain to remove materials from the atmosphere and is in agreement with the less accurate value that can be deduced from the Be^7 data (*26, 61*).

TABLE V
SOME PRE-1954 TRITIUM DATA

Material	Tritium content (TU)
Rain water (Continental, Chicago)	7.0
River water (Mississippi)	6.0
Lake water (Michigan)	1.6
Ocean surface	0.24
Marine rain	1.0
Atmospheric hydrogen	15,000
Antarctic snow	16.0
French wines (corrected for decay)	4.5

Earlier measurements made in the Southern Hemisphere shortly after these tests showed no increase in tritium activity which was interpreted as showing that the tritium produced by the thermonuclear explosions was confined to the troposphere and that the tropospheric atmospheres of the Northern and Southern Hemispheres do not mix (*174*). The former conclusion was quite unexpected since the other products of these explosions are largely ejected into the stratosphere and it was difficult to account for differences in the behavior of the tritium and the other radioactive products in the explosion. However subsequent observations do not confirm these data. Direct measurements of the tritium content of the stratosphere have now been reported. These show that the artificially injected tritium amounts to about four times the natural content, that is to say about 2.4×10^{27} atoms of artificial tritium. The ratio of artificial T/artificial C^{14} in 1959 was about 0.4. The stratospheric tritium concentration in T.U. is about 4×10^5–10^6. The accuracy is poor because of insufficient knowledge of the water content of the stratosphere. In the same paper it is confirmed that the tritium in the troposphere is removed to the sea with the usual wash-out kinetics (*130*). Clearly most of the artificial tritium joins the artificial radiocarbon in the stratospheric reservoir.

D. The Production and Distribution of the Tritium

Because of the short half-life of tritium it is even more important than in the case of radiocarbon to develop a dynamic model of the production and distribution processes. The mixing processes in the hydrogenous reservoir that the tritium can enter are often slow compared with the half-life of the activity.

1. *Tritium Life Cycle*

The tritium is produced, at least to a considerable extent, in the stratosphere. It is quickly oxidized to water and is then gradually introduced into the troposphere, this mixing process having a half-life comparable with that of the tritium (*177*). It leaves the atmosphere in the rain. On land it then enters the biosphere and the rivers. The rivers carry the tritium to the sea, joining that part reaching the sea directly from the rain in the surface waters of the oceans. From the surface waters it slowly leaks into the deep waters, but the half-life for this process is long compared with that of tritium. Because of the re-evaporation of surface waters and the oceans into the atmosphere the tritium content of continental rain is higher than that of marine rain, since the tritium suffers greater dilution on mixing with the ocean surface water than it does on falling on a land mass (*55*).

a. Stratospheric-tropospheric mixing. The tritium observations provide an interesting confirmation of the conclusion, from fallout data (see Section VI), that the half-life for stratospheric-tropospheric mixing is about 7 yr. It was shown in Table V that the tritium content of atmospheric hydrogen is many times greater than that of rain. Now the atmospheric hydrogen results from the photodecomposition of water vapor in the stratospheric region as is shown by the identity of their deuterium-hydrogen ratios and the difference from the equilibrium value for the hydrogen-water system (*129*, *133*, *134*, *261*). In addition, it can be expected that most of the natural tritium formed in the atmosphere will be formed in the stratosphere. If, therefore, the stratospheric water mixes only slowly with the rest of the atmosphere, its tritium content should be much higher than that of the tropospheric water because only a small part of the atmospheric water is contained in the stratosphere. Bearing in mind that hydrogen and water vapor reach isotopic equilibrium only very slowly indeed, the tritium content of the atmospheric hydrogen can be regarded as representative of the tritium content of stratospheric water, after allowing for the decay of the tritium during the time taken for the hydrogen to be mixed into the troposphere.

In effect, slow mixing of the stratosphere and troposphere means that the tritium in atmospheric hydrogen will not have suffered the dilution, corresponding to the different water contents of the stratosphere (6×10^{-3} gm/cm$_e^2$) and troposphere (2.54 gm/cm$_e^2$), that reduces the activity of the rain.

The observations are consistent with half-life for the mixing process of about 7 yr (*55*).

Further data on this question has been obtained from Sr^{90} fall-out and C^{14} measurements. These are considered in Sections VI,B and C.

2. Calculated Rate of Production of Tritium

The rate of production of tritium can be calculated in a manner similar to that already described for the calculation of the rate of production of Be^7. It suffers from the same limitations and like that calculation the probable error should be taken rather cautiously. The tritium is produced both in the very energetic processes and also, to some extent, by a reaction involving neutrons of moderate energy. Until a few years ago no satisfactory cross sections for the energetic processes were available, but values are now available for tritium production by proton bombardment of nitrogen and oxygen for a number of energies in the 400 Mev to 6 bev range (*97–99,62*) A still more extensive coverage of the cross section as a function of the incident particle energy would be desirable. Using this data the estimates of tritium production in Table VI were made (*112*). From these estimates it can be safely said that the cosmic ray production of tritium can hardly exceed 0.5 T/cm$_e^2$ sec.

TABLE VI
CROSS-SECTIONS FOR TRITIUM PRODUCTION

Process	Energy range (Mev)	6 millibarns	T/cm$_e^2$ sec.
N^{14} (n,t)	4.4	11 ± 2	0.1–0.2
O^{16} (p,t)	100	30	0.1
			0.25
O^{16} (p,t) N^{14} (p,t)	100	25	0.08
N^{14} (n,t)	10	11	0.05
O^{16} (p,t) N^{14} (p,t)	10–100		0.01
N^{14} (μ,t) (γ,t)			0.001
			0.14

3. Experimental Rate of Production

The rate of production of tritium can also be calculated from the experimental data on the tritium content of the hydrogeneous components of small sections of the earth by consideration of the material balance in the system chosen. Two particular systems have been chosen for this treatment, the Mississippi valley and the central Atlantic Ocean. In both cases the initial calculations omitted important factors but arrived at results compatible with the calculation of the previous section (*42*, *112*, *151*).

a. Mississippi valley data. It was first assumed that the tritium lost from the continental atmosphere by runoff down the rivers into the oceans and holdup in the land must be balanced by the production and transport of ocean vapor onto the continent. On this basis the experimental data on Mississippi rain gave a production rate of 0.16 T/cm_e^2 sec. Such a balance, however, ignores the extensive transport of water vapor from the continent to the oceans in the vapor state. Geographical and meteorological data have shown this to amount to about four times the run off from rivers. After taking this vapor transport into account a much larger tritium production is obtained, amounting to approximately 1 T/cm_e^2 sec (*52*, *55*).

b. Ocean balance. The earlier calculations supposed the rate of production of tritium equalled the rate of loss by marine rain less the rate of supply by evaporation of ocean surface waters (*42*). This calculation also led to about 0.12 T/cm_e^2 sec. However the radiocarbon data (see Section IV) showed the importance of mixing between the surface and deep sea waters, the process having a half-life of about 300 yr (*55*). Although this process is slow compared to the half-life of tritium, it means that the tritium is continually leaking into the deep sea. Correction for this leak on the basis of a residence time of 15 yr in the surface layers for the tritium raises the required production rate from the ocean data to more than 1 T/cm_e^2 sec. This model requires more than half the tritium inventory to be found in the deep sea at very great dilution (*52*, *55*). Further measurements bearing on the oceanic mixing processes are very necessary. A stratification of the tritium content of the superficial layers of the arctic ocean has been detected and it has been suggested that the deep Arctic ocean is supplied with water from the shelf of the Canadian archipelago (*114*). This interpretation of the observations, however, has met with some criticism (*37*, *115*).

4. Source of the Tritium

All these tritium production figures are subject to rather large errors. Nevertheless it seems very doubtful that the cosmic radiation can account for all the tritium production. Mayne, from consideration of the He^3 content of the atmosphere, has suggested that appreciable amounts of the gas, as well as the associated tritium, are supplied to the atmosphere by the volatilization of meteoric dust. However, very large amounts of dust would be necessary to account for the observed T production or He^3 concentration (*64, 201, 202*). A most interesting recent speculation suggested by Feld and Rossi (*52, 55*) is the possibility of direct accretion of tritium from the sun by the earth.

Clearly tritium measurements are yielding extremely valuable information about terrestrial and possibly even solar processes (*22, 113, 281*).

VI. Artificial Activities

For more than fifteen years man has been increasing the radioactive content of the atmosphere by the release of gaseous fission products during the processing of nuclear fuels and at various times by the detonation of nuclear weapons and, more recently, of thermonuclear devices. The three modes of contamination of the atmosphere produce rather different effects. The first only introduces true radioactive gases; the second distributes the radioactive fission products as well as, sometimes, radioactive isotopes of other elements, within the troposphere. Much of this activity is deposited quite locally near the test site, the remainder is largely removed from the atmosphere by rain—washout—in the same way as the Be^7 and with the same chronological pattern (*127, 180, 199, 200, 258*). The debris from thermonuclear tests includes much larger amounts of the same species as are formed by the atomic weapons together with large amounts of tritium, and, from the surplus neutrons produced, radiocarbon. Nearly all the fission product activities are projected in this case into the stratosphere.

A. GASEOUS FISSION PRODUCT ACTIVITIES

The most important of these are the Xe^{133} and the Kr^{85}. The former is too short-lived (5.3 days) to become thoroughly mixed throughout the atmosphere of the relevant hemisphere. But the krypton isotope with its 10.4-yr half-life now confers activity on all recently separated samples of the element. A measurement by de Vries in 1955 showed the current specific activity of krypton to be $2 \cdot 5 \cdot 10^4$ dis/mole min (*72*). The present value is at least four times this figure. Supposing that all of the fission product krypton activity is released into the atmosphere during the chemical processing of irradiated uranium and expressing the plutonium used in nuclear weapons entirely as equivalent U^{235}, it can be calculated from the fission yield of Kr^{85} (0.24) and the abundance of krypton, that the total U^{235} suffering fission up to the date of de Vries' measurement was about 5500 kg. The specific activity of krypton, therefore, provides a useful monitor of the total fission taking place (*54*). A comparison of the specific activities of samples of krypton from the northern and southern hemispheres would be most interesting.

B. THE FALLOUT

In the last few years a great deal of attention has been paid to the fate of the radioactive products from the nuclear weapon tests and a very extensive literature has accumulated. Two of the longer-lived fission products, the biologically important Sr^{90} and the more easily measured long-lived Cs^{137}, have been studied exhaustively. The latter isotope is gamma active, but both Sr^{90} and its shorter-lived daughter Y^{90} are purely beta emitters. The radioactive strontium deposited as fallout distributes itself over the biosphere and because of the close similarity in properties generally becomes associated with the much commoner calcium. Most animals and plants discriminate against the strontium when assimilating from a calcium–strontium mixture, reduction by factors of 4 or greater being commonly observed (*46*); some radiostrontium is acquired however by animals, plants, and human beings (*6, 158, 159*). Although the specific activity of the strontium remains fairly high in such media, the total activities in samples of reasonable size, not exceeding 100 gm for example, are very small, and therefore to permit accurate measurements, with reasonably high efficiency of detection, the strontium must be separated from the large excess of calcium before measurement of the activity. A number of satisfactory procedures for this separation and measurement have been described, but a more rapid and cheaper method would be valuable (*39, 94, 124, 209*). A critical report on these methods is also available (*264, 265*). Data on Sr^{90} are often presented in "Sunshine Units" (SU) $\equiv$ $\mu\mu$c. of Sr^{90}/gm Ca (*178*).

Earlier measurements of fall-out were often made by collecting the activity after allowing the air to impinge on a gummed strip. However, since the tropospheric fall-out takes place largely by the wash-out mechanism this technique is unreliable and it is more satisfactory to collect the rain in stainless steel or polythene pots (*89*). Several descriptions of the procedures used by the U.S. Atomic Energy Commission have now appeared both in the general literature and in the methods of the New York Health and Safety Laboratory (HASL reports) (*84*).

The Sr^{90} projected into the stratosphere appears to adsorb on submicron particles and suffers little or no gravitational deposition (*199*). It is presumably transformed to the carbonate, although the deposited Sr^{90} is said to be water-soluble. However this is very possibly due to bicarbonate formation. There is some evidence that the local fall-out in the vicinity of the test and the stratospheric fall-out are chemically different kinds of aerosol (*126*). The Sr^{90} is mostly retained by a few inches of soil and not much is leached out by the drainage of the rain (*203*).

Because of the slow stratospheric-tropospheric mixing the ratio of two activities of different half-lives and known fission yields, such as Sr^{89} and Sr^{90}, does not provide a simple measure of the age of the atmospheric fission products (*199*). Even the appropriate fission yields may be somewhat uncertain (*104, 123*).

A good deal of data on the fall-out has now appeared. One of the most interesting values is the current Sr^{90} content of the stratosphere. This has been calculated both on the basis of estimates of the total injection of Sr^{90} into the stratosphere coupled with fall-out observations and more recently by direct integration of the Sr^{90} content of the stratosphere as a function of altitude and latitude (*85, 89, 95, 136, 137*). Estimates by the former method suggest that about 6.4 Mc of Sr^{90} have been injected into the stratosphere up to October 1958, of which 2.1 Mc have already deposited on the earth and 4.3 remain in the stratosphere (*89*). The direct stratospheric measurements suggest a much smaller content of the reservoir, totalling about 1 Mc, distributed between the northern and southern hemispheres in ratio 0.7:0.3 (*95*). A curious feature of the stratospheric Sr^{90} sampling is the report of a maximum content at 65,000 ft. whereas the C^{14} content is still rising up to 90,000 ft. (see below) (*95, 130*).

1. *Kinetics of the Stratospheric Fall-out of the* Sr^{90}

One of the most interesting features of these observations is the complexity of the atmospheric mixing revealed by the pattern of the Sr^{90} fall-out. The meteorologists' suspicion that the mixing of the stratosphere and troposphere is a slow process has been confirmed (*34, 82, 191, 192*). However, the data are conflicting as to the exact value of the half-life for the process, estimates ranging from 6 months to 12 years (*85, 89, 95, 178–180, 199*).* Thus the largest part of the fission product activity from the thermonuclear weapons tests only reaches the earth's surface quite slowly. The slow step is the transfer across the tropopause (*130*); removal from the troposphere following the usual wash-out pattern (*180, 199*). Mixing within the stratosphere both horizontally and vertically also appears to take an appreciable time. A half-life of a few months may be involved (*199*). As the C^{14} data show (*130*) (see below) the latitude of maximum stratospheric concentration does not appear to coincide with the latitude of injection of the activity. The fall-out appears greatest in the middle latitudes (*85, 89, 95, 193*), which might be connected with the mixing occurring through the overlap of the high tropical tropopause and the lower polar tropopause (*95*). There is also a seasonal variation in fall-out manifesting itself in an abnormally high fall-out in the Spring (*89, 199, 257*). Whether this is a

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* ***Footnote added in Proof:*** **Recent studies tend to support a value near the lower limit of this range.**

reflection of the choice of the autumn for several of the weapon tests (*7, 199*) or indicates an especially rapid mixing in the Spring is not yet clear. Sr^{89}/Sr^{90} ratios support the former explanation. Certainly neither the latitude or seasonal variations in fall-out appear noticeable in the Southern hemisphere (*199*). It is possible that the stratospheric-tropospheric mixing half-time is a function of the latitude, although this would require a relatively slow horizontal mixing time within the stratosphere (*95*). The North-South hemispheric mixing time in the stratosphere must be fairly long but the W^{185} data confirms that it is not more than a few years at most, for material injected near the equator.

In 1956 Libby estimated that about 16 mc/mile^2 of Sr^{90} had been deposited, but that 12 mc/mile^2 remained in the stratosphere. Taken in conjunction with the Kr^{85} data this information implies that up to about 1956 nearly one-third of all the fission taking place had occurred in weapon tests (*54*).

C. ARTIFICIAL TRITIUM AND RADIOCARBON

Some of the effects of the artificial T and C^{14} production have already been described (See Sections V,C,*2* and IV,B,*2,c*). The sudden disturbance of the dynamic equilibrium distribution of the natural T and C^{14} by the injection of a substantial amount of each activity into the stratosphere will permit invaluable data to be obtained over the next year or two on the kinetic characteristics of the processes referred to in the last section, provided of course no further weapon tests take place.

The direct measurements (*130*) of the stratospheric T and C^{14} content reveal an artificially injected T/C^{14} ratio of about 0.4. The tritium has thus risen to about four times its previous concentration. More extensive and more reliable data on the C^{14} content of the stratosphere have been obtained. The excess C^{14} is almost three-fourths of the natural amount (*130, 181*). The distribution of C^{14} in the stratosphere both in respect of altitude and latitude are shown in Fig. 5. Most features of this distribution are difficult to explain, the maximum appears at an unexpected latitude with respect to the related weapon tests. Many more measurements of this kind are urgently necessary.

The appearance of this excess C^{14} activity in the biosphere has already been discussed (See Section IV,B,*2,c*). A number of discussions of the biological significance of this increased activity have appeared (*169, 226, 269*).

D. OTHER ARTIFICIAL ACTIVITIES REPORTED IN THE ATMOSPHERE

Neutron capturing elements have been used in bomb casings to facilitate measurement of the efficiency, or extent of fission, in various types of weapons. Cobalt-60 is one of the activities now reported as present in the atmosphere that might have such an origin (*260*). Tungsten was used for the same purpose in the 1958 Hardtack trial conducted by the U.S. Atomic Energy Commission. A considerable number of measurements of the atmospheric W^{185} arising in this way have been reported (*185*). It is interesting that although these trials are conducted in the Northern Hemisphere at a low latitude, the W^{185} has been found in both the Northern and Southern Hemispheres.

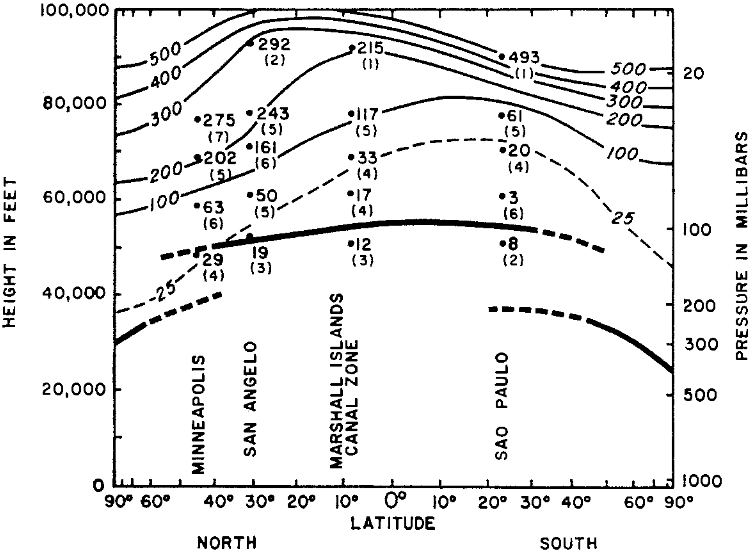

FIG. 5. Altitude-latitude cross section of the atmosphere showing the mean excess radiocarbon distribution as of 1 July, 1955. Concentrations in 10^5 atoms per gram of air are indicated near points identifying the altitude. Numbers in parentheses show the number of samples from which the mean concentration was computed. Thin lines are isolines of carbon-14; heavy lines indicate the position of the tropopause. [From Hagemann *et al.* (*130*).]

Finally two activities have recently been reported, Sr^{46} and Cs^{134}, for which no mechanism of formation has so far been advanced (*157*).

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