RECENT FLUCTUATIONS OF ATMOSPHERIC CARBON-14 CONCENTRATIONS

THESIS

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SUMMARY

Natural fluctuations of atmospheric C-14 concentrations over time periods from several hundred to several thousand years are known to have occurred during the last 6 millenia. The fluctuations represent deviations from the basic assumption of the radiocarbon dating method and, although their origin is not fully understood, probably stem from the variation of one or more of the geophysical parameters which control carbon circulation. The scope of past studies was limited by the availability of complete series of samples of precisely known origin. Consequently it has not been possible to establish whether natural atmospheric C-14 concentrations are constant over shorter time periods of several years.

In this research annual variations of atmospheric C-14 concentrations over the past century have been studied through analyses of plant seeds, wines and spirits. Using exchange rate data obtained from recent investigations of the transport of artificial "bomb" C-14, the magnitude of the "Suess effect" during the past century has been assessed theoretically and compared with the experimental results. Predictions of the "Suess effect" to 2,025 A.D. suggest a marked

increase in atmospheric CO_2 concentrations to levels about 50% above natural. It is concluded that the enhanced infrared absorption in the atmosphere implied by such an increase may be sufficient to raise world temperatures by several degrees.

Correction of observed atmospheric C-14 activities for "Suess effect" dilution revealed that between 1890 and 1950 natural fluctuations appear to have occurred over the 11-year sunspot cycle in inverse correlation with solar activity. It is suggested that the origin of this correlation lies in the variable mixing rates of stratospheric and tropospheric air masses caused by modulation of the incident U.V. and corpuscular radiation over each solar cycle. A general decrease in atmospheric C-14 concentrations was also observed and is attributed to a reduction in the mean C-14 production rate through increased solar activity. The results therefore support theories of solar-sensitive atmospheric circulation. In addition they imply the probability of increased errors in radiocarbon age determinations and endorse the universal use of the N.B.S. modern standard in C-14 assay.

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I INTRODUCTION

Historical

More than twenty years have passed since the feasibility of the radiocarbon dating method was demonstrated by Libby. During this period there have been considerable refinements in experimental methods and understanding of C-14 geochemistry (Table 1). The improved sensitivity of modern counting techniques has allowed the measurement of C-14 activities and ages to an accuracy that was unattainable with the original screen wall counting method. More significantly, however, the sensitivity of C-14 analysis now permits an assessment of the basic assumptions of the radiocarbon dating method.

The dating method is based on the principle that C-14 is produced in the upper atmosphere by cosmic ray interaction with nitrogen atoms (N-14 $\xrightarrow{n,p}$ C-14). The C-14 is oxidised to carbon-14 dioxide which, when mixed with the inactive carbon dioxide in the atmosphere, enters the natural carbon cycle (Figure 1). It is assumed that the distribution of C-14 in the carbon reservoirs has remained constant throughout the time period covered by the dating method, i.e. the past 50,000 years. This assumption of equilibrium implies constancy of the C-14/C-12

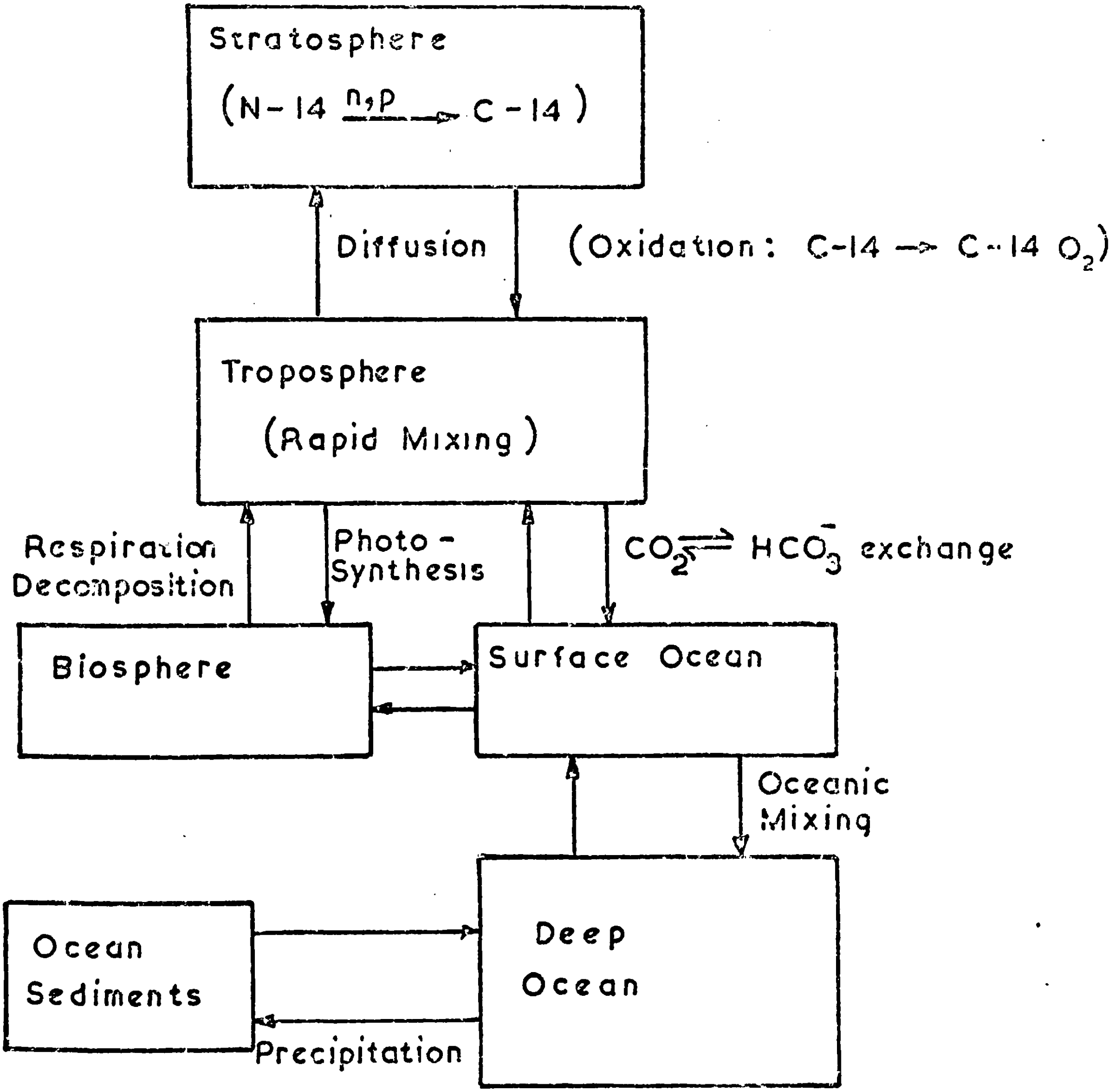
TABLE 1

THE DEVELOPMENT OF RADIOCARBON DATING AND GEOCHEMISTRY

PERIOD	PRINCIPLE ADVANCES	REFERENCES
1930-1940	(a) Reaction N-14 $\xrightarrow{n,p}$ C-14 discovered.	1-3
	(b) Cosmic ray production of neutrons in the atmosphere detected.	4,5
	(c) Development of screen wall counter.	6
	(d) Production of C-14 in detectable quantity.	7,8
1940-1950	(e) Realisation of potential dating method.	9,10
	(f) Natural C-14 discovered.	11,12
	(g) First half-life value assumed (5,568 years).	10,13
	(h) First radiocarbon dates published.	13
	(i) Dating method proved reliable within experimental error.	13,14
1950-1960	(j) Proportional gas counting and liquid scintillation counting developed.	15-18
	(k) Discovery of fossil fuel CO_2 dilution of atmospheric C-14.	19
	(l) Onset of nuclear era and artificial C-14 input to atmosphere.	20
	(m) First measurements of bomb C-14 distribution.	21,22
	(n) Several calculations of C-14 mixing rates published.	21,23,24
	(o) Universal system of C-14 activity calculation established.	25
	(p) First observations of pre-1900 atmospheric C-14 fluctuations.	23,26
1960-1969	(q) New C-14 half-life accepted (5,730 years).	27
	(r) Further natural fluctuations of atmospheric C-14 detected.	28-30
	(s) Evolution of theories to explain natural fluctuations	28-31
	(t) Increased nuclear C-14 input.	20
	(u) Many studies of inter-reservoir exchange rates based on bomb C-14 distribution.	32-37

FIGURE I.

THE CARBON CYCLE.



ratio of all reservoirs of the cycle, of the C-14 production rate, and of the carbon exchange rates between the reservoirs. During the lifetime of living materials an equilibrium is established whereby assimilation of C-14 is balanced by radioactive decay. At death, however, C-14 uptake ceases while decay of the C-14 continues. On the assumption that the material remains a closed system, the C-14 concentration decreases with time according to the half-life of radiocarbon, 5,730 ± 40 years. Accurate measurement of the residual C-14 activity allows the age of the sample to be calculated.

As a check on the validity of a dating method, the first radiocarbon age measurements were made on samples whose ages were known from archaeological studies. The statistical errors on each radiocarbon age lay in the region of ± 200 years. That agreement between radiocarbon and known ages was achieved implied that to a first approximation the assumptions of C-14 equilibrium were valid. As the analytical accuracy of the method was improved, significant deviations between radiocarbon dates and true ages have been found.

Deviations between C-14 and known ages reflect disequilibrium in the C-14 distribution in the carbon cycle which may stem from the variation of one or more of the controlling geophysical parameters. The important parameters involved are (1) the C-14 production rate, and (2) the exchange rates of C-14 between reservoirs, i.e. atmosphere/ocean, ocean/atmosphere, atmosphere/biosphere, biosphere/atmosphere, surface ocean/deep ocean, deep ocean/surface ocean.

The C-14 production rate is a function of cosmic-ray flux intensity and the C-14 exchange rates are dependent on reservoir temperatures and sizes. Whatever the cause of disequilibrium the quantity most significantly altered is the atmospheric C-14 activity. Any perturbation of the general C-14 distribution is temporarily amplified in the atmosphere because (1) the atmospheric carbon content is only 1.5% of the earth's exchangeable carbon and (2) the ocean response time is several hundred years. The amplified atmospheric deviation is transmitted as a corresponding error in the radiocarbon age of any living material grown at that time.

The fluctuations of atmospheric C-14 concentration are significant for at least two reasons;

(1) a deviation of atmospheric C-14 concentration of only 1% alters the radiocarbon age by about 80 years,

and (2) the size and duration of the variations permit an understanding of the geochemical and geophysical processes which control C-14 distribution.

Fluctuations of Atmospheric Carbon-14 Concentrations.

Variations in atmospheric C-14 concentrations are either naturally or artificially induced. The former are caused by variation of the C-14 production rate or of the C-14 exchange processes. Artificial deviations stem from the activities of mankind.

Natural Fluctuations of Atmospheric Carbon-14 Concentrations.

(a) Method of Detection.

Past variations of atmospheric C-14 content are most commonly detected by measurement of the C-14 activity in tree rings whose true ages have been determined by dendrochronological methods. The dendrochronology of the long-lived species *Sequoia gigantea* and *Pinus aristata* as developed in Arizona is believed to be reliable and has recently been extended back to 5,000 years B.C. (38, 39). The assumption is made that no carbon has been added to or removed from the tree rings since their formation. Although this assumption remains unproved in detail, Stuiver (30) has estimated from the agreement between archaeological and tree ring sample activities that the average carbon exchange between rings must be less than 0.01% per year.

The detection of past fluctuations of atmospheric C-14 can also be achieved by radiocarbon analysis of lake sediments. These sediments can often be dated independently by the "varved clay" chronology. The basis of this dating method lies in the yearly formation of sediment layers deposited by melting waters from glaciers. Lake sediment analyses have extended our knowledge of atmospheric C-14 concentrations back to the 12th millenium before present (B.P.). The method is less sensitive than dendrochronological techniques because of the increased opportunities for the exchange of carbon between layers.

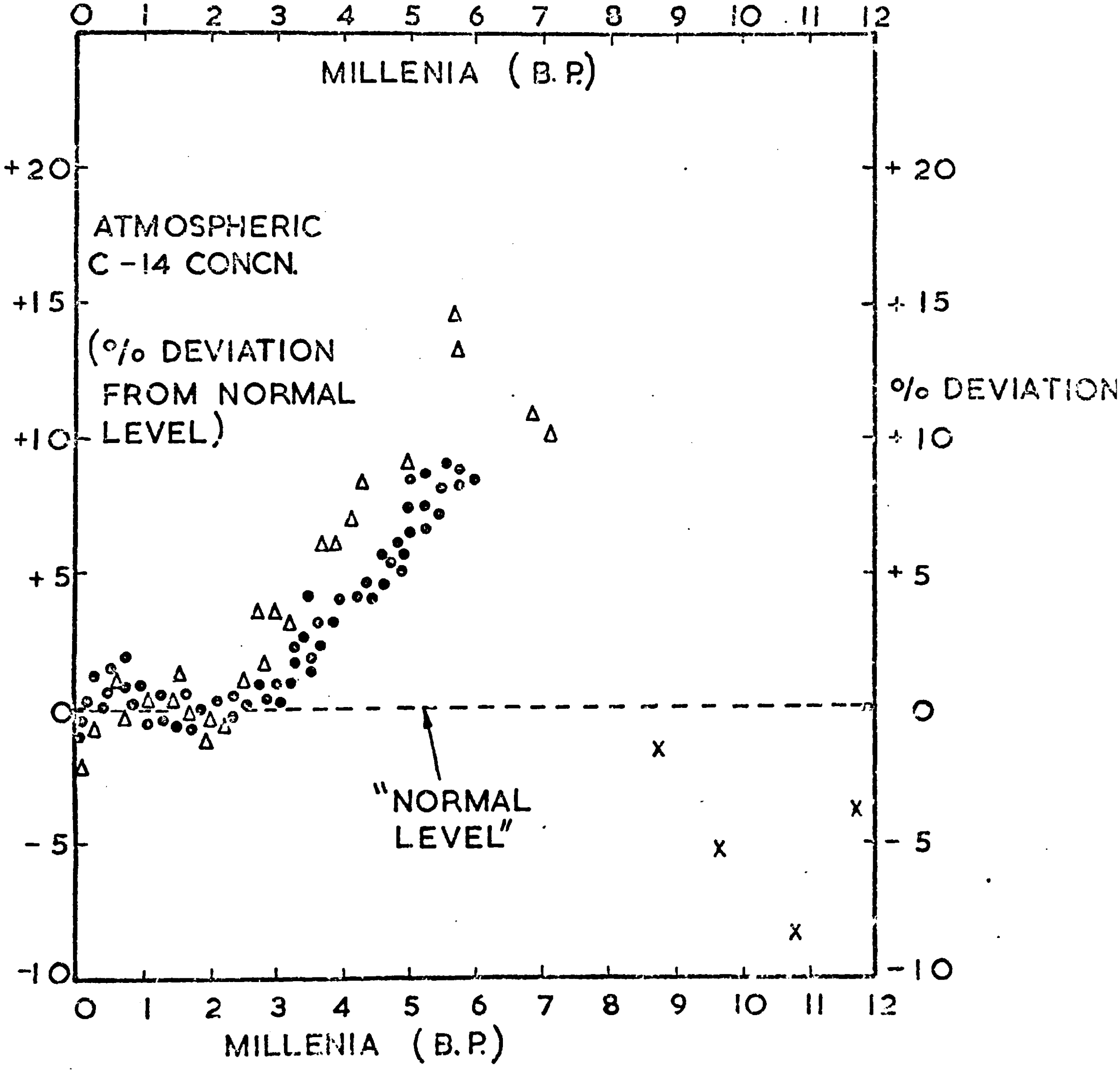
(b) Magnitude of Fluctuations.

The variation of past atmospheric C-14 activities is shown in Figure 2. The limited number of results allows the detection of long-term fluctuations occurring over at least a few centuries. The detection of variations on a shorter time scale would require an increased frequency of sampling.

Fluctuations of atmospheric C-14 content appear to be of two types; (1) short-term changes of a few percent over a few centuries, and (2) a long-term increase of about 14% from ca. 2,500 B.P. to 6,000 B.P.. At the present time it is not certain whether the increase continues towards 10,000 B.P.. Stuiver (42) and Suess (41) favour the continuation of the deviation to a value about 30% above the normal level at 10,000 B.P.. Damon (28), however, suggests maximum deviation of about 15% above

FIGURE 2.

SECULAR VARIATIONS OF ATMOSPHERIC CARBON-14 ACTIVITY.



DENDROCHRONOLOGY Δ } DAMON ET AL. (28,40)
VARVE CHRONOLOGY X }
DENROCHRONOLOGY ● SUESS (29,41)

normal at 6,000 B.P. falling to the natural level about 9,000 B.P..

A well-defined example of the short-term fluctuations is the "De Vries effect" at ca. 1600 - 1800 A.D. when atmospheric C-14 concentrations rose to 2% above normal about 1690 A.D.. In general the short-term changes are most noticeable during the past two millenia. That many more samples from this period have been analysed could explain this observation.

Unless they are accurately determined, fluctuations in past C-14/C-12 ratios can introduce considerable errors into radiocarbon age-assessment. Concentrated research into precise measurement of these variations is therefore a marked feature of many radiocarbon projects. Walton and Baxter (43), however, have recently pointed out that, where intercomparison is possible, the results obtained by different laboratories are not always in agreement. For example, Suess attributes a C-14 concentration of 7.2% above normal to the time 5,700 B.P., while Damon finds a deviation of 14.8% for the same period. Again, bearing in mind that 1% deviation in C-14 activity yields an 80 year change in radiocarbon age, such discrepancies are highly significant.

When past fluctuations are precisely known the conversion of radiocarbon ages to true ages will be possible. If, for example, the deviation in atmospheric C-14 concentration is 7.5% above normal at 5,000 B.P., then a radiocarbon age of 4,400 years B.P. would be expected. Some workers have already published conversion curves for this purpose (29, 44). Because of inter-laboratory discrepancies, however, these calibration curves seem unreliable.

(c) Causes of Fluctuations.

Natural variations of atmospheric C-14 content can be attributed to (1) change in the natural C-14 production rate, and/or (2) modulation of the inter-reservoir carbon transfer processes.

The production of C-14 by cosmic ray neutrons implies dependence of the formation rate on cosmic ray intensity. The latter can be significantly influenced by (1) change in solar activity, and (2) change in the earth's magnetic field. A common index of solar activity is the sunspot number. Sunspots are small areas of intensely localised magnetic field on the solar surface. Increased solar activity, as shown by high sunspot numbers, causes a deflection in the galactic cosmic ray flux which, in turn, reduces the cosmic ray intensity and thus the C-14 production rate in the earth's upper atmosphere. Stuiver (30) has shown that an inverse correlation between atmospheric C-14 concentrations and relative sunspot numbers through production rate modulation appears to explain the

"De Vries effect".

Variations in the earth's magnetic dipole moment alter the cosmic ray flux in the atmosphere as the deflection of the cosmic rays varies with the field intensity. The total C-14 production rate is approximately inversely proportional to the square root of the field intensity. Although paleo-magnetic measurements are imprecise, evidence from determinations of remanent magnetism in pottery samples does indicate a variable magnetic field intensity during the past 6,000 years (45, 46).

Changes in inter-reservoir carbon exchange processes may occur by variation of ocean mixing rates. Since the oceans contain about 95% of the earth's exchangeable carbon inventory, any changes in its mixing rate would cause marked deviation in the C-14 content of the atmosphere. The ocean mixing rate is dependent on pH, reservoir size, and climate. A 1% increase in ocean temperature would produce an increase of about 6% in atmospheric CO_2 and a corresponding decrease in C-14 activity. The melting of glaciers during geological time would also lower atmospheric C-14 concentrations through an increase in ocean volume. Since the atmospheric CO_2 content is dependent on equilibrium with the marine carbonate/bicarbonate system, it must also be a function of ocean pH. It seems likely, however, that the buffering action of ocean salts has prevented any appreciable change in pH during geological time (47).

Because our knowledge of the past environment is uncertain, it is not possible to define precisely the cause of the long-term fluctuations in atmospheric C-14 content. It appears, however, that these variations show marked correlation with climatic changes. High C-14 concentrations are associated with a cold terrestrial climate. The increase in atmospheric C-14 activities from 100 B.C. to 4,000 B.C. would therefore represent a relic of the last ice age. The short-term fluctuations also seem climate-dependent through variation of solar activity. Thus the high C-14 concentrations associated with the "De Vries effect" correspond to the cold period known as the "little ice age". Since changes in world climate are accurately documented only within the last few centuries, C-14 analyses may extend our knowledge of past world climates indirectly. The mechanism of the dependence of the long-term variation in atmospheric C-14 activities on climate is uncertain. Production rate modulation may account for both the long-term and the short-term deviations. Alternatively the long-term variations may stem from perturbations of the oceanic mixing processes.

Artificial Fluctuations of Atmospheric Carbon-14 Concentrations.

(a) "Suess effect".

The "Suess effect" is the decrease in atmospheric C-14 concentrations caused by the combustion of large quantities of C-14 - free fossil fuels. It originated with the industrial revolution but did not become pronounced until the late 19th century (19). Since then the decrease in C-14 activity of the atmosphere is approximately linear, reaching a value of about 3% by 1950, and, by extrapolation, about 4.2% by 1970.

The total amount of inactive CO_2 released has been estimated by Revelle and Suess (24) as 2%, 12%, and 20% of the normal atmospheric CO_2 content by 1900, 1950, and 1970 respectively. Only one fifth of the total quantity released to date has therefore remained in the atmosphere, so that the majority must have been absorbed by the oceanic reservoir. The decrease in the C-14 concentration of the oceans, however, is difficult to assess because of the influence of C-14 produced in nuclear weapon tests. The upwelling of old water masses in certain regions can also present difficulties in the interpretation of oceanic data. Some pre-test samples analysed by Broecker (48) and Brannon et al (49) suggest a decrease in the C-14 concentration of the surface ocean of about 1% to 2% due to the "Suess effect". Here the surface ocean represents the mixed ocean layer to about 200 metres depth.

Besides the universal decrease in atmospheric C-14 concentrations attributable to the "Suess effect", local variations can occur. For example, areas near industrial centres experience more intense fossil fuel CO_2 contamination than rural areas. In a recent study, Walker (50) found that contamination by fossil fuel CO_2 varied by 18% from central Glasgow to rural areas 20 miles away. A similar dilution gradient appears to exist between the hemispheres. Thus Fergusson (51) reported a southern hemisphere dilution of 2% at the same time as Suess found 3% for the industrialised northern hemisphere.

The "Suess effect" is particularly important in radiocarbon age studies. Prior to its detection 20th century wood samples were frequently used as the modern standards to which all samples were compared. With the discovery of the "Suess effect", however, it was shown that radiocarbon ages based on these standards could be too young by 200 years. Therefore the primary standard activity is now the decay-corrected C-14 activity of 1890 wood.

The "Suess effect" may be considered as a "tracer" experiment on a global scale and can be used to evaluate some of the parameters controlling carbon circulation. For example, Revelle and Suess (24) estimated a value of about 10 years for the mean residence time of CO_2 in the atmosphere prior to oceanic or biospheric absorption.

The "Suess effect" also reflects the general increase in atmospheric CO_2 which has occurred during the past century. The present atmosphere contains about 318 p.p.m. CO_2 compared with 290 p.p.m. in 1890. According to Bischof and Bolin (52) the increase in atmospheric CO_2 concentration is now 0.7 p.p.m./year. Since CO_2 absorbs in the infrared, increased concentrations will produce increased downward flux of radiation in the atmosphere and a rise in surface temperatures. An increase of 30%/century in atmospheric CO_2 concentrations will produce a temperature increase of 1.1°C./century (53). Such a rise is very close to the average increase so far in the 20th century. It seems possible that the additional CO_2 from the continued burning of fossil fuels could appreciably change the climate over the next few hundred years.

(b) "Atomic bomb effect".

The "atomic bomb effect" is the result of the addition to the atmosphere of considerable quantities of C-14 produced through the activation of atmospheric nitrogen (N-14 $\xrightarrow{n,p}$ C-14) by bomb neutrons. The neutron yield of a nuclear device is related to the total energy yield. Thus Table 2, which presents the total energy yields of weapons tested during the period 1945 to 1968 (20), gives a direct measure of the bomb C-14 production. It is significant that a "surface" test will yield considerably less C-14 than a corresponding "air" burst. Based on an available neutron yield for activation of $2x10^{26}$n./Mton. of fission and fusion in the case of an "air" burst and $1x10^{26}$n./Mton. for a "surface" burst, the total production of artificial C-14 to date is estimated at 10^{29} atoms. This would be sufficient to raise the C-14 concentration by a factor of four were it to be contained in the troposphere.

Increases in the C-14 activity level of the atmosphere were, in fact, first observed in 1954 following the onset of the thermonuclear era in 1952. Since then, C-14 has been injected sporadically into the atmosphere, and the C-14 level has followed a general but irregular increase (21, 22, 54, 55). Figure 3 presents a profile of this irregular increase of atmospheric C-14

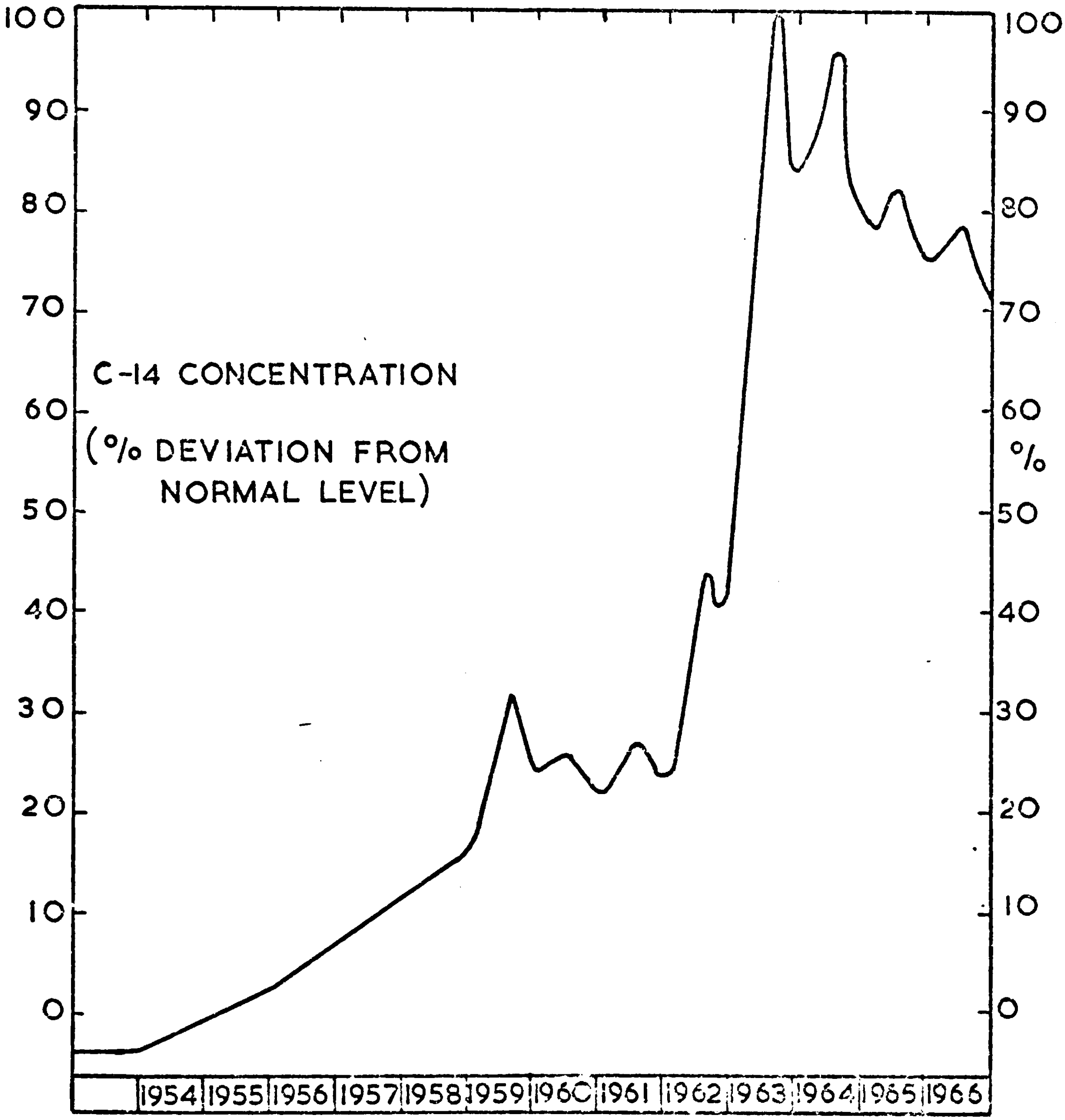
TABLE 2

FISSION AND FUSION ENERGY YIELDS OF NUCLEAR DEVICES.

PERIOD	FISSION AND FUSION YIELD (Mton.)	
	AIR TESTS	SURFACE TESTS
1945-51	0.19	0.57
1952-54	1.0	59.0
1955-56	11.0	17.0
1957-58	57.0	28.0
1959-60	TEST MORATORIUM	
1961	120.0	-
1962	217.0	-
1963-68	16.3	0.2
TOTAL	422.5	105.0

FIGURE 3

CARBON-14 CONCENTRATIONS IN THE NORTHERN HEMISPHERE TROPOSPHERE (1954-66)

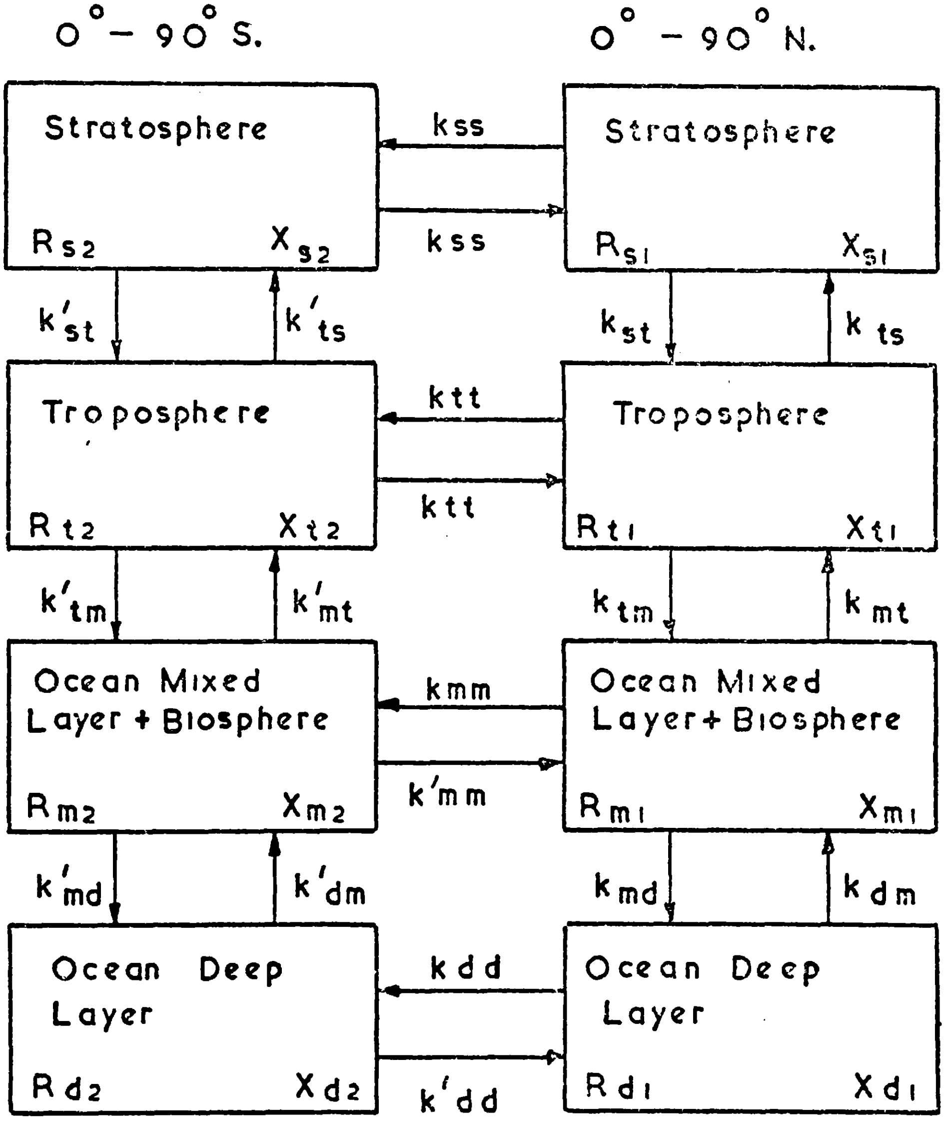


concentrations for the period 1954-1966 for the northern hemisphere troposphere. Since the majority of the artificial C-14 was first injected into the stratosphere of the northern hemisphere, the peak in northern tropospheric C-14 concentrations occurred in 1963, about two years after the period of maximum C-14 production. This lag time is attributable to the finite stratospheric residence time of carbon. Following the maximum in the northern troposphere, C-14 concentrations have shown a gradual decrease with time as the C-14 distribution tends towards equilibrium through mixing with the southern troposphere and absorption by the oceans and biosphere.

Although a considerable quantity of artificial C-14 has been produced it represents only a very small fraction of the total atmospheric carbon content, and thus it can safely be assumed that the carbon exchange equilibrium is undisturbed. Therefore the rate of movement of this excess C-14 within the various carbon reservoirs presents an ideal opportunity for the "tracer" study of the parameters controlling carbon circulation. Figure 4 shows a typical "box model" of the dynamic carbon cycle and the various parameters which can be studied. In particular, exchange rate constants, k_{ij}, can be examined in detail. The exchange rate constant is defined by the equation $N_t = N_o e^{-k_{ij}t}$, which describes the decrease with time of

FIGURE 4

A TYPICAL "BOX MODEL" OF CARBON-14 CYCLE.



R_{ij} indicates the amount of C – 12 in each reservoir

K_{ij} are the exchange rate constants

X_{ij} is the excess C – 14.

the number of C-14 atoms, N_t, in one reservoir, i, through transfer to an adjacent reservoir, j.

A comparison of the exchange rate constants determined by several workers (32-37, 54) shows that agreement is not always achieved. For example, the rate constant k_{tm}, which describes the absorption rate of tropospheric C-14 by the surface oceans, has been attributed values ranging from 0.04 to 0.30. The corresponding exchange time, τ_{tm}, has therefore been found to be between 25 years and 3.3 years ($\tau_{tm} = 1/k_{tm}$). However, as the excess C-14 distribution tends further to equilibrium additional observations should permit increased accuracy in the exchange rate constant determinations.

To the radiocarbon dating method the bomb-produced C-14 constitutes a significant source of contamination. Whereas a 1% contamination of a 17,000 year old sample by natural modern carbon introduces an age error of 570 years, the same degree of contamination by nuclear era carbon could introduce an error of 1,100 years. The danger of contamination by modern carbon is most significant for inorganic samples which may allow ion exchange with carbonate of atmospheric origin.

A second effect of bomb C-14 on radiocarbon dating lies in the long-term disruption of atmospheric C-14 concentrations. Even if further weapons testing is curtailed, many hundreds of years will be required before the distribution of the excess C-14 throughout the carbon cycle will reach complete equilibrium. It is therefore of some importance that atmospheric concentrations of C-14 are followed during future years. In the very long term, the high C-14 activities of the mid 20th century will introduce the need for accurate conversion of radiocarbon ages into true ages. The nuclear era can in this respect be likened to a period of natural fluctuation of atmospheric C-14 concentrations. The problem of age ambiguity will also arise for the nuclear era as for times of natural variations. A plant sample grown in 1963 will be indistinguishable by activity measurement from a specimen grown 700 years hence.

Purpose of Research Project.

Several natural fluctuations of atmospheric C-14 concentrations are known to have occurred during the past 10 millenia. Because of the scarcity of samples of accurately known age, the studies until now have been concerned with fluctuations occurring over long time periods. Little is known about the short-term behaviour of atmospheric C-14 activity levels. Since the availability of samples of known age is highest for recent times a detailed study of annual C-14 concentrations should be feasible.

The artificial fluctuations of atmospheric C-14 concentrations have provided an opportunity to study the parameters which control short-term activity levels. A project combining a study of artificial and natural C-14 distributions during the past century would therefore benefit from an accumulation of knowledge from both fields.

Furthermore, little is known of the yearly fluctuations in atmospheric C-14 due to the "Suess effect". The values of atmospheric C-14 dilution attributed to specific years are interpolated from only a few observations. It is therefore of interest to obtain a more detailed profile of the "Suess effect" during the past century since such information could further our knowledge of carbon exchange rates between reservoirs.

The object of the research was therefore twofold;

(1) to study quantitatively the fluctuations in atmospheric C-14 concentrations during the past century,

and (2) to evaluate the importance of these fluctuations with respect both to the radiocarbon dating method and to the geochemical and geophysical processes which control carbon distribution.

Natural and artificial fluctuations of atmospheric C-14 are of definite significance both to the geochemist and to the radiocarbon geochronologist. To the former they appear as periods of disequilibrium within the dynamic cycle. As such they offer an opportunity to evaluate rates and mechanisms of carbon exchange and distribution. To the latter they represent deviations from the conditions assumed by the dating method. They require accurate measurement and necessitate modification of some aspects of the method. Eventually they may assist an understanding of some features of the environment of past times.

II

EXPERIMENTAL METHODS IN RADIOCARBON ASSAY

Introduction

C-14 is a low energy beta emitter (maximum energy 0.158 MeV.) and is present in natural carbon in very low concentrations (ca. 10^{-12}g. C-14/g.C). The specific activity of pre-bomb carbon is estimated at 13.56 ± 0.07 d.p.m./g.C (56). The low specific activity and beta energies of natural C-14 require (1) that the C-14 detector has a high efficiency, and (2) that sample activities are statistically high relative to background count rates.

The determination of C-14 concentrations relative to the natural level involves the precise intercomparison of modern standard and sample activities. It is therefore important that the counting system be stable in performance over long periods. In addition relatively long counting times (overnight) are necessary to reduce statistical errors below ±1%. During these counting periods the background count rate must also be stable.

A C-14 counting system should therefore have the following basic characteristics,

(1) high beta detection efficiency,

(2) low background count rate,

(3) long-term stability of background and beta detection efficiency.

Two distinct counting techniques are currently employed for radiocarbon assay;

(1) internal gas counting,

(2) liquid scintillation counting.

Of 52 radiocarbon laboratories surveyed in 1967, 45 used gas proportional counting methods. In 1965 gas proportional systems appeared to exhibit superior counting characteristics (57) with C-14 detection efficiencies better than 90% compared with 60% for liquid scintillation. Background count rates of less than 10 c.p.m. for proportional counters were common and less than those obtainable with scintillation techniques. In addition, the characteristics of proportional counters were more stable with respect to high voltage, gain, discriminator, and temperature drifts. Even at present some problems of the double pulsing, memory effects, and instability of scintillation photomultipliers remain. It was also expected that the size of samples to be analysed in this research might be small (ca. 1g. C), and thus the superior facility of liquid scintillation systems for counting large samples was unnecessary.

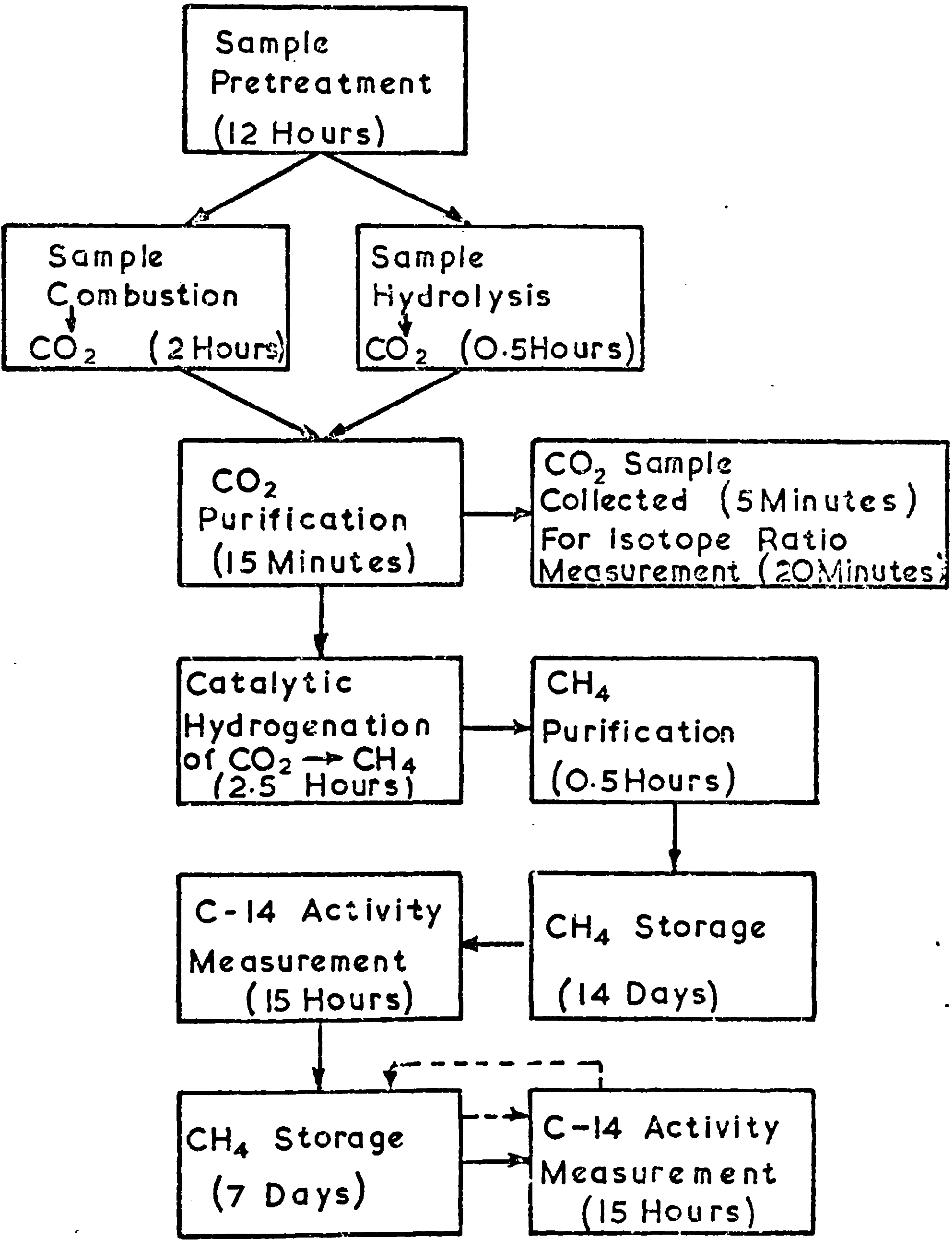
The choice of counting gas was based on Burke and

Meinschein's observation (58) that the counting characteristics of methane are considerably less sensitive to electronegative impurities than the more widely used CO_2. Recent improvements in the methods of conversion of CO_2 to CH_4 (59) confirmed the choice of CH_4 as counting gas. A survey in 1967 of laboratories which used proportional counting methods showed that 60% still employed CO_2, 20% used CH_4, and 20% either C_2H_6 or C_2H_2. The latter alternative counting gases were rejected for this research because of the tedious chemical procedures involved in their syntheses.

Figure 5 presents a block diagram of the procedures involved in routine analysis with approximate times required for each operation included as a guide.

FIGURE 5

BLOCK DIAGRAM OF LABORATORY PRACTICE



Chemical Preparation System.

(a) Sample Pretreatment.

It is essential in radiocarbon studies that the sample contain the original carbon atoms present when it ceased to be involved in the environmental exchange processes. During the time interval between removal from the exchange reservoir and analysis, the sample may become contaminated with foreign carbonaceous materials. This contamination may be "chemical" or "superficial". The former involves replacement, normally by ion-exchange, of sample carbon. The opportunities for "chemical" contamination are therefore most significant in the case of inorganic samples. Bone or shell carbonates, for example, are frequently found to have undergone exchange with the carbonate/bicarbonate of ground waters. For organic samples the only possibility of chemical alteration stems from structural breakdown by putrefaction. Mass-spectrometric corrections can be made for this type of isotopic modification.

"Superficial" contamination can involve impregnation of a sample by non-contemporaneous materials. Contaminating agents commonly found are rootlets, and soil components such as humic acids, carbonates, sand, and the soil itself. These species generally enter the sample matrix through ground water infiltration. No ion replacement or chemical bonding to the sample occurs.

If sample contamination is not eliminated the non-contemporaneous carbon atoms can introduce errors in sample activities which in dating become more significant with increasing sample age. Table 3 indicates the size of the errors which can result from contamination of old and nuclear era samples by varying amounts of modern and inactive carbon.

The basic pretreatment of solid organic samples consists firstly of visual examination for intrusive rootlets. The sample is then boiled successively in distilled water, 5% HCl, distilled water, 5% NaOH, distilled water, 5% HCl, and distilled water. These washings ensure the elimination of carbonate and humic acid contaminants and are followed by oven drying over-night at 100°C.. Shells and marble samples are leached in 5% HCl to remove about 20% by weight. The removal of outer surfaces of inorganic materials is generally successful in freeing the samples from carbonate contaminant. Wines and spirits require pretreatment through distillation to remove colouring matter.

(b) Sample Combustion.

All organic samples are combusted in an O_2-rich atmosphere to yield CO_2 (Figure 6). Five litre-atm. of CO_2 are generally prepared.

TABLE 3

ERRORS CAUSED BY SAMPLE CONTAMINATION

(a) CONTAMINATION OF OLD SAMPLES BY MODERN CARBON

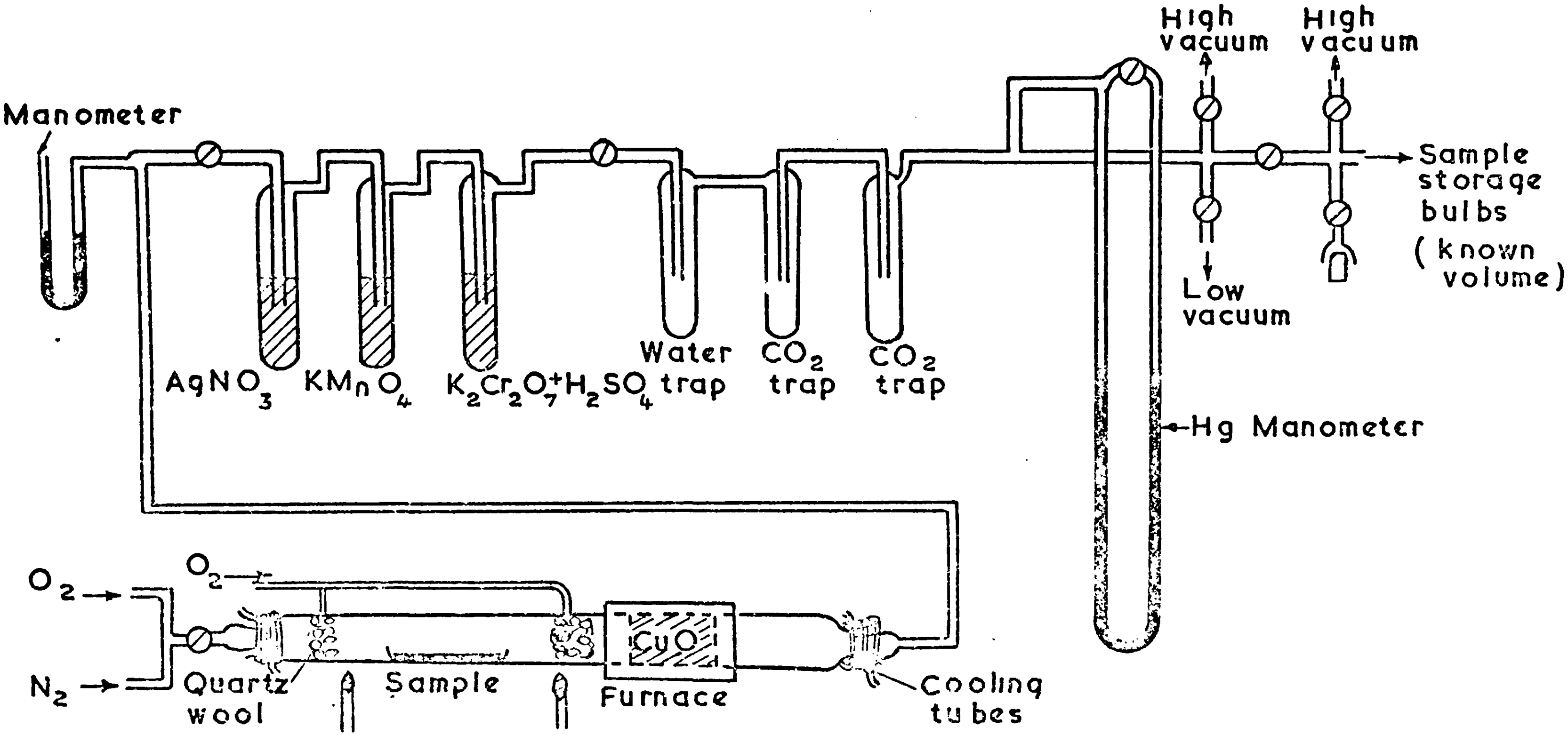
True Age of Sample (years)	Radiocarbon Age of Sample (years) Degree of Contamination with Modern Carbon 1%	0.1%	0.01%
5,570	5,490	5,560	5,570
11,140	10,900	11,120	11,140
22,280	21,080	22,160	22,270
44,560	32,260	42,760	44,350

(b) CONTAMINATION OF NUCLEAR ERA SAMPLES BY DEAD CARBON

True C-14 Concentration of Sample (% deviation from normal level)	Observed C-14 Concentration (% deviation from normal level) Degree of Contamination with Dead Carbon 10%	5%	1%
+ 40.0	+ 26.0	+ 33.0	+ 38.6
+ 60.0	+ 44.0	+ 52.0	+ 58.4
+ 80.0	+ 62.0	+ 71.0	+ 78.2
+ 100.0	+ 80.0	+ 90.0	+ 98.0

FIGURE 6

COMBUSTION SYSTEM.

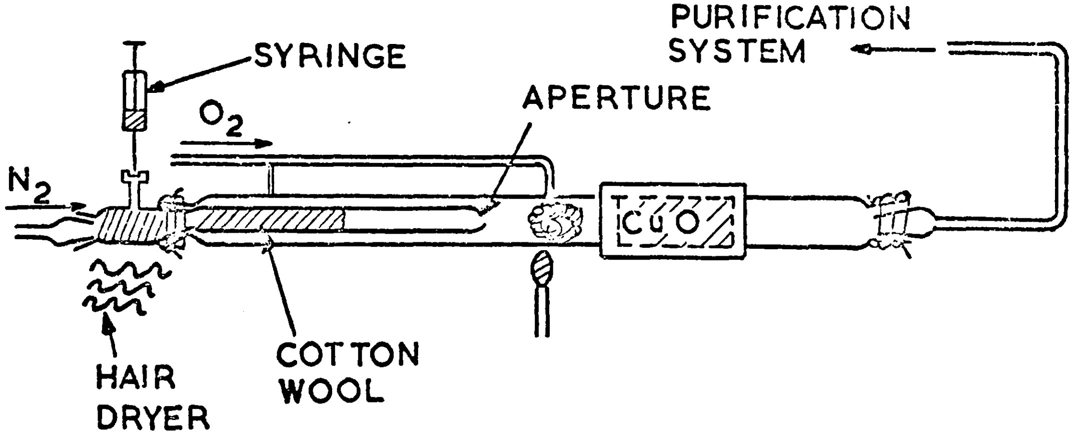


The samples are contained in porcelain boats positioned as shown within the quartz glass tube, but in cases where samples are bulky the boats are not used. A stream of O_2 and N_2 is passed over the sample which is heated from below by a Meker burner. The amount of O_2 initially made available to the sample is dependent on the nature of the material. For volatile samples the flow rate is 100 cc./min. with a N_2 flow of 400 cc./min.. For more stable samples such as charcoal the initial O_2 rate is 300 cc./min.. In the main combustion area an O_2 flow rate of 600 cc./min. is maintained from the sidearm. The rate of combustion is carefully controlled by varying the sample heating rate, and throughout the reaction the system is kept at slightly reduced pressure, by controlled pumping, to prevent pressure build-up. As the combustion proceeds, the O_2 flow rate over the sample is increased to 600 cc./min., the N_2 flow rate reduced to 100 cc./min., and the sample heating rate increased.

For alcohol samples the modified combustion system shown in Figure 7 is used. An inner tube packed with cotton wool is fitted inside the outer combustion tube. A 1mm. aperture at the tip of the inner tube permits the passage of gases through the system. A stream of N_2 (500 cc./min.) is passed through the inner tube. The

FIGURE 7.

ALCOHOL COMBUSTION SYSTEM.



alcohol/water mixture from the distillation is injected by a syringe in 1cc. quantities through a self-sealing septum and is absorbed by the wool. This area is heated gently using a hairdryer and the alcohol vapour is swept through the inner tube and burned at the quartz wool plug. In this way the vaporisation and combustion rates are carefully monitored.

When the initial combustion is complete, the product vapours are purified by the following stages;

(1) passage through a CuO furnace at 500°C. to ensure complete oxidation,

(2) an $AgNO_3$ bubbler to extract halogens and their acids,

(3) a $KMnO_4$ bubbler to remove oxides of sulphur and nitrogen,

(4) an $H_2SO_4/K_2Cr_2O_7$ bubbler to extract sulphur and nitrogen oxides and act as a drying agent,

(5) a dry ice trap (-76°C.) to remove water vapour.

The CO_2 is then condensed in the first liquid N_2 trap (-196°C.) and pumped to less than 1μ to remove all gases (including O_2) which have an appreciable vapour pressure at -196°C.. Finally the CO_2 is distilled into the second liquid N_2 trap and pumped below 1μ to remove any occluded gases. This purification scheme is adequate for 90% of the samples encountered.

In the combustion of materials of high nitrogen content (certain species of tree seeds) a deep blue contaminant is observed in the condensed CO_2. This contaminant is believed to be N_2O_3 as encountered by De Vries (60). At room temperature the N_2O_3 is unstable and partially decomposes into NO and NO_2, and although NO and NO_2 can, theoretically, be pumped off from frozen CO_2, this method of purification is not effective. Trace contamination of the CO_2, however, does not appear to effect the purity of the CH_4 prepared from it. Where gross contamination is evident, the CO_2 is adsorbed in KOH solution and released by acid hydrolysis.

The time required for combustions varies markedly for different sample types. Charcoal requires 1 hour while alcohol and peat samples may take up to 2½ hours. It is noteworthy, however, that the combustion of alcohol samples, although time-consuming, is trouble-free.

Before routine analyses began a number of determinations of combustion yields were performed with various materials. For oxalic and benzoic acids yields of 95 - 100% were obtained. Although uncertainty in the carbon content of wood and plant materials precluded precise yield determination the combustion of these materials was found to proceed satisfactorily. Blank runs proved that no CO_2 was being produced from impurities in the system.

After each combustion the quartz tube is roasted in a stream of O_2 to remove any carbon residues and replenish the CuO furnace.

A small aliquot of CO_2 is expanded into a glass sampler for mass-spectrometric analysis.

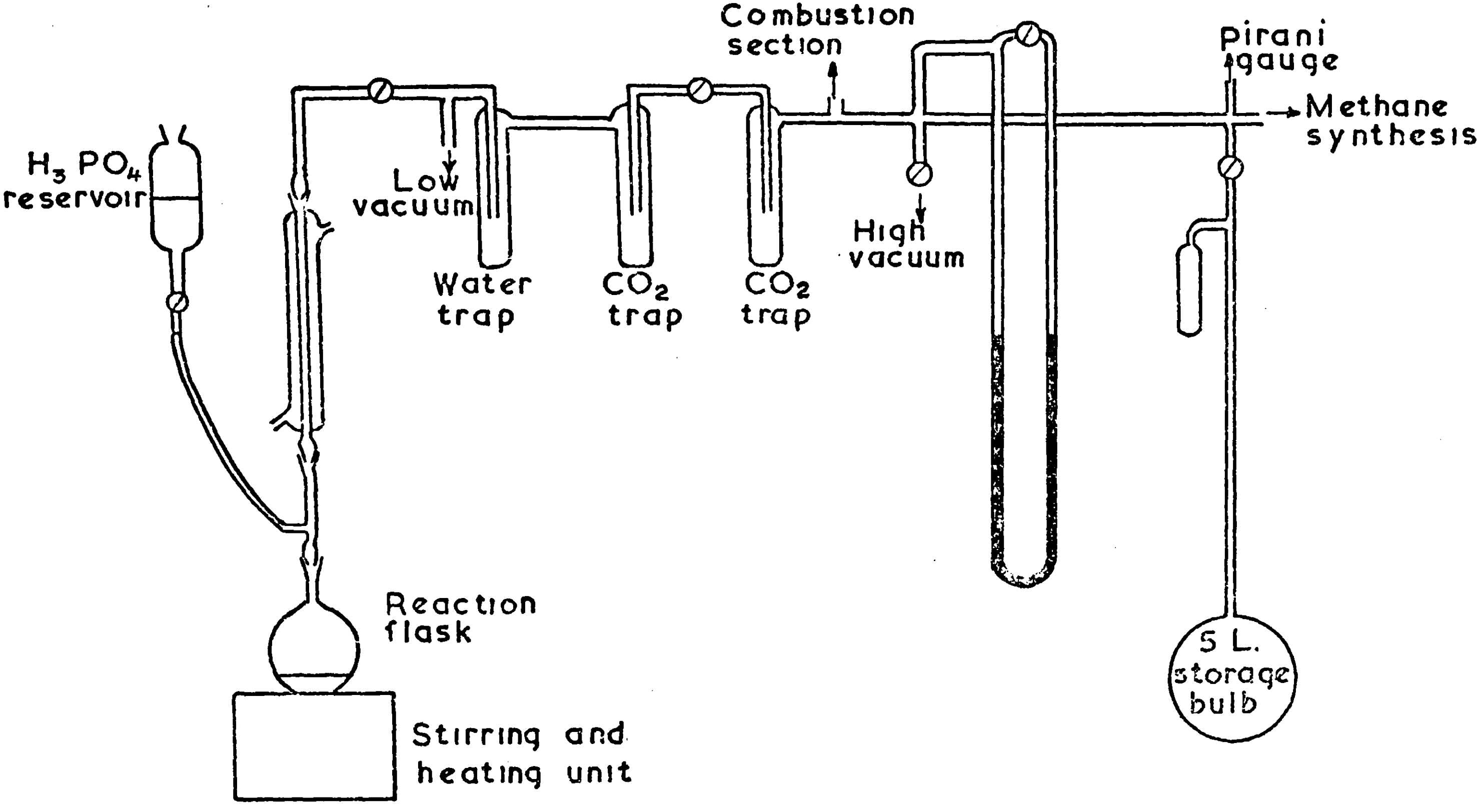
(c) Sample Hydrolysis.

Inorganic materials such as marble, shells, mortars, and K_2CO_3 are hydrolysed in the apparatus shown in Figure 8. Solid samples are fragmented to increase the surface area and are placed in the reaction flask with 50 cc. distilled water. Phosphoric acid (50% v/v) is used as the hydrolysing agent.

The rate of reaction can be controlled by varying (1) the rate of acid addition, (2) the temperature of the reactants, (3) the rates of stirring, and (4) the pressure in the reaction vessel. In most cases no heating is necessary and the pressure is several cm.Hg. Water vapour is removed from the product CO_2 by passage through a condenser and a dry ice trap. The CO_2 requires no further chemical purification. Pumping to less than 1 μ , distillation and repumping is sufficient to remove occluded impurities.

FIGURE. 8

HYDROLYSIS SYSTEM.



In the hydrolysis of mortar samples, large-scale "frothing" of reactants can become a problem. This is partially overcome by the addition of a non-carbonate "defrothing tablet" to the reaction mixture. Mortar hydrolyses are also hindered by difficulty in stirring the reactants and thus the overall reaction time is somewhat longer (ca. 2½ hours).

The hydrolysis system is also used for the wet oxidation of standard oxalic acid samples. The oxidising agent used is saturated $KMnO_4$ in 0.5 M. acid solution. The reaction is rapid and requires only gentle stirring.

A CO_2 sample is collected for isotope ratio analysis and the bulk CO_2 transferred to a 5 litre bulb for yield measurement and storage. Although precise yield calculation is not possible for hydrolyses of samples of variable carbon content such as mortars and marbles, the conversion of pure $CaCO_3$ and oxalic acid samples to CO_2 gave yields of 98 - 100%.

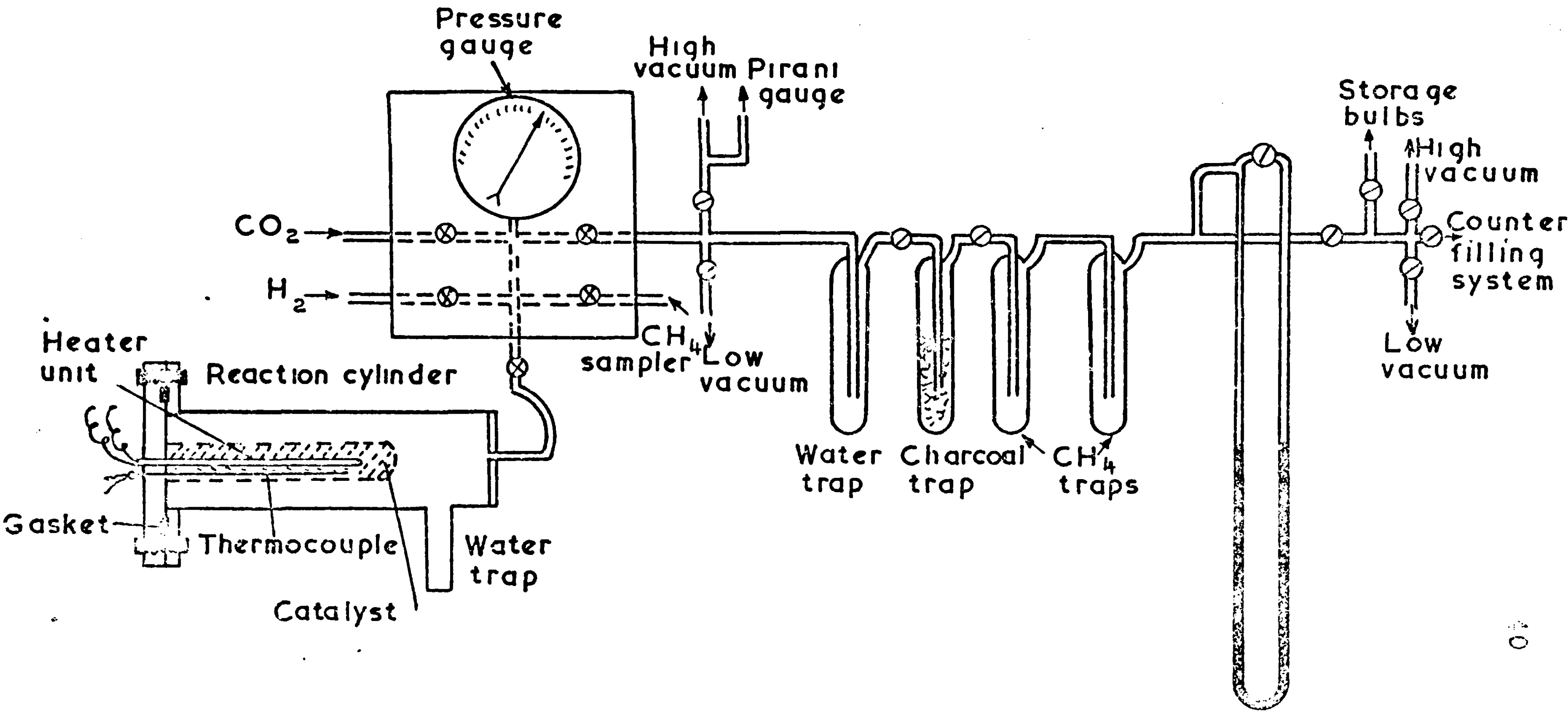
(d) Methane Synthesis.

A catalytic process is used to convert CO_2 to CH_4 (59). Gas pressures up to 10 atm. and catalyst temperatures of about 500°C. are employed with a catalyst of 0.5% ruthenium on ⅛ in. alumina pellets (Engelhard Industries Ltd

(Figure 9).

FIGURE 9

METHANE SYNTHESIS SYSTEM.

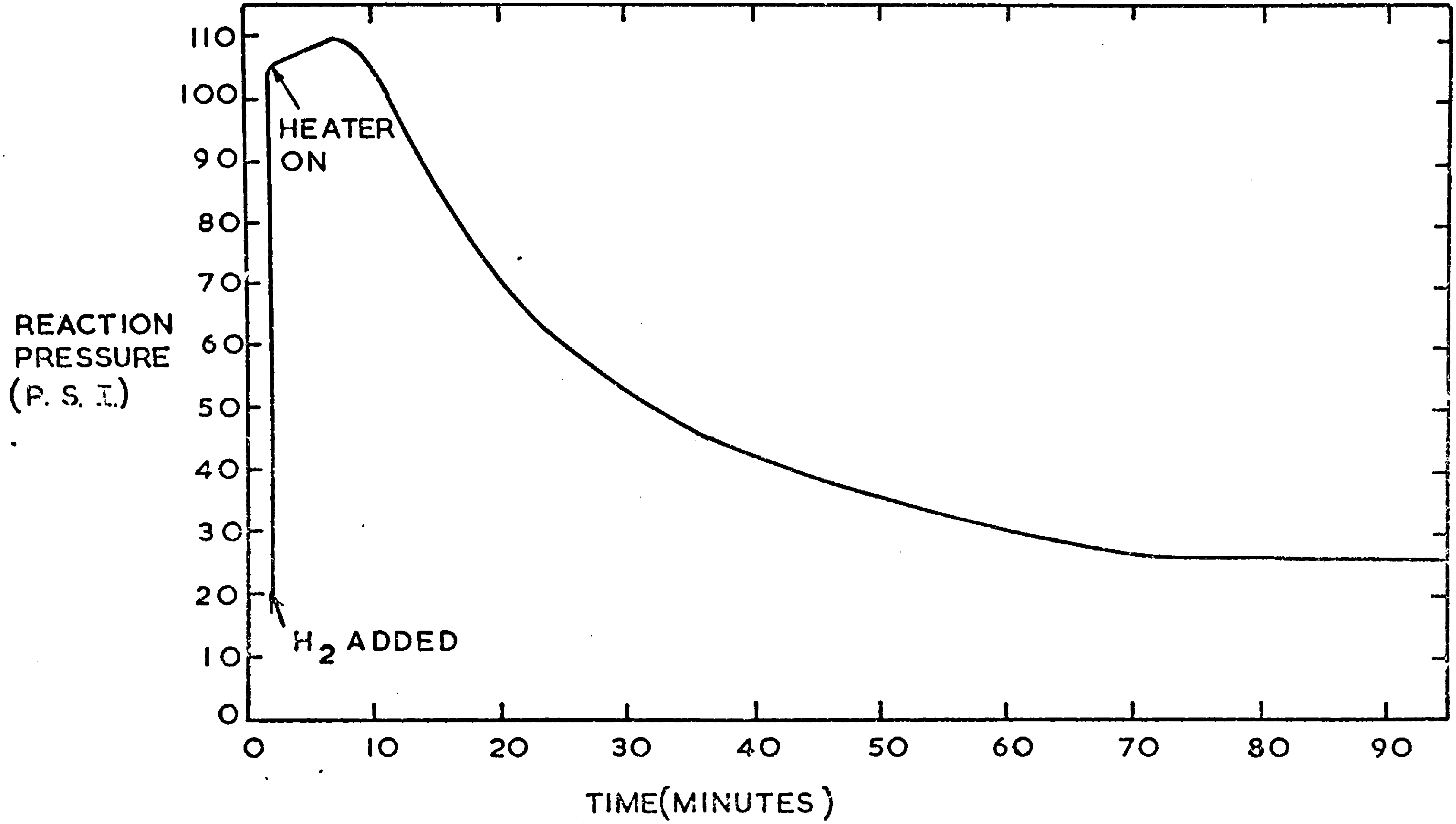


The stainless steel reaction vessel is 4.5 litres in volume with a 150 ml. sidearm attached. About 300 g. of the catalyst pellets are packed within the central steel mesh cage which contains the 1000 watt cartridge heater and associated thermocouple. A composition gasket, clamped by eight steel bolts through the top flange, ensures efficient vacuum and pressure holding performance of the system.

CO_2 is first condensed from a storage bulb into the reactor sidearm and then allowed to expand until a constant gas pressure is recorded. A slight excess (5%) of the H_2 requirement for complete conversion of the CO_2 to CH_4 is added ($CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O$). A dry ice bath is then placed around the reactor sidearm to freeze out product H_2O. The heater unit is switched on and the catalyst temperature rises to 500°C, in about 12 minutes. A pressure increase of 5 p.s.i. occurs during the first 10 minutes as the gases expand and subsequently a pressure drop associated with a 5 to 1 volume reduction occurs. After about 1 hour a constant pressure reading is recorded and a further 30 minutes is allowed to elapse to ensure complete reaction. A typical reaction pressure profile is shown in Figure 10. The half-reaction time for these conditions appears to be constant at 14 minutes so that first order kinetics are suggested. Although the reaction mechanism is not known, it seems likely that formaldehyde

FIGURE 10

PRESSURE CHANGE DURING METHANE SYNTHESIS.



is an intermediate.

Rotation of the reaction vessel to ensure complete evaporation of CO_2 was recommended by Fairhall et al (59) but was found unnecessary in our system since the pressure drop recorded in all reactions was within 1 p.s.i. of the predicted stoichiometric value.

The CH_4 extraction and purification method differs from the Fairhall technique in that the CH_4 is not liquefied in the reactor sidearm prior to pumping away the excess H_2. Instead the CH_4 and excess H_2 gases are directly transferred to the evacuated purification line. Water vapour is extracted by the dry ice trap. CH_4 and H_2 are adsorbed on the activated charcoal trap at $-196^{\circ}C$. and the subsequent liquid N_2 traps condense any excess CH_4. When adsorption of gases by the charcoal ceases, slow pumping of the remaining gases over the charcoal removes the majority of the excess H_2. The reaction vessel is closed from the purification line and the charcoal trap warmed. The effluent CH_4 is condensed in the two liquid N_2 traps. When transfer is complete a small pressure of excess H_2 remains in the trap system. This is removed by pumping for one second on the liquid (or solid) CH_4 to reduce the vapour pressure below 12 mm.Hg. Such a direct pumping technique, as opposed to high vacuum pumping of the CH_4 on charcoal, is also recommended by Olson and Nickoloff (61). The charcoal trap is then isolated from the two cold traps containing the CH_4. To ensure the complete removal of water vapour, the liquid N_2 around the second cold trap is replaced by dry ice and the CH_4 transferred by distillation into a sample storage bulb.

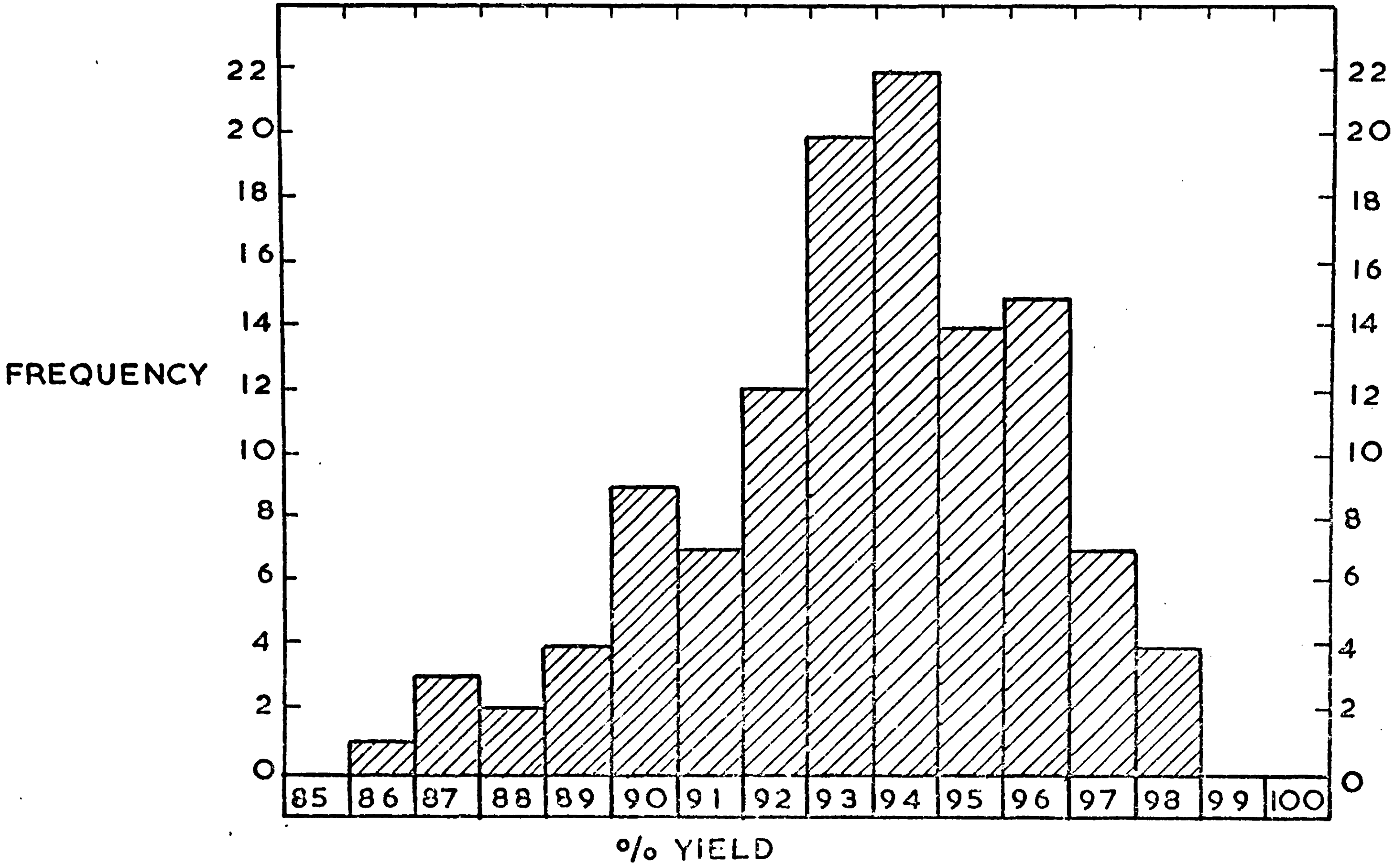
From the pressure changes recorded during the reaction the CO_2 to CH_4 conversion yields are believed to be close to 100%. The finite vapour pressure of CH_4 at -196°C. precludes 100% CH_4 recovery but a mean yield of 94%, as determined from the results of 120 syntheses, compares well with the data obtained by other laboratories (59, 61, 62). A histogram of the overall yields is shown in Figure 11. The purity of the product CH_4 was confirmed by mass-spectrometry. The gas contains no CO_2 and only p.p.m. quantities of hydrocarbons up to molecular weight 140.

Although the reaction time itself is consistently 90 minutes, the overall time for CO_2 introduction, reaction, and purification is almost double this figure. Direct supervision is required for 1 hour.

The catalyst life appears to be long. More than 120 syntheses have been performed with the last filling and no deterioration in efficiency has been observed. Care is taken, however, in the degassing of the reaction vessel and catalyst unit. After each reaction the

FIGURE 11

OVERALL YIELDS OF METHANE SYNTHESES.



product water is pumped off and the vessel evacuated to 1μ at 600°C.. This procedure requires about 6 hours of pumping but appears sufficient to maintain the catalyst condition and eliminate memory effects. If the catalyst is not thoroughly degassed synthesis is slow with reaction times of about 3 hours, and in these cases the overall yields can be less than 90%. It is necessary also to degas the charcoal between syntheses to eliminate the possibility of memory effects and to reactivate the adsorbent. The charcoal is therefore heated by a furnace to 200°C. and pumped to 1μ for 30 minutes.

(e) Sample Storage and Counter Filling Systems.

Storage of freshly-prepared CH_4 samples is necessary to allow any radon contamination to decay. Since radon (Rn - 222) is an alpha-emitter with beta-emitter daughters its presence in the counting gas can introduce significant errors. The radon commonly originates from the radium content of calcium compounds. For this reason the CH_4 samples prepared from inorganic materials contain most radon. The mean radon content of CH_4 samples freshly prepared from inorganic and organic materials amounts to 0.5 c.p.m./litre CH_4 and 0.1 c.p.m./ litre CH_4 respectively. The maximum level observed was 8 c.p.m./litre CH_4 for gas prepared from a mortar sample.

Although some organic samples such as high-clay peats can produce significant amounts of radon, the acid washings during pretreatment eliminate 95% of the isotope (60). Since radon has a half-life of 3.83 days, a storage period of 14 days will generally reduce the radon contamination to immeasurable values. After each sample has been counted it is stored for another week and recounted. Comparison of the two sample activities determines whether significant radon contamination has occurred. Storage and counting is repeated until consistent results are obtained.

Fourteen 5-litre bulbs are available for sample storage. This number permits permanent storage of 5 background and modern standard samples plus 3-week sample storage facilities on the basis of a turnover of 3 samples per week. Each bulb has a cold thimble attached so that sample transfer losses due to the vapour pressure of CH_4 at $-196^{\circ}C$. are minimised. A manometer in the storage frame allows measurement of bulb filling pressures. Each storage bulb is evacuated to less than 1μ prior to filling.

An alternative method of sample storage using 50 ml. metal sparklets was studied. These were found to be unsatisfactory, however, because (1) when filled to 10 atm. pressure leakage occurred in 96% of those tested, and (2) metallic dust from the sparklets constituted a hazard to the counter performance.

The counter is filled to the routine filling pressure of 5 atm. through the all-metal system shown in Figure 12. The detector is first pumped below 1μ over a period of about one hour. Both the counter filling system and sample storage frame are then isolated from vacuum and the sample gas distilled into the stainless-steel trap cooled by liquid N_2. After the filling system is isolated from the storage frame via a needle valve the CH_4 can be expanded into the counter. After 15 minutes no further pressure change occurs and the excess CH_4 is carefully returned to the storage bulb as the counter-filling pressure is adjusted to 5 atm.. The counter valve is closed and the CH_4 remaining in the filling system is condensed in the storage bulb. The filling pressure can be read to an accuracy of 0.2 p.s.i. (±0.25%).

The filling temperature is monitored by a thermometer probe within the counter shield. Since overall temperature variations between 15°C. and 21°C. have been observed during a two year period, all sample activities are normalised to a constant filling temperature of 18°C. (Figure 13) (Appendix A).

FIGURE 12

COUNTER FILLING SYSTEM.

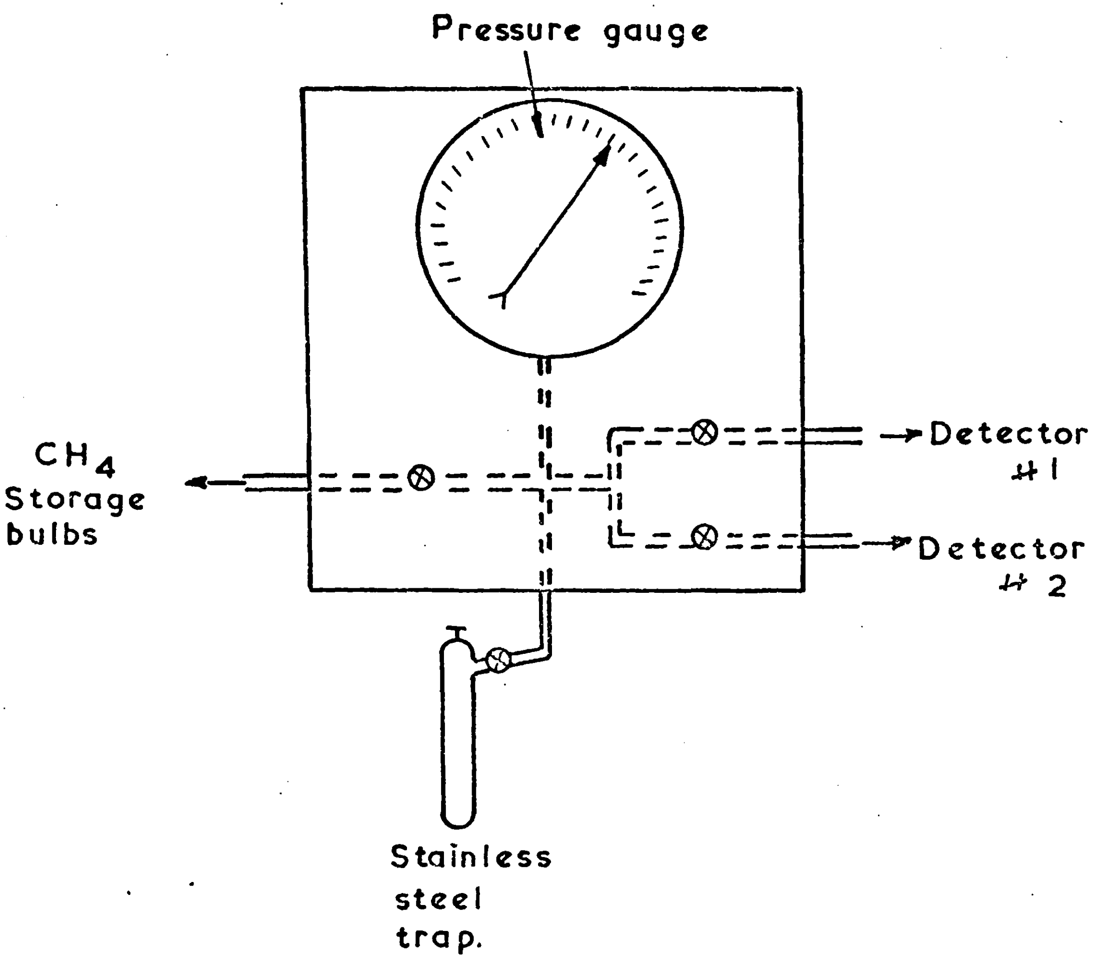
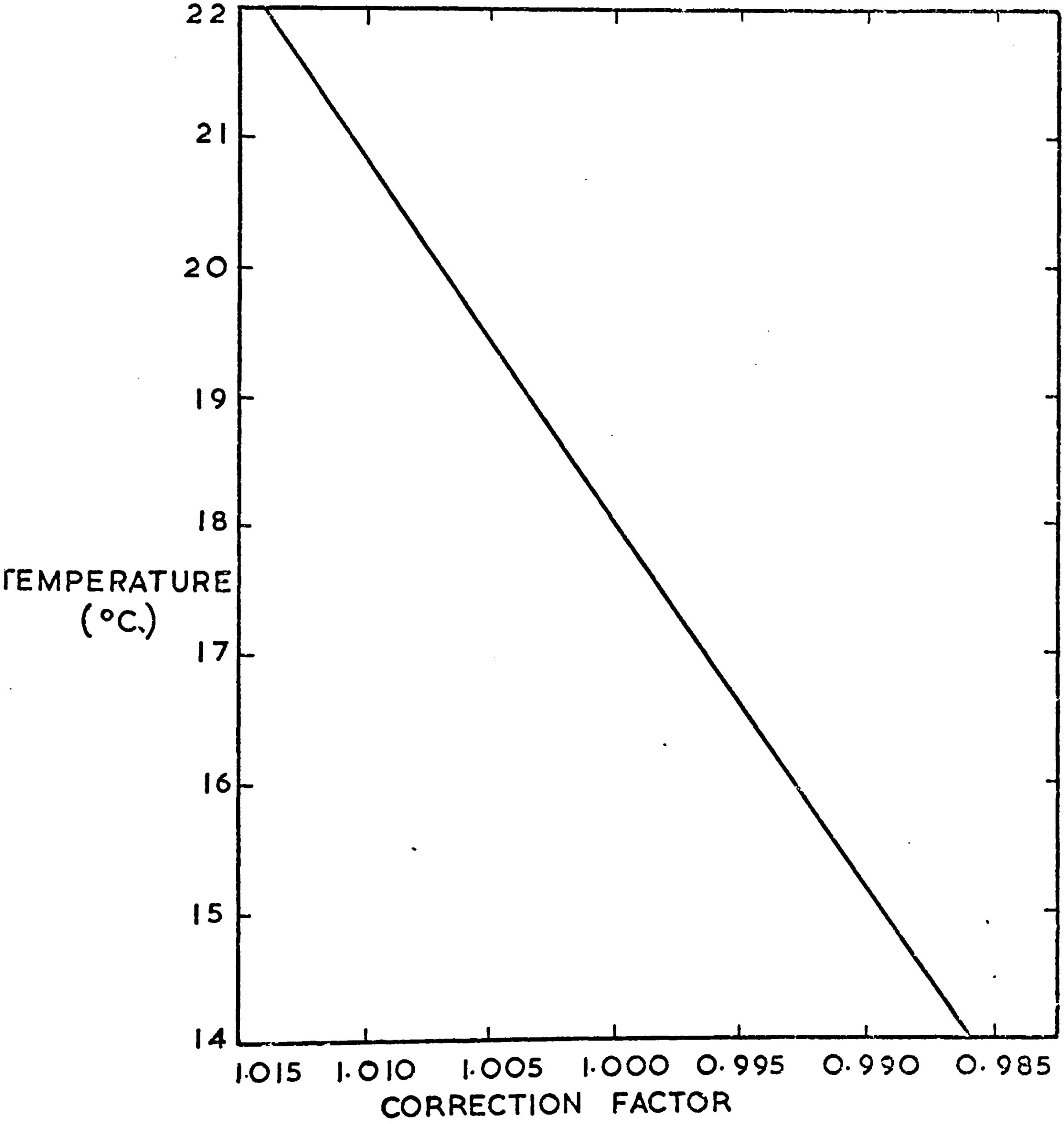


FIGURE 13.
COUNTER FILLING TEMPERATURE CORRECTION FACTOR.



Counter Assembly.

(a) General.

Internal gas proportional counters (0.5 litre) supplied by Beckman Instruments Inc., California, are used as sample detectors. Two detectors are in general use although only one is involved in this research project. A concentric-wall multiple anode anticoincidence counter surrounds the detectors and the entire assembly is encased within a lead shield (J. Girdler & Co., London). Counter electronics, anticoincidence system and power supply are of Beckman design (57). A block diagram of the internal gas counting system is presented in Figure 14.

(b) Sample Detector.

The detector was machined from a solid ingot of O.F.H.C. copper thus providing a 1.8 cm. copper lining to the shield (Figure 15). A layer of pure nickel electroplated on to the interior surface of the detector absorbs any alpha particles from the copper and eliminates memory effects occasionally observed with pure copper cathodes. Stainless steel wire (diameter 0.001 in.) stretched to 90% of its elastic limit constitutes the anode. Teflon is used as insulator material and the end plates of the detector are O-ring sealed. This arrangement facilitates satisfactory vacuum and pressure holding

FIGURE 14
BLOCK DIAGRAM OF COUNTING SYSTEM

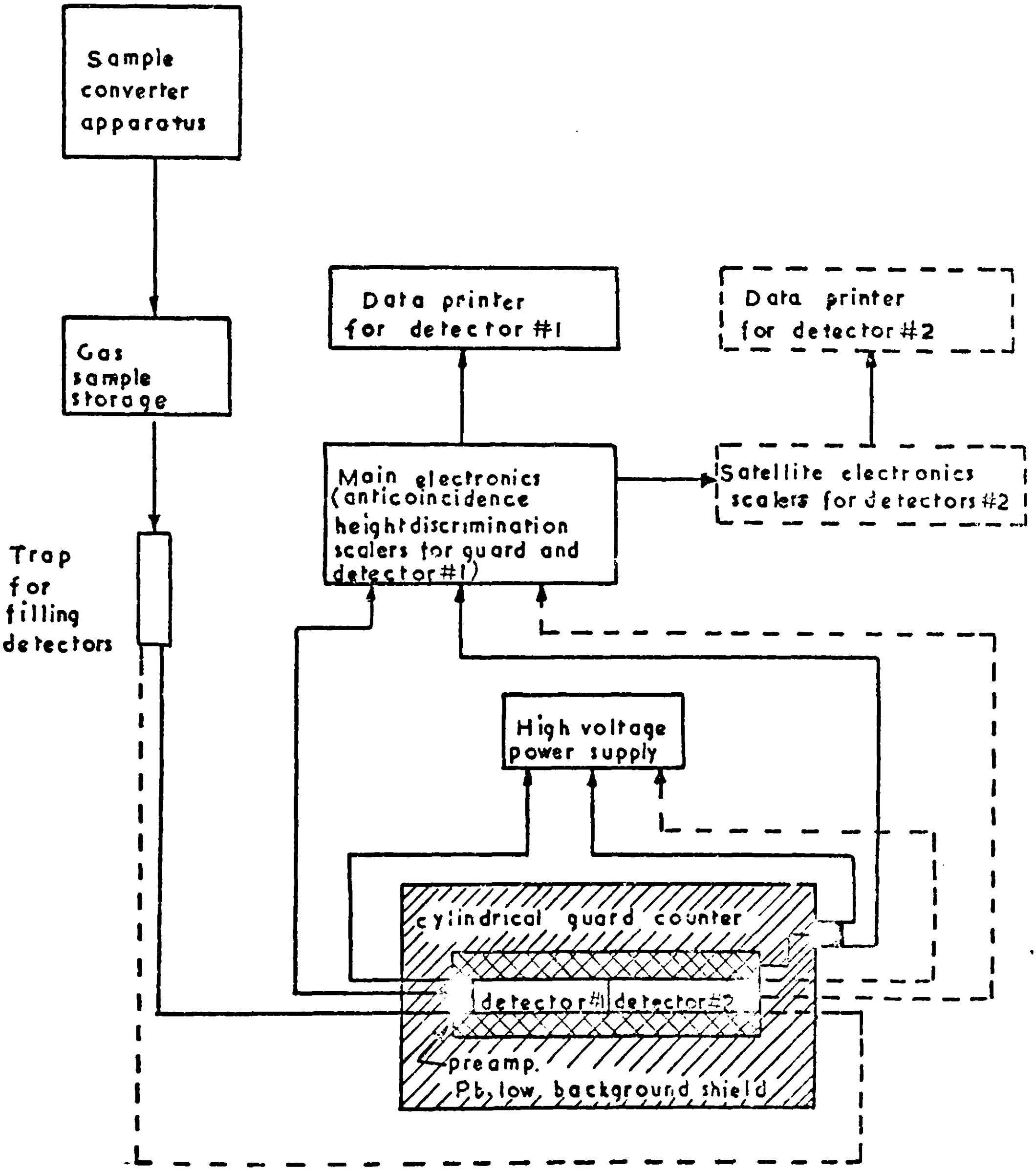
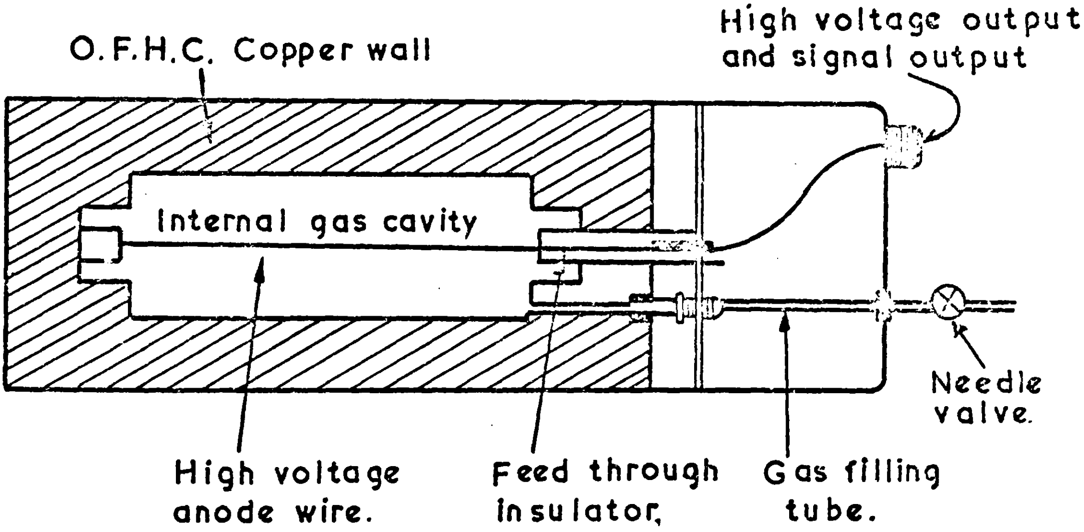


FIGURE 15.

CROSS SECTION DIAGRAM OF SAMPLE DETECTOR.



performance. A disadvantage of the detector is that it cannot be dismantled for cleaning without the anode wire being broken. The detector can be operated at gas filling pressures of 1 to 10 atm. (2.5 g. C as CH_4).

(c) Anticoincidence Guard Counter.

The inner and outer walls of the concentric-wall guard counter are heavy wall O.F.H.C. copper pipe with a combined thickness of 2.5 cm.. Together with the detector wall this provides an O.F.H.C. copper shield liner over 4 cm. thick. The guard counter fits closely inside the shield to increase the efficiency of interception of the mu-mesons producing gamma showers in the shield. Anode wire, teflon insulators, and O-ring seals are similar to those in the detector. Unlike the sample detector, however, the outer sleeve of the guard is easily removable to allow inspection and cleaning.

The guard counter is normally filled to 80 cm.Hg with inactive CH_4, each fill having a lifetime of 4 to 6 months. Both noise and cosmic radiation can be detected as efficiently as by the sample detector so that effective cancellation of simultaneous pulses in both counters is achieved.

In this counting system, the "wall effect", due to recoil electrons produced by gamma interactions in the counter walls, is believed to contribute 20-40% of the background count rate (57). Counters of the "Oeschger" design with guard and detector combined in a single unit offer reduced opportunities for this effect. The Beckman system, however, compensates for the increased background by a reduction in dead volume.

(d) Shield Assembly.

The shield is constructed of 4in. thick lead and has overall dimensions of 16in. x 16in. x 36in.. Its weight is 2,960 lb.. It is manufactured from "aged" lead, known to be relatively free from natural radioactivity and fission products.

At each end the shield is fitted with a close-fitting lead plate door which opens freely on a thrust-bearing. This provides ready access to the counter unit inside.

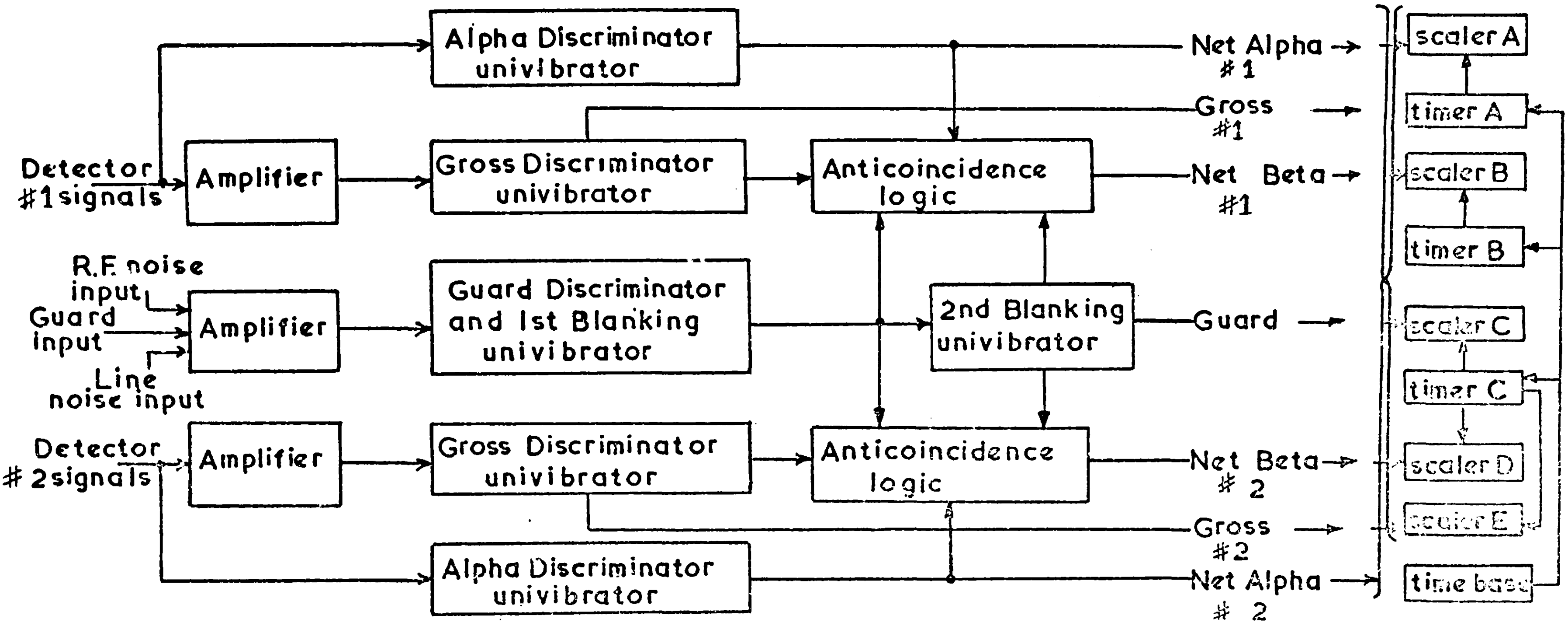
(e) Electronics.

Seven data outputs are provided from the main electronics; net alpha counts, gross unguarded counts, and net beta counts for each detector, and the guard counts (Figure 16). Five scalers are available to switch to any of the seven outputs. The alpha data channels are triggered by an adjustable upper level discriminator which is usually set at 200 MeV..

To eliminate environmental electrical noise the power line and a radio-frequency pickup antenna are

FIGURE 16

MAIN ELECTRONICS BLOCK DIAGRAM.



coupled into the anticoincidence circuit. This ensures that the anticoincidence circuit is more sensitive to noise than the detectors.

A further feature of the electronics design is the incorporation of a circuitry test programme. Three internal test pulses are provided, simulating detector pulses at the detector input, mu-meson pulses coincident at the detector and guard inputs, and alpha pulses at the detector inputs. Using the seven data outputs and five scalers a 105 step test programme can check every circuit board in a few minutes.

The high voltage power supply incorporates three separately adjustable channels, each with an output range of 1,000 to 10,000 volts. Two extractor fans are required to cool the unit and maintain dust levels at a minimum.

Since C-14 activity measurement requires long counting times, four of the five scaler units are linked to an automatic data printer. A print-out each 30 minutes allows examination of data for statistical reproducibility.

Counter Characteristics.

(a) Plateaux.

All initial counter calibration experiments were performed using "pure tank" CH_4, obtained from Beckman Instruments Ltd., Glenrothes, and believed to be free from radioactive contamination. Experience has shown these results to be reproducible and in excellent agreement with data obtained from CH_4 synthesised from inactive materials in the laboratory.

Detector plateaux are routinely monitored using an external Cs-137 source to increase the count rate and improve statistics. The detector plateaux are of length 1,000 to 2,000 volts with slopes less than 0.5% per 100 volts (Figure 17). Guard plateaux are 500 to 1,000 volts long with a slope less than 1% per 100 volts. At the routine filling pressures of 5 atm. and 1.05 atm., the detector and guard working voltages are 6.7 KV. and 3.7 KV. respectively.

The variation of detector working voltage with filling pressure is presented in Figure 18. Five atm. was chosen as the normal filling pressure for two reasons; (1) the high voltage power unit indicated some instability at continuous operating voltages above 8 KV., and (2) the amount of CH_4 required for a 5 atm. counter filling is compatible with efficient handling of the chemical procedures. A minimum of about 3.5 litre-atm.

FIGURE 17

DETECTOR AND GUARD PLATEAUX.

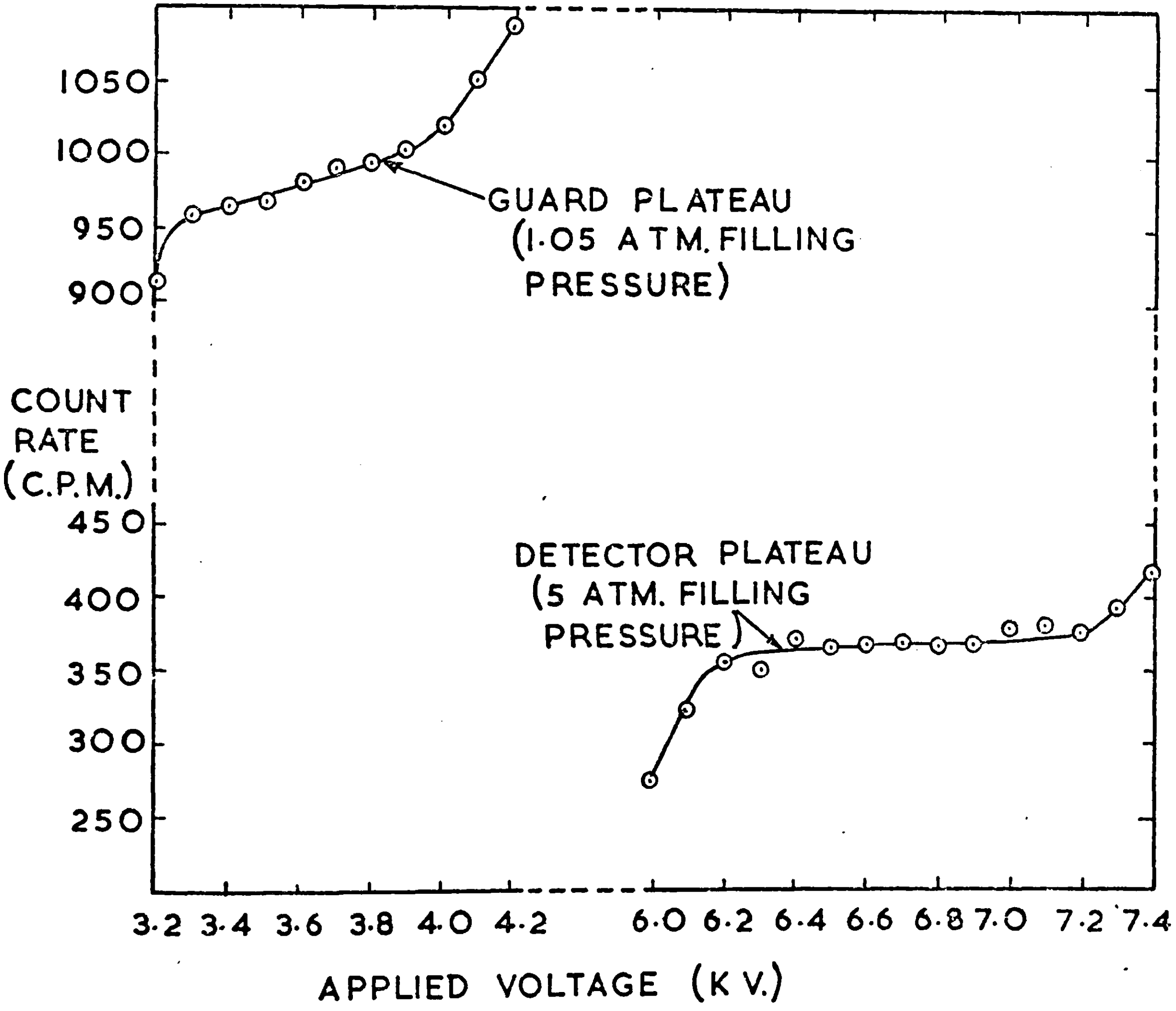
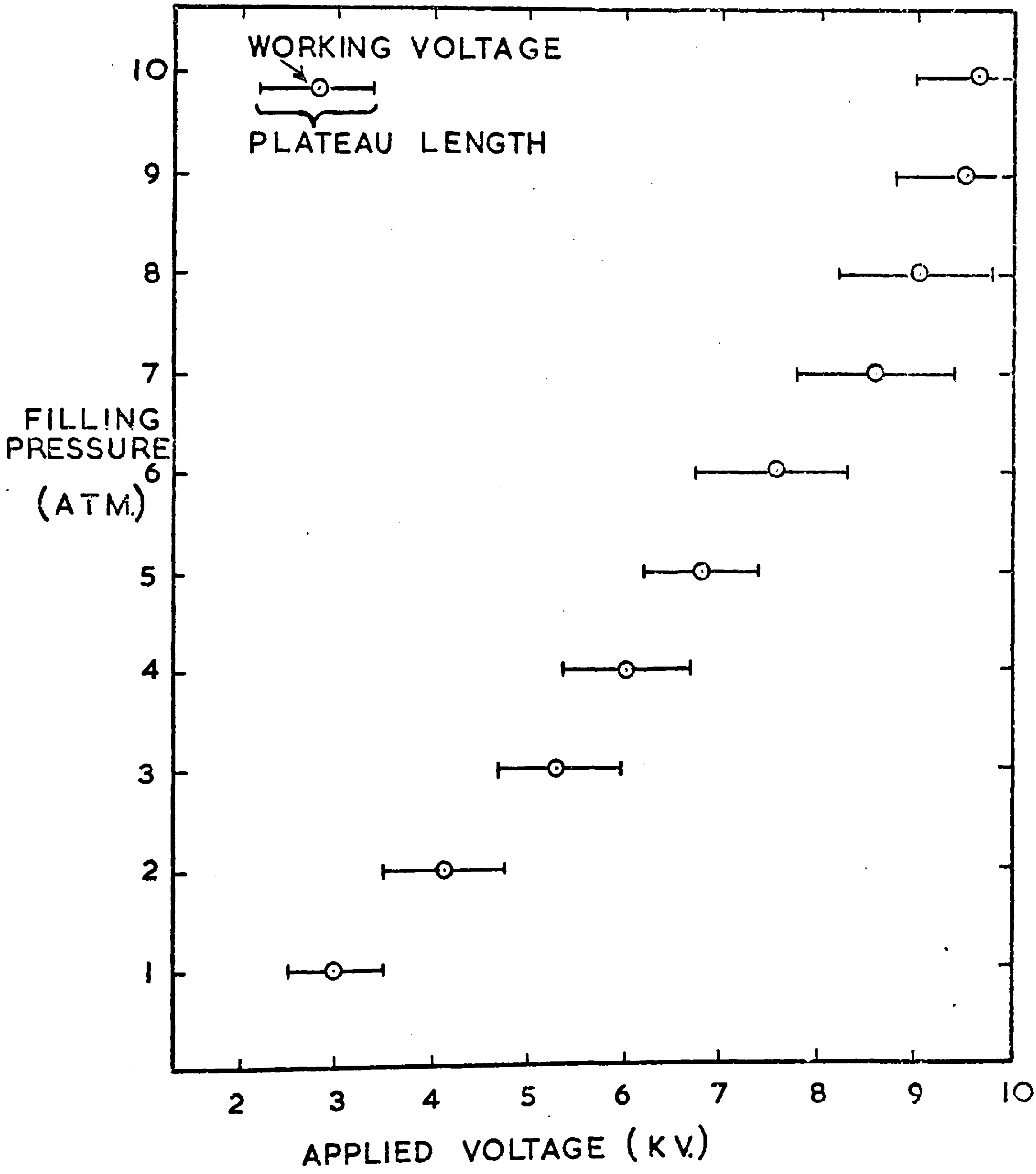


FIGURE 18

VARIATION IN DETECTOR PLATEAU WITH FILLING PRESSURE.

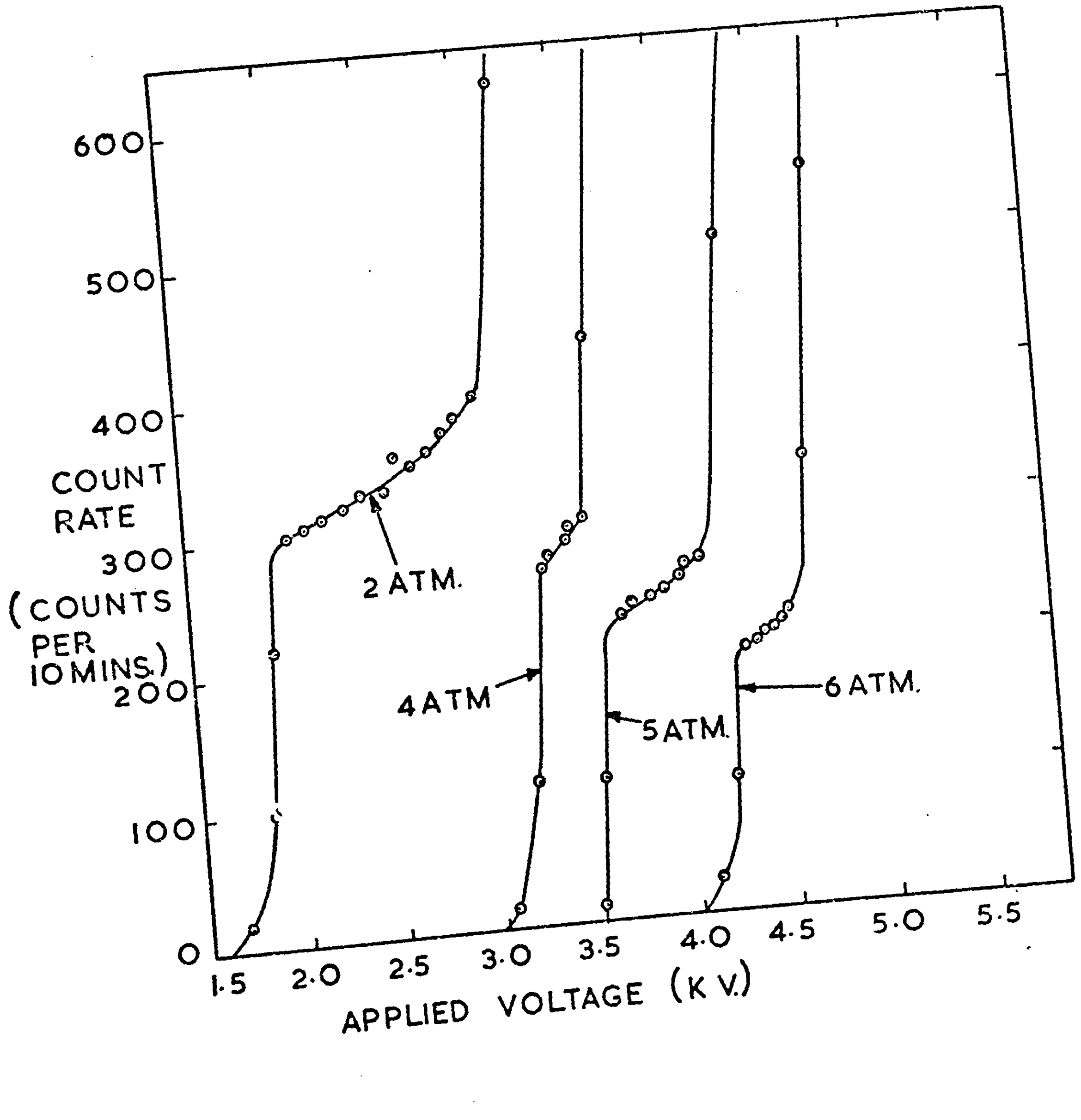


of CH_4 is required for 2 or 3 activity measurements. Filled to 5 atm. the counter contains 1.25g. carbon. Although counting times would be reduced by counting at higher filling pressures, a routine turnover of more than 3 samples/week could not be maintained by the sample preparation system. Here the rigorous degassing required by the CH_4-synthesis reactor is the time-consuming stage.

Because the pulses of the alpha particles of radon are larger than the pulses of cosmic rays and beta particles, it should be possible to detect radon contamination by counting at a lower voltage. Here the gas amplification is too small to bring the smaller pulses over the threshold. This hypothesis was tested by allowing a 10g. sample of pitchblende to emanate radon overnight into a CH_4 atmosphere. The contaminated CH_4 was then swept into the detector. An alpha plateau was determined and the variation of alpha working voltage with filling pressure was evaluated (Figure 19). Although the alpha plateaux are short, preliminary alpha counting of samples provides a valuable indication of the presence or absence of radon contamination. No attempt was made to use alpha counting to provide a quantitative correction factor for the radon contribution to the sample activity. This, in effect, would be an alternative to sample storage. The increased statistical

FIGURE 19

DETECTOR ALPHA PLATEAUX.



error, the relatively ill-defined alpha plateaux, and the much increased counting time make radon correction undesirable in this system, since storage for decay does not interfere with the overall rate of sample analyses.

(b) Background Measurements.

The background count rate at 5 atm. filling pressure and 1 atm. barometric pressure is 3.65 ± 0.08 (± 2σ). This is the value found both with "tank" CH_4 and with samples prepared from anthracite and marble. The background count rate can be attributed to radiation undetected by the anticoincidence system and to natural radioactivity in the counter environment. The former is caused primarily by external gamma and cosmic ray meson radiations. Apart from guard efficiency considerations, the particles can penetrate the sample counter undetected by the guard by entry through the ends of the guard ring ("end effect").

The variation of background count rate with filling pressure is shown in Figure 20. This plot is non-linear presumably because at higher filling pressures the gamma detection efficiency tends to 100%. The curve indicates also that any activity in the background gas is small.

Background count rates vary with atmospheric pressure by -0.11 c.p.m./cm.Hg or -0.08 c.p.m./10mb. at 5 atm. filling pressure (Figure 21). To obtain this correction

FIGURE 20

BACKGROUND COUNT RATE AS A FUNCTION OF COUNTER FILLING PRESSURE.

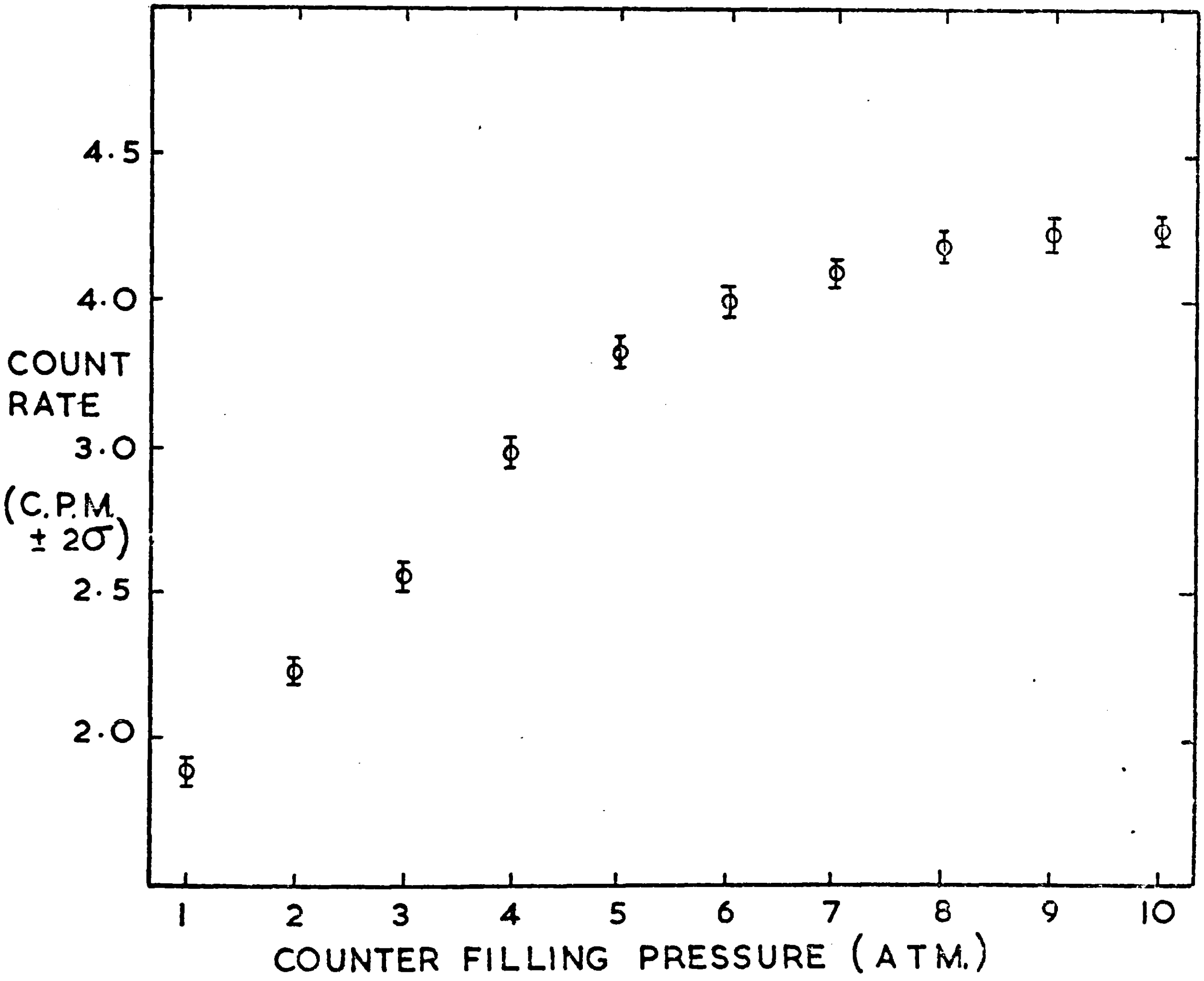
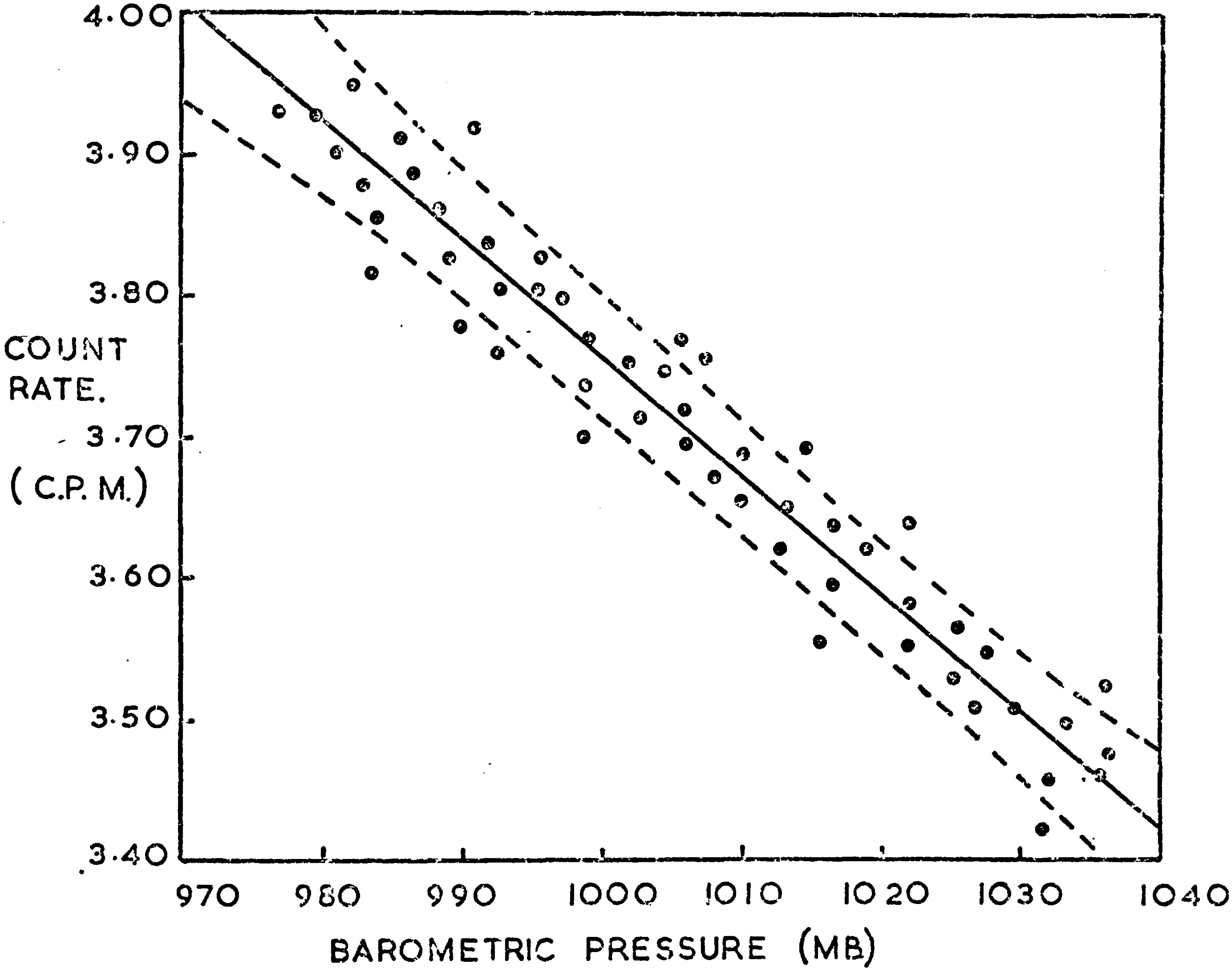


FIGURE 21.
BACKGROUND COUNT RATE AS A FUNCTION OF BAROMETRIC PRESSURE.



factor a continuous record of atmospheric pressure, corrected to sea level, is monitored by a laboratory barograph. Regular intercalibration with the records of the Glasgow Weather Centre ensures the accuracy of the barograph readings. During the period of routine sample counting, barometric pressures ranged between limits of 970 and 1035 mb. with occasional overnight variations up to 30 mb.. Because of this pressure variability, the mean barometric pressure is calculated for each counting period.

Computer regression analysis allowed calculation of the precise mathematical dependence of background count rate on atmospheric pressure. This relationship was calculated for several periods and found not to vary. The standard deviation on the predicted background count rates is estimated by calculation of the standard deviation on the regression coefficient. A range in background error from 0.06 c.p.m. at 1035 mb. and 980 mb. to 0.04 c.p.m. at 1010 mb. is found. Background count rates are monitored on a weekly basis to ensure the stability of the counting system.

Significant positive deviations of the background count rates from the "tank" values were observed in samples prepared from anthracite and marble using an alternative supply of hydrogen (Air Products, Ltd.). Samples synthesised from the same materials using

Messrs. Griesheims' tritium-free hydrogen recorded background levels in agreement with the "tank" CH_4 values. Table 4 presents a comparison of background data for the three sample types. The contaminant activity in Air Products' samples is not radon since no significant decay occurred over a 6-month period. Nor can the activity be due to C-14 since the same samples were used for synthesis with Griesheim hydrogen. The contamination is probably due to tritium. Unfortunately the opportunities for tritium-contamination during the manufacturing processes could not be assessed as neither manufacturer would provide details of their methods. Most commercial hydrogen, however, is a product of the electrolysis of sea water. In addition, ground waters have been contaminated by artificial tritium produced by nuclear weapons. Based on this assumption, the mean "tritium" contribution to the background count rate at 5 atm. filling pressure is 0.27 ± 0.04 c.p.m. ($\pm 2\sigma$). This corresponds to a tritium content of the hydrogen supply amounting to 0.1 c.p.m./litre H_2, or 15.5 tritium units (1 T.U. corresponds to a T/H ratio of 10^{-18}). This tritium concentration is typical of those in the surface ocean during recent times (34).

(c) Mass-Spectrometry.

C-13/C-12 ratios were determined by mass-spectrometry

TABLE 4

COMPARISON OF BACKGROUND DATA

(a) SAMPLES MADE USING AIR PRODUCTS' HYDROGEN

Sample	Count Rate (c.p.m. ± 2σ)	Barometric Pressure (mb.)	Corresponding "Tank" Value (c.p.m. ± 2σ)	Difference "Tritium" (c.p.m. ± 2σ)
Marble 1	4.02 ± 0.08	997	3.79 ± 0.10	+ 0.23 ± 0.13
"	4.32 ± 0.12	986	3.88 ± 0.11	+ 0.44 ± 0.15
Marble 2	3.95 ± 0.10	1015	3.64 ± 0.08	+ 0.31 ± 0.13
"	4.06 ± 0.11	995	3.81 ± 0.10	+ 0.25 ± 0.15
Anthracite 1	3.92 ± 0.06	1020	3.59 ± 0.09	+ 0.33 ± 0.11
"	3.78 ± 0.11	1021	3.58 ± 0.09	+ 0.20 ± 0.14
"	3.84 ± 0.06	1019	3.60 ± 0.09	+ 0.24 ± 0.11
"	4.10 ± 0.06	985	3.89 ± 0.11	+ 0.21 ± 0.12
"	3.79 ± 0.05	1023	3.57 ± 0.10	+ 0.22 ± 0.11
			Mean difference	+ 0.27 ± 0.04

TABLE 4 (cont.)

COMPARISON OF BACKGROUND DATA

(b) SAMPLES MADE USING GRIESHEIM HYDROGEN

Sample	Count Rate (c.p.m. ± 2σ)	Barometric Pressure (mb.)	Corresponding "Tank" Value (c.p.m. ± 2σ)	Difference "Tritium" (c.p.m. ± 2σ)
Marble 3	3.74 ± 0.06	1013	3.65 ± 0.08	+ 0.09 ± 0.10
"	3.63 ± 0.07	1012	3.66 ± 0.08	- 0.03 ± 0.11
"	3.48 ± 0.11	1023	3.57 ± 0.10	- 0.09 ± 0.15
"	3.48 ± 0.07	1025	3.55 ± 0.10	- 0.07 ± 0.12
"	3.70 ± 0.10	1015	3.64 ± 0.08	+ 0.06 ± 0.13
"	3.63 ± 0.07	1010	3.68 ± 0.08	- 0.05 ± 0.11
"	3.76 ± 0.08	996	3.80 ± 0.10	- 0.04 ± 0.13
Anthracite 2	3.72 ± 0.08	1014	3.63 ± 0.08	+ 0.09 ± 0.11
"	3.81 ± 0.07	996	3.80 ± 0.10	+ 0.01 ± 0.12
			<u>Mean difference</u>	<u>0.00 ± 0.04</u>

for every sample assayed for C-14 activity. The deviation in isotope ratio from a standard sample ratio was used to correct the sample activity for isotopic fractionation.

Fractionation of the carbon isotopes may occur in the laboratory during processes where sample loss is incurred. Since CH_4 is not suitable for mass-spectrometric measurement of sample C-13/C-12 ratios the determinations are carried out on CO_2 samples. Correction is therefore made for deviations in isotope ratio caused both by natural and CO_2 production processes. However, for any fractionation occurring in CH_4-synthesis, purification, or storage, no correction is made. Because of the finite vapour pressure of CH_4 at liquid N_2 temperatures these processes do involve sample losses. Despite the mean overall CH_4-synthesis loss of 6% and the transfer losses during counter filling and storage, there is significant evidence to suggest that fractionation is negligible;

(1) $CO_2 \longrightarrow CH_4$ conversion efficiencies are high (98-100%),

(2) the majority of samples show activity agreement after 2 counting periods, involving at least 3 CH_4 distillations,

(3) 3 modern standard samples have been counted up

to 12 times each without observable variation in C-14 activity (Table 5),

(4) 2 CO_2 samples previously counted in a CO_2 proportional counter were converted to CH_4 and their activity found to agree with the CO_2 data (samples (g) and (h) in Table 6).

That fractionation seems negligible in this system confirms the results of Long (62) who found that only with CH_4-synthesis yields of 80% and less did fractionation cause measurable errors in activity determination.

Sample C-13/C-12 ratios are measured at the National Physical Laboratory, Middlesex, using an MS3 mass-spectrometer. This spectrometer is fitted with twin ion collectors which permit direct measurement of the deviation in sample C-13/C-12 ratio from the standard ratio. The primary standard for carbon isotope studies is the P.D.B. belemnite limestone standard. At the National Physical Laboratory, a secondary standard has been intercalibrated with the belemnite standard. The mean of ten measurements of the deviation (C-13/C-12 sample - C-13/C-12 standard) is used in the activity correction. The measurement of each sample deviation is accurate to ± 1‰ (± 2σ). Details of the correction procedure are included in Appendix A.

(d) Modern Standard Activity.

After correction for background, filling temperature, and isotopic fractionation, C-14 activities are converted to Δ units, which represent the % difference in C-14 concentration from the "natural" level (Appendix A). The "natural" level is assumed equal to 95% of the C-14 concentration of an oxalic acid standard (National Bureau of Standards). The factor of 0.95 is based on the results of Broecker and Olson (25) which indicated that 95% of the N.B.S. standard C-14 activity equals the decay-corrected C-14 activity of 1890 wood samples. These wood samples are assumed free from the "Suess effect". For all radiocarbon work, therefore, 95% of the standard activity represents the constant atmospheric activity assumed by Libby.

Since Broecker and Olson's derivation of the 0.95 factor was made in 1958, present day activities of the N.B.S. standard require a minor correction for C-14 decay since that time. The correction factor is 0.12‰/year. A further correction of the standard activity must be made for the isotopic fractionation effect which can occur to varying degrees in different laboratories. In 1960, Craig (63) carefully measured the C-13/C-12 ratios of 24 CO_2 samples prepared from the standard in

13 different laboratories throughout the world. His work established that the "best" value for the C-13/C-12 ratio of the standard is -19‰ relative to P.D.B. belemnite. All modern standard activities are therefore corrected for fractionation relative to -19‰

Regular monitoring of the modern standard activity is necessary since (1) a large number of measurements reduce the statistical error associated with the standard, and hence all sample activities, and (2) reproducible standard count rates indicate stable detection efficiencies. The modern standard activity is therefore measured at least twice each month. Table 5 indicates the standard activities observed during the past 18 months and the calculation of 95% of the corrected mean activities for different samples. Good internal agreement is evident.

A useful guide to the gas purity of every sample is found to be derived from the difference between gross count rate (i.e. before coincidence) and net count rate (i.e. after coincidence). At 5 atm. filling pressure this function should be 90 ± 2 c.p.m.. An impure gas has a value smaller than 90 ± 2 c.p.m. due presumably to reduced detection efficiency through electron capture by the contaminant. Since the counting characteristics of CH_4 can tolerate up to 0.35% of air contamination (64), significantly impure samples were encountered very rarely and amounted to less than 2% of all gases. No cleaning

TABLE 5

MODERN STANDARD ACTIVITIES

STANDARD 1		STANDARD 2		STANDARD 3	
Counting Date	Corrected Activity (c.p.m. ± 2σ)	Counting Date	Corrected Activity (c.p.m. ± 2σ)	Counting Date	Corrected Activity (c.p.m. ± 2σ)
1-11-67	18.60 ± 0.29	28-3-68	18.45 ± 0.27	16- 9-68	18.43 ± 0.26
14-11-67	18.66 ± 0.35	2-4-68	18.71 ± 0.28	7-10-68	18.59 ± 0.29
15-12-67	18.57 ± 0.29	16-4-68	18.44 ± 0.29	21-10-68	18.47 ± 0.27
10- 1-68	18.54 ± 0.30	2-5-68	18.63 ± 0.31	4-11-68	18.60 ± 0.30
25- 1-68	18.68 ± 0.28	27-5-68	18.57 ± 0.33	15-11-68	18.46 ± 0.28
29- 1-68	18.65 ± 0.33	4-6-68	18.88 ± 0.29	4-12-68	18.55 ± 0.29
8- 2-68	18.64 ± 0.28	14-6-68	18.38 ± 0.30	19-12-68	18.61 ± 0.27
22- 2-68	18.65 ± 0.29	2-7-68	18.48 ± 0.29	5- 1-69	18.49 ± 0.29
5- 3-68	18.68 ± 0.26	16-7-68	18.67 ± 0.28	20- 1-69	18.45 ± 0.30
		1-8-68	18.52 ± 0.29	7- 2-69	18.55 ± 0.27
Mean (A')	18.63 ± 0.10	15-8-68	18.57 ± 0.30	20- 2-69	18.71 ± 0.30
		2-9-68	18.54 ± 0.31	3- 3-69	18.66 ± 0.25
				20- 3-69	18.42 ± 0.30
		Mean (A')	18.57 ± 0.09	4- 4-69	18.37 ± 0.30
				25- 4-69	18.40 ± 0.29
				15- 5-69	18.47 ± 0.28
				Mean (A')	18.50 ± 0.07

TABLE 5 (cont.)

MODERN STANDARD ACTIVITIES

Fractionation-corrected Activity $(A_f)^+$;

STANDARD 1 no isotope measurement available

STANDARD 2 $A_f = 18.66 \pm 0.09$ c.p.m.

STANDARD 3 $A_f = 18.68 \pm 0.07$ c.p.m.

Decay-corrected Activity (A_o);

STANDARD 1 $A_o = 18.65 \pm 0.10$ c.p.m.

STANDARD 2 $A_o = 18.68 \pm 0.09$ c.p.m.

STANDARD 3 $A_o = 18.70 \pm 0.07$ c.p.m.

0.95 Standard Activity* $= \underline{17.76 \pm 0.06}$ c.p.m. $(\pm 2\sigma)$

$+ \; A_f = A' \left(1 - \frac{2(\delta C\text{-}13 + 19)}{1000}\right)$

* mean of samples 2 and 3 since no δC-13 for sample 1

procedure was found satisfactory for purification of these samples. The substantial vapour pressure of CH_4 at -196°C. prevents the quantitative removal of contaminants.

(e) Reliability of System.

As a check on the reliability of the laboratory and counting techniques a number of samples were requested from various established laboratories for intercalibration purposes. The radiocarbon ages found for these samples are compared with the results of others in Table 6. The majority of these results have been reported elsewhere (65).

Agreement between these results is satisfactory. Where disagreement outwith statistical error occurs, as for the wood and peat samples, there is good evidence that the discrepancy may be due to sampling difficulties. Thus denaturing of the wood sample prevented identification of the tree rings.

The intercalibration experiments and the long-term stability of background and standard count rates confirmed the reliability of the system.

TABLE 6

RESULTS OF INTERCALIBRATION SAMPLES

(1) DATING SAMPLES

Sample	Radiocarbon Age (years ± 1σ)	Others' Results (years ± 1σ)
(a) Charcoal	2,064 ± 55	2,100 ± 80
		1,908 ± 60
(b) Charcoal	2,370 ± 40	ca. 2,300*
(c) Peat	12,158 ± 218	11,205 ± 177
		11,828 ± 132
(d) Wood	3,702 ± 69	3,847 ± 60
(e) Wood	4,623 ± 69	ca. 5,000*

* archaeological estimates.

(2) RECENT SAMPLES

Sample	Δ (% ± 1σ)	Others' Results (% ± 1σ)
(f) Whisky	+ 86.08 ± 1.08	+ 86.80 ± 2.10
(g) Tropospheric CO_2	+ 58.71 ± 0.80	+ 58.90 ± 0.92
(h) Tropospheric CO_2	+ 59.73 ± 0.79	+ 60.21 ± 0.90

III

PLANT MATERIALS AS INDICATORS OF ATMOSPHERIC CARBON-14 CONCENTRATIONS.

Introduction

Information regarding atmospheric C-14 concentrations during the past century may only be obtained if the C-14 content of samples accurately reflects the prevailing atmospheric activity at their place of "growth". For the detection of any annual variations it is essential that these samples should indicate the mean atmospheric C-14 concentration during a time period less than one year. Furthermore, the samples must have remained closed systems with respect to carbon exchange since their removal from the carbon exchange cycle. Plant materials seemed to provide the most suitable source for this type of study since a correlation between C-14 activities in atmospheric CO_2 and biospheric (tree leaves and grain) samples had previously been indicated by the results of Broecker and Walton (21) and Nydal (66). Such a correlation is of course basic to the radiocarbon dating method. (The validity of the radiocarbon method does not necessarily confirm, however, that plant materials will accurately reflect short-term fluctuations of atmospheric C-14 activities. Nor does the use of plant materials to detect atmospheric C-14 fluctuations occurring over hundreds or thousands of years confirm that any annual variations will be precisely indicated.)

The basis of a correlation between plant and atmospheric C-14 concentrations lies in the direct fixation by plants of atmospheric CO_2 for cell synthesis. If, however, plants also incorporate carbon from the soil environment via the roots then a direct correlation may be disturbed. Soil CO_2 is produced at a rate of about 2 tons/acre/month (67) and, in addition to the contribution from plant respiration, significant amounts of CO_2 may be derived from (1) decaying vegetation, and (2) carbonate materials in the soil environment. The C-14 activity of the former is a function of past years' atmospheric activities, and soil carbonates may be completely C-14 free, as in limestone. Thus the possible uptake of non-contemporaneous carbon by plants may cause atmospheric and plant C-14 activities to differ. Kursanov et al (68) used tracer methods and found that as much as 20% of the carbon synthesised by bean seedlings could be introduced through the roots. Broecker and Olson (22) suggested that 30% of the carbon content of a sample of tree leaves was derived from the soil. Although Stolwijk and Thimann (67) confirmed that soil CO_2 uptake values greater than a few percent are uncommon, the correlation between plant and atmospheric C-14 concentrations seemed to require further investigation. The marked variations in atmospheric C-14 content caused by nuclear weapons testing offered ideal conditions for such a study in the environment.

The Selection of Suitable Plant Materials.

The choice of plant materials to be studied as indicators of atmospheric C-14 concentrations was based on

(1) sample availability during the past century,
(2) sample purity, i.e. freedom from contamination or carbon exchange since "death",
(3) sample definition, i.e. knowledge of the exact time and location of plant growth.

Although, by analogy with conventional radiocarbon studies, annual tree rings appeared to offer a source of suitable samples, these were not used. The "death" of a tree ring is followed by a gradual transformation of sapwood, containing soluble carbonaceous material, into hardwood. This change has been observed to take up to 100 years for completion (69). During transformation the soluble components of the sapwood may well be in equilibrium with the sapwood of adjacent rings. Thus Broecker and Olson (70) found the C-14 concentration of the 1952 growth ring of an oak tree felled in 1959 to be -0.1% (Δ) compared to the 1952 atmospheric level of about -3%. This discrepancy implies incorporation into the 1952 tree ring of about 20% post-1952 carbon containing bomb-produced C-14. Tree ring analysis may be a reliable technique for time periods during which significant year to year variations in atmospheric C-14 concentrations do not occur. For a study of short-term variations, however, uncertainties in the assumptions basic to tree ring studies make the method undesirable. In addition tree rings were unsuitable for this study since in many cases irregularities in ring formation can introduce error in identification of the growth year and since the size of samples required for C-14 analysis can necessitate the use of sections containing several annual growth rings.

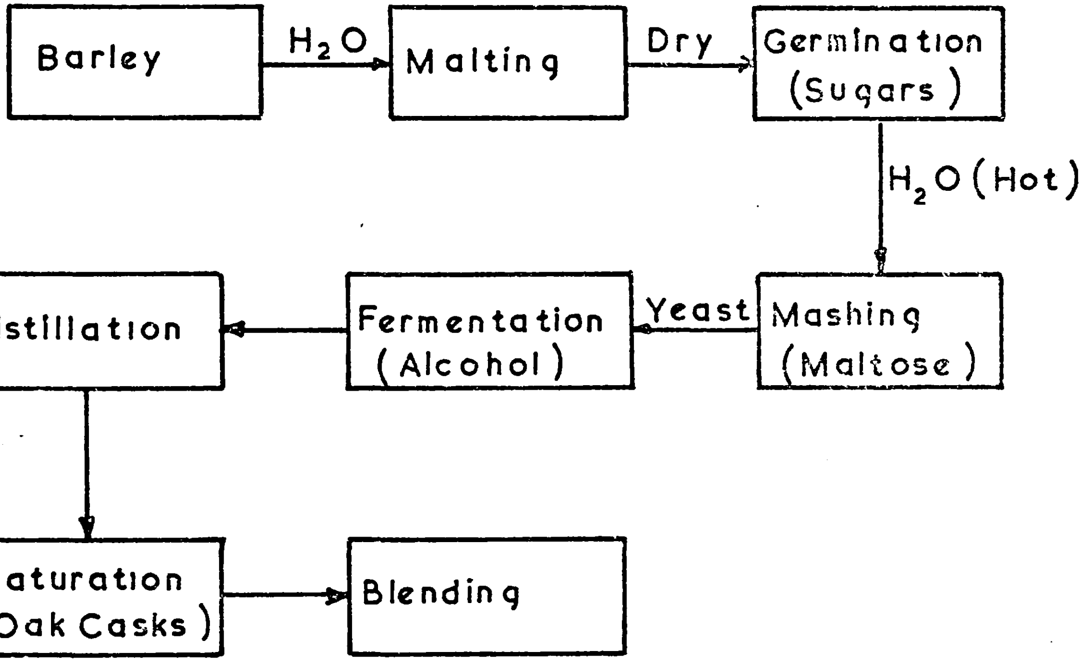
The materials of plant origin which seemed to satisfy the requirements were (a) spirits and wines and (b) tree and plant seeds. It is assumed in the use of spirits and wines that the C-14 concentration of the alcohol fraction is closely related to the C-14 concentration of the plant materials from which it was manufactured. The correlation between the C-14 concentrations in cereal and atmospheric samples appear to be particularly reliable (22, 71). Furthermore, vintage wines and spirits are available on an annual basis during the past century, and the location and year of manufacture is accurately known.

In the preliminary investigation of the correlation between alcoholic material and atmospheric C-14 activities, malt whiskies were analysed. Since malt whiskies are manufactured exclusively from barley grown in Scotland, the origin of the grain was known. This is in contrast to "blended" whiskies where the grain may be a mixture from various regions. Because it was important to determine whether there existed any additional sources of carbon other than the grain, the processes involved in whisky production were examined (Figure 22). Three possible sources do in fact exist; water, yeast, and colouring matter. In our experiments the colouring matter was removed in the laboratory distillation. Of the remaining constituents yeast acts primarily as a catalyst in the sugar - to - alcohol conversion and the water was not expected to contribute any carbon to the alcohol fraction. The chemical processes involved in wine manufacture are analogous to those in whisky production so that for both materials no substantial source of carbon contamination seemed probable.

Recent plant seeds are collected and preserved by various agricultural laboratories and by the Forestry Commission. The history of these seeds is accurately recorded and samples grown at various latitudes are available.

FIGURE 22.

MANUFACTURE OF MALT WHISKIES.



Tree seeds were used for the evaluation of seed materials as atmospheric C-14 indicators. These seeds had been cleaned and stored in vacuo since collection so that no contamination should have occurred. During growth, however, it is possible that the seeds incorporated carbon via root uptake from the soil environment. As a precaution against this type of contamination by inactive carbon, seeds from trees grown on limestone soils were not selected for the intercalibration experiments.

Since cereals and plant seeds grow predominantly during the summer months it is most probable that carbon uptake will only occur during this period. Heinicke and Childers (72) have shown that the photosynthetic activity of a tree can vary from 200g. CO_2/month in May to a maximum of 5,000g. CO_2/month in July, falling to less than 500g. CO_2/month in November. Therefore plant materials, if they indicate accurately the atmospheric C-14 concentrations during a 6-month period, may be used to detect any year to year variations which may have occurred during the pre-nuclear era.

Sample Analysis

(a) Whisky Analysis.

The results of C-14 measurements of malt whiskies are shown in Table 7. Since whisky is usually manufactured during the year following the grain harvest, the year of barley growth is recorded for comparison purposes. Figure 23 presents the comparison of atmospheric and whisky C-14 activities where the former have been averaged over the grain growth season (April - September) and the corresponding winter months for each year. The atmospheric C-14 concentrations were derived from analyses of CO_2 samples collected in the middle and upper latitudes of the northern hemisphere (21, 22, 34). These data were chosen in view of the rapid mixing of C-14 believed to occur in the troposphere within the 42°N. to 78°N. latitude band (73). In Figure 23, the brackets indicate the total C-14 activity range within each growth season. Each spirit C-14 concentration is accompanied by a shaded area whose ordinate represents the standard deviation associated with the activity determination.

In all cases the whisky C-14 activities fall within the atmospheric C-14 activity ranges for the growth periods. In a preliminary study (74), the true ages of the first 7 samples analysed were known only to the distillers. Based on its C-14 activity each sample was then allocated a

TABLE 7

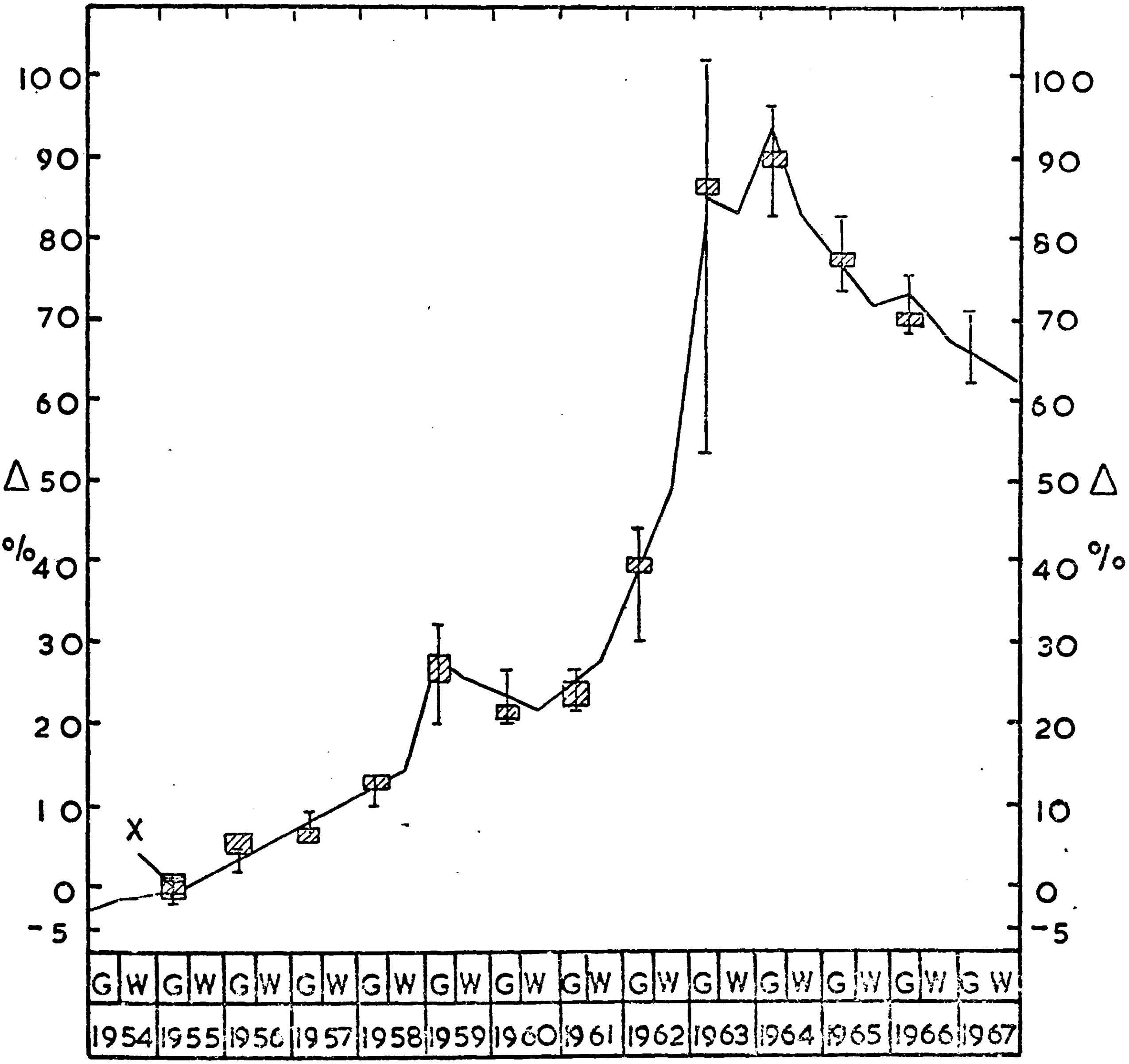
C-14 CONCENTRATIONS OF MALT WHISKIES (1955-66)

Year of Barley Growth	δ C-14 $\pm 1\sigma$ (%)	δC-13 (‰) $\pm$ 1‰ (2σ)	Δ $\pm 1\sigma$(%)
1955*	+ 0.60 ± 1.10	-25.0	+ 0.60 ± 1.12
1955(1939,1951)*	+ 1.40 ± 1.31	-17.5	- 0.10 ± 1.31
1956*	+ 5.20 ± 1.22	-26.7	+ 5.60 ± 1.24
1957	+ 6.56 ± 0.67	-25.1	+ 6.58 ± 0.70
1958	+ 12.29 ± 0.68	-28.2	+ 13.02 ± 0.73
1959*	+ 27.50 ± 1.46	-21.0	+26.50 ± 1.47
1960	+ 20.20 ± 0.70	-27.9	+ 20.91 ± 0.75
1961*	+ 22.70 ± 1.48	-25.7	+ 22.90 ± 1.50
1962	+ 39.19 ± 0.78	-24.9	+ 39.16 ± 0.83
1963	+ 86.08 ± 1.08	-25.0	+ 86.08 ± 1.12
1963*	+ 86.80 ± 2.07	-25.1	+ 86.80 ± 2.11
1964	+ 87.88 ± 0.97	-30.0	+ 89.75 ± 1.03
1965	+ 76.04 ± 1.20	-29.0	+ 77.45 ± 1.26
1966	+ 68.35 ± 1.19	-29.5	+ 69.87 ± 1.25

* Analysed at the National Physical Laboratory (74)

FIGURE 23

CORRELATION BETWEEN C-14 CONCENTRATIONS IN ATMOSPHERIC CO_2 AND WHISKY.



G BARLEY GROWTH SEASON

W CORRESPONDING "WINTER" SEASON.

probable year of grain growth and in all cases the "C-14 age" agreed with the true age. Sample X (Figure 23) was exceptional in that it was a blend of predominantly 3 individual whiskies - some 1939, some 1951, but mainly 1955. That this sample was assigned to 1955 implied that the method was sufficiently sensitive to detect the major component of a blended whisky of that period. This might not be the case, however, for blends of different composition. Thus the correlation between the C-14 activities of whisky and atmospheric samples is sufficiently good to justify this technique as a dating method for certain spirits. An application of such a method could be in the detection of illicit blenders and distillers.

Figure 24 presents a comparison of C-14 concentrations in whiskies and in Danish cereals as determined by Tauber (71). The direct correlation confirms that whisky manufacturing processes do not contaminate the cereal carbon. Small deviations may be attributable to slightly different growth periods of the Copenhagen and Glasgow samples. Certainly the results indicate that barley is a good measure of atmospheric C-14 activity via the spirits produced from it. That wines are also reliable indicators is evident from Figure 25 which is based on the analysis in 1968 of a series of German wines by L'Orange and Zimen (75). C-14 analysis of alcoholic materials is therefore

FIGURE 24

COMPARISON OF C-14 CONCENTRATIONS IN SCOTTISH MALT WHISKIES AND DANISH CEREALS.

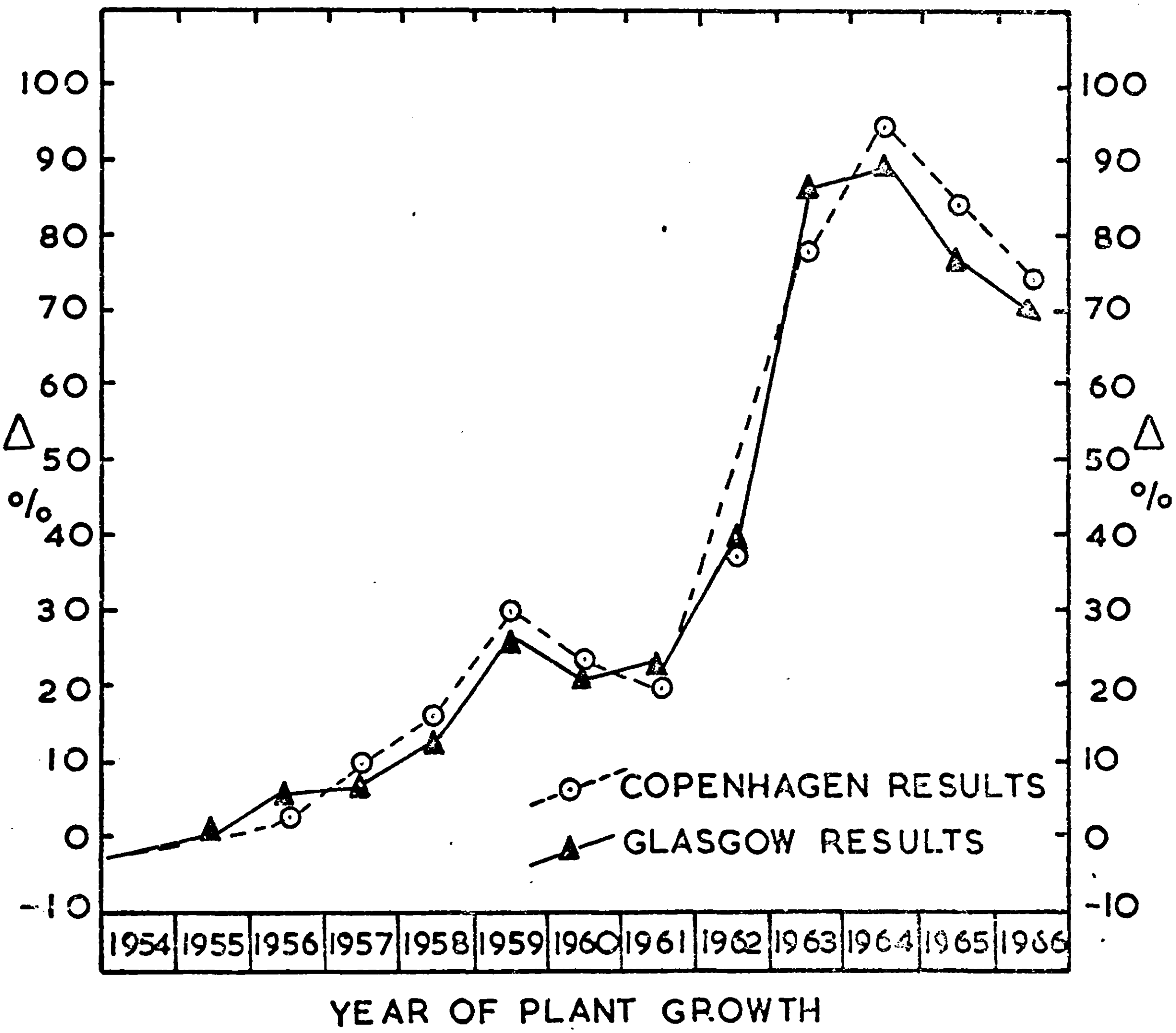
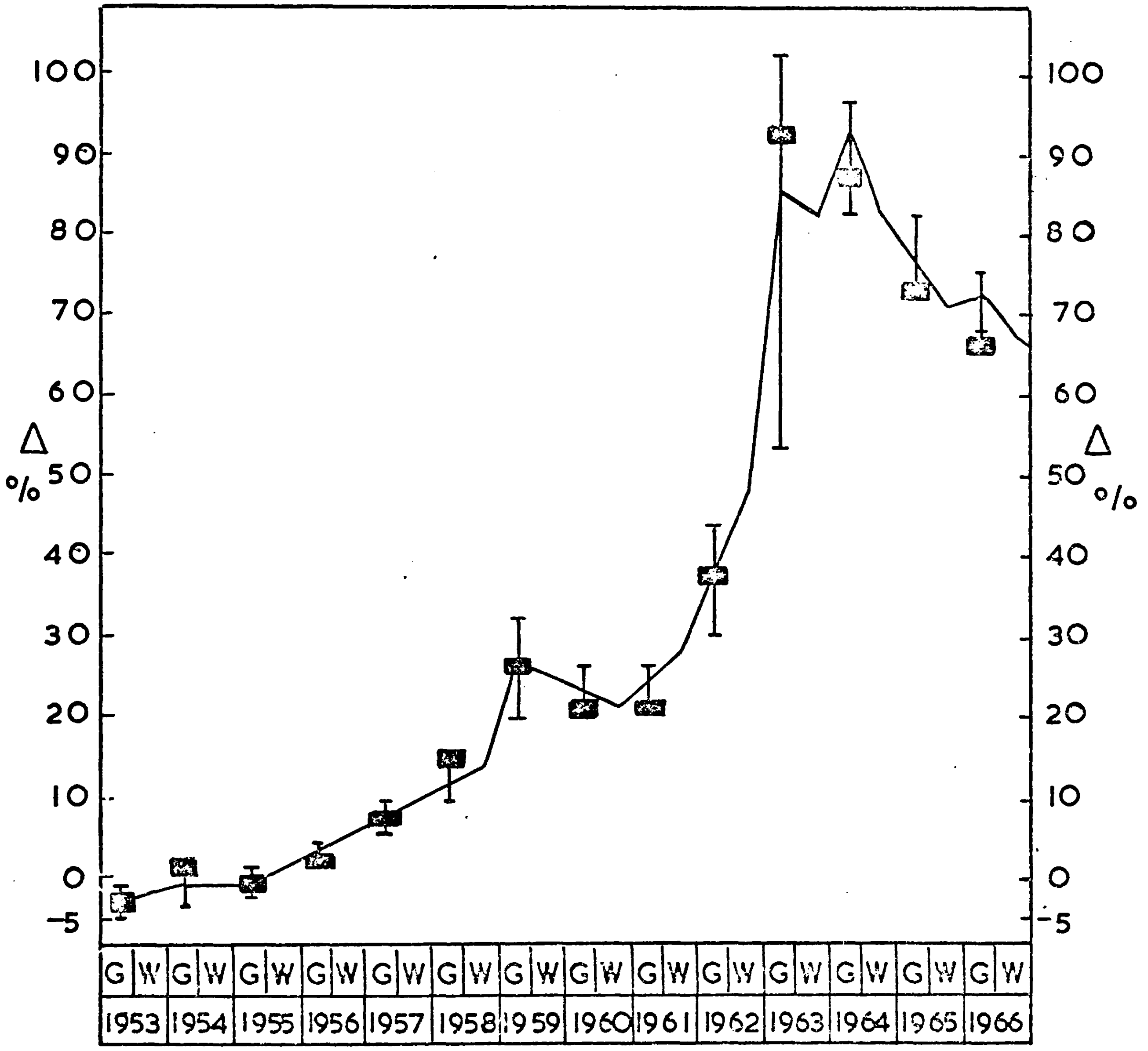


FIGURE 25.

CORRELATION BETWEEN C-14 CONCENTRATIONS IN ATMOSPHERIC CO_2 AND VINTAGE WINE.



G GRAPE GROWTH SEASON

W CORESPONDING "WINTER" SEASON

a reliable technique for determination of yearly atmospheric C-14 concentrations for time periods when direct measurements were not possible.

(b) Tree Seed Analysis.

Two series of tree seeds, from Northern Scotland and Oregon, U.S.A., were analysed to compare the C-14 activities of seeds grown in different locations in the northern hemisphere (Table 8). These results are plotted in Figure 26 together with the atmospheric C-14 activities prevailing during the seed growth periods. Brackets represent the overall variation in atmospheric C-14 concentration during June to November, and the ordinate of each seed activity "box" represents the statistical standard deviation of the analysis.

For each year atmospheric and seed C-14 activities seem directly correlated within experimental errors. Discrepancies between the two seed series, although predominantly statistical, may also be due to slightly different growth periods and to minor disequilibrium in the atmospheric C-14 distribution through variable injection of artificial C-14 from the stratosphere at preferred latitudes. The contribution to seed growth of any inactive or non-contemporaneous carbon from the soil CO_2 appears to be negligible, so that plant seeds may be used with confidence

TABLE 8

C-14 CONCENTRATIONS IN TREE SEEDS (1959-68)

(1) NORTH SCOTLAND SERIES (57°30'N.)

Growth Year	Tree Species	δ C-14 $\pm 1\sigma$ (%)	δ C-13 (‰) $\pm$ 1‰ (2σ)	Δ $\pm 1\sigma$ (%)
1960	*Tsuga mertensiana*	+ 18.69 ± 0.64	-24.9	+ 18.67 ± 0.66
1961	*Pinus mugo*	+ 21.56 ± 0.60	-28.9	+ 22.50 ± 0.62
1962	*Pinus mugo*	+ 29.45 ± 0.70	-26.2	+ 29.76 ± 0.72
1963	*Pinus sylvestris*	+ 85.42 ± 1.15	-26.8	+ 86.08 ± 1.20
1964	*Pinus sylvestris*	+ 93.75 ± 1.20	-26.7	+ 94.41 ± 1.26
1965	*Pinus sylvestris*	+ 72.90 ± 0.96	-26.9	+ 73.54 ± 1.02
1966	*Pinus sylvestris*	+ 69.88 ± 0.75	-29.4	+ 71.37 ± 0.78
1967	*Larix decidua*	+ 62.68 ± 0.69	-25.7	+ 62.91 ± 0.71
1968	*Picea sitchensis*	+ 59.40 ± 0.70	-29.8	+ 60.94 ± 0.73

TABLE 8 (cont.)

C-14 CONCENTRATIONS IN TREE SEEDS (1959-68)

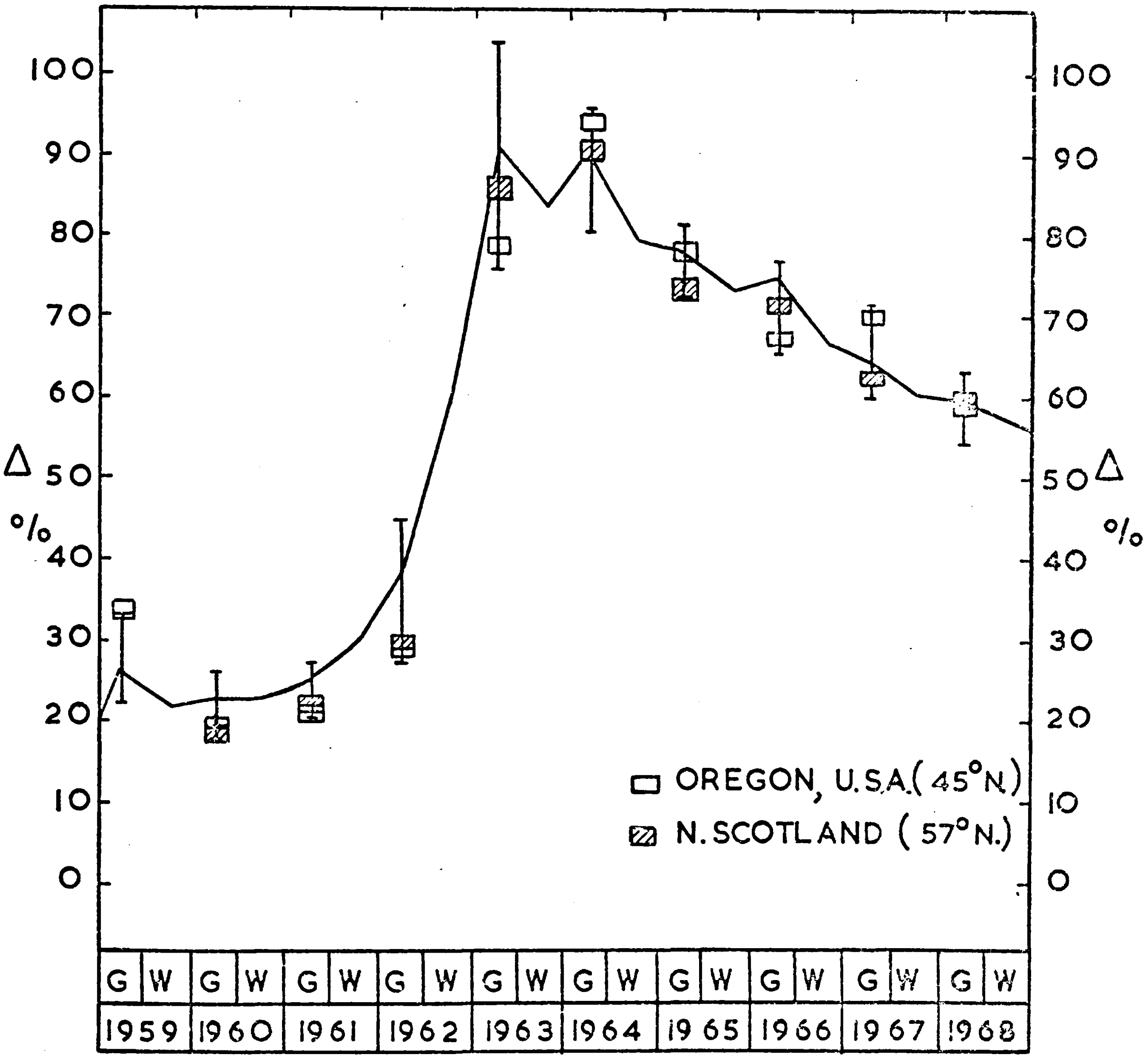
(2) OREGON, U.S.A. SERIES (45°N.)

Growth Year	Tree Species	δ C-14 $\pm 1\sigma$(%)	δ C-13 (‰) $\pm$ 1‰ (2σ)	Δ $\pm 1\sigma$(%)
1959	<u>Pseudotsuga taxifolia</u>	+ 33.39 ± 0.95	(-28.0)	+ 34.19 ± 0.98
1960	<u>Abies grandis</u>	+ 18.47 ± 0.54	-30.6	+ 19.80 ± 0.56
1961	<u>Picea sitchensis</u>	+ 19.93 ± 0.59	-26.5	+ 20.29 ± 0.61
1962	<u>Abies nobilis</u>	+ 28.66 ± 0.80	-25.6	+ 28.81 ± 0.83
1963	<u>Pinus contorta</u>	+ 78.72 ± 1.06	-26.3	+ 79.18 ± 1.09
1964	<u>Pinus contorta</u>	+ 89.19 ± 1.18	-29.6	+ 90.92 ± 1.21
1965	<u>Abies amabilis</u>	+ 77.58 ± 0.97	(-28.0)	+ 78.65 ± 1.02
1966	<u>Abies amabilis</u>	+ 67.57 ± 1.05	-23.9	+ 67.19 ± 1.07
1967	<u>Abies nobilis</u>	+ 70.33 ± 1.05	-26.1	+ 70.69 ± 1.07
1968	<u>Abies nobilis</u>	+ 58.73 ± 0.72	-28.4	+ 59.81 ± 0.75

(δC-13 values in brackets are estimates for samples for which mass-spectrometric measurements were not available).

FIGURE 26

CORRELATION BETWEEN C-14 CONCENTRATIONS IN ATMOSPHERIC CO_2 AND TREE SEEDS.



G SEED GROWTH SEASON

W CORRESPONDING "WINTER" SEASON.

as indicators of atmospheric C-14 concentrations.

Further Studies

(a) Latitudinal Variations of Atmospheric C-14 Concentrations.

It is known that latitudinal variations in tropospheric C-14 concentrations occur through downflux of stratospheric C-14 at preferred latitudes. To investigate the magnitude of these variations a series of 1965 tree seeds grown at different latitudes in the northern hemisphere was analysed. Table 9 and Figure 27 present the results of this study. The results are by no means conclusive. Certainly the C-14 activities which are scattered outside the statistical errors indicate disequilibrium in northern latitudes. Peak concentrations, which occurred at 51°-54°N. and 45°N. may well reflect injection of stratospheric C-14 into the troposphere in the vicinity of these latitudes. However, the influence of local "Suess effect" and of short time-lags in plant growth seasons may also contribute to the observed variability.

(b) The Incorporation of Soil Carbon During Seed Growth.

In consultation with the Forestry Commission, the seeds used as atmospheric C-14 indicators were selected from trees of various species which are not grown on limestone soils. This precaution minimised the opportunity for introduction

TABLE 9

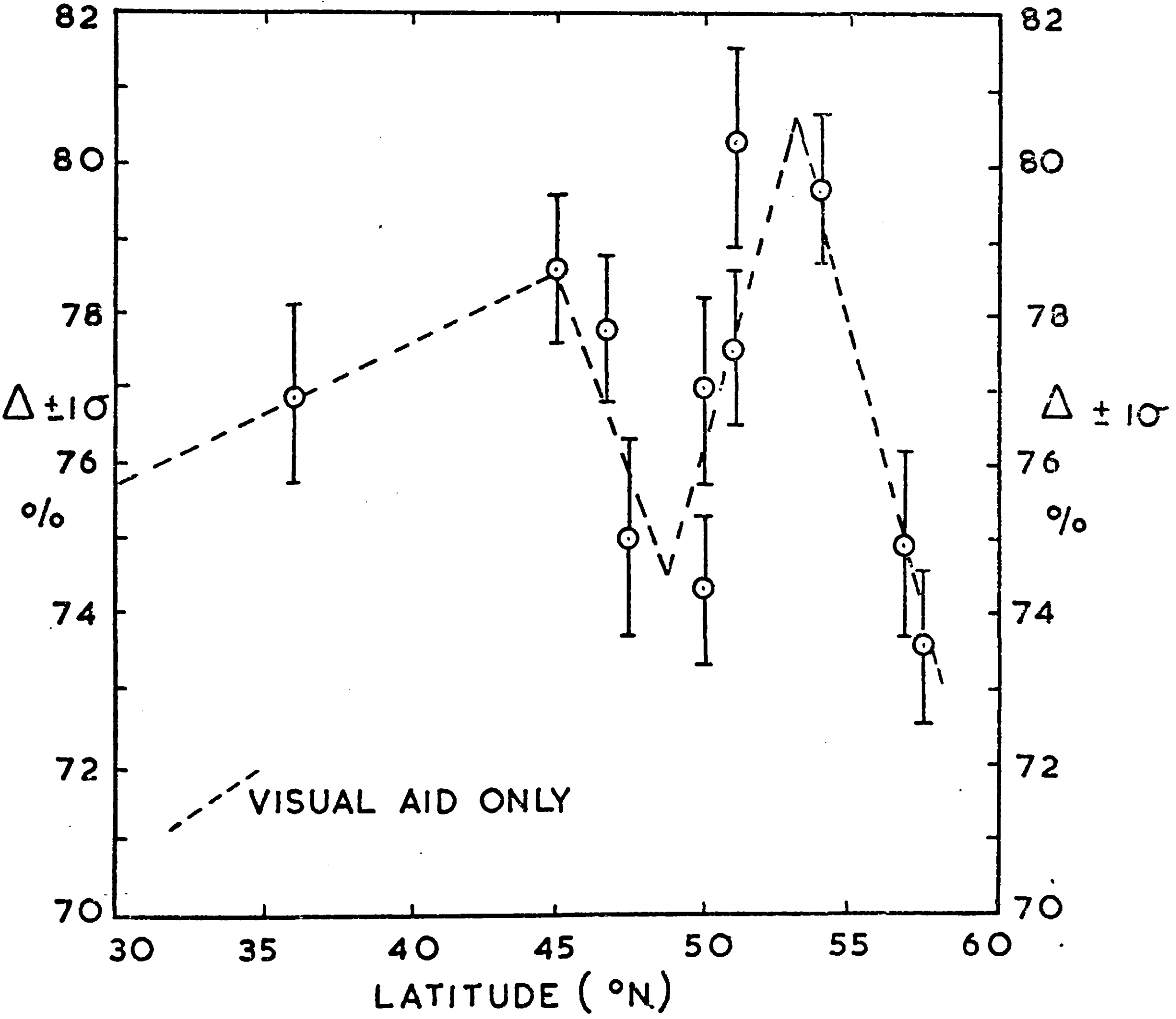
C-14 CONCENTRATIONS OF 1965 TREE SEED SERIES

Location and Latitude of Seed Growth		Tree Species	δC-14 $\pm$ 1σ (%)	δC-13 (‰) $\pm$ 1‰ (2σ)	$\Delta \pm 1\sigma$ (%)
Moray, Scotland	$57^{\circ}30'$N.	*Pinus sylvestris*	+ 72.90 ± 0.96	-26.9	+ 73.54 ± 1.02
Alaska, U.S.A.	$56^{\circ}50'$N.	*Pinus contorta*	+ 73.74 ± 1.22	-28.4	+ 74.94 ± 1.26
N.W. England	54°N.	*Pinus sylvestris*	+ 77.36 ± 0.94	-31.6	+ 79.69 ± 0.98
Campine, Belgium	51°N.	*Alnus glutinosa*	+ 79.18 ± 1.30	(-28.0)	+ 80.26 ± 1.35
S.E. England	51°N.	*Pinus sylvestris*	+ 76.90 ± 0.99	-26.8	+ 77.54 ± 1.03
Homburg, Germany	50°N.	*Larix decidua*	+ 75.93 ± 1.21	-28.1	+ 77.01 ± 1.25
Br. Columbia, Canada	50°N.	*Pinus contorta*	+ 73.68 ± 0.92	-26.9	+ 74.32 ± 0.96
Styria, Austria	$47^{\circ}30'$N.	*Larix decidua*	+ 73.93 ± 1.29	(-28.0)	+ 74.98 ± 1.33
Washington, U.S.A.	$46^{\circ}40'$N.	*Picea sitchensis*	+ 76.73 ± 0.93	(-28.0)	+ 77.79 ± 0.97
Oregon, U.S.A.	45°N.	*Abies amabilis*	+ 77.58 ± 0.97	(-28.0)	+ 78.65 ± 1.02
Nagano, Japan	36°N.	*Larix leptolepis*	+ 75.93 ± 1.16	(-28.0)	+ 76.99 ± 1.20

(δC-13 values in brackets are estimates for samples for which mass-spectrometric measurements were not available)

FIGURE 27

LATITUDINAL VARIATION OF C - 14 CONCENTRATIONS IN TREE SEEDS —1965.



of inactive carbon into the growing seeds.

To investigate the size of the error which could have arisen without this precaution, a sample of beechnuts, grown in 1967 on a limestone-rich soil at Cirencester, England ($51^{\circ}40'$N), was analysed with the following results;

$$\delta\text{C-14} = 55.74 \pm 0.72\% \quad (\pm 1\sigma)$$
$$\delta\text{C-13} = -33.00 \pm 1‰ \quad (\pm 2\sigma)$$
$$\Delta = 58.23 \pm 0.75\% \quad (\pm 1\sigma).$$

The atmospheric C-14 concentrations prevailing at that time had a mean value of $\Delta = 65\%$ and concentrations in this region were observed in the 1967 seeds grown on non-calcareous soils. The beechnut sample therefore appears to have obtained a minimum of 5.5% of its carbon via root uptake from the soil. This figure, however, assumes that the soil carbon is completely C-14 free. If it is assumed that the soil carbon is derived from root respiration (60%), decaying vegetation grown during the previous 3 years (20%), and limestone (20%), the percentage incorporation of soil carbon into the seed materials amounts to 30%. It is evident therefore that unless samples are carefully selected the uptake of soil carbon by plant seeds can introduce significant errors into the assessment of atmospheric C-14 activities. It is also important to note that plant materials grown on limestone soils may yield erroneous C-14 ages. Thus a sample 1,000 years old would be dated as about 1,450 years old assuming 5.5% uptake of inactive carbon.

(c) Rate of Equilibration of Atmospheric C-14 Concentrations.

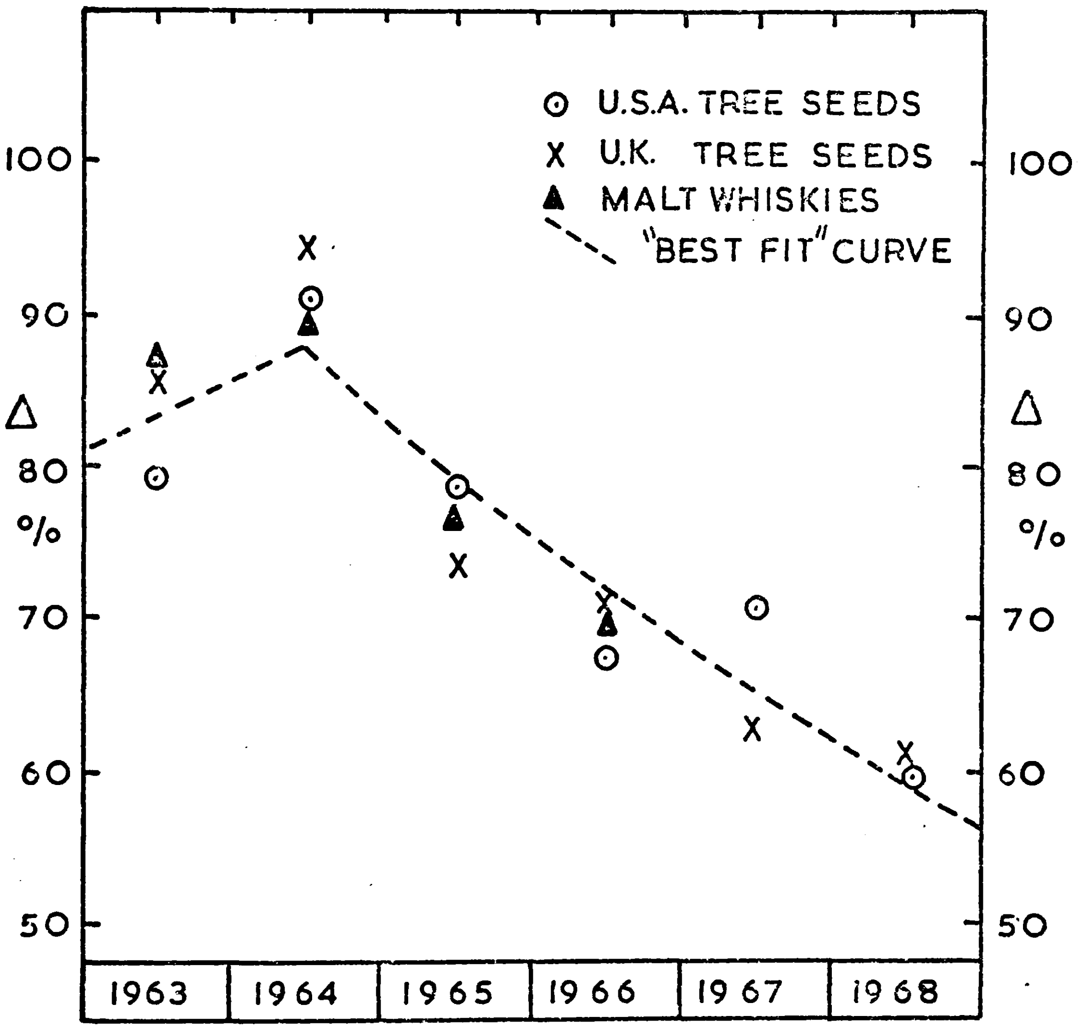
It was shown earlier (Figure 3) that since 1963 the concentrations of C-14 in the northern troposphere have been decreasing exponentially as the distribution of bomb C-14 tends towards equilibrium. The rate of this decrease is a significant factor in the assessment of inter-reservoir exchange rates.

Superimposed on the steady decrease in tropospheric C-14 activities are annual fluctuations of up to ± 5% caused by downflow of stratospheric C-14 during the spring of each year. These variations tend to obscure the downward trend in C-14 activities making a precise assessment of the overall gradient more complex. Since plant analyses can indicate atmospheric C-14 concentrations during the same months of consecutive years this technique offers a means of evaluating the regular decrease in C-14 activities with a minimum of interference by these annual perturbations.

The exponential decrease in northern tropospheric C-14 activities indicated by the whisky and two series of tree seed analyses was calculated by computer for each of these three sets of plant samples (Figure 28). For the individual series and for the combination of all three, the half-life of the decrease is 7 years. The relationship

FIGURE 28

C-14 CONCENTRATIONS OF RECENT PLANT MATERIALS (1963-1968).



YEAR OF PLANT GROWTH

governing annual northern tropospheric C-14 concentrations is found to be $\Delta_t = 97e^{-0.10t}$ where Δ_t is the tropospheric C-14 concentration (%) at time t years after 1963.

An implication of this study may be that by 2,000 A.D. tropospheric C-14 concentrations will have fallen to about 5% above the "natural" level. This value represents a uniform distribution of artificial C-14 throughout the dynamic reservoirs, so that after 2,000 A.D. the atmospheric C-14 excess will decrease with a half-life of 5,730 years. This estimate, however, neglects the expected increase in the "Suess effect" which by 2,000 A.D. may reach values sufficient to reduce the "net" atmospheric C-14 concentration below the "natural" level.

Furthermore, the prediction based on the trend during recent years must be regarded only as an approximation since northern tropospheric C-14 activities have been strongly influenced by C-14 input from the stratosphere and by a "net" transfer of excess C-14 to the southern hemisphere. As the total atmosphere (troposphere + stratosphere) attains complete equilibrium, the excess C-14 activity in the atmosphere will decrease only through oceanic uptake. Since stratospheric input of C-14 to the troposphere has been larger than the "net" interhemispheric transfer within the troposphere, the approximation represents an underestimate of the rate of oceanic uptake. In addition the return of excess C-14 from the surface ocean to the atmosphere has been assumed negligible. Therefore the rate constant of 0.10 in the earlier relationship represents a minimum value of the exchange rate constant for uptake of tropospheric C-14 by the oceans and biosphere. This corresponds to a maximum mean exchange time of 10 years, an upper limit which is in agreement with the majority of estimates of this parameter (22, 32-34).

IV

A THEORETICAL APPROACH TO THE "SUESS EFFECT"

Introduction.

During recent years the predominant influence of bomb-produced C-14 on atmospheric C-14 concentrations appears to have reduced scientific interest in the "Suess effect". Between its detection in 1955 and the period of large scale weapons testing in 1961 many studies were published (19, 24, 48, 49, 51, 76-78). Since 1961, however, little has been added to our knowledge of the magnitude or implications of the "Suess effect" despite marked advances in our understanding of the geophysical processes controlling carbon circulation. In particular the nuclear era has allowed more accurate evaluations of inter-reservoir exchange rates, parameters which are fundamental to studies of the excess CO_2 distribution. A reassessment of the "Suess effect" could therefore be achieved with increased precision. Furthermore a detailed reappraisal of the effect seemed necessary in view of the following inadequacies which appear in earlier approaches;

(1) All previous investigations were based on the assumption that deviations in atmospheric C-14 concentrations from the "natural" level during the

period 1890 to 1950 were due solely to the "Suess effect". This assumption seems unrealistic in view of the frequent natural fluctuations of atmospheric C-14 activities during the last few millenia (Figure 2). Indeed, atmospheric C-14 concentrations appear to have been within 1% of the "natural" level for only about 45% of the past 6,000 years.

(2) A number of investigators (24, 51, 76-78) have calculated inter-reservoir carbon exchange rates based on appropriate "box-models" and measurements of early 20th century atmospheric C-14 activities. The exchange rate assessments may be in error if the initial estimates of the "Suess effect" were incorrect. Thus the mean exchange time of CO_2 for troposphere/surface ocean transfer based on "Suess effect" studies generally appears longer (5-20 years (24, 51, 76-78)) than values calculated from the distribution of artificial C-14 (1.5-7 years (32-34, 73, 79)).

(3) Of the few previous workers who assumed exchange rates and used these to calculate the size of the "Suess effect" in 1950, Broecker and Olson (22), Broecker (48), and Bolin and Eriksson (78) found -4% (△), -3 to -4%, and -3 to -5% respectively,

compared to the observed values of -2 to -3% (21, 22, 24, 51, 80). In a recent study, Houtermans et al (80) calculated an atmospheric "Suess effect" amounting to -2 to -6% by 1940. In addition, Broecker (48) estimated that the dilution of oceanic C-14 concentrations should be up to 2% greater than those actually observed in 1950 (ca. -1%). Deviations of this nature were commonly attributed to inadequacies in the "box-models" used in theoretical treatments. Certainly the assumptions made regarding exchange rates involved greater uncertainty than at present. The theoretical models nevertheless appeared satisfactory for quantitative interpretation of the more marked "bomb effect". It seems possible therefore that the deviations may reflect inaccuracy in the assumption that the "Suess effect" was the only cause of the variations in atmospheric C-14 concentrations during the early 20th century. Certainly it seems reasonable that this possibility should be considered.

(4) Atmospheric C-14 concentrations during the period 1890 to 1950 have not yet been studied on a yearly basis. The majority of experimental measurements were based on the use of tree rings as atmospheric C-14 indicators. Since tree rings may be subject

to carbon exchange these analyses could be in error. In addition, any annual fluctuations of atmospheric C-14 activities may not be detected in analyses of tree ring sections which yield only mean C-14 concentrations for the growth periods contained in the sections.

(5) In all previous theoretical studies the release of fossil fuel CO_2 into the atmosphere was assumed to have occurred at discrete times up to 20 years apart. Although this assumption permits simplification of the mathematical calculations, such widely spaced injection periods must introduce significant errors into the assessments, particularly at years close to the injection time.

(6) Studies of the "Suess effect" have invariably been based on a summary of industrial fossil fuel CO_2 production published in 1957 by Revelle and Suess (24). This summary provided estimates of the excess CO_2 production for each decade since 1860. As a check on the reliability of these data and since a more detailed estimate is essential to a theoretical treatment involving more frequent CO_2 injection, the industrial fossil fuel CO_2 production figures should be recalculated.

For these reasons it seemed necessary to reinvestigate the "Suess effect" from basic principles using a treatment which would

(1) permit the possibility that factors other than the "Suess effect" may have contributed to pre-1950 atmospheric C-14 concentrations,

(2) achieve increased accuracy through the use of inter-reservoir exchange rates determined from recent studies of bomb-produced C-14,

(3) involve recalculation of industrial fossil fuel CO_2 production,

(4) incorporate a suitable mathematical model assuming annual fossil fuel CO_2 injection,

(5) include experimental measurement of atmospheric C-14 concentrations prevailing at specific years using plant seeds, wines, and spirits as indicators (Chapter V).

The Production of Fossil Fuel CO_2.

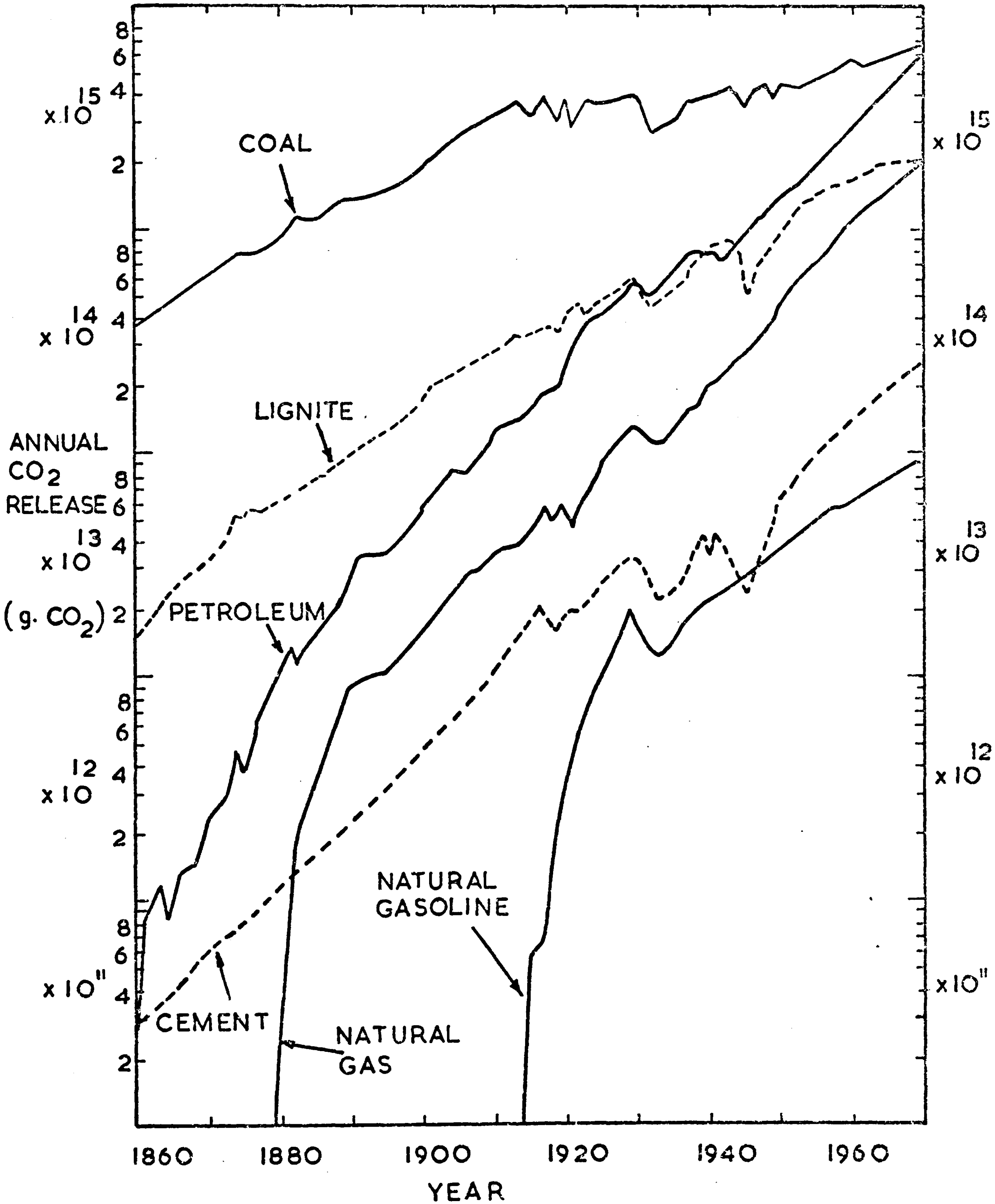
The release of inactive CO_2 to the atmosphere is a result of the combustion of coal, lignite, petroleum, natural gasoline, natural gas and of the decomposition of limestone in cement manufacture. Details of the production of these materials since 1860 were obtained from several sources (Statistical Yearbooks of the League of Nations and of the United Nations, the United Nations' review of world energy requirements (81) and personal communication with the Ministry of Power) for the purpose of calculating the amount of CO_2 released from these sources. Since fuel consumption figures are not available it was assumed that these are closely related to production estimates. The annual fuel and cement production figures are tabulated in Appendix B. Some of the data on natural gas and gasoline have been estimated from production in the U.S.A. and its share in world production. According to the United Nations (81) the possible error of these estimates is small.

It is further assumed that the injection of fossil CO_2 into the atmosphere prior to 1860 was negligible. This seems reasonable since industrial use of coal did not become common until the late 18th century. Indeed, until 1880, wood was the major source of energy throughout the world (82).

For the conversion of fuel production figures to estimates of the annual excess CO_2 output, assumptions must be made regarding the carbon content and combustion efficiencies of the various materials. The carbon contents of coal, lignite, petroleum, natural gasoline, and natural gas were assumed to be 80%, 73%, 85%, 83% and 76% respectively (83-86). For petroleum combustion it was further assumed that losses amounting to 10% were incurred through liquid and vapour escape and through conversion into fixed carbon products (85). For other fuels 100% conversion to CO_2 was assumed. The mean CaO content of cements was taken to be 60% (87) and the carbon content of limestone assumed to be 12% with 100% kilning efficiency. Thus the combustion of 1 metric ton of coal, crude petroleum, gasoline, and lignite produces 2.93×10^6g. CO_2, 2.81×10^6g. CO_2, 3.04×10^6g. CO_2, and 2.67×10^6g. CO_2 respectively from each source. The combustion of 1 cubic metre of natural gas releases 2.43×10^3g. CO_2 and the manufacture of 1 metric ton of cement yields 4.71×10^5g. CO_2. Using these conversion factors the production figures for excess inactive CO_2. were calculated. Annual data are tabulated in Appendix B. Figure 29 presents the annual variations in CO_2 production from each source during the period 1860-1969. The effects on CO_2 production of major world crises

FIGURE 29.

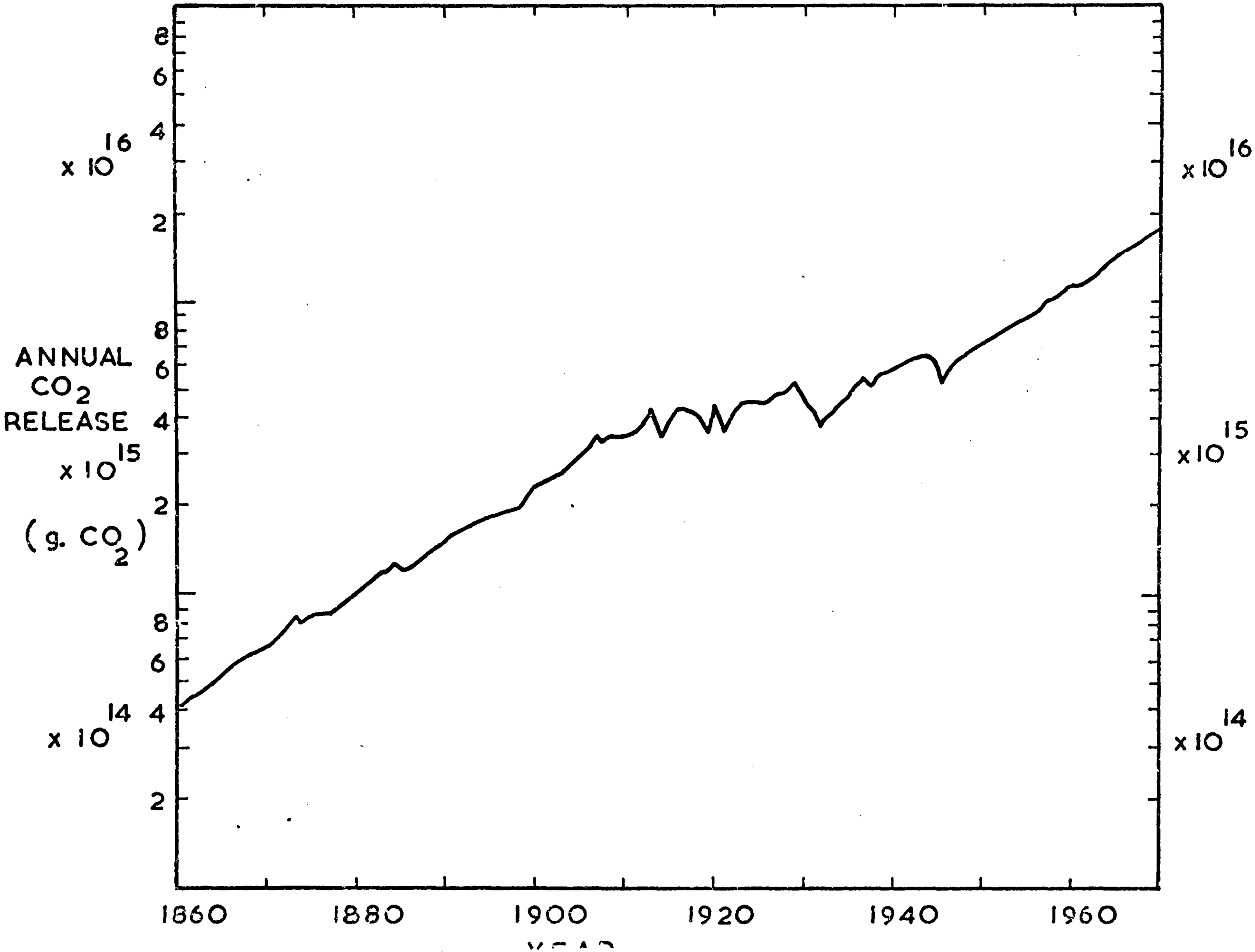
ANNUAL FOSSIL FUEL CO_2 RELEASE FROM EACH SOURCE.



(2 world wars and the depression of ca. 1930) are evident. The total CO_2 production from all sources, as presented in Figure 30, shows the marked increase in output during recent years. Thus the production rate of inactive CO_2 has doubled since 1954 when the first measurements of the "Suess effect" were made.

These estimates of the output of fossil fuel CO_2 are within 5% of the less detailed figures calculated by Revelle and Suess (24). Thus the CO_2 released between 1860 and 1950 was estimated by Revelle and Suess at 2.76×10^{17}g. CO_2 compared to the value of 2.65×10^{17}g. CO_2 found in this study. The total excess CO_2 produced between 1860 and the present amounts to 4.96×10^{17}g. CO_2 compared to 4.95×10^{17}g. CO_2 predicted by Revelle and Suess. Hence the cumulative total of excess CO_2 has doubled since 1945 when the majority of wood samples analysed for "Suess effect" studies were growing. The natural CO_2 content of the atmosphere for the mid 19th century was assumed to be 290p.p.m. or 120mg./cm.^{2} (Callendar (88), Libby (10)) corresponding to a natural CO_2 content of 2.26×10^{18}g.. Thus the total production of fossil fuel CO_2 between 1860 and 1969 amounts to ca. 22% of the normal atmospheric CO_2 content. The annual excess CO_2 production, X(t), expressed as a percentage of the natural atmospheric CO_2 content

FIGURE 30.
TOTAL ANNUAL FOSSIL FUEL CO_2 RELEASE.



approximately follows the exponential expression $X(t) = 0.05e^{0.03t}$, where t represents time in years since 1880. The rapid increases in CO_2 production during the past decade, however, suggest that future CO_2 output figures may considerably exceed the predictions of this equation.

A Mathematical Model for "Suess effect" Calculation.

The distribution and transport of bomb-produced C-14 throughout the dynamic carbon cycle has been assessed by several workers (22, 32-34, 73, 89-92) using "box-models" of the form shown in Figure 4. These models, most of which incorporate at lease 6 "boxes", have been rather complex because of the marked disequilibrium in world-wide C-14 concentrations caused by weapons testing. As the excess C-14 distribution tends towards equilibrium, however, its rate of movement may be theoretically described using simpler models. Thus Ergin (89) has interpreted the excess C-14 distribution during 1967 and 1968 with a simple model containing only 4 boxes (stratosphere, troposphere, surface ocean + biosphere, and deep ocean). The complexity of the model is therefore dependent on the extent of disequilibrium within the carbon cycle. Since, in comparison to the "bomb effect", the "Suess effect" represents a more moderate disturbance over a longer time period, a relatively simple model should be adequate for its interpretation.

Exchange rate data derived from studies of artificial C-14 have shown that

(1) the CO_2 exchange time for interhemispheric mixing within the troposphere is about 1 year (32, 73, 89-91),

(2) the CO_2 exchange time for interhemispheric mixing within the stratosphere is about 5 years (32, 73, 89, 91),

(3) the CO_2 exchange time from stratosphere to troposphere is between 0.8 and 4.5 years (32, 33, 73, 89, 91, 92).

Because these atmospheric exchange times are short in comparison to the time period covered by the "Suess effect" it seems reasonable to treat the atmospheric reservoirs as a single unit.

For a satisfactory treatment of the oceans, however, 2 reservoirs were incorporated in the model, viz.,

(1) the surface ocean; situated above the thermocline in direct contact with the atmosphere and constituting about 2% of the total ocean (93),

(2) the deep ocean; situated beneath the thermocline.

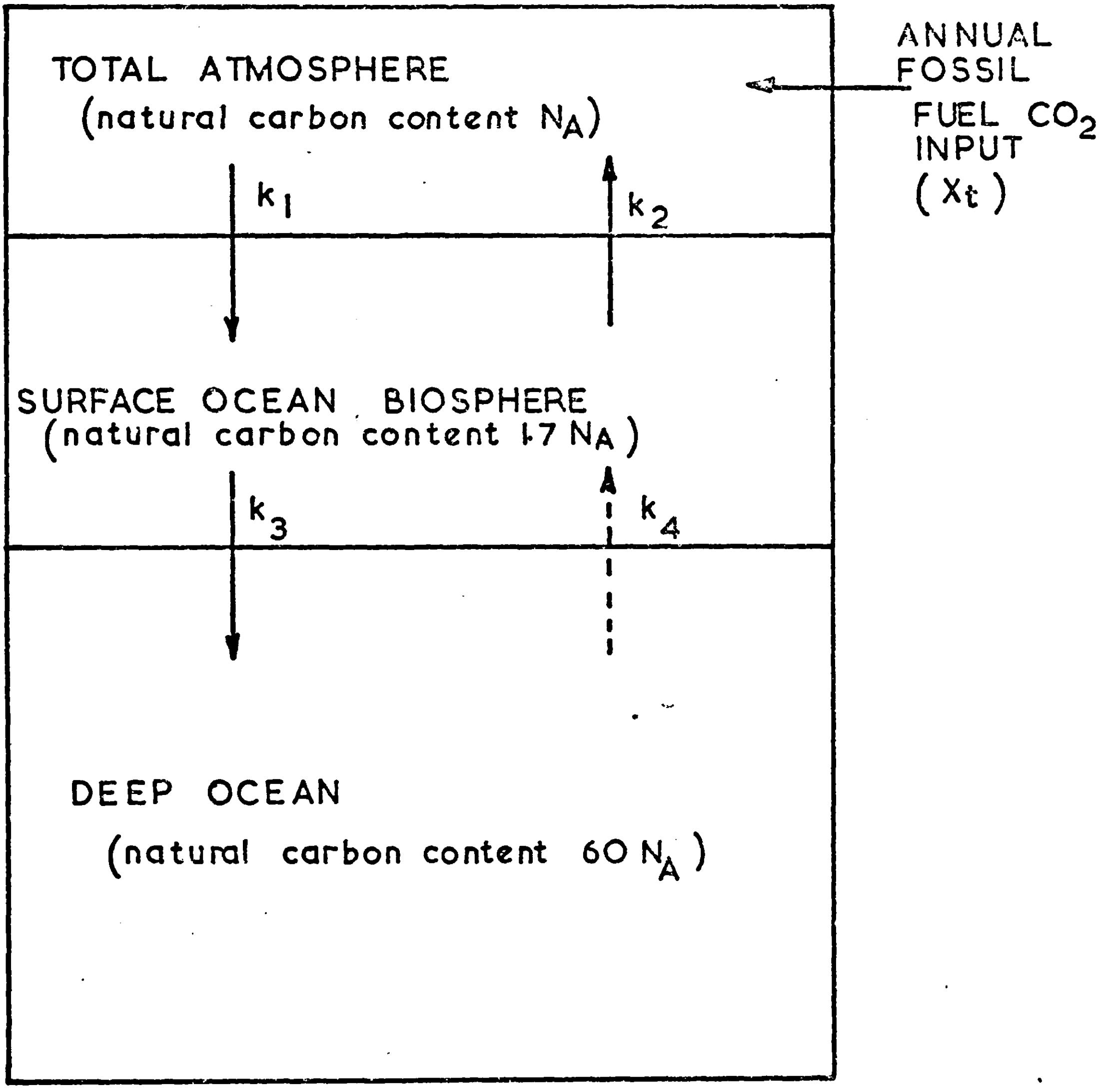
The surface ocean, well-mixed through wind action and convection, has a CO_2 residence time of 5 to 8 years (25, 93, 94). The deep ocean, however, mixes slowly and has a CO_2 residence time of 500 to 1,000 years (78, 89, 93, 94). The residence time of CO_2 in the surface ocean therefore controls the rate of transport of fossil fuel CO_2 from the atmosphere to the deep ocean. Thus the assumption by Revelle and Suess that the ocean may be regarded as one well-mixed reservoir does not seem adequate.

The model designed for evaluation of the "Suess effect" is shown in Figure 31, where k_1, k_2, k_3, and k_4 are the inter-reservoir CO_2 exchange rate constants. In accordance with Mydal's procedure (32, 91) the biosphere was included with the surface ocean since both are involved in direct CO_2 exchange with the atmosphere. The rate constant, k_4, may be neglected since the 500 to 1,000 year CO_2 residence time in the deep ocean is long in comparison to the time period covered by the "Suess effect". This assumption was confirmed by Bolin and Eriksson (78) who found that the atmospheric "Suess effect" was virtually independent of deep sea residence times of greater than 500 years.

The mathematical treatment of the "box model" to enable calculation of the "Suess effect" was as follows,

FIGURE 31

THEORETICAL MODEL FOR "SUESS EFFECT" ESTIMATION.



where all quantities of excess CO_2 are expressed as percentages of the normal CO_2 content of the atmosphere;

let x_t = the annual output of fossil CO_2 for the t^{th} year after 1859,

a_t = the resultant cumulative CO_2 excess in the atmosphere after t years,

and b_t = the resultant cumulative CO_2 excess in the surface ocean + biosphere after t years.

At t = 1 (1860) x_1 was injected into the atmosphere. By the definition of exchange rate, during the first year $(x_1\ k_1)$ of the excess was absorbed by the surface ocean (+ biosphere).

$(x_1\ k_1)\ k_2$ was returned to the atmosphere, and $(x_1\ k_1)\ k_3$ entered the deep ocean. Therefore after 1 year the oceanic excess, b_1, is expressed by

$$\begin{aligned} b_1 &= (x_1\ k_1) - (x_1\ k_1\ k_2) - (x_1\ k_1\ k_3) \\ &= \underline{x_1\ k_1\ (1-k_2-k_3)} \end{aligned}$$

Similarly the atmospheric CO_2 excess after 1 year, a_1, is described by

$$\begin{aligned} a_1 &= x_1 - (x_1\ k_1) + (x_1\ k_1)\ k_2 \\ &= \underline{x_1\ (1-k_1+k_1k_2)}. \end{aligned}$$

x_2 was then injected into the atmosphere, producing an initial atmospheric CO_2 excess of (a_1+x_2). $(a_1+x_2)\ k_1$ entered the surface ocean producing an excess CO_2 content of $\left[(a_1+x_2)\ k_1 + b_1\right]$. Of this $\left[(a_1+x_2)\ k_1 + b_1\right] k_3$ entered the deep ocean and $\left[(a_1+x_2)\ k_1 + b_1\right] k_2$ returned to the atmosphere so that

$$\begin{aligned} b_2 &= \left[(a_1+x_2)\ k_1 + b_1\right] - \left[(a_1+x_2)\ k_1 + b_1\right] k_2 \\ &\quad - \left[(a_1+x_2)\ k_1 + b_1\right] k_3 \\ &= \underline{\left[(a_1+x_2)\ k_1 + b_1\right]\ (1-k_2-k_3)} \end{aligned}$$

and
$$\begin{aligned} a_2 &= (a_1+x_2) - (a_1+x_2)\ k_1 + \left[(a_1+x_2)\ k_1 + b_1\right] k_2 \\ &= \underline{(a_1+x_2)\ (1-k_1+k_1k_2) + b_1\ k_2} \end{aligned}$$

For the general case therefore:-

$$\underline{a_t = (a_{t-1}+x_t)\ (1-k_1+k_1k_2) + b_{t-1}k_2}$$

and $$\underline{b_t = \left[(a_{t-1}+x_t)\ k_1 + b_{t-1}\right]\ (1-k_2-k_3)}$$

If x_t, k_1, k_2, and k_3 are known the solution of these equations by computer can be readily achieve (Appendix C). The percentage decrease in atmospheric C-14 concentrations (i.e. "Suess effect") for each year is directly related to the calculated increase in atmospheric fossil CO_2 concentrations.

Inter-Reservoir Exchange Rates.

Values of the CO_2 exchange rate constants, k_1, k_2, and k_3 may be estimated from studies of the transfer of bomb-produced C-14 if isotopic fractionation is neglected. Craig (93) has shown that fractionation in the atmosphere/ocean CO_2 exchange process causes a deviation in exchange rate constants expressed by $k_2^*/k_1^* = 0.988\ k_2/k_1$ where k_1^* and k_2^* are the C-14 exchange rates corresponding to k_1 and k_2 in Figure 31. The error (1.2%) in the assumption that C-14 and CO_2 rate constants are identical lies within the limits of accuracy of the C-14 rate constant assessment so that it seemed valid to neglect isotopic fractionation in these processes. In addition fractionation during carbon transfer between the surface and deep ocean reservoirs was believed to be negligible since exchange occurs primarily through transport of the ocean water itself.

In the assessment of appropriate exchange rate values, assumptions must be made regarding the natural carbon inventories of the reservoirs in the theoretical model. For this study the following natural carbon distribution was assumed;

(1) the stratospheric carbon content is 16% of the total atmospheric inventory, N_A (95),

(2) the biospheric exchangeable carbon content is

equivalent to 50% of the atmospheric inventory (78),

(3) the surface ocean contains 1.2 times the atmospheric carbon content (93),

(4) the deep sea carbon inventory is 60 times the atmospheric content (93).

Since theoretical models used for calculations of the exchange rates of excess C-14 have been more complex than the "Suess effect" model, the rate constants required modification to suit the simpler situation. Furthermore the assumption of values for the rate constants, k_1, k_2, and k_3 should be based on the parameters which have been most reliably determined in recent studies. The value of k_1, the rate constant for exchange between the total atmosphere and the surface ocean + biosphere, was therefore assessed from determinations of the rate constant for the troposphere/surface ocean + biosphere exchange. This approach avoided the present disagreement over the relative contributions of the individual uptake rates by the surface ocean and biosphere to the overall troposphere/surface ocean + biosphere transfer rate (91, 32). This controversy has caused wide variation in results for the troposphere/surface ocean rate constant (0.04 (36) to 0.30 (79)). The rate constant, k_{tu}, describing troposphere/surface ocean + biosphere exchange was assumed to be 0.23

based on results of 0.25, 0.22 and 0.22 from detailed studies by Nydal (32, 91) and Munnich and Roether (34) respectively. From the definition of exchange rates $k_{tu} = \frac{N_A}{N_T} k_1$, where N_A and N_T represent the carbon inventories of the total atmosphere and troposphere respectively. Thus $k_1 = 0.84 \times 0.23 = 0.19$, corresponding to an exchange time for atmosphere/surface ocean + biosphere carbon transfer of about 5.3 years. From the distribution of k_{tu} results the estimate is believed to be accurate to within 10%.

Since $k_1/k_2 = N_U/N_A$ where N_U is the carbon content of the surface ocean + biosphere, k_2 is immediately defined. Thus $k_2 = 0.19/1.7 = 0.11$ (±10%).

Accurate assessment of k_3, the rate constant for surface ocean + biosphere/deep ocean transfer, has not been possible until the present due to the delay in oceanic uptake of the excess C-14. In a recent study, however, Ergin (89) found a value of 0.058 for k_{md}, the surface ocean/deep ocean rate constant, corresponding to an exchange time of about 17 years. Since terrestrial biospheric/deep ocean exchange is an unreal concept, k_3 must be derived from k_{md} according to $k_3 = \frac{N_M}{N_U} k_{md}$ where N_M is the carbon content of the ocean surface layer alone. Thus $k_3 = 0.71 \times 0.058 = 0.041$ (±10%), corresponding to an exchange time of about 24.4 years.

These values of k_{md} and k_3 define k_4, the exchange time for deep sea/surface ocean transfer, at about 860 years which is in general agreement with previous estimates (78, 93, 94) based on the distribution of natural C-14.

The interpretation of data from recent studies of the exchange of bomb-produced C-14 therefore produced the following values of k_1, k_2, and k_3 for estimation of the "Suess effect",

$k_1 = 0.19 \pm 0.02$

$k_2 = 0.11 \pm 0.01$

$k_3 = 0.041 \pm 0.004$.

Results of Theoretical Study.

The results of the "Suess effect" assessment are presented in Table 10 and Figure 32. Dotted lines represent the maximum and minimum values within the limits of error of the rate constant estimations. Thus the maximum "Suess effect" levels were obtained with $k_1 = 0.17$, $k_2 = 0.10$, $k_3 = 0.037$, and minimum levels with $k_1 = 0.21$, $k_2 = 0.12$, $k_3 = 0.045$. The value of the effect at 1950 is $-3.20 \pm 0.22\%$ which seems larger than the observed atmospheric dilution at that time (average -2 to -3%). Nevertheless the estimate is in better agreement with the observed decrease than previous studies (22,48, 78, 80) which indicated a mean value of -4% at 1950. Present day levels are assessed at about -5.94% increasing by 0.2% (Δ)/annum.

The "Suess effect" increase between 1880 and 1969 can be subdivided into 3 distinct periods of exponential growth (Figure 33);

(1) 1880 - 1915, during which the effect doubled each 15 years according to $S_t = -0.30e^{0.046t}$ (%) where S_t is the magnitude of the "Suess effect" t years after 1880,

(2) 1915 - 1950, during which the effect doubled in 33 years according to $S_t = -1.55e^{0.021t}$ (%) where t is in years since 1915,

TABLE 10

RESULTS OF "SUESS EFFECT" ESTIMATION (1860-1969)

	"SUESS EFFECT"		"SUESS EFFECT"		"SUESS EFFECT"
YEAR	Δ (%)	YEAR	Δ (%)	YEAR	Δ (%)
1860	-0.02	1883	-0.34	1906	-1.00
1861	-0.03	1884	-0.36	1907	-1.06
1862	-0.04	1885	-0.38	1908	-1.10
1863	-0.05	1886	-0.40	1909	-1.15
1864	-0.06	1887	-0.42	1910	-1.20
1865	-0.08	1888	-0.44	1911	-1.25
1866	-0.09	1889	-0.46	1912	-1.30
1867	-0.10	1890	-0.48	1913	-1.37
1868	-0.11	1891	-0.51	1914	-1.41
1869	-0.12	1892	-0.53	1915	-1.45
1870	-0.14	1893	-0.56	1916	-1.50
1871	-0.15	1894	-0.58	1917	-1.56
1872	-0.16	1895	-0.60	1918	-1.60
1873	-0.18	1896	-0.63	1919	-1.63
1874	-0.19	1897	-0.66	1920	-1.69
1875	-0.21	1898	-0.69	1921	-1.72
1876	-0.22	1899	-0.71	1922	-1.76
1877	-0.24	1900	-0.75	1923	-1.82
1878	-0.25	1901	-0.79	1924	-1.87
1879	-0.26	1902	-0.82	1925	-1.91
1880	-0.28	1903	-0.87	1926	-1.96
1881	-0.30	1904	-0.91	1927	-2.02
1882	-0.32	1905	-0.95	1928	-2.08

TABLE 10 (cont.)

RESULTS OF "SUESS EFFECT" ESTIMATION (1860-1969)

	"SUESS EFFECT"		"SUESS EFFECT"
YEAR	Δ (%)	YEAR	Δ (%)
1929	-2.15	1952	-3.39
1930	-2.18	1953	-3.48
1931	-2.21	1954	-3.58
1932	-2.22	1955	-3.69
1933	-2.24	1956	-3.81
1934	-2.28	1957	-3.94
1935	-2.32	1958	-4.07
1936	-2.37	1959	-4.21
1937	-2.44	1960	-4.36
1938	-2.49	1961	-4.50
1939	-2.54	1962	-4.64
1940	-2.61	1963	-4.80
1941	-2.68	1964	-4.97
1942	-2.74	1965	-5.15
1943	-2.81	1966	-5.34
1944	-2.87	1967	-5.53
1945	-2.89	1968	-5.73
1946	-2.93	1969	-5.94
1947	-2.97		
1948	-3.06		
1949	-3.13		
1950	-3.20		
1951	-3.30		

FIGURE 32

THEORETICAL RESULTS OF "SUESS EFFECT" INCREASE.

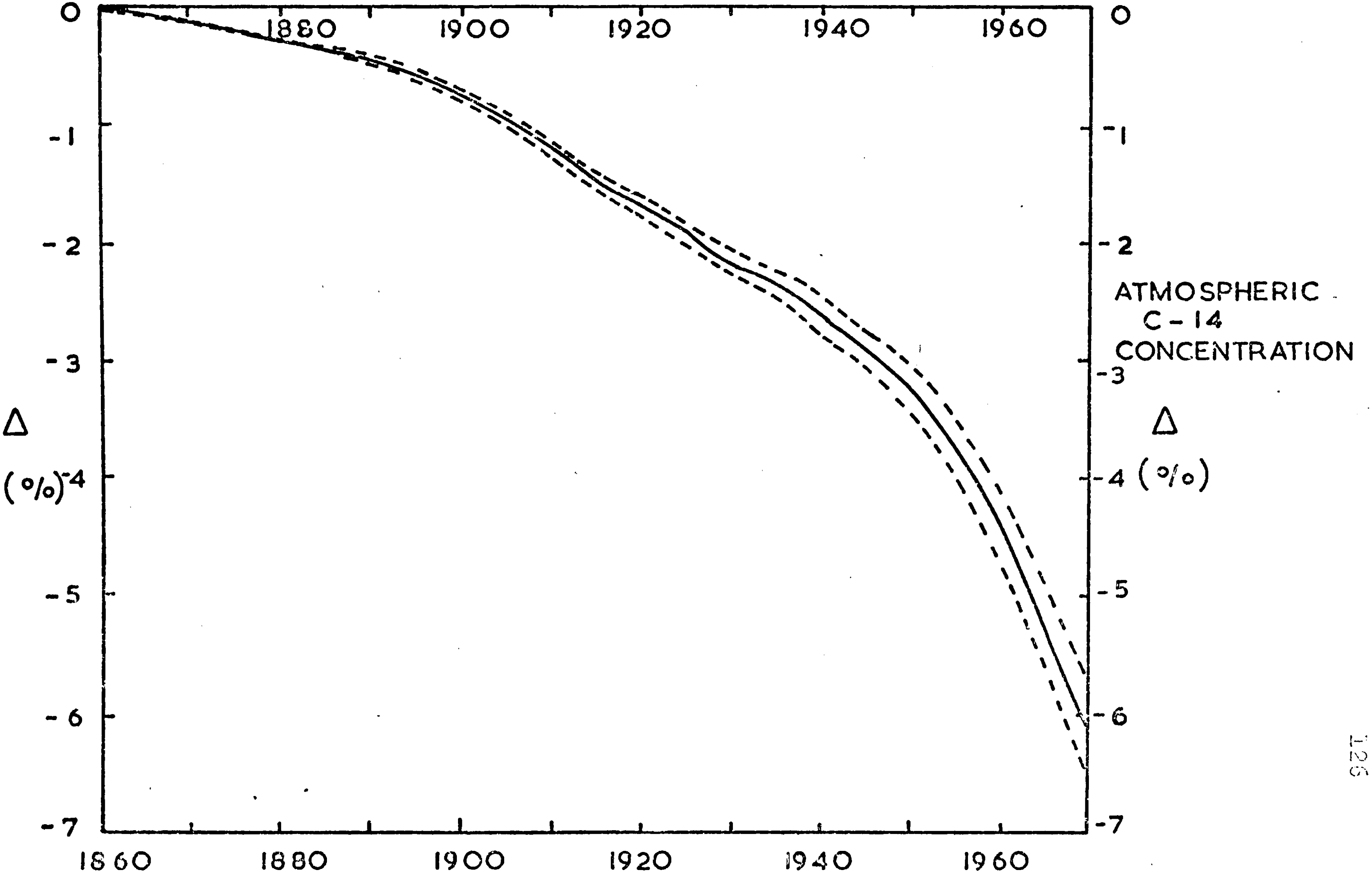
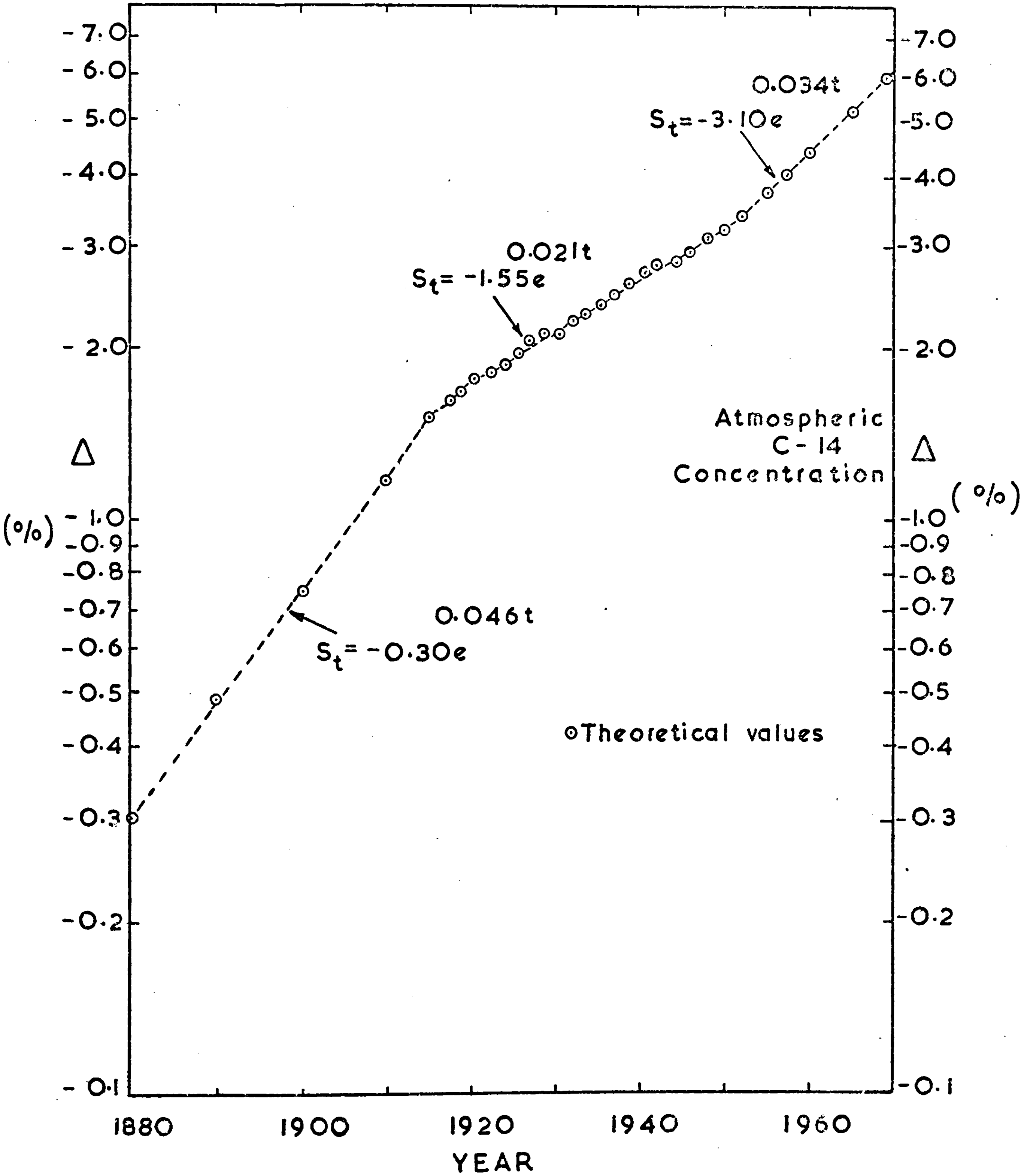


FIGURE 33

GROWTH OF "SUESS EFFECT."



and (3) 1950 - 1969, during which the "Suess effect" had a doubling time of 21 years described by $S_t = -3.10e^{0.034t}$ (%) where t is in years since 1950.

Figure 34 shows the increase in the surface ocean "Suess effect", reaching -2.0 ± 0.1% (△) in 1950 as compared to the observed values of -0.5 to -2.0% (48, 49). Present levels are about -3.5% with an annual increase of 0.13% (△). Three distinct growth periods are noticeable; (1) 1885-1920 when $S'_t = -0.20e^{0.046t}$, (2) 1920-1955 when $S'_t = -1.04e^{0.021t}$, and (3) 1955-1969, when $S'_t = -2.20e^{0.034t}$. The 5-year phase shift between periods of steady atmospheric and oceanic increase arises from the atmospheric CO_2 residence time.

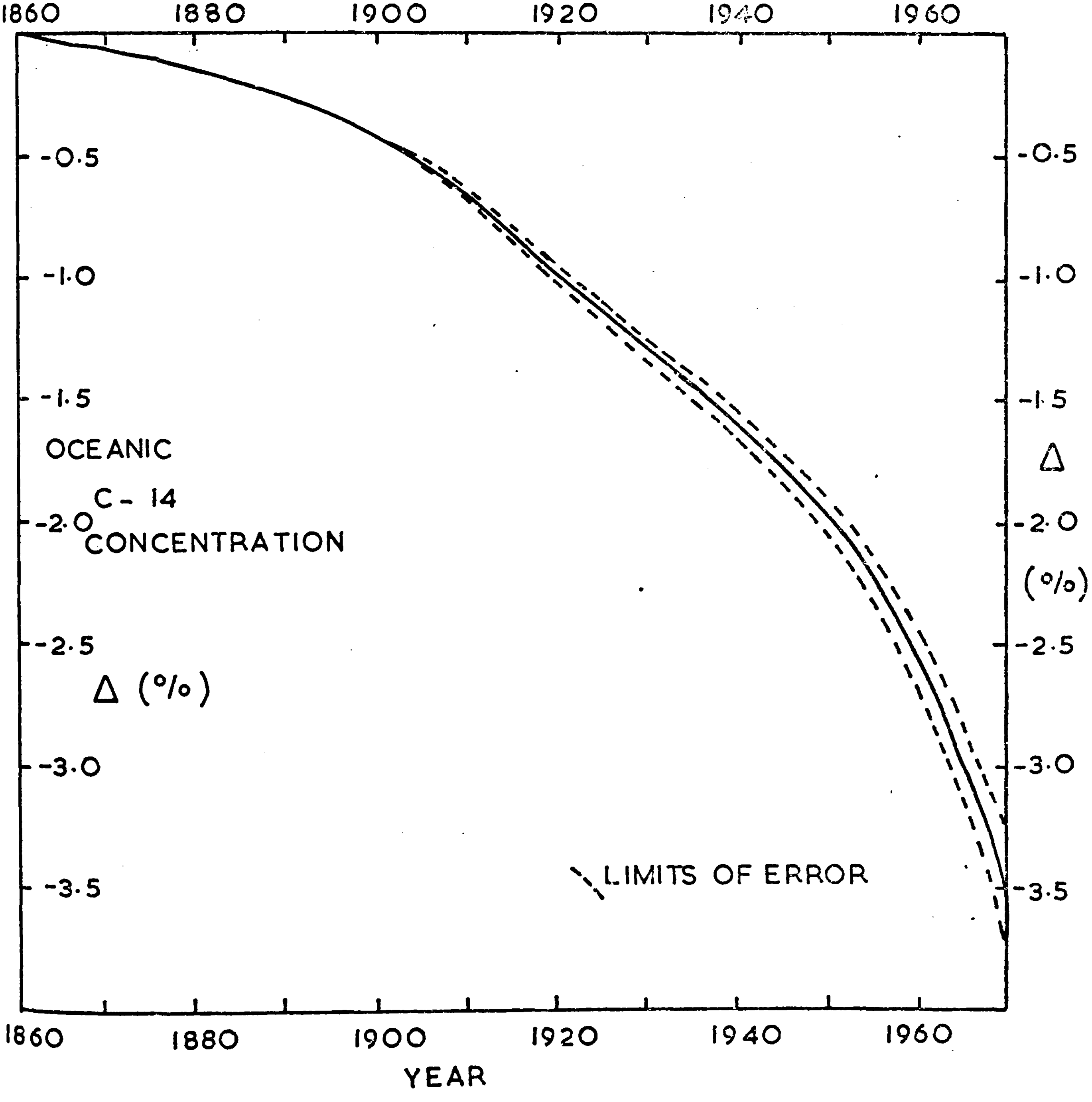
Discussion and Implications of Results.

(a) Atmospheric C-14 Concentrations (1860-1969).

Theoretical values of the "Suess effect" appear slightly larger than many observations of pre-1950 C-14 concentrations. This finding may suggest errors in either the experimental or theoretical methods or in the assumption that fossil CO_2 dilution was the only cause of the observed deviations. Since the theoretical treatment was based on models which have assessed the more complex "bomb effect" its results should be reliable.

FIGURE 34

THEORETICAL INCREASE OF SURFACE OCEAN "SUESS EFFECT."



It seemed essential therefore that a series of experimental measurements of pre-1950 atmospheric C-14 concentrations be made to permit accurate comparison with theoretical "Suess effect" values (Chapter V).

It is interesting to note that despite the increased values of the "Suess effect" during this decade recent studies of bomb-produced C-14 transport have neglected its influence. The resultant error in assessment of the gradient of decrease in atmospheric C-14 concentrations amounts to a maximum of 5% and introduces an error of about 3.5% in calculations of the atmosphere/ocean exchange rate constant. Since this error lies within the limits of accuracy of most determinations the practice of neglecting the "Suess effect" seems justified.

(b) Implications for the Radiocarbon Dating Method.

The results of the theoretical study of the "Suess effect" are relevant to the assumption in modern radiocarbon dating practice that 1890 wood, the primary modern standard material, was free from fossil CO_2 dilution. From the theoretical treatment, the "Suess effect" in 1890 amounted to -0.48 ± 0.02%. It seems certain therefore that the atmospheric C-14 activity at that time was already significantly diluted by inactive CO_2. If it is assumed that no other effects contributed to variations in atmospheric C-14 concentrations during this period then a basic assumption of the dating method is in error. The size of such an error, however, would be small, amounting to -0.25% in △ (ca. 20 years) for a sample 5,570 years old and halving with each C-14 half-life. The error involved in the analyses of samples from the nuclear era would be more significant with a maximum of 1% (△) for a sample 100% above the "natural" level.

(c) Prediction of Future "Suess effect" (1969-2,025).

Prediction of the "Suess effect" is dependent on an accurate estimate of future trends in fossil fuel consumption. These trends are uncertain, however, since the future contributions to the world's energy needs of nuclear and solar energy sources are not precisely known. The recoverable reserves of conventional fossil fuels are estimated at about $3x10^{15}$ tons of coal and lignite and $4.5x10^{14}$ equivalent tons of oil products and natural gas (S1). These reserves are sufficient to permit the continued consumption of primary fuel at present levels for about 500 years. Future trends through 2,025 A.D. are, therefore, largely dependent on the economics of energy alternatives.

In 1955 the United Nations predicted an average compound rate of increase in fossil fuel utilisation of 3.5%/annum. At this rate the cumulative total excess CO_2 emission by 2,025 would amount to about 180% of the natural atmospheric CO_2 content, requiring 50% of the present fuel reserves. Based on this estimate the annual injections of fossil CO_2 were calculated and the resultant "Suess effect" predicted using the theoretical model. The results indicated that the "Suess effect" would amount to -8.6%, -16.0% and -31.1% in 1980, 2,000 and 2,025 respectively.

Since the United Nations prediction of 1955, however, annual fuel consumption has increased on average by 4.5%/annum. If present trends continue the total excess of CO_2 would amount to more than 205% of the natural atmospheric CO_2 inventory by 2,025 and would exhaust 56% of the present fuel reserves. If the rate of increase of 4.5%/annum is maintained the "Suess effect" would amount to -8.9%, -18.7% and -40.7% in 1980, 2,000, and 2,025 respectively.

Extrapolation of the increase in the "Suess effect" between 1950 and 1969 ($S_t = -3.1e^{0.034t}$) predicts values of -8.6%, -17.0% and -39.7% in 1980, 2,000, and 2,025 respectively.

These predictions therefore imply very marked increases in atmospheric concentrations of fossil CO_2 during the next 55 years amounting to about 9.5%, 23% and 50% of the normal atmospheric CO_2 content by 1980, 2,000, 2,025 respectively. Admittedly the bases of these estimates are somewhat uncertain, but it seems unlikely that they could be in error by an order of magnitude since the contribution of nuclear energy to the world's energy requirements is not expected to exceed 20% of the total needs during this period (82). Indeed it seems possible that the predictions may be underestimates because of the following factors;

(1) According to the theoretical treatment by Bolin and Eriksson (78) large-scale addition of CO_2 to the oceans could lower the pH and thereby decrease the dissociation of H_2CO_3 to HCO_3^-/CO_3^{2-}. The partial pressure of CO_2 in equilibrium with the ocean reservoir is proportional to the number of CO_2 and H_2CO_3 molecules in the water. Therefore an increase in the CO_2 partial pressure would occur which would be much larger than the increase in total carbon content of the oceans. The result would be a reduction in the atmosphere/ocean mixing rate with an atmospheric "Suess effect" larger than predicted.

(2) The increased atmospheric CO_2 content implied by the rise in the "Suess effect" could significantly increase

equilibrium surface temperatures through enhanced absorption and emission of infrared radiation to the earth's surface. A temperature rise initiated by this mechanism would be reinforced by increased atmospheric H_2O concentrations leading to additional downward infrared flux. At the same time a decreased cloud cover due to lower rates of radiational cooling at cloud tops would allow more direct solar radiation to reach the earth's surface. An increase of 50% in atmospheric CO_2 concentrations by 2,025 could increase earth temperatures by about 2°C. (53). The secondary effects would reinforce this rise. A minor increase in ocean temperatures could result from these effects with a subsequent rise in the CO_2 content of the atmosphere (69). Since this excess CO_2 would be of a lower specific C-14 content the "Suess effect" would be increased.
(3) The return of inactive carbon from the deep ocean reservoir was neglected in the theoretical treatment. In the future, however, the increased release of fossil CO_2 over the longer time period could result in return from the deep ocean of quantities of inactive CO_2 sufficient to raise the atmospheric "Suess effect" by 1 to 5%.

For these reasons it seems possible that the "Suess effect" could increase by a factor of 10 during the next 50 to 100 years. Indeed, based on the prediction of the bomb-produced C-14 distribution (Chapter III), it seems possible that the "net" atmospheric C-14 concentration could decrease below the "natural" level by about 1990. Thereafter concentrations may fall markedly.

It is also significant that atmospheric CO_2 concentrations are likely to increase through (1) the present exponential increase in world population, and (2) the decrease in size of the plant biosphere through substitution of woods for cropland, and cities and industrial areas for rural land. According to Putnam (82) the reduction in the total volume of plant life has prevented removal from the atmosphere of quantities of CO_2 several times as large as those injected by fossil fuel consumption. Certainly a decrease in carbon fixation by plants (amounting to about 1.63×10^6 tons of carbon/annum (96)) could significantly increase atmospheric CO_2 concentrations. In addition the CO_2 released through the breathing of animal life could increase from 0.9×10^{11} tons of CO_2 during 1800-1850 (82) to 2.8×10^{11} tons of CO_2 during 1950-2,000, and to about 4.1×10^{11} tons of CO_2 during 2,000-2,050 as the world population increases from 8.9×10^8 in 1880 to about 4×10^9 by 2,000 and 7.2×10^9 by 2,050 (82). Thus the calculated increase in atmospheric CO_2 concentrations through emission of fossil fuel CO_2 alone amounts at present to 6.3% compared to the observed increase, from 290p.p.m. to 318p.p.m. (52), of 9.7%. It seems certain therefore that the increase in atmospheric CO_2 content during the next century will be larger than that due to fossil fuel consumption alone. Since a 100% increase in atmospheric CO_2 content would raise world temperatures by at least 4°C.(53) it seems probable that significant climatic changes will occur. One result of such a change could be a rise in sea level due to melting of polar ice sheets. This process is slow, however, since doubling the CO_2 content of the atmosphere increases the downward energy flux by approximately 0.01 $cal./cm^2.min.$(53). Assuming 10% of this energy is absorbed by the ice, it would take 15,000 years to melt an ice sheet 1 km. in thickness. Nevertheless it seems possible that the sensitive equilibrium processes of the carbon cycle could be significantly altered during the next century. It is essential therefore that future world energy requirements be met by new economical energy sources other than fossil fuels.

V

ATMOSPHERIC CARBON-14 CONCENTRATIONS (1890-1950).

Sample Analysis.

A detailed series of plant materials of known ages and locations of growth was required for the measurement of annual atmospheric C-14 concentrations during the past century. Although the ideal number of samples (1 per year) was not obtainable, a satisfactory series was collected and analysed. The materials consisted of either (a) malt whiskies and vintage wines or (b) flax seeds and cereals. The latter were assumed to be accurate indicators of atmospheric C-14 activities by analogy with tree seeds and with the results of Tauber (71). In addition, 4 wool samples were analysed. These were assumed to be valid indicators of atmospheric C-14 concentrations based on the results of a 1962 sample (grown 1961-62) which had a C-14 content of 21.73 ± 0.61% (Δ), typical of 1961 atmospheric C-14 activity levels.

The results of all C-14 analyses are shown in Tables 11-13. One markedly anomalous result was obtained; the 1918 wine sample (Table 12) had a C-14 activity typical of 1963 atmospheric C-14 activities. No satisfactory explanation of this observation was found although the high C-14 activity must have been due either to an error

TABLE 11

C-14 CONCENTRATIONS OF PRE-1954 MALT WHISKIES

Year of Plant Growth	δC-14 (%) $\pm 1\sigma$	δC-13 (‰) $\pm$ 1‰ (2σ)	Δ(%) $\pm 1\sigma$
1919	- 1.58 ± 0.58	- 27.09	- 1.17 ± 0.59
1920	- 1.97 ± 0.58	- 25.67	- 1.84 ± 0.59
1925	- 3.38 ± 0.57	- 27.72	- 2.85 ± 0.59
1933	+ 0.06 ± 0.64	- 19.94	- 0.95 ± 0.66
1935	- 1.74 ± 0.52	- 27.60	- 1.23 ± 0.54
1937	- 1.14 ± 0.54	- 19.94	- 2.14 ± 0.56
1939	- 3.49 ± 0.57	- 28.08	- 2.90 ± 0.59
1941	- 2.68 ± 0.66	- 26.61	- 2.37 ± 0.68
1945	- 4.32 ± 0.68	- 23.81	- 4.55 ± 0.70
1947	- 5.69 ± 0.47	- 27.86	- 5.15 ± 0.49
1947	- 5.88 ± 0.73	- 29.11	- 5.09 ± 0.75
1949	- 3.13 ± 0.68	- 24.01	- 3.16 ± 0.70
1951	- 2.81 ± 0.62	- 29.52	- 1.93 ± 0.64
1953	- 3.60 ± 1.47	- 26.40	- 3.30 ± 1.49

TABLE 12

C-14 CONCENTRATIONS OF PRE-1950 WINES

Year of Plant Growth	δC-14 (%) ± 1σ	δC-13 (‰) ± 1‰ (2σ)	Δ(%) ± 1σ
1897	- 1.69 ± 0.52	- 30.16	- 0.68 ± 0.54
1906	- 2.81 ± 0.57	- 29.17	- 2.00 ± 0.59
1907	- 4.73 ± 0.50	- 38.34	- 2.19 ± 0.54
1907	- 2.70 ± 0.52	- 27.80	- 2.15 ± 0.54
1908	- 3.34 ± 0.53	- 29.86	- 2.40 ± 0.54
1914	- 2.36 ± 0.52	- 30.52	- 1.28 ± 0.54
1914	- 0.96 ± 1.08	- 29.35	- 0.10 ± 1.09
1917	- 4.01 ± 0.56	- 31.58	- 2.75 ± 0.58
1918	97.63 ± 1.74	- 29.61	+99.45 ± 1.77
1920	- 1.63 ± 0.52	- 30.51	- 0.54 ± 0.54
1926	- 3.26 ± 0.57	- 28.67	- 2.55 ± 0.59
1927	- 4.56 ± 0.47	- 31.58	- 3.30 ± 0.49
1928	- 3.15 ± 0.58	- 32.02	- 1.79 ± 0.60
1928	- 2.19 ± 0.52	- 28.37	- 1.53 ± 0.54
1929	- 2.25 ± 0.53	- 31.67	- 0.95 ± 0.55
1929	- 2.81 ± 0.52	- 31.36	- 1.57 ± 0.54
1929	- 2.14 ± 0.57	- 29.78	- 1.20 ± 0.59

TABLE 13

C-14 CONCENTRATIONS OF PRE-1950 FLAX SEEDS, CEREALS AND WOOL

Flax and cereals grown near Belfast ($54^{\circ}35'$N.)

(a) FLAX SEEDS (Linum usitatissimum)

Year of Plant Growth	δC-14 (%) $\pm 1\sigma$	δC-13 (‰) $\pm$ 1‰ (2σ)	Δ(%) $\pm 1\sigma$
1934	- 3.49 ± 0.57	- 33.21	- 1.91 ± 0.59
1936	- 4.33 ± 0.52	- 29.94	- 3.38 ± 0.54
1938	- 4.73 ± 0.69	- 32.60	- 3.28 ± 0.71
1938	- 4.50 ± 0.47	- 30.66	- 3.42 ± 0.49
1940	- 3.77 ± 0.52	- 30.11	- 2.79 ± 0.54
1942	- 3.83 ± 0.57	- 32.10	- 2.46 ± 0.59
1943	- 4.45 ± 0.53	- 30.68	- 3.36 ± 0.55
1944	- 5.29 ± 0.55	- 32.64	- 3.84 ± 0.58
1945	- 5.80 ± 0.51	- 30.69	- 4.73 ± 0.53
1946	- 6.08 ± 0.52	- 31.99	- 4.77 ± 0.55
1947	- 5.99 ± 0.39	- 30.72	- 4.92 ± 0.42
1948	- 6.08 ± 0.56	- 31.04	- 4.95 ± 0.59
1950	- 5.07 ± 0.57	- 29.08	- 4.29 ± 0.59

TABLE 13 (cont.)

C-14 CONCENTRATIONS OF PRE-1950 FLAX SEEDS, CEREALS AND WOOL

(b) CEREALS AND WOOL

Sample	Year of Growth	δC-14 (%) ± 1σ	δC-13 (‰) ± 1‰ (2σ)	Δ(%) ± 1σ
Oats†	1935	- 2.35 ± 0.50	- 30.26	- 1.32 ± 0.52
Barley*	1936	- 4.00 ± 0.57	- 30.01	- 3.04 ± 0.59
Wool$^{\phi}$	1851	- 3.04 ± 0.75	- 31.79	- 1.72 ± 0.77
Wool	1851	- 2.31 ± 0.74	- 27.46	- 1.83 ± 0.76
Wool	1944	- 4.11 ± 0.53	- 30.52	- 3.05 ± 0.55
Wool	1962	+20.36 ± 0.59	- 30.68	+21.73 ± 0.61

† species Avena sterilis

* species Hordeum distichum

ϕ wool samples grown in Yorkshire, England (ca. 54°N.).

in identification or to sample contamination. Since the sample activity was higher than any other measured in the laboratory, contamination during CH_4- preparation seems unlikely. Indeed contamination by natural carbon could not produce such a high C-14 concentration, so that it seems likely that the result was due to mistaken identity of the sample.

Several samples belonging to 1945-47 were analysed as a check on the validity of the low Δ values found for this period.

Comparison of Atmospheric C-14 Activities and "Suess effect" Data.

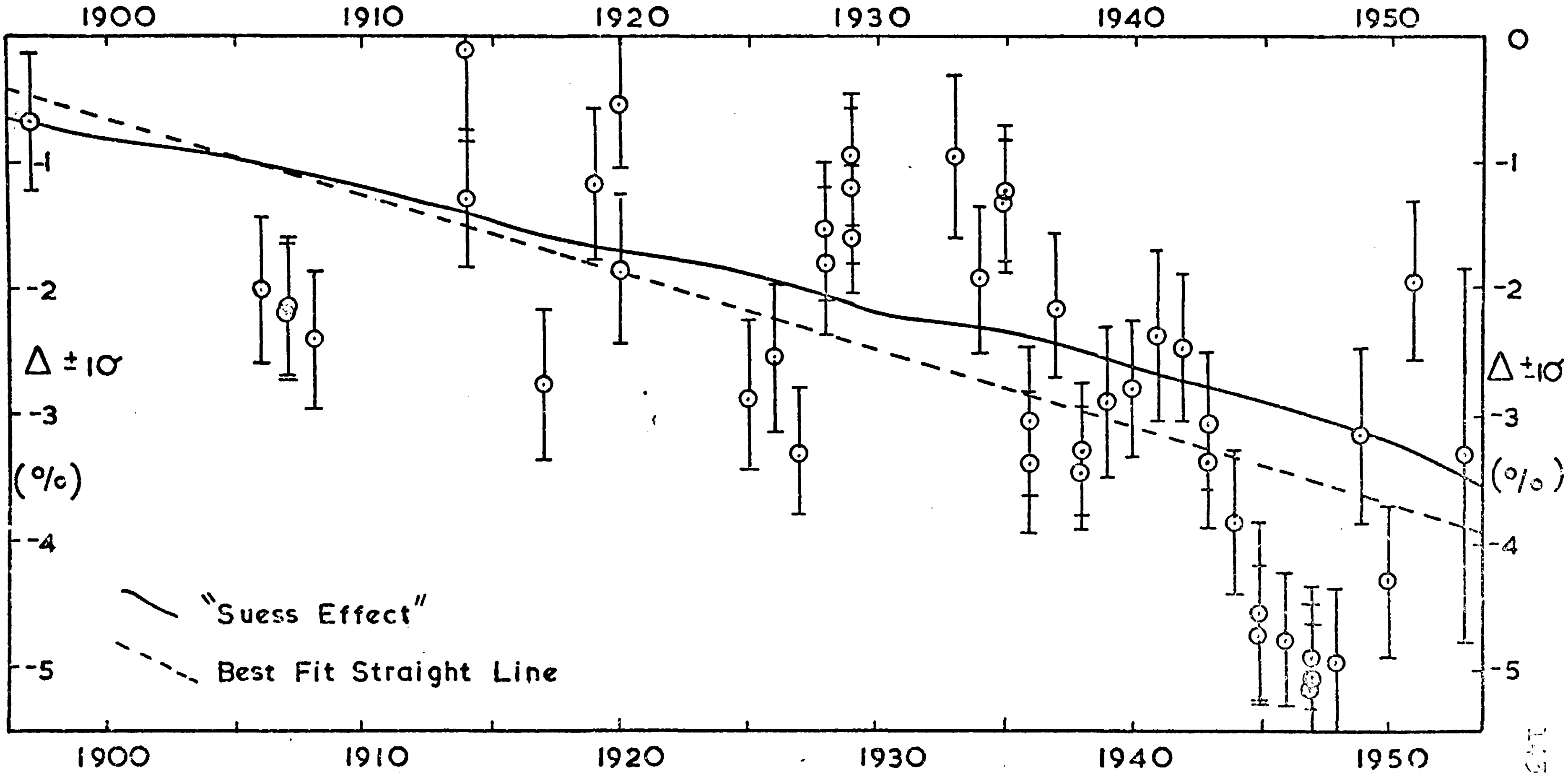
Figure 35 presents a comparison of the sample C-14 concentrations and the theoretical "Suess effect" values calculated in Chapter IV. The plot shows that

(1) the "Suess effect" curve passes through the observed C-14 activities within 0.5% of the best fit straight line through the data defined by $\Delta_t = 0.14-0.01t$ (%) where t is time in years since 1895. The "Suess effect" values, however, are consistently smaller than the deviations predicted by this equation,

and (2) the observed points are scattered well outwith statistical errors. Thus, for example, the mean 1935 and 1945 C-14 activities differ by

FIGURE 35

ATMOSPHERIC C-14 CONCENTRATIONS (1890 – 1954).



-3.36 ± 1.14% (2σ) whereas a deviation of 0.57% is implied by consideration of the "Suess effect" alone.

The non-statistical scatter of results would therefore appear to indicate annual deviations in atmospheric C-14 activities due to influences other than the "Suess effect". That the theoretical fossil CO_2 dilution curve passes through the observed points with a slightly less steep gradient implies that the other effect on its own would have (1) fluctuated about the "natural" level, and (2) caused an average decrease of ca. 0.5% in atmospheric C-14 concentrations during the period 1890-1950.

The observed C-14 concentrations appear to be slightly lower than the average results of some workers. Agreement was found, however, with the results of Broecker and Olson (-3.2% at 1938, -3.0% at 1954 (70)) and Cowan et al (ca. -2.5% at 1923 (97)). Because of the possibility that an additional perturbation factor exists the results of Suess and of early investigators who used a pre-1890 wood as their modern standard may not be directly comparable with data based on the N.B.S. oxalic acid standard. Walton and Baxter (43) have pointed out that analyses based on pre-1890 wood as standard may differ significantly from conventional analyses based on the N.B.S. standard. Thus the results of the 1851 wool samples (Table 13) suggest a C-14 concentration in 1850 of ca. -1.75% relative to the 1890 level. Analyses based on these samples as modern standard would therefore suggest C-14 activity deviations during the early 20th century ca. 1.75% smaller than those found using the conventional standard.

Natural Fluctuations of Atmospheric C-14 Concentrations (1890-1950).

A measure of the secular variations of atmospheric C-14 concentrations in the absence of the "Suess effect" during the period 1890 to 1950 was achieved by correction of the observed experimental data with the results of the theoretical study for fossil CO_2 dilution. Thus $\Delta_N = \Delta - \Delta_S$, where Δ_N represents the effect of the additional perturbation and Δ_S represents the theoretical "Suess effect" value. Δ_N values are presented in Table 14. Since the errors on Δ_N do not differ significantly from the errors on Δ the scatter of Δ_N values is again markedly outwith the 2σ statistical errors indicating that the deviations are significant. A plot of these corrected results (Figure 36) reveals a cyclic fluctuation which appears to be closely in phase and negatively correlated with the 11-year sunspot cycle. Thus in the diagram, annual mean sunspot numbers, obtained from the Royal Greenwich Observatory, are plotted on an inverse scale.

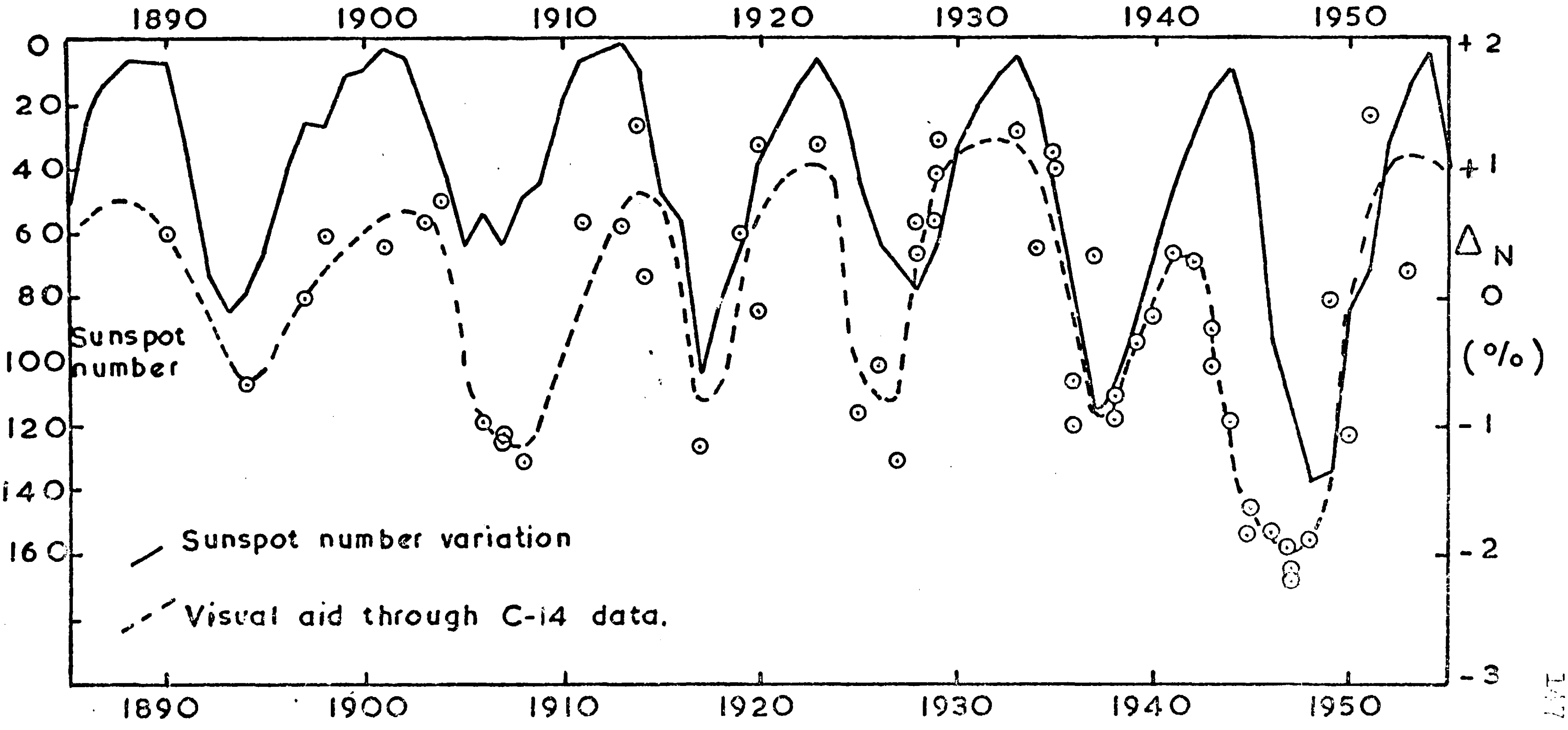
TABLE 14

ATMOSPHERIC C-14 CONCENTRATIONS (1890-1954) CORRECTED FOR "SUESS EFFECT" DILUTION

Year	Δ (%) ± 1σ	Δ_S (%) ± 1σ	Δ_N (%) ± 1σ
1897	- 0.68 ± 0.54	- 0.66 ± 0.02	- 0.02 ± 0.54
1906	- 2.00 ± 0.59	- 1.00 ± 0.02	- 1.00 ± 0.59
1907	- 2.19 ± 0.54	- 1.06 ± 0.02	- 1.13 ± 0.54
1907	- 2.15 ± 0.54	- 1.06 ± 0.02	- 1.09 ± 0.54
1908	- 2.40 ± 0.54	- 1.10 ± 0.02	- 1.30 ± 0.54
1914	- 1.28 ± 0.54	- 1.41 ± 0.04	+ 0.13 ± 0.54
1914	- 0.10 ± 1.09	- 1.41 ± 0.04	+ 1.31 ± 1.09
1917	- 2.75 ± 0.59	- 1.56 ± 0.05	- 1.19 ± 0.59
1919	- 1.17 ± 0.60	- 1.63 ± 0.05	+ 0.46 ± 0.60
1920	- 1.84 ± 0.59	- 1.69 ± 0.05	- 0.15 ± 0.59
1920	- 0.54 ± 0.54	- 1.69 ± 0.05	+ 1.15 ± 0.54
1925	- 2.85 ± 0.59	- 1.91 ± 0.06	- 0.94 ± 0.59
1926	- 2.55 ± 0.59	- 1.96 ± 0.06	- 0.59 ± 0.59
1927	- 3.30 ± 0.49	- 2.02 ± 0.06	- 1.28 ± 0.49
1928	- 1.79 ± 0.60	- 2.08 ± 0.06	+ 0.29 ± 0.60
1928	- 1.53 ± 0.54	- 2.08 ± 0.06	+ 0.55 ± 0.54
1929	- 0.95 ± 0.55	- 2.15 ± 0.07	+ 1.20 ± 0.55
1929	- 1.57 ± 0.54	- 2.15 ± 0.07	+ 0.58 ± 0.54
1929	- 1.20 ± 0.59	- 2.15 ± 0.07	+ 0.95 ± 0.59
1933	- 0.95 ± 0.66	- 2.24 ± 0.08	+ 1.29 ± 0.66
1934	- 1.91 ± 0.59	- 2.28 ± 0.08	+ 0.37 ± 0.59
1935	- 1.23 ± 0.54	- 2.32 ± 0.08	+ 1.09 ± 0.55
1935	- 1.32 ± 0.52	- 2.32 ± 0.08	+ 1.00 ± 0.53
1936	- 3.38 ± 0.54	- 2.37 ± 0.08	- 1.01 ± 0.55
1936	- 3.04 ± 0.59	- 2.37 ± 0.08	- 0.67 ± 0.60
1937	- 2.14 ± 0.57	- 2.44 ± 0.09	+ 0.30 ± 0.58
1938	- 3.28 ± 0.71	- 2.49 ± 0.09	- 0.79 ± 0.72
1938	- 3.42 ± 0.49	- 2.49 ± 0.09	- 0.93 ± 0.50
1939	- 2.90 ± 0.59	- 2.54 ± 0.09	- 0.36 ± 0.60
1940	- 2.79 ± 0.54	- 2.61 ± 0.10	- 0.18 ± 0.55
1941	- 2.37 ± 0.69	- 2.68 ± 0.10	+ 0.31 ± 0.70
1942	- 2.46 ± 0.59	- 2.74 ± 0.10	+ 0.28 ± 0.60
1943	- 3.36 ± 0.55	- 2.81 ± 0.10	- 0.55 ± 0.56
1943	- 3.05 ± 0.55	- 2.81 ± 0.10	- 0.24 ± 0.56
1944	- 3.84 ± 0.58	- 2.87 ± 0.10	- 0.97 ± 0.59
1945	- 4.55 ± 0.70	- 2.89 ± 0.10	- 1.66 ± 0.71
1945	- 4.73 ± 0.54	- 2.89 ± 0.10	- 1.84 ± 0.55
1946	- 4.77 ± 0.55	- 2.93 ± 0.10	- 1.84 ± 0.56
1947	- 5.15 ± 0.49	- 2.97 ± 0.11	- 2.18 ± 0.50
1947	- 5.09 ± 0.76	- 2.97 ± 0.11	- 2.12 ± 0.77
1947	- 4.92 ± 0.42	- 2.97 ± 0.11	- 1.95 ± 0.43
1948	- 4.95 ± 0.59	- 3.06 ± 0.11	- 1.89 ± 0.60
1949	- 3.16 ± 0.70	- 3.13 ± 0.11	- 0.03 ± 0.71
1950	- 4.29 ± 0.59	- 3.20 ± 0.11	- 1.09 ± 0.60
1951	- 1.93 ± 0.64	- 3.30 ± 0.12	+ 1.37 ± 0.65
1953	- 3.30 ± 1.49	- 3.48 ± 0.13	+ 0.18 ± 1.50

FIGURE 36

ATMOSPHERIC C-14 CONCENTRATIONS (CORRECTED FOR "SUESS EFFECT").



In addition a few results of other workers (25, 97, 98) are included where gaps in C-14 data coincided with times of sunspot maxima and minima (Table 15). Care was taken to ensure that these additional results were based on the N.B.S. standard activity and that analyses of tree ring sections were excluded. For the 46 pairs of C-14 and sunspot data a correlation coefficient of -0.482 was obtained. For all 55 pairs of data the correlation coefficient was -0.550 increasing to a maximum of -0.673 for a 1 year positive phase shift such that Δ_N maxima precede sunspot minima by 1 year. The variation of the correlation coefficient with phase shift is plotted in Figure 37. The magnitude of these correlations is surprising although the high degree of serial correlation which exists in both the sunspot and C-14 data must reduce the degrees of freedom of the estimate. Assuming a reduction of 50%, the maximum correlation remains highly significant corresponding to a probability of only 1 in 1,000 that Δ_N and sunspot number are unrelated.

By regression analysis the mean relationship between Δ_N and sunspot number, R, at time t was found to be

$$\Delta_N(t) = -0.017\ R(t+1) + 0.78.$$

This expression, however, provides only an approximate fit to the observed fluctuations. The less detailed

TABLE 15

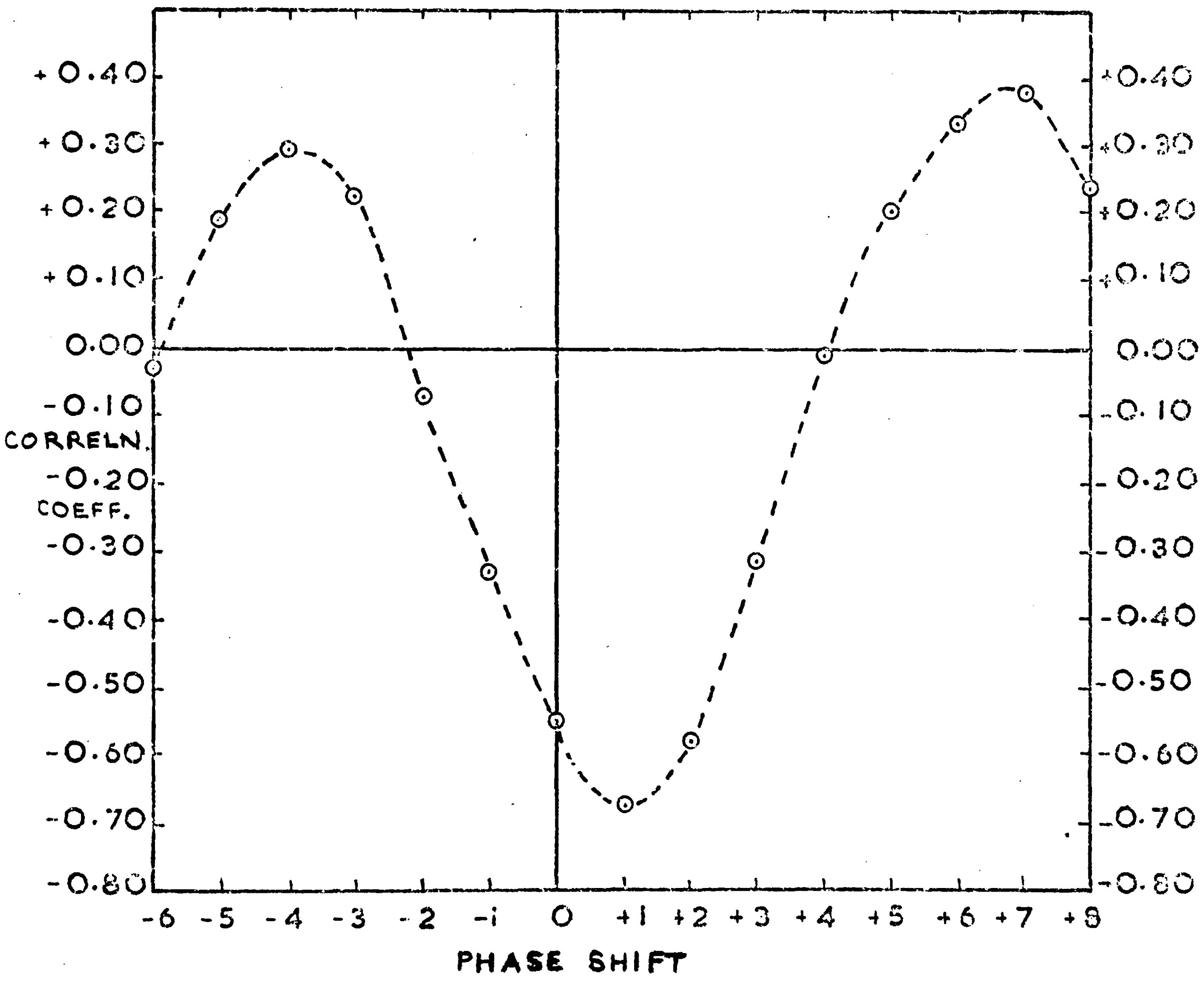
ADDITIONAL C-14 DATA

Growth Year*	Reference	Δ (%) $\pm 1\sigma$	Δ_S (%) $\pm 1\sigma$	Δ_N (%) $\pm 1\sigma$
1890	25	0.00 ± 0.00	- 0.48 ± 0.02	+ 0.48 ± 0.02
1894	97	- 1.26 ± 0.00	- 0.58 ± 0.02	- 0.68 ± 0.02
1898	98	- 0.23 ± 0.16	- 0.69 ± 0.02	+ 0.46 ± 0.16
1901	98	- 0.42 ± 0.18	- 0.79 ± 0.02	+ 0.37 ± 0.18
1903	97	- 0.29 ± 0.00	- 0.87 ± 0.02	+ 0.58 ± 0.02
1904	98	- 0.15 ± 0.16	- 0.91 ± 0.02	+ 0.76 ± 0.16
1911	98	- 0.69 ± 0.16	- 1.25 ± 0.03	+ 0.56 ± 0.16
1913	97	- 0.84 ± 0.00	- 1.37 ± 0.04	+ 0.55 ± 0.04
1923	97	- 0.66 ± 0.00	- 1.82 ± 0.05	+ 1.16 ± 0.05

* All samples single tree rings.

FIGURE 37

VARIATION OF CORRELATION COEFFICIENT WITH PHASE SHIFT.



relationships,

$$(\Delta_N)_{maximum} = -0.023\ R_{minimum} + 0.93$$

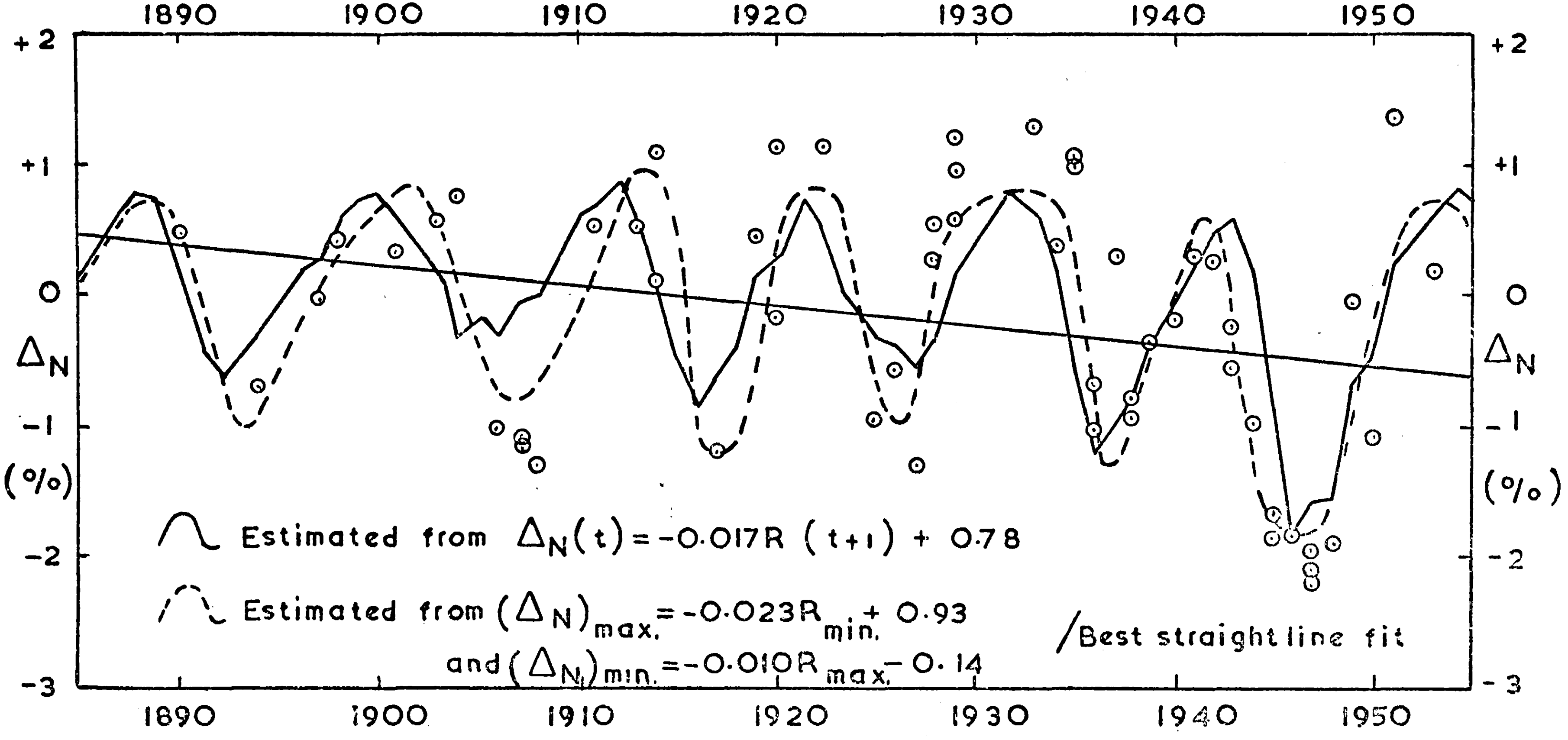
and $$(\Delta_N)_{minimum} = -0.010\ R_{maximum} - 0.14$$

define more precisely the amplitude of each cyclic deviation (Figure 38). Also shown in Figure 38 is the best straight line fit to the observations. This indicates that the general trend during the 60 year period was a decrease in atmospheric C-14 concentrations amounting to 0.5% (Δ_N). Such a trend appears similar to fluctuations of atmospheric C-14 concentrations observed in the more distant past.

Variations of atmospheric C-14 concentrations on a yearly basis have also been observed by Dyck (99) in the annual growth rings of a fir tree. Thus between 822 and 831 A.D. and 1616 and 1627 A.D. C-14 activities showed an overall variation of about 3% (Δ). Since detailed sunspot records for these periods are not available, however, it was not possible to evaluate a correlation with solar activity.

FIGURE 38

THE RELATIONSHIP BETWEEN Δ_N AND SUNSPOT NUMBER, R.



Causes of the Natural Fluctuations (1890-1950).

Recently Stuiver (30, 42, 44) has shown that long-term deviations of atmospheric C-14 concentrations from the "natural" level (e.g. the "De Vries effect") appear negatively correlated with solar activity. The cause of this observation is believed to be the modulation of the cosmic-ray flux, and hence of the C-14 production rate, by the increased magnetic fields associated with high sunspot activity. In a detailed study Lingenfelter (100) has shown that the C-14 production rate varies according to the expression $Q = 2.61-0.53(R-9.1)/178.4$ where Q is the C-14 production rate in atoms/cm.^{2}/second, and R is the mean sunspot number. Based on this relationship the mean C-14 production rate during 1890 to 1950 was 2.50 atoms/cm.^{2}/second or about 4×10^{26} atoms/year, with overall variations from 3.3 to 4.4×10^{26} atoms/year. Averaged over the 6 solar cycles between 1890 and 1954 the production rate varies from about 3.6 to 4.4×10^{26} atoms/year between solar maximum and minimum (ca. 5 years). Thus the annual variations in C-14 input to the stratosphere can amount to a maximum of 2×10^{25} atoms/year.

Fluctuations of tropospheric C-14 concentrations from +1.5% to -1.5% (Δ) during a sunspot cycle require overall variations in the C-14 budget of the troposphere by about 1×10^{27} atoms or 2×10^{26} atoms/year. Therefore the changes in C-14 production rate are about one order of magnitude too small to account for the observed deviations. In addition, the concepts of a steady state equilibrium within the atmospheric carbon reservoirs and of a finite stratospheric residence time imply that any excess C-14 produced in the atmosphere is injected to the troposphere relatively slowly and in small quantities. Thus the probability that modulation of the C-14 production rate is the mechanism of the observed tropospheric fluctuations is reduced even further. Furthermore, it is known (100) that cosmic-ray flux variations are in direct phase agreement with changes in solar activity, so that if production rate modulation was the causal mechanism tropospheric C-14 maxima would follow sunspot minima by a few years as determined by the stratospheric residence time. That the optimum correlation of tropospheric C-14 concentrations with solar activity is obtained with a 1 year phase shift in the opposite sense appears to confirm that variations in production rate are not primarily responsible for the fluctuations.

It is of interest to consider the phase shift expected if the long-term fluctuations of atmospheric C-14 activity (i.e. fluctuations occurring over several hundred years) are correlated with solar activity via production rate variation. Since the stratospheric residence time is negligible in these cases, maximum C-14 production would seem to be required not in direct phase agreement with the maximum of C-14 concentrations (as implied by most workers) but at the time of maximum increase of C-14 concentrations. Thus in these cases C-14 activity maxima should follow minima in solar activity by a significant period (e.g. in the case of the "De Vries effect" by up to 50 years).

The observed C-14 fluctuations over 1 solar cycle certainly appear to reflect a variable input of C-14 into the troposphere. The input mechanism must be sensitive to variations in solar activity through the modulation of the flux of incident radiation. If production rate changes are not responsible it would appear that the variable input must result from fluctuation of the carbon exchange rate between the troposphere and one (at least) of the adjacent reservoirs (atmosphere, biosphere, surface ocean). Biospheric activity could be sensitive to solar activity through variations in climate (99) but since increased uptake of C-14 would involve uptake of C-13 and C-12 and since biospheric turnover is relatively rapid the resultant C-14 concentration would not be changed significantly over short time periods. Annual variations of tropospheric/surface ocean mixing rates seem unlikely since the ocean reservoir is large and slow-mixing in comparison with the troposphere. Furthermore the effects of variations in solar activity are much reduced at lower altitudes so that biospheric and oceanic response should be negligible. It seems possible, however, that stratosphere/troposphere exchange could be correlated with solar activity since

(1) the inter-reservoir boundary, the tropopause, is flexible and subject to marked variation in height and stability (e.g. tropopause gaps, tropopause folding),

(2) the stratosphere and upper troposphere are exposed to variations in incident solar radiation,

(3) the internal motions of the atmosphere are controlled by heat and related pressure gradients (101),

(4) variable input of air from the stratosphere is known to occur over a 1 year cycle as shown by the annual "spring peak" in fission product concentrations in the troposphere.

Under equilibrium conditions the mean C-14 production rate must equal the "net" transfer rates of C-14 from the stratosphere to the troposphere and from the troposphere to the surface ocean + biosphere (neglecting radioactive decay). For the period 1890 to 1950 the mean production rate and hence mean inter-reservoir exchange rates were about 4 x 10^{26} atoms/year. To estimate the variation in stratospheric C-14 input to the troposphere required to explain the observed fluctuations, the uptake of tropospheric C-14 by the surface oceans + biosphere was assumed to be constant at 4 x 10^{26} atoms/year. Table 16 presents the mean annual variations of Δ_N, sunspot number, tropospheric C-14 content and hence of C-14 input from the stratosphere averaged over the 6 solar cycles during 1890 to 1953. These estimates are based on the "natural" C-14 content of the troposphere of 3.0 x 10^{28} atoms calculated from a natural tropospheric CO_2 content of 290 p.p.m. (88) and a mean C-14 activity of 13.56 d.p.m. (56). The results indicate that maximum input of C-14 to the troposphere occurs on average within the 2 year period following sunspot maximum when tropospheric C-14 concentrations are rising most rapidly. Minimum C-14 input from the stratosphere appears to occur on average 3 years before sunspot maximum. Due to the variable intensity of solar cycles and to the statistical errors on the C-14 analyses, these phase estimates are believed to be accurate only to within ±2 years. The stratospheric C-14 input to the troposphere appears to vary during a solar cycle by about ±50% of the mean value. Based on the results of

TABLE 16

THE VARIATION OF THE TROPOSPHERIC C-14 BUDGET DURING ONE SOLAR CYCLE

Year	Mean Sunspot Number	Δ_N (%)	Tropospheric C-14 Content ($\times10^{28}$ atoms)	C-14 Input from Stratosphere ($\times10^{26}$ atoms)
1	4.7	+ 0.80	3.024	3.1
2	13.4	+ 0.50	3.015	2.2
3	49.0	- 0.10	2.997	1.9
4	80.2	- 0.80	2.976	2.8
5	87.8	- 1.20	2.964	4.6
6	90.5	- 1.00	2,970	5.8
7	70.2	- 0.40	2.988	5.8
8	56.0	+ 0.20	3.006	5.2
9	32.9	+ 0.60	3.018	4.6
10	19.7	+ 0.80	3.024	4.6
11	11.4	+ 1.00	3.030	3.4

Lingenfelter (100) and a mean "natural" C-14 content of 5.7 x 10^{27} atoms the variations in the stratospheric C-14 budget can also be estimated (Table 17). The results show that a cyclic fluctuation of stratospheric C-14 activities should occur in direct correlation with solar activity with a phase shift of 1 year (i.e. C-14 maximum preceding a sunspot maximum by 1 year). Thus the cyclic fluctuations in the troposphere would be inversely correlated with the stratospheric variations, with maximum C-14 concentration gradients across the tropopause of ±7 to ±8% (Δ) around solar maxima and minima.

The long-term trend of decreasing tropospheric C-14 concentrations between 1890 and 1950 (amounting to ca. -0.5% in 1950) may be a direct result of production rate modulation, since sunspot activity during this period was significantly higher than mean values during the past 2,000 years. Thus the mean maximum sunspot number between 1890 and 1950 was about 100 compared to the overall mean of about 85 (102). (Bray (31) has predicted a tropospheric C-14 activity of about -0.7% (Δ) for a period of this level of solar activity.) Furthermore, by analogy with the "Suess effect" calculation, the cumulative deficit of C-14 required to produce a general decrease of 0.5% in tropospheric C-14 concentrations is

TABLE 17

THE VARIATION OF THE STRATOSPHERIC C-14 BUDGET DURING ONE SOLAR CYCLE

Year	Mean Sunspot Number	C-14 Production ($x10^{26}$ atoms)	C-14 Input to Troposphere ($x10^{26}$ atoms)	Stratospheric C-14 Content ($x10^{27}$ atoms)	Δ (%)
1	4.7			5.42	- 4.9
		4.3	3.1		
2	13.4			5.54	- 2.0
		4.1	2.2		
3	49.0			5.73	+ 0.5
		4.0	1.9		
4	80.2			5.94	+ 4.2
		3.9	2.8		
5	87.8			6.05	+ 6.1
		3.7	4.6		
6	90.5			5.96	+ 4.6
		3.7	5.8		
7	70.2			5.75	+ 0.9
		3.9	5.8		
8	56.0			5.56	- 2.5
		4.0	5.2		
9	32.9			5.44	- 4.6
		4.1	4.6		
10	19.7			5.39	- 5.4
		4.1	4.6		
11	11.4			5.34	- 6.3
		4.2	3.4		

about 1.2% of the natural atmospheric C-14 inventory or 3.6 x 10^{26} C-14 atoms (Chapter IV). From Lingenfelter's relationship between the C-14 production rate and sunspot number (100) the production rate for the mean sunspot number of 100 is 0.06 x 10^{26} atoms/year less than the production rate at the "normal" level of 85. On the assumption, therefore, that the level of solar activity between 1890 and 1950 exceeded the mean "natural" level in the ratio of these maximum sunspot numbers, the cumulative deficit of C-14 resulting from production rate modulation would be 3.6 x 10^{26} atoms, sufficient to have caused the observed deviation.

The Mechanism of Short-term Fluctuations of Atmospheric C-14 Concentrations.

The enhancement in solar emission of extreme U.V. radiation by increased sunspot activity is thought to occur through local increases in coronal temperatures. The temperature increases are caused by hydromagnetic movement along the magnetic field lines associated with the sunspots (103). In addition, solar maximum is correlated with an increase in "solar wind", the stream of charged particles, mainly protons, emitted by the sun. Thus, according to Willett (101), the intensified bursts of U.V. and corpuscular energy are absorbed in the upper atmosphere and the resulting temperature variations at high levels expressed as pressure differences in the "normal" pattern of tropospheric circulation. Thus Jacchia (104) has estimated from observations of satellite drag that the upper atmosphere is extremely responsive to solar control, deviating in density from the mean by a factor of 100 and varying in temperature by hundreds of degrees at times of high solar activity. In the troposphere, however, increased solar activity appears to produce lower temperatures. The explanation of this paradox is believed to lie in the effects of variable insolation of the general atmospheric circulation (105). (It is of interest in this respect that the theories of Suess (41, 80) and Stuiver (30, 42) assume that periods of high solar activity correspond to periods of increased earth temperatures whereas meteorological evidence implies the opposite effect.) In fact, the increased corpuscular radiation at solar maximum appears to be diverted by the earth's magnetic field towards the poles and thus preferential heating of the upper air of the polar regions occurs (101, 105). . As a result zonal circulation is disrupted and there is a greater latitudinal transfer of air with accompanying storminess and temperature extremes.

A contributing mechanism to stratospheric/tropospheric mixing lies in the altitude variation of the tropopause, a high tropopause corresponding to a period of increased exchange (106). Kulkarni (107) has provided evidence that the mean tropopause height in the southern hemisphere could be related to sunspot numbers. Lawrence (106, 108) has closely studied tropopause height variations in recent years and although data are not available from a long period of observation, a direct correlation of mean tropopause height and sunspot numbers is indicated. Thus mean tropopause heights over south-east England reached a maximum in 1959 (2 years after sunspot maximum) with lowest values in 1954 (a sunspot minimum) and 1963 (1 year before sunspot minimum). Mean tropopause height variations over an 11-year solar cycle would therefore be analogous to the variations known to occur over the annual cycle (109) which are responsible, in part, for the monthly fluctuations of fission product concentrations observed in recent years.

Since the annual "spring peaks" are believed to be the result of increased energy input to the stratosphere during the late winter (110) it seems reasonable that the high energy fluxes associated with solar maximum could produce similar intensification of atmospheric circulation. By analogy with the annual variations the mechanism of the increased vertical transfer of C-14 could therefore involve enhanced tropopause folding and input through the "jet- streams" besides the altitude variation of the tropopause. Thus input of C-14 from the stratosphere to the troposphere would reach maximum levels during the periods of high tropopause and enhanced atmospheric circulation which appear correlated with the years during and immediately following solar maximum.

Additional Evidence of Variable Stratospheric C-14 Input to Troposphere.

(a) Carbon-14 Data.

Since 1963 Nydal (32, 54, 66, 91) has continuously monitored atmospheric C-14 concentrations and has interpreted these observations in terms of carbon exchange rate constants. In a review of his findings (1968) it was observed that, based on the same theoretical model, the stratosphere/troposphere exchange time appeared to have increased during 1963 (1.4 years), 1964 (2.2 years) and 1965 (3.3.years) by over 100%. As 1968-1969 is a period of high solar activity, a minimum in stratospheric input to the troposphere would be expected about 1965-1966 with an increased rate of downflux since then. The variation in exchange time may, however, be attributed to a non-uniform distribution of the excess C-14 in the stratosphere resulting from its initial injection at specific latitudes and altitudes. Harkness (95), however, has shown that in the northern hemisphere stratosphere the latitudes and altitudes of maximum injection closely corresponded to the regions of maximum production of natural C-14 (ca. 50-70°N., 60,000 feet), so that the movement of bomb-produced C-14 could be expected to reflect the transport of natural C-14. In addition, if the stratospheric distribution of excess C-14 is regarded as non-uniform the variation in apparent exchange time from 1963 through 1965 might be expected to follow a decrease rather than the observed increase due to slow downward movement of the excess from 60,000 feet to the tropopause region about 30,000 to 50,000 feet (109).

It is also of interest that stratospheric residence times estimated between 1957 and 1960 were significantly shorter (ca. 1 year) than subsequent determinations. During 1957-1958 solar activity reached its highest recorded level (mean sunspot number ca. 190) (102), and thus an increased rate of stratospheric input at that time would be expected. In addition, stratospheric studies performed by Feely (111) in 1963 and 1964 predicted an exponential decrease in the stratospheric excess C-14 burden which, according to Ergin (89), can be described by the relationship $X(t) = 39.16e^{-0.12t}$ where $X(t) \times 10^{27}$ atoms is the stratospheric excess C-14 content at time t months after January 1963.

Extrapolation of this curve to January 1968 predicts a stratospheric C-14 concentration of ca. 100% (Δ). Harkness (95), however, has found that the C-14 concentration in January 1968 was closer to 74% (Δ). This evidence therefore suggests further that the rate of injection of stratospheric C-14 into the troposphere increased towards the period of solar maximum in 1968-1969. It is also interesting to note that a natural C-14 gradient across the tropopause of about 8% (Δ) would be predicted for 1968 (i.e. stratospheric levels ca. 8% above tropospheric values). This result agrees with the observed difference and suggests that the bomb-produced C-14 excess may have already attained equilibrium in the atmospheric reservoirs. If this is the case a reversal of gradient should have occurred by 1975.

(b) Ozone and Tritium Data.

In 1967 Aegerter et al (112) observed that H-3 concentrations in six profiles of Greenland ice were inversely correlated with sunspot activity. The overall variation in H-3 concentration between 1925 and 1955 was from 100 T.U. at solar minimum to 30 T.U. at solar maximum. Since H-3 is produced in the stratosphere by a mechanism analogous to C-14 formation and must enter the troposphere prior to "rain-out" it seems probable that variable stratospheric injection may be responsible for the fluctuations. As the deviations in H-3 content at solar minimum are of the same magnitude as nuclear era H-3 concentrations (1961, 1962, 1965) in rainfall (113), it seems unlikely that the sunspot correlation is due to production rate variation. In addition a mechanism involving production rate modulation alone would be expected to cause a significant lag (which is not observed) between solar minimum and H-3 maximum.

Further evidence of solar-sensitive atmospheric circulation stems from the observation by Willett (114) that for the period 1933 to 1959 a highly significant negative correlation was found between sunspot numbers and the worldwide average of total atmospheric O_3. Maximum correlation occurred for a phase shift where O_3 maxima preceded solar minima by 1 to 2 years. Thus O_3 and C-14 concentrations are in direct phase agreement. Since O_3 is in photochemical equilibrium above 35 km. a study of variations in total O_3 refers essentially to altitudes below 35 km. (107). Annual variations in atmospheric O_3 content can therefore be attributed to variations in large-scale vertical motion as required to explain the C-14 fluctuations. It is also possible that variations in atmospheric O_3 content reinforce tropopause height fluctuations since the reduced infrared cooling in the upper troposphere, resulting from high O_3 concentrations, appears to cause a lower equilibrium tropopause height (106, 107, 115).

Implications of Results.

(a) Geophysical Implications.

The observed C-14 fluctuations appear to confirm the belief that atmospheric circulation is extremely sensitive to variations in solar activity. The correlation is thought to stem from the influence of changes in incident energy fluxes (U.V. and corpuscular) experienced in the upper atmosphere. Resultant temperature gradients are expressed as pressure differences which intensify atmospheric circulation leading to increased mixing of stratospheric and tropospheric air masses shortly after solar maximum. An increase in the average height of the tropopause reinforces the intensified mixing processes.

It appears, therefore, from these findings that the concept of a constant stratospheric residence time may not be adequate for detailed theoretical studies of "tracer" distributions. In certain respects the variations in transfer of stratospheric C-14 to the troposphere over a solar cycle resemble the fluctuations known to occur during the annual cycle. The variations also provide an explanation for the range of values (0.8 to 5 years) found for the stratosphere/troposphere exchange time during the past decade.

The results provide some support for meteorological theories that climatic variation is related to solar activity although at lower levels of the troposphere such effects may be negligible.

(b) Implications for the Radiocarbon Dating Method.

The observations indicate that between 1890 and 1950 tropospheric C-14 concentrations (corrected for "Suess effect" dilution) fluctuated by up to ±1.5% of the "natural" level in approximate phase agreement with solar activity. A study of the results indicate that stratospheric C-14 concentrations should also fluctuate (by ca. ±6% of the "natural" level) in phase with, but in opposite sense to, the tropospheric variations. As a result the total atmospheric C-14 content remains constant unless the C-14 production rate deviates significantly from the mean value. Thus fluctuations of tropospheric C-14 concentrations in the more distant past may be caused by C-14 production rate modulation or by variation of other geophysical parameters (ocean mixing rates, geomagnetic field strength). Variable stratospheric mixing is therefore a cause of short-term fluctuations alone.

If these fluctuations of tropospheric C-14 concentrations have occurred continuously during the past, however, they represent a significant deviation from the basic assumption of radiocarbon dating. As such they require modification of the treatment of errors associated with radiocarbon dates since all samples which take part in carbon exchange for short-time periods (less than 10 years) may be subject to significant deviations in initial C-14 concentration. Materials such as grain and leaves may have C-14 activities differing by 1.5% (Δ) from the "natural" level with a resultant error in C-14 age amounting to 120 years. Analyses of individual tree rings for calibration of past atmospheric C-14 activities may also be subject to such errors so that unless several samples are measured during each decade the accuracy of the determinations may be limited. Dating of wood sections and materials which "live" over longer time periods may not be significantly affected due to cancellation of the annual deviations. Thus it would seem necessary to increase the 1σ error on radiocarbon ages of short lived materials by 80 years.

The results are also relevant to the current assumption that the C-14 activity of 1890 wood reflects the mean "natural" level. It has already been observed that 1890 atmospheric C-14 activities seem likely to have been significantly diluted by fossil fuel CO_2 (by ca. 0.5%). Although the short-term fluctuations of atmospheric C-14 concentrations were measured relative to 1890 activities their overall amplitude would be identical relative to any standard activity. That the deviations in C-14 concentrations were virtually symmetrical about the 1890 level, however, implies the validity of the standard as a representative measure of the mean "natural" level. Thus at 1890 the "Suess effect" dilution was compensated by a positive natural deviation associated with a year following sunspot minimum. Non-conventional pre-1890 modern standards may, however, be in significant error unless the mean activity over an 11-year cycle is used. Thus 1850 atmospheric C-14 activities as indicated by the 1851 wool samples (Table 13), were about -1.75% (△), in agreement with solar data since 1850 immediately followed a strong sunspot maximum during a period of generally high solar activity. The short-term fluctuations of atmospheric C-14 concentrations and the annual increases in the "Suess effect" therefore appear to support, perhaps fortuitously, the universal use of the N.B.S. oxalic acid standard.

APPENDIX A

METHOD OF CALCULATION OF RESULTS

(1) Determination of Net Sample Count Rate.

The gross sample count rate, N_S (c.p.m.), is converted to a net activity, A_S,

by (1) correction for the mean background count rate, B_S, via established relationship between background and barometric pressure (Figure 21),

and (2) normalisation of the counter gas fill to constant temperature (18°C.) through the correction factor, 1 (Figure 13).

Thus $A^*_S = N_S - B_S$ and $A_S = 1A^*_S$, the standard deviation on A_S, $\sigma(A_S)$, being calculated by combination of the individual errors on N_S and B_S (i.e. $\sigma(A_S) = 1\sqrt{\sigma^2(N_S) + \sigma^2(B_S)}$). For known-age samples which are analysed to reflect atmospheric C-14 concentrations during their growth periods, net activities are corrected for decay since "death" using a half-life of 5,730 years (27) ($A^o_S = A^t_S . e^{\lambda t}$).

(2) Determination of δC-14, δC-13 and Δ.

The method of calculation of δC-14, δC-13 and Δ is based on the Lamont formulation (25, 70) as interpreted by Callow et al (116). Thus $\delta C\text{-}14 = (A_S/0.95A_M - 1).1000$ (‰), where $0.95A_M$ is the net C-14 activity of the N.B.S. standard (Table 5) normalised to the activity of age-corrected 1890 wood. The variance on δC-14 is expressed by $\sigma^2(\delta C\text{-}14) = \left[\frac{1000}{0.95A_M}\right]^2 \left\{\sigma^2(A_S) + \left(\frac{A_S}{A_M}\right)^2 . \sigma^2(A_M) + \left(\frac{A_S - A_M}{A_M}\right)^2 . \sigma^2(B_S)\right\}$ (‰).

The fractionation of C-13 and C-12 isotopes is expressed by δC-13 where $\delta C\text{-}13 = (R_S/R_P - 1).1000$ (‰) and R_S and R_P represent the C-13/C-12 ratios of sample and P.D.B. belemnite standard respectively. The standard deviation of the δC-13 measurement is consistently 0.5‰.

Sample C-14 concentrations are then normalised to the same C-13/C-12 ratio by conversion to Δ expressed by $\Delta = \delta C\text{-}14 - (2\,\delta C\text{-}13 + 50)\,(1 + \delta C\text{-}14/1000)$ (‰) where the factor -50 brings the Δ value of 1890 wood close to zero.

$$\sigma^2(\Delta) = \left[1 - \frac{(2\,\delta C\text{-}13 + 50)}{1000}\right]^2 . \sigma^2(\delta C\text{-}14) + 4\left[1 + \frac{\delta C\text{-}14}{1000}\right]^2 . \sigma^2(\delta C\text{-}13)$$

(3) Age Determination.

To avoid revision of all published radiocarbon dates it is current practice to calculate C-14 ages using the Libby half-life value of 5,568 years. These dates are converted to values based on the 5,730 year half-life through multiplication by the factor 1.03.

The sample age T_S, in years, is defined by

$T_S = 8033 \log_e \frac{1}{1+\Delta.10^{-3}}$ (where $8033 = t_{\frac{1}{2}}/0.693$).

Limits of age $(T_S + t_1, T_S - t_2) = 8033 \log_e \frac{1}{1+(\Delta\pm\sigma(\Delta))10^{-3}}$.

All radiocarbon ages are expressed in years B.P., where B.P. designates years before 1950.

APPENDIX B

(1) FOSSIL FUEL CONSUMPTION AND CEMENT MANUFACTURE (1860-1969).

Annual fuel consumption figures are given in millions of metric tons, except for natural gas combustion which is in thousand millions of cubic metres. Cement manufacture data are also presented in millions of metric tons.

Year	Coal	Lignite	Petroleum	Natural Gasoline	Natural Gas	Cement
1860	132.1	6.1	0.1			0.6
1861	139.5	6.6	0.3			0.7
1862	138.7	7.3	0.4			0.8
1863	149.4	7.7	0.4			0.8
1864	162.3	8.6	0.3			0.9
1865	171.7	9.3	0.4			1.0
1866	181.4	9.4	0.5			1.1
1867	194.4	10.1	0.5			1.1
1868	192.4	10.7	0.5			1.2
1869	199.3	11.6	0.6			1.2
1870	203.5	12.2	0.8			1.3
1871	227.1	14.2	0.8			1.3
1872	246.6	15.5	0.9			1.4
1873	263.3	17.4	1.5			1.5
1874	255.8	19.2	1.6			1.6
1875	263.8	19.0	1.4			1.7
1876	266.8	19.9	1.5			1.8
1877	272.5	19.7	2.2			1.9
1878	272.6	20.5	2.5			2.1
1879	287.3	21.7	3.2			2.3
1880	313.9	23.1	4.1		0.1	2.5
1881	337.7	24.5	4.4		0.3	2.9
1882	362.6	25.7	4.9		0.6	3.2
1883	387.9	27.4	4.1		0.8	3.3
1884	389.5	28.1	4.9		1.1	3.8
1885	380.6	29.0	5.0		1.5	4.1
1886	381.6	29.8	6.5		1.9	4.4
1887	408.1	31.1	6.5		2.4	4.6
1888	441.2	33.2	7.1		2.8	4.8
1889	448.0	35.4	8.4		3.3	4.9
1890	474.6	38.9	10.5		3.8	5.1

Year	Coal	Lignite	Petroleum	Natural Gasoline	Natural Gas	Cement
1891	493.8	41.6	12.5		3.9	5.6
1892	498.5	42.2	12.2		4.1	6.3
1893	487.1	43.9	12.6		4.2	6.9
1894	509.3	45.2	12.2		4.3	7.4
1895	536.3	49.2	14.2		4.5	7.9
1896	551.8	52.2	15.7		5.1	8.4
1897	577.2	56.6	16.7		5.7	8.9
1898	608.2	60.2	17.2		6.2	9.4
1899	667.0	63.9	18.0		6.7	9.9
1900	700.7	71.5	20.5		7.1	10.5
1901	717.5	76.8	23.0		7.9	11.6
1902	733.8	75.3	24.9		8.4	12.6
1903	807.4	78.4	26.7		8.9	13.6
1904	812.4	81.5	29.9		9.3	14.7
1905	857.5	87.0	29.5		10.6	15.8
1906	925.9	93.3	29.2		11.7	16.8
1907	1022.7	102.0	36.2		12.2	17.7
1908	968.1	105.6	39.1		12.1	19.0
1909	1010.4	107.5	40.9		14.4	20.0
1910	1056.6	108.4	44.9		15.3	21.0
1911	1076.8	112.6	47.2		15.4	23.1
1912	1133.8	124.4	48.3		16.9	25.2
1913	1216.3	128.8	53.7	0.1	17.5	27.3
1914	1086.1	120.9	55.9	0.2	17.7	29.4
1915	1069.5	123.7	59.1	0.2	18.9	31.5
1916	1152.1	131.9	62.5	0.3	22.6	35.7
1917	1215.3	134.9	69.2	0.7	23.9	37.8
1918	1194.9	141.4	69.5	0.8	21.6	44.1
1919	1040.0	133.1	77.5	1.0	22.4	38.0
1920	1192.5	157.5	99.2	1.2	24.0	39.9
1921	993.2	168.4	107.4	1.3	19.9	44.1
1922	1061.8	182.7	119.9	1.5	22.9	44.1
1923	1205.5	163.4	141.5	2.4	30.2	46.2
1924	1189.0	173.1	141.3	2.7	34.2	51.4
1925	1185.1	186.9	148.8	3.3	36.1	58.1
1926	1177.1	187.7	152.8	4.0	39.7	62.4
1927	1275.1	202.9	175.2	4.7	43.6	67.8
1928	1246.1	219.4	184.2	5.3	47.5	72.2
1929	1325.1	232.4	206.6	6.6	57.9	75.5
1930	1216.9	197.2	196.6	6.5	54.2	71.8
1931	1074.5	181.6	189.5	5.4	52.6	60.6
1932	955.2	170.2	180.7	4.5	49.1	48.9
1933	1000.0	174.4	197.2	4.2	49.4	47.7
1934	1088.0	191.3	208.2	4.5	56.2	57.4
1935	1111.5	205.8	226.2	4.8	57.5	64.0

Year	Coal	Lignite	Petroleum	Natural Gasoline	Natural Gas	Cement
1936	1250.0	205.2	245.0	5.2	66.6	75.2
1937	1302.0	252.0	280.0	6.0	74.0	82.9
1938	1214.0	264.0	273.0	6.3	70.6	86.0
1939	1288.0	292.0	285.6	6.4	75.9	84.1
1940	1363.0	319.2	292.0	6.9	81.8	81.0
1941	1422.0	331.2	279.0	7.9	86.6	91.1
1942	1429.0	334.0	263.0	8.0	94.2	87.0
1943	1430.0	348.0	288.0	8.2	105.2	78.2
1944	1379.0	316.0	324.0	8.9	114.2	64.0
1945	1188.0	187.2	342.0	9.7	125.0	51.0
1946	1216.0	256.0	376.0	10.2	129.3	78.0
1947	1374.0	274.0	414.0	10.7	143.2	88.0
1948	1429.0	299.2	468.0	11.7	161.2	104.0
1949	1342.0	332.0	466.0	12.2	170.3	118.0
1950	1454.0	360.8	523.0	13.6	197.0	132.4
1951	1524.0	396.8	592.0	14.6	233.2	148.6
1952	1499.0	423.2	623.0	15.0	250.8	158.6
1953	1500.0	450.0	658.0	15.7	263.3	175.3
1954	1475.1	493.9	690.7	16.2	278.7	188.6
1955	1597.1	535.2	773.8	17.6	302.8	217.0
1956	1686.1	564.8	841.7	17.8	328.1	235.0
1957	1733.5	593.2	886.3	17.7	357.0	247.0
1958	1815.3	612.5	906.7	18.0	386.6	263.0
1959	1890.0	616.7	978.6	18.6	431.1	294.0
1960	1982.0	638.4	1053.9	19.6	484.2	314.0
1961	1807.3	661.9	1122.5	20.8	507.0	333.0
1962	1852.3	683.8	1217.4	21.6	553.5	358.0
1963	1923.6	718.0	1305.8	23.5	605.0	378.0
1964	1992.4	747.2	1410.0	26.1	660.0	415.0
1965	2042.4	742.0	1511.8	27.4	705.7	434.0
1966	2076.8	738.1	1641.4	28.4	765.0	463.0
1967	2125.7	750.0	1810.0	29.5	828.0	485.0
1968	2200.0	770.0	2000.0	30.5	890.0	510.0
1969	2270.0	800.0	2200.0	31.5	950.0	540.0

APPENDIX B

(2) ANNUAL PRODUCTION OF FOSSIL CO_2 FROM EACH SOURCE (1860-1969).

All quantities of fossil CO_2 are expressed in g. CO_2.

Year	Coal ($x10^{14}$ g.)	Lignite ($x10^{13}$ g.)	Petroleum ($x10^{12}$ g.)	Natural Gasoline	Natural Gas	Cement ($x10^{12}$ g.)	Total ($x10^{14}$ g.)
1860	3.87	1.63	0.28			0.30	4.04
1861	4.09	1.76	0.84			0.35	4.28
1862	4.06	1.95	1.12			0.40	4.27
1863	4.38	2.06	1.12			0.42	4.60
1864	4.76	2.30	0.84			0.48	5.00
1865	5.03	2.48	1.12			0.50	5.29
1866	5.32	2.51	1.41			0.54	5.59
1867	5.70	2.70	1.41			0.56	5.99
1868	5.64	2.86	1.41			0.57	5.95
1869	5.84	3.10	1.69			0.59	6.17
1870	5.96	3.26	2.25			0.60	6.31
1871	6.65	3.79	2.25			0.65	7.05
1872	7.23	4.14	2.53			0.70	7.68
1873	7.71	4.65	4.22			0.75	8.22
1874	7.49	5.13	4.50			0.80	8.06
1875	7.73	5.07	3.93			0.85	8.28
1876	7.82	5.31	4.22			0.90	8.40
1877	7.98	5.26	6.18			0.95	8.58
1878	7.99	5.47	7.03			1.05	8.62
1879	8.42	5.79	8.99			1.16	9.10

Year	Coal ($x10^{14}$ g.)	Lignite ($x10^{13}$ g.)	Petroleum ($x10^{12}$ g.)	Natural Gasoline	Natural Gas ($x10^{12}$ g.)	Cement ($x10^{12}$ g.)	Total ($x10^{14}$ g.)
1880	9.20	6.17	11.50		0.24	1.25	9.95
1881	9.89	6.54	12.40		0.73	1.45	10.69
1882	10.62	6.86	13.80		1.46	1.55	11.47
1883	11.37	7.31	11.50		1.94	1.65	12.25

Year	Coal ($x10^{15}$ g.)	Lignite ($x10^{14}$ g.)	Petroleum ($x10^{13}$ g.)	Natural Gasoline	Natural Gas ($x10^{13}$ g.)	Cement ($x10^{12}$ g.)	Total ($x10^{15}$ g.)
1884	1.141	0.75	1.38		0.27	1.85	1.234
1885	1.115	0.77	1.41		0.36	1.95	1.212
1886	1.118	0.80	1.83		0.46	2.10	1.223
1887	1.196	0.83	1.83		0.58	2.30	1.305
1888	1.293	0.89	2.00		0.68	2.35	1.411
1889	1.313	0.95	2.36		0.80	2.40	1.442
1890	1.391	1.04	2.95		0.92	2.50	1.536
1891	1.447	1.11	3.51		0.95	2.75	1.605
1892	1.461	1.13	3.43		1.00	3.00	1.621
1893	1.427	1.17	3.54		1.02	3.25	1.593
1894	1.492	1.21	3.43		1.04	3.50	1.661
1895	1.571	1.31	3.99		1.09	3.75	1.757
1896	1.617	1.39	4.41		1.24	4.00	1.817
1897	1.691	1.51	4.69		1.39	4.25	1.907
1898	1.782	1.61	4.83		1.51	4.50	2.011
1899	1.954	1.71	5.06		1.63	4.75	2.197
1900	2.053	1.91	5.76		1.73	5.00	2.324

Year	Coal ($x10^{15}$g.)	Lignite ($x10^{14}$g.)	Petroleum ($x10^{13}$g.)	Natural Gasoline	Natural Gas ($x10^{13}$g.)	Cement ($x10^{12}$g.)	Total ($x10^{15}$g.)
1901	2.102	2.05	6.46		1.92	5.50	2.396
1902	2.150	2.01	7.00		2.04	6.00	2.447
1903	2.366	2.09	7.50		2.16	6.50	2.678
1904	2.380	2.18	8.40		2.26	7.00	2.712
1905	2.512	2.32	8.29		2.58	7.50	2.860
1906	2.713	2.49	8.21		2.84	8.00	3.081
1907	2.997	2.72	10.20		2.96	8.50	3.409
1908	2.837	2.82	11.00		2.94	9.00	3.267
1909	2.960	2.87	11.50		3.50	9.50	3.407
1910	3.096	2.89	12.60		3.72	10.00	3.558
1911	3.155	3.01	13.30		3.74	11.00	3.637

Year	Coal ($x10^{15}$g.)	Lignite ($x10^{14}$g.)	Petroleum ($x10^{14}$g.)	Natural Gasoline ($x10^{13}$g.)	Natural Gas ($x10^{14}$g.)	Cement ($x10^{13}$g.)	Total ($x10^{15}$g.)
1912	3.322	3.32	1.36		0.41	1.20	3.853
1913	3.564	3.44	1.51	0.03	0.43	1.30	4.115
1914	3.182	3.23	1.57	0.06	0.43	1.40	3.718
1915	3.134	3.30	1.66	0.06	0.46	1.50	3.692
1916	3.376	3.52	1.76	0.09	0.55	1.70	3.985
1917	3.561	3.60	1.94	0.21	0.58	1.80	4.193
1918	3.501	3.78	1.95	0.24	0.53	2.10	4.150
1919	3.047	3.55	2.18	0.30	0.54	1.80	3.695
1920	3.494	4.20	2.79	0.37	0.58	1.90	4.274

Year	Coal (x10^{15}g.)	Lignite (x10^{14}g.)	Petroleum (x10^{14}g.)	Natural Gasoline (x10^{13}g.)	Natural Gas (x10^{14}g.)	Cement (x10^{13}g.)	Total (x10^{15}g.)
1921	2.910	4.50	3.02	0.40	0.48	2.00	3.734
1922	3.111	4.88	3.37	0.46	0.56	2.00	4.016
1923	3.532	4.36	3.98	0.73	0.73	2.20	4.469
1924	3.484	4.62	3.97	0.82	0.83	2.42	4.459
1925	3.472	4.99	4.18	1.00	0.88	2.74	4.514
1926	3.449	5.01	4.29	1.22	0.97	2.94	4.517
1927	3.736	5.42	4.92	1.43	1.06	3.19	4.922
1928	3.651	5.86	5.18	1.61	1.15	3.40	4.920
1929	3.883	6.21	5.81	2.01	1.41	3.56	5.282
1930	3.566	5.27	5.52	1.98	1.32	3.38	4.731
1931	3.148	4.85	5.32	1.64	1.28	2.85	4.338
1932	2.799	4.54	5.08	1.37	1.19	2.30	3.917
1933	2.930	4.66	5.54	1.28	1.20	2.25	4.105
1934	3.188	5.11	5.85	1.37	1.37	2.70	4.462
1935	3.257	5.49	6.37	1.46	1.40	2.95	4.627
1936	3.663	5.48	6.88	1.58	1.62	3.53	5.148
1937	3.815	6.73	7.87	1.82	1.80	3.81	5.511
1938	3.557	7.05	7.67	1.92	1.72	3.96	5.260

Year	Coal (x10^{15}g.)	Lignite (x10^{15}g.)	Petroleum (x10^{15}g.)	Natural Gasoline (x10^{13}g.)	Natural Gas (x10^{14}g.)	Cement (x10^{13}g.)	Total (x10^{15}g.)
1939	3.774	0.780	0.803	1.95	1.84	4.23	5.603
1940	3.994	0.852	0.821	2.10	1.99	3.82	5.925
1941	4.166	0.884	0.784	2.40	2.10	4.28	6.111
1942	4.187	0.892	0.739	2.43	2.29	4.10	6.112

Year	Coal (x10^{15}g.)	Lignite (x10^{15}g.)	Petroleum (x10^{15}g.)	Natural Gasoline (x10^{13}g.)	Natural Gas (x10^{14}g.)	Cement (x10^{13}g.)	Total (x10^{15}g.)
1943	4.190	0.930	0.809	2.49	2.56	3.67	6.246
1944	4.040	0.844	0.910	2.71	2.78	3.01	6.130
1945	3.481	0.500	0.961	2.95	3.04	2.40	5.300
1946	3.563	0.684	1.057	3.10	3.14	3.67	5.686
1947	4.026	0.732	1.163	3.25	3.48	4.14	6.343
1948	4.187	0.800	1.315	3.56	3.92	4.90	6.708
1949	3.932	0.886	1.309	3.71	4.14	5.56	6.634
1950	4.260	0.963	1.470	4.13	4.79	6.24	7.276
1951	4.465	1.059	1.664	4.44	5.67	7.00	7.869
1952	4.392	1.130	1.751	4.56	6.09	7.47	8.002
1953	4.395	1.202	1.849	4.77	6.40	8.26	8.216
1954	4.322	1.319	1.941	4.92	6.77	9.09	8.399
1955	4.680	1.429	2.174	5.36	7.36	10.20	9.175
1956	4.940	1.508	2.365	5.41	7.97	11.11	9.775
1957	5.079	1.584	2.491	5.38	8.68	11.59	10.192
1958	5.318	1.635	2.548	5.48	9.39	12.42	10.619
1959	5.538	1.647	2.750	5.65	10.48	13.81	11.178
1960	5.807	1.705	2.961	5.96	11.77	14.78	11.858
1961	5.295	1.767	3.154	6.35	12.32	15.70	11.569
1962	5.427	1.826	3.421	6.55	13.45	16.93	12.254
1963	5.636	1.917	3.669	7.14	14.70	17.80	12.941
1964	5.838	1.995	3.962	7.92	16.04	19.49	13.673

Year	Coal ($\times 10^{15}$ g.)	Lignite ($\times 10^{15}$ g.)	Petroleum ($\times 10^{15}$ g.)	Natural Gasoline ($\times 10^{13}$ g.)	Natural Gas ($\times 10^{15}$ g.)	Cement ($\times 10^{14}$ g.)	Total ($\times 10^{15}$ g.)
1965	5.983	1.981	4.248	8.33	1.715	2.04	14.214
1966	6.085	1.970	4.612	8.62	1.859	2.18	14.830
1967	6.228	2.003	5.086	8.97	2.012	2.28	15.647
1968	6.446	2.056	5.620	9.27	2.163	2.40	16.618
1969	6.651	2.136	6.182	9.58	2.309	2.54	17.628

APPENDIX C

COMPUTER PROGRAMMES

The following computer programmes were used in the theoretical studies associated with this research project; with the assistance of the Computing Department, Glasgow University they were programmed in Algol language for use in the K.D.F.9 computer.

(1) Programme for Determination of Best Straight Line Fit Through Observed Points.

```
begin  comment  This programme works out m and c for the
           equation y = mx + c by least squares from n
           pairs of x and y and gives the rms error
           (sqrt([v↑2]/(n - 2) ) plus the individual
           deviations in y ;

integer  n, i, p;
real  sx, sy, sxy, sx2, sy2, m, c, d;
open(20);  open(70);
start:  n:= read(20);
begin  array  x,y, e [1:n];
sx:=sy:=sxy:=sx2:=sy2:=0.0;
for i:=1 step 1 until n do
begin  x[i]:= read(20);
       y[i]:= read(20)
end;
for i:=1 step 1 until n do
begin sx:= sx + x[i];
      sy:= sy + y[i];
      sxy:=sxy + x[i]×y[i];
      sy2 := sy2 + y[i]↑2;
      sx2:=sx2 + x[i]↑2
end;

d:= n×sx2 -sx↑2;   m:= (n × sxy -sx × sy)/d;
c:= (sx2 × sy - sx × sxy)/d;
```

```
d:= sqrt((sy2 - sy × c - sxy × m)/(n - 2));

for i:= 1 step 1 until n do
  begin

  e[i] := y[i];
  y[i] :=  y[i] - m × x[i] - c
  end;

write text (70, [[4c] m*=*]);
write (70, format ([-d.ddddd₁₀-nd]), m);
write text (70, [[3s]c*=*]);
write (70, format([-d.ddddd₁₀-nd]), c);
write text (70, [[3s] rms*error*=*]);
write (70, format ([-d.ddddd₁₀-nd]), d);
write text (70, [[3c][6s]y*obs[8s]y*calc [7s]deviation[2c]]);
for i := 1 step 1 until n do
  begin
    write (70, format ([2s -d.dddd₁₀-nd]), e[i]);
    write (70, format ([3s -d.dddd₁₀-nd]), m × x[i] + c);
    write (70, format ([3s -d.dddd₁₀-ndc]), y[i])
end;
comment  if another set of data is to
follow punch 1 otherwise 0;

p := read (20);
if p = 1 then goto start;
close (70);
close (20);
comment The data tape consists of n followed by n pairs of
    values of x and y.  A 1 is punched after each set of n
    pairs if another set follows, and a zero after the
    final set;

end   end   →
```

(2) Programme for Estimation of the "Suess effect"

```
begin comment  This programme works out the
yearly fossil CO2 content of atmosphere
and oceans(BETA and GAMMA resp) resulting
from the annual release of ALPHA inactive
CO2 to the atmosphere for all combinations
of exchange rates k1,k2 and k3;
integer i,fa,fb,fc,fd;
real kone,ktwo,kthree,alpha,beta,gamma;
real array ALPHA,BETA,GAMMA[1860:1969];
open(20);
open(70);
fa:=format([snd.ddd]);
fb:=format([sssdddd]);
fc:=format([ssndddd.ddd]);
fd:=format([sssndddd.dddc]);
for i:=1860 step 1 until 1969do
ALPHA[i]:=read(20);
for k one:=0.33,0.20,0.143,0.10,0.05,0do
for k two:=0.50,0.20,0.10,0do
for k three:=0.05,0.10,0.20 do
begin write text(70,[[p]K*ONE*=*]);
write (70,fa,k one);
write text (70,[*****K*TWO*=*]);
write (70,fa,k two);
write text (70,[*****K*THREE*=*]);
write (70,fa,k three);
new  line (70,2);beta:=gamma:=0;
write text (70,[***YEAR******ALPHA*******BETA******GAMMA[cc]]);
for i:=1860 step 1 until 1969 do
begin alpha:=ALPHA[i];
GAMMA[i]:=(gamma +(alpha + beta )×k one) ×
          (1.0 - k two - k three);
BETA[i]:=beta:=(alpha+beta)×(1.0-k one ×(1.0-k two))+
                   gamma×k two;
gamma:=GAMMA[i];
write (70,fb,i);
write (70,fc,alpha);
write (70,fc,beta);
write (70,fd,gamma)
end close(20);close(70)
comment The data tape consists of the annual CO2 input
data (expressed as percent of natural atmospheric CO2
content); the output gives ALPHA,BETA and GAMMA values
for each year
end end→
```

(3) Programme for Determination of Best Exponential Fit Through Observed Points

```
begin comment This programme estimates by regression
 analysis the best values for A and k in the expression
 y=Aexp(-kt) within a given range of k values to fit
 n observed points;
 integer k,j,i,n,f1,f4;
 real sum1,sum2,a,a1,b1,d1,c1,s;
open(20); open(70); k:=read(20);
for j:=1 step 1 until k do
begin n:=read(20);
begin real array x,y,e1,e2[1:n];
b1:=read(20);
d1:=read(20);
c1:=read(20);
for i:=1 step 1 until n do
begin x[i]:=read(20);
      y[i]:=read(20)
end;
for a1:=b1 step d1 until c1 do
begin sum1:=sum2:=0;
for i:=1 step 1 until n do
begin sum1:=sum1+exp(-2×a1×x[i]);
      sum2:=sum2+y[i]×exp(-a1×x[i])
end;
a:=sum2/sum1;
    s:=0.0;
for i:=1 step 1 until n do
begin e1[i]:=a×exp(-a1×x[i]);
       e2[i]:=e1[i]-y[i];
      s:=e2[i]×e2[i]
end;
f1:=format([7s-d.ddd₁₀+nd]);
f4:=format([10s-d.ddd₁₀+ndc]);
write(70,f1,a1);
write(70,f1,s);
write(70,f4,a)
end;
end;
close(20); close(70)
comment  The data tape consists of the number of
separate sets of data,then the number of pairs of
```

```
points,n,followed by the lower limit of k ,then
the increment in k desired, then the upper limit
of k, and finally the coordinates of the n points
(y,t);the output lists values of s , which is
related to the deviation between observed and calculated
points, so that the best values of A and k correspond
to the minimum value of s;
end end→
```

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SUMMARY

Natural fluctuations of atmospheric C-14 concentrations over time periods from several hundred to several thousand years are known to have occurred during the last 6 millenia. The fluctuations represent deviations from the basic assumption of the radiocarbon dating method and, although their origin is not fully understood, probably stem from the variation of one or more of the geophysical parameters which control carbon circulation. The scope of past studies was limited by the availability of complete series of samples of precisely known origin. Consequently it has not been possible to establish whether natural atmospheric C-14 concentrations are constant over shorter time periods of several years.

In this research annual variations of atmospheric C-14 concentrations over the past century have been studied through analyses of plant seeds, wines and spirits. Using exchange rate data obtained from recent investigations of the transport of artificial "bomb" C-14, the magnitude of the "Suess effect" during the past century has been assessed theoretically and compared with the experimental results. Predictions of the "Suess effect" to 2,025 A.D. suggest a marked

increase in atmospheric CO_2 concentrations to levels about 50% above natural. It is concluded that the enhanced infrared absorption in the atmosphere implied by such an increase may be sufficient to raise world temperatures by several degrees.

Correction of observed atmospheric C-14 activities for "Suess effect" dilution revealed that between 1890 and 1950 natural fluctuations appear to have occurred over the 11-year sunspot cycle in inverse correlation with solar activity. It is suggested that the origin of this correlation lies in the variable mixing rates of stratospheric and tropospheric air masses caused by modulation of the incident U.V. and corpuscular radiation over each solar cycle. A general decrease in atmospheric C-14 concentrations was also observed and is attributed to a reduction in the mean C-14 production rate through increased solar activity. The results therefore support theories of solar-sensitive atmospheric circulation. In addition they imply the probability of increased errors in radiocarbon age determinations and endorse the universal use of the N.B.S. modern standard in C-14 assay.