IAEA-116

INTERPRETATION OF ENVIRONMENTAL ISOTOPE DATA IN HYDROLOGY

REPORT OF A PANEL
SPONSORED BY THE
INTERNATIONAL ATOMIC ENERGY AGENCY
AND HELD IN VIENNA,
24-28 JUNE 1968

A TECHNICAL REPORT PUBLISHED BY THE
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FOREWORD

The following papers, oral contributions and discussions, were assembled informally by the Scientific Secretariat of the Panel Meeting on Interpretation of Environmental Isotope Data in Hydrology (Vienna, Austria, 24-28 June 1968). They have not been edited formally, so that minor changes have not been cleared with the original authors. They are reproduced for informal distribution as they may be helpful to hydrologists and others interested in the application of envieonmental isotopes in hydrologic studies.

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1. INPUT OF ENVIRONMENTAL ISOTOPES TO HYDROLOGICAL SYSTEMS

1.1 GENERAL PATTERNS OF DEUTERIUM AND OXYGEN-18 CONTENT OF THE PRECIPITATION. Summary of the contribution made by Prof. W. Dansgaard.

During the hydrologic cycle, the stable isotopic components of the water are exposed to several fractionation effects. One of these effects occurs because the vapour pressure of the light isotopic component, $H_2{}^{16}O$, is higher than the heavier components HDO and $H_2{}^{18}O$. Another important effect is the molecular exchange between water in the liquid and gas phases which is a complicated process. For several years IAEA has carried out, in cooperation with WMO, a collection of the precipitation samples in a world-wide network of about 110 meteorological stations. These samples have been measured for tritium, deuterium and oxygen-18 content, and the following discussion is based on these data.

Fig. (1) shows the mean oxygen-18 content [*] of the precipitation in January. The values presented are the weighted means of several January samples.

High oxygen-18 values are found in the mid-Atlantic and along the equator. The water which evaporates from the oceans condenses in such a way so that initially the oxygen-18 content of the precipitation is relatively high. As the condensation proceeds however, the water vapour and consequently precipitation originating from it is more and more depleted in oxygen-18. This is the main cause for the change in oxygen-18 with latitude seen in Fig. (1). A noticeable feature is a broad tongue of high values in the northern Atlantic. This, which is probably an indication of exchange between the atmospheric water vapour and the ocean surface is also supported by the low tritium values perhaps resulting from molecular exchange. However, the oxygen-18 and tritium variation over the northern Atlantic could also be correlated by the precipitable water over this region, which would tend to increase the oxygen-18 content of precipitation while decreasing the tritium content.

The "inland effect" is also illustrated in the same figure. In North America precipitation decreasing inland is accompanied by a decrease in oxygen-18 content of precipitation. The same trend is observed in South-America, South Africa and in Europe

This effect is also observed over the other high mountain ranges such as the Andes and Rocky Mountains of the American continent, and the Alps and mountains in Norway in Europe.

Fig. 2 shows the mean oxygen-18 content of the precipitation in July. The patterns are almost the same as those of January but show a shift of oxygen-18 content toward higher values. In the Indian Ocean high values of oxygen-18 can be explained by the fact that monsoon precipitation represents the first stage of condensation.

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[*] Expressed in relative deviation with respect to SMOW.

Fig. 3 shows the annual mean values for deuterium and oxygen-18 content of the precipitation for all the stations of the network. The correlation is linear and the slope of the line is 8. In arid zones the scattering can be explained partly by the kinetic effect introduced by the evaporating raindrops.

The location of the annual values on a line with slope 8 and a positive intercept is explained by the following process: The ocean water, when evaporated, produces a vapour which is lighter than the water vapour but which is in equilibrium with the ocean water. The difference is larger for oxygen-18 than for deuterium. Also upon condensation the water vapour produces precipitation which is in equilibrium with the vapour phase. Thus, the stable isotope composition of the precipitation is slightly lower than the ocean water, the difference being larger for oxygen-18 than for deuterium. When the process of condensation continues, both the water vapour and the precipitation composition move along a line with slope 8, which is defined initially by the water vapour originating from the oceans. The intercept of the line with deuterium axis is generally found to be + 10‰, but in certain regions intercepts higher than + 10‰ have been found. The above correlation is made among stations, but when monthly values of oxygen-18 and deuterium for a given individual station are plotted versus each other, a different regression line, which does not necessarily have the slope 8 nor the intercept + 10‰, is obtained.

Evaporation from water causes the enrichment of remaining water with respect to stable isotopes. When the initial isotopic composition of such waters is the same (as in raindrops), the evaporated waters are found on a δ_{18} - δ_D graph along a line passing by the composition of the original water with a slope less than 8.

The altitude effect was studied in Innsbruck (600 m), Austria, and a station 6 km from Innsbruck, Hafelekar, which is 700 m higher. The oxygen-18 content of the precipitation in June showed significantly lighter isotopic composition in Hafelekar precipitation. In these mid-Alpine regions precipitation is released from clouds nearly all at the same altitude so there should not be an orographic type altitude effect. Fig. 4 shows that the difference of the isotopic composition of the precipitation in Innsbruck and in Hafelekar is due to the evaporation. The intermediate values are from Honeburg, which is about 400 m higher than Innsbruck. The line joining Hafelekar and Honeburg values has a slope lower than 8, which indicates evaporation.

Fig. 5 shows the oxygen-18 content of the precipitation in winter in the same region. As expected, they are much lower than the summer values· the difference between Innsbruck and Hafelekar is not systematically positive, as it is in summar precipitation. This does not mean that there was no evaporation, or rather sublimation, from the precipitation in fall but it is due to the fact that sublimation from the snow flakes cannot bring the same type of fractionation as that from raindrops. In a snow flake or crystal sublimation takes place layer by layer, without any mixing process.

Fig. 6 shows the so-called amount effect in Kinshasa (Leopoldville), Congo precipitation which can also be used in hydrological studies. The oxygen-18 content of intense and long duration rains must be lower than the oxygen-18 content of less intense rains with short duration. Monthly precipitation is also given at the lower part of the figure. There is an antiphase correlation and a correspondence of maximum and minimum values for the amount of the precipitation and its oxygen-18 content. At higher latitudes the same amount effect is observed in summer as shown in Fig. 7 which shows the monthly precipitation and its oxygen-18 content in Tokyo. The amount effect vanishes in winter due to the solid state of the precipitation.

In polar regions the altitude effect is much greater than at the lower latitudes because no fractionation by evaporation can take place from solid precipitation. At higher latitudes the altitude effect for oxygen-18 amounts to 0.6‰ per 100 meters of altitude difference. At low and mid-latitudes the altitude effect is 0.2‰ per 100 meters.

1.2 ENVIRONMENTAL ISOTOPE VARIATIONS IN THE PRECIPITATION, SURFACE WATERS AND IN TREE RINGS IN CANADA.

Summary of the contribution made by R.M. Brown.

1.2.1 Deuterium in Precipitation and Surface Waters

A survey of the deuterium content of precipitation and surface waters across Canada is under way. Precipitation from 15 precipitation stations and river waters from 100 sites are being analyzed every second month for a two year period. Measurements to date show that seasonal variability is not more than ± 2 ppm in surface streams in spite of being up to ± 10 ppm in precipitation. Fig. 8 shows concentrations observed in December 1967. Concentrations are expressed relative to SMOW - 157.6 ppm derived from recent absolute calibration work in our laboratory.

Main features of the distribution of deuterium across Canada are:

(a) High concentrations in the east and west coastal regions with a sharp drop inland from the west coast because of the Rocky Mountains.

(b) Low concentrations in northern Canada where temperatures are low, and central Canada which derives its moisture from northern air masses.

(c) High concentrations in the Great Lakes where a long residence time affords opportunity for extensive evaporative enrichment.

Figures 9 and 10 show deuterium concentrations along the drainage systems of central Canada and the Great Lakes - St. Lawrence River. The latitude effect is apparent in the Saskatchewan Rivers - high deuterium in the South Saskatchewan River, low deuterium in the North Saskatchewan River. The concentration increases in Lake Winnipeg because of the admixture of water from southern Manitoba originating in the Gulf of Mexico - Mississippi Valley air mass system. In the Great Lakes - St. Lawrence system, local precipitation and tributary streams have lower deuterium than the main stream indicating enrichment has occurred in the Great Lakes. An enrichment of 2 ppm occurs across Lake Erie. Lower concentrations are observed down the St. Lawrence River where the admixture of local drainage, much of it from the north. dilutes the Great Lakes deuterium.

1.2.2 Storm-to-storm Variation of Tritium and Deuterium in Precipitation

Figure 11 shows the storm-to-storm variability of deuterium and tritium in Ottawa precipitation, 1961. An inverse correlation of the deviations of individual tritium and deuterium values from their respective mean curves is observed. Studies of air mass trajectories show that the high tritium and low deuterium values are associated with air masses of northern origin, low tritium and high deuterium with air masses of southern origin.

1.2.3 Tritium in Tree Rings

The distribution of tritium in the annual growth rings of trees has been investigated as a possible means of learning the history of tritium deposition at sites for which past data is not available. The method involves mechanical separation of individual rings, chemical separation of cellulose, removal of any labile tritium (the three hydroxyl hydrogens of the cellulose unit) by boiling in 0.5 N HCl solution made up with tritium-free water, combustion of the dried cellulose, electrolytic enrichment and low level counting.

Trees growing in tritiated groundwater in the CRNL Liquid Disposal Area were examined first to see if recent tritium was incorporated in older wood. Figure 12 shows the pattern observed. Although the high tritium concentrations of recent years penetrated the tree moisture back to 1945, it was not incorporated in cellulose formed prior to the time of its appearance in groundwater of the area. This work gave the history of tritium dispersal in this area.

Somewhat in contradiction to the foregoing, we have not been able to obtain values less than 50 TU on 1920-30 wood grown at an uncontaminated site. For the present, we have accepted this as a background level which we subtract from the measured concentrations of more recent rings to deduce the tritium pattern of the thermonuclear period. Figure 13 compares concentrations observed in a tree grown on well-drained, sandy soil at Deep River with mean concentrations of Ottawa precipitation for the growth period of each year. Excess tritium appears in the rings of 1960, 61, 62, but evidence from a few Deep River precipitation samples indicates that some reactor tritium from CRNL (6 miles downwind) was deposited at Deep River at this time.

1.2.4 Perch Lake Evaporation Study

It was reported that P.J. Barry and W.F. Merritt are making an extensive study of evaporation from a small lake at Chalk River. Perch Lake has been uniformly labelled with about 0.5 μCi/l tritium as a result of reactor liquid waste disposals. Absolute measurements of evaporation can be obtained by observing HTO vapour profiles over the lake. The site is fully instrumented for meteorological and hydrological measurements to obtain evaporation data by the various conventional methods (e.g. pan evaporation, water and energy budgets) for comparison with the tritium results. It was suggested that it would be valuable to make deuterium measurements in the course of this work to learn more about D/H fractionation in natural evaporation.

1.3 Discussions on the factors affecting the environmental isotope content of precipitation.

The most important "effects" to be used in hydrological work were the so-called "altitude", "inland" and "temperature" effects, due to the rather local nature of the most hydrological and hydro-geological problems. The basic relation to be studied was the temperature effect because this is probably the cause of the altitude and latitude effects.

Temperature however, is closely related to the moisture content of the air, i.e. the lower is the temperature the lower is the capacity of the air to hold moisture. Therefore, the stable isotope content - temperature relation has an intermediate step, namely, the moisture content of the air. Air with a low moisture content is expected to contain less deuterium and oxygen-18 because, starting from its production in oceanic environments it should have gone through several processes of condensation and consequently of depletion with respect to stable isotopes. On the other hand, the influence of temperature on the value of the fractionation factor is a negligible secondary effect which would be difficult to detect even in the condensation of water in nature.

In arid regions in the lower latitudes, evaporation of the raindrops during their fall is important and affects the stable isotope content of the precipitation. The initial stable isotope content of the raindrop can be modified considerably toward heavier values during its fall. Precipitation on the southern slopes of the Sierra-Nevada Spain and the Taurus, Turkey, mountain ranges shows a significant altitude effect as well as some deviation from the equilibrium line.

A question was raised concerning the antiphase variation of the tritium and deuterium content of the Canadian precipitation. The cause of this antiphase correlation could be that the storms with high turbulence contain more stratospheric air with high tritium and low deuterium content. However the meteorologic investigations, which were carried out together with these isotope studies, indicate that this variation could only be due to the different sources of moisture.

A more general explanation of this antiphase correlation between tritium and deuterium content of the precipitation (which is observed in almost every region of the world) can be made by considering the moisture content of the atmosphere. Dry polar air masses are likely to contain moisture with high tritium content and low deuterium content. On the other hand, oceanic moist air masses have low tritium content and high deuterium content, reflecting their immediate marine origin. When such problems are studied it is important to start with factors, such as temperature, moisture content, and to also consider the origin of the air.

In many actual applications of the environmental isotopes, meteorologists and hydrologists are interested in the time variations of the isotopes at a given locality. The negative correlation between the tritium and deuterium contents of the precipitation raises interesting questions, such as the mechanism of atmospheric vapour transport. The fluctuations about the recession line probably represent the local effects. The overall effect can be obtained by the superposition of the flux or the vapour transport effect with the local effect. This might lead to the quantitative evaluation of the both, provided a proper model is chosen.

1.4 Discussion of the variations of tritium content of the precipitation in Scandinavian precipitation, by E. Eriksson

As there is only a limited number of precipitation stations where tritium has been measured for more than several years it is necessary to correlate the tritium content of the precipitation in stations with short tritium records with neighbouring stations having longer records.

The tritium-precipitation network in Scandinavia is extensive and has operated collecting monthly samples since 1961. It is possible to calculate the annual mean values of tritium in the precipitation and doing so to remove the seasonal variation. In the present analysis the Stockholm (Huddinge) meteorological station, which belongs to the WMO/IAEA network, was used as a benchmark.

There are a number of other stations in Sweden where samples for tritium are collected and 10 of these stations have 6 years of tritium record as does Huddinge station. The ratio of the annual mean tritium concentrations of these stations to the annual mean tritium concentrations at Huddinge were calculated. These ratios varied considerably, both from one place to another and one year to another. The lowest value was 0.64 and the highest was a little higher than 1.50. The purpose of this study was to find the error of the estimate of the mean annual tritium content of the precipitation using the annual tritium data in a neighbouring station. This can be done by using the well known analysis of variance technique with two ways of classification, which are classification by stations and classification by years.

Such an analysis allows elimination of the variations among stations and the variations among the years. The variability among years indicates broad changes in climate from year to year.

Table I shows the final analysis of variance. The estimates of variances made with respect to stations and years are very significant compared to the residual. This means that there is a difference of tritium deposition from one station to another but even more significant is the fact that the deposition pattern of tritium varies considerably from one year to another.

Table I

Table of Analysis of Variance

Origin of variation	D.F.	Variance estimate	f
Among stations	9	0.2470	16.41
Among years	5	0.1829	12.11
Residual	45	0.0151	

These changes affect all the stations in any region. The remaining variability can be explained as changes which affect only some stations, not all of them. The standard deviation of an individual estimate is 12%, of which approximately 5% results from analytical errors. If the above analysis were done on a monthly basis, the variability of "f" values would be higher. These results agree well with the results obtained by the chemistry of precipitation.

1.5 A GLOBAL SURVEY OF ENVIRONMENTAL ISOTOPE DATA.

By G. Lewis Meyer

The Data

Since 1961, monthly precipitation samples for the IAEA/WMO Isotopes-In-Precipitation Network have been collected at more than 100 meteorological stations in 67 countries and territories. To give the global coverage needed for a representative basic data network, stations at Argentine Islands in Antarctica Thule in Greenland, Uaupes in the upper Amazon Basin and Ouargla in the Sahara have been requested to cooperate. Fig. 14 shows the stations in the network.

Stationkeepers participating in the network collect and composite total rainfall for each month for tritium, deuterium and oxygen-18 analysis and bottle half-litre and 20-ml samples of the composite for tritium and for deuterium-oxygen-18 analysis respectively. The deuterium-oxygen-18 samples are shipped to Copenhagen for measurement under a contract from the IAEA with the Oersted Institute, University of Copenhagen. Approximately half of the tritium samples and selected weather data from all network stations are sent to the IAEA Laboratory in Vienna for analysis. The remainder of the tritium samples are forwarded to cooperating tritium laboratories in Canada, India, New Zealand, Sweden and the USA for analysis. Supplementary isotope data are received by the IAEA from other tritium laboratories in France, Germany, Iceland, the United Kingdom and the USA.

The IAEA acts as a collection and coordinating agency for the isotope and meteorological data necessary for hydrologic investigations. It has published the data at regular intervals. Data now (1968) included for each monthly sample are tritium, deuterium and oxygen-18 content, type and amount of precipitation, and mean temperature and relative humidity. These data are now computer-compatible and are available upon request on magnetic tape in the Fortran format. All old isotope and meteorological data available will be reissued in yearly blocks in a format prepared by the computer. These will begin to appear late in 1968 and new data will be issued yearly.

Similar but less extensive networks for collection of river and ocean water samples for isotope analysis have been established within the framework of the IHD. Two networks, one of 21 major river stations and the other of 11 ocean stations, collect regular monthly instantaneous samples. As the programming workload permits the data will be integrated into a common computer storage system for an "isotope-in-water" data file along with the precipitation data.

1.6 Discussion.

Some questions raised in the discussions were·

Is the monthly sampling really necessary?
Would a weighted composite annual sample be satisfactory in environmental isotope studies in hydrology?

These questions, it was suggested, could be partly answered if the existing data are properly analyzed and interpreted, depending in part on the type of application of the environmental isotope data. Averaging is a good practice if done in the bottle. It was also pointed out that the theory of sampling could supply part of the answer on the frequency of sampling: If the frequency spectrum of the tritium output is considered it is seen that many fast molds are damped by the hydrologic system, so that there is no point of collecting very frequent samples in the input. However one should also be careful to collect environmental isotope data to handle unforeseen situations and problems which may arise in the future.

The use of environmental isotopes in hydrometeorological and groundwater studies requires different sampling methods. In hydrometeorological work a high frequency of sampling the precipitation and broad areal coverage are necessary due to the high variability of the environmental isotope content of the precipitation both in time and space. On the other hand, the groundwater hydrologists normally require only the mean isotope input to the groundwater systems. This can be obtained from the mean values for the isotope content of the precipitation if collected when the precipitation is closely related to the recharge to the groundwater. This is valid only in some regions where the precipitation is concentrated in a well defined period of the year (examples: mediterranean and monsoon climates). In Europe for example, the summer precipitation probably seldom reaches the groundwater and is largely transpired by plants. Thus the isotopic composition of only the winter precipitation, in such a case should be considered if a relation is sought between the isotopic composition of the precipitation and the groundwater. Monthly sampling is needed, therefore, to estimate the input concentrations with more precision.

Quarterly sampling was also proposed as a compromise between the requirements imposed by the cost of the analysis and the reliability of estimates of the environmental isotope input concentrations to the hydrologic systems.

1.7 THE RELATIONSHIP BETWEEN ISOTOPIC COMPOSITION OF PRECIPITATION AND LYSIMETER PERCOLATES.

By. E. Halevy

1.7.1 Introduction

Realizing the importance of climatic and pedologic conditions on the quality and isotope composition of water in the unsaturated zone, the International Atomic Energy Agency set up a cooperative programme to study the changes in and relationship between precipitation and soil water, as reflected in the composition of lysimeter percolates. Lysimeter stations were selected to represent a broad spectrum of climates and soil conditions. This paper presents and discusses results from lysimeter stations for which data accumulated for at least two years. Results of other stations will be published when more data becomes available. Although two years may not be enough for conclusive studies of this nature, the data accumulated so far have interesting implications which may stimulate similar studies elsewhere.

1.7.2 Description of lysimeters and sampling methods

Each lysimeter was at least 2 x 2 x 2 meters (except Petzenkirchen), kept under natural regime (with one exception, Taastrup, discussed later) including natural drainage (without suction).

Juprelle, Belgium (50°41'N 5°26'E); filled with a loess soil, texture clay loam, good drainage (krilium added to ensure good drainage).

Mol, Belgium (51°11'N 5°7'E); sandy white soil. Excellent drainage. Data for this lysimeter are available for one year only. However, results are included for comparison with Juprelle and other stations.

Taastrup, Denmark (55°39'N 12°18'E); sandy soil covered with alfalfa. In summer 1967 the lysimeter was irrigated. Samples of irrigation water were taken and regarded as "precipitation" for the purpose of the present study.

Coshocton, Ohio, USA (40°16'N 81°50'W); constructed in a silt loam residual soil (Muskingum series, a Gray-Brown Podzolic soil) on a slope of 23.2%. Good drainage, covered with pasture grass. Lysimeter Y101A was not fertilized whereas Y101C was fertilized. In operation since 1944.

Petzenkirchen, Lower Austria (48°6'N 15°12'E); size 1 x 1 x 1.3 m, filled with colluvial brown loam. Lysimeter 1 has no cover and developed spaces between well and monolith. Lysimeter 3 is grass covered. In operation since 1953.

Precipitation was collected on site, in a standard rain gauge. Water collected during one month was combined for a weighted average. The lysimeter percolates, with one exception, were collected in a covered container, mixed at the end of the month for a weighted sample. In Coshocton, the lysimeter data represent water collected on the last day of each month.

Results and discussion

The results are shown in Figs. 15 - 18. There are several common features to all data worth pointing out:

(a) Except in Mol, a pure sand lysimeter. the isotopic composition of the percolates show a relative degree of stability, not reflecting the annual or seasonal variations.

(b) The weighted yearly average of stable isotopes in the percolate is depleted with respect to the precipitation.

(c) The tritium curves are receding. as a function of time, in a regular manner resembling the atmospheric recession.

(d) The weighted yearly averages of tritium concentration in the percolate is higher than that of the precipitation.

Tritium Data

The main features of the tritium data are the recession trend and the difference between the weighted averages of the precipitation and percolation. Although the percolate tritium line shows in most cases a large degree of buffering caused by mixing and dispersion in the soil, the distinct recessive trend indicates vertical flow that keeps a temporal identity.
The degree of buffering and the turn-over time depend on soil texture and are more pronounced in loamy textured soils than in sandy soils.

Owing to the present moratorium on atmospheric nuclear testing, tritium in the atmosphere is characterized by recession following the 1963-4 peak.

The higher than average concentration of tritium in the percolate in comparison with the precipitate indicates that the bulk of the percolated water is infiltration from the previous year or even earlier. The longest set of data on tritium is provided by Petzenkirchen. Here, we find also the only exception; 1965 tritium values in the percolate are lower than the assumed average of the precipitation (the assumed value was reached by comparing the yearly weighted averages Vienna and Petzenkirchen. Vienna values in 1966 and 1967 were 20 TU higher. In 1965 the average for Vienna was 876 and thus a value of 850 was chosen for Petzenkirchen. This value seems to be reasonable from the Petzenkirchen data available for the period April-December 1965).

If this peak is an actual reversal of the generally observed trend, it may belong to the peak year of the percolate activity and thus give us a rate of movement of 2 years because the atmospheric peak of tritium in Vienna occurred in 1963. However, it is possible, as will be discussed from stable isotopes data, that computations based on yearly averages are not correct in all cases. The stable isotopes data, in cases where the precipitation - percolation ratio is high, are strongly biased towards winter precipitation. As observed, tritium values in winter precipitation are generally lower than in spring and early summer. The weighted average for the following winters (October-March) are:

year	precipitation	percolation
1963/64	1772 TU	-
1964/65	577	~ 750
1965/66	303	~ 650
1966/67	208	~ 400

These comparisons show further that at least a one-year delay occurs unless there is an immediate effective percolation of spring-summer precipitation which raises the average tritium concentration in the percolate. In Austria the summers of 1965 and 1966 had excessive rain falls. This may explain the relatively high values for percolate 1965/66 which otherwise should be interpreted as originating prior to 1964/65: and the same may be said for 1966/67 which show a pre 1965/66 value.

In Juprelle the weighted average for the percolate in 1967 is slightly lower than the precipitation of 1966 and thus indicates a delay of about one year. In Taastrup the weighted averages of percolate and precipitate are close to each other and in 1966 they are equal. Thus, if the average for the whole year is considered, the turn-over time is less than one year. However, the sharp decline in composition of June 1967 caused by application of irrigation water which was followed by low values in July and August, does not show up in the percolate of the end of 1967 and thus the turn-over time may be longer than half a year, but less than a full year.

Stable isotope data

Here too, in spite of the highly fluctuating input values, the output exhibits a large degree of stability. In no case does the deviation from the weighted mean exceed one delta unit for ^{18}O. (Note: Deuterium values are not shown because they follow the same general pattern. However, the relationship between D and ^{18}O is in some cases very useful and will be discussed separately).

Assuming that the years under consideration represent the normal climatic conditions, it is then possible to use the stable isotopes data to compute the relative contribution of winter and summer input to the percolate since its average composition reflects the weighted mean of the effective infiltration.
For instance, the Coshocton data for the period 1966 and 1967 shows:

Weighted average of percolate		- 9.5‰
" "	of winters (Jan/Mar, Oct/Dec)	- 11‰
" "	of summers (Apr.-Sept.)	- 5.7‰

Had the percolate consisted only of winter input, its composition should have been different. If, however, we attribute 70% of winter input and 30% of summer the actual composition is the outcome. As discussed above, there exists an average delay of at least one year between input and output and thus such calculations are only justified if the previous years were not substantially different from 1966/67. An attempt to compare the tritium data of Coshocton and Chicago in order to obtain past records for Coshocton showed a poor correlation and could not be applied to this case. As a test the assumed 70-30% effective input was applied to the 1966 tritium data in Coshocton in order to predict the 1967 percolate composition. This resulted in a calculated value of 288 TU against the actual value of 313 TU. This may either be caused by a longer delay period (higher values in 1965) or larger summer contribution. The second assumption is not consistent with the stable isotope data. The same analysis for Juprelle shows an equal contribution of winter and summer. The application to tritium data results in a discrepancy of 40 TU (actual is lower than calculated). In Taastrup both tritium and stable isotope averages for input and output are close to each other and this type of calculation cannot be applied.

1.8 Discussion of the lysimeter studies.

It was reported that similar tritium output curves were obtained in lysimeter experiments made in Heidelberg, Federal Republic of Germany. The considerable smoothing of the tritium in the lysimeter percolates was first attributed to mixing, but soil cores showed that there was no significant mixing of water layers having different tritium contents, although some smoothing due to diffusion did occur. The second effect, which is much more important, is the preferential intake of the precipitation falling during different periods of the year. The summer rains, with high tritium content, are more or less consumed by the plants and do not reach the lysimeter bottom. The same is true also for late winter and spring precipitation. The early winter precipitation, which has relatively low tritium content, does reach the lysimeter bottom. In the lower part of the lysimeters, the capillary fringe may also contribute to the smoothing of the tritium variations. The process of movement of soil moisture is a complicated one; the mean passage time depends on the moisture content and on the depth of the lysimeter. The smooth curves of tritium which have values close to the annual mean tritium concentration in precipitation, are not due to the mixing they result from a process of selecting the precipitation which has a tritium concentration not very different from the annual mean.

Isotope data may provide valuable information on moisture movement in the soil, even in cases where basic hydrological data are missing. If a system is stable, and if deuterium and tritium contents of the precipitation and the percolate are available, information on the evaporation and mass transfer are not necessary.

The method of accounting for moisture can also be used to solve problems of soil moisture movement. In this method, however, the physical mechanism of the moisture transfer cannot be studied. It is possible to use both methods, i.e., moisture accounting and variations of the environmental isotopes in the input and output of the lysimeter study area. Certainly more information can be obtained in this way. The major objective of the lysimeter studies was the investigation of changes in the isotopic composition of the water between its infiltration into the soil and its percolation into the zone of saturation. In this way the environmental isotope data of the precipitation can be used to estimate the isotope content of the input or recharge to groundwater systems.

Also reported were studies on large lysimeters (400 m^2 surface area and 4 m deep). Three lysimeters having different plant covers are being studied with particular emphasis on C-14 analysis but samples are collected also for analysis of tritium and deuterium content of the water. Such studies require long periods of time because the water percolates very slowly in the lysimeters.

1.9 THE USE OF ENVIRONMENTAL ISOTOPES IN INFILTRATION STUDIES.

BY L. Thilo and K.O. Münnich.

H-3 and C-14 in shallow groundwater

The rise of both ^{3}H and ^{14}C concentrations in nature due to the atmospheric tests of nuclear weapons opened the way for a number of useful applications in which these radioactive isotopes are used as tracers. In particular, the way in which the increase of the ^{3}H (as well as that of ^{14}C concentration) are reflected in shallow groundwater can be used to check the reliability of ^{3}H and ^{14}C ages of groundwater. Under favourable conditions bomb-produced tritium in uppermost groundwater also allows a determination of the recharge rate.

The validity of the isotope ages is based on a comparison of the bomb increase of both isotopes in the groundwater. An older age from ^{14}C data than from ^{3}H means that there has been exchange in the ^{14}C with carbonate compounds in the transit of water from the land surface to the groundwater sampling point. The average recharge rate, on the other hand, is determined by comparison of the total bomb tritium found in the upper groundwater with the average tritium concentration in post-bomb rain. The principles and the conditions for application and preliminary results in a few cases are given by Münnich /̅1_7. With the technique described in detail elsewhere extensive sampling has been done in the area of Sandhausen (Rhinevalley near Heidelberg). A tritium profile taken at the same place previously has been reported by Münnich /̅1_7. At that time a specially drilled observation well in which a filter tube had been blocked by rubber balloons, thus confining a certain depth interval, was sampled. All tritium depth-profiles obtained are shown in Fig. 19. The total amount of tritium found below the water table (integral under TU vs. depth-curve) for the individual profiles is given in Table I.

Table I

Sandhausen a, b, c and d

Site,	Date	TU x meter/ε	Depth of half value below water table
a	IX, 67	900	2.3
a	XII, 67	1160	2.8
a	I, 68	1360	3.0
b	X, 66	1220	3.5
b	VI, 67	980*)	?
b	XII, 67	1390	3.2
c	I, 68	1020	2.0
d	III, 68	1310	4.2

*) admixture from below during sampling

In Table I the variations with sampling site as well as with the sampling date are larger than was originally expected. Although the values for site A (Fig. 19a) seem to be rising with time, this increase is too rapid to be attributed to the continuous tritium input by recharge. That recharge is not the cause of the increase can also be seen from the shape of the curves in Fig. 19a where only the upper part of the curves is pushed down whereas the lower part is similar. The differences from one sampling site to another are not as serious as one might assume in view of possible inhomogeneities in the aquifer. Although the sampling sites are quite near to each other (from 10 to 20 meters) small scale irregularities could still have an influence, since the flow velocity of the groundwater is only a few centimetres a day. The slight indications of peaks or other details in the individual profiles may also be attributable to small irregularities in the aquifer. Although it is tempting to ascribe such peaks to the corresponding variations of tritium concentration in rain, it is unlikely that such an effect would still be observed after the water has been flowing in the aquifer for almost ten years. Nevertheless, with the obtained recharge rate of 170 mm/year and an assumed porosity of $\varepsilon = 0.35$, the variations of tritium-concentration in rain, if "projected" into the aquifer are shown in Fig. 20. The sampling technique proved not to result in a vertical mixing of water in the aquifer even if larger samples are taken for ^{14}C measurement. (See Fig. 19d). To determine the recharge rate by measuring the tritium accretion in groundwater, it is necessary to take more than one tritium-profile to determine an average value for the tritium amount. From all the profiles measured in Sandhausen an average value of (1200 ± 180) xε-TU metre -*) below the water table is obtained. ε is the porosity. The standard deviation of 15% is not too serious if compared to uncertainties in the porosity and moisture content above the water table.

The rise of ^3H concentration in shallow groundwater can be compared with that of ^{14}C. Since the laboratory experiments with aquifer material from Sandhausen indicate a surface-layer carbon exchange taking place between the solid and liquid phase, this should also occur in nature, as the material we used in the column was untreated. As was explained in [1], such an exchange would not influence equilibrium conditions where the surface layer of the solid has been loaded to equilibrium with ^{14}C. In the case of a rising ^{14}C concentration in the water, however, the establishment of a new exchange equilibrium results in the same delay effect as observed in the column experiments. This effect can be sought by comparing the increase of ^3H and ^{14}C concentrations of groundwater at different depths.

Samples for ^{14}C analysis were taken in the same way as samples for tritium. Since larger samples are needed (60 liters for groundwater of medium hardness approx. 200 m mole of CO_2 are needed for the measurement) care must be taken to prevent vertical mixing in the aquifer during sampling. In the initial sampling technique with the moveable filter such mixing did occur, as has been shown by tritium measurement of the same samples (see profile of June 66 in Fig. 19b). With the new sampling technique (sampling downwards) no such mixing occurred (tritium values in Fig. 19d). The depth profile of ^{14}C concentration

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*) the uncertainty in ε causes an additional error in the total amount of tritium in the groundwater.

in the groundwater is shown in Fig. 21. The profile for June 67 corresponds to sampling site of Fig. 19b and that for March 68 to Fig. 19d. The values for the June 67 profile for 5 and 6 metres might be higher, since the tritium values indicated admixture from below. The ^{13}C values are indicated. As the undisturbed ^{14}C concentrations show, the initial value is around 60% whereas the values normally found for groundwater are around 85%. This indicates that the input of CO_2 into the groundwater happens in such a way that, after dissolution of $CaCO_3$ in the water containing CO_2 the resulting HCO_3 solution is no longer in contact with the CO_2 source. This is confirmed by the ^{13}C values being around - 11‰ (against PDB) instead of around - 16‰ where after dissolution of $CaCO_3$ the water remains in contact with the CO_2 supply. This raises the ^{14}C concentration from about 60% to 85% and causes ^{13}C to change from - 12‰ to about - 16‰. A depth profile of the $CaCO_3$ content of the aquifer in Sandhausen is shown in Fig. 22. As there is little $CaCO_3$ above the water table in the unsaturated zone, the CO_2 can reach the water table in the gas-phase by diffusion. It dissolves in the water causing dissolution of $CaCO_3$.

The exchange between the resulting HCO_3^- solution at the water table and the CO_2 gas phase is much less than it is between soil moisture and CO_2 in the unsaturated zone. This is due to (1) considerable diffusion resistance in the gas phase and (2) the absence of turbulence in the liquid. Thus, a liquid layer even of moderate thickness reduces diffusion to a minimum. Direct measurements of CO_2 concentrations in the unsaturated zone made by J. Fantidis resulted in values between 0.3 and 0.5% by volume. Such concentrations can keep about 3 m mole HCO_3^- and 0.2 m mole CO_2 in solution. The total carbonate hardness of the water as measured from the samples increased from about 3 m mole just below the water table to nearly 5 m mole 7.5 meters deeper (see Fig. 23). The $\delta^{13}C$ values of the CO_2 above the water table being - 22 and - 20‰ against PDB indicate the CO_2 to be from plant origin. The origin of the CO_2 is important when looking for a delay of ^{14}C increase in the groundwater. If from plant origin (humus), an additional delay of more than 2 years in the biosphere occurs. In Fig. 24 the ^{14}C increase in the atmosphere is "projected" into the groundwater with and without this delay of 2 years. Even without the two years delay no delay of ^{14}C incrase can be seen if compared to the ^{14}C input. With the half value-depth more than 3 meters below the water table, there also is no delay compared with the tritium profiles where the half value-depth is close to 3 meters below the water table also.

This result, on the other hand should not be surprising if one thinks of the delay factor (see this report and [1]) which is calculated as $\beta = 1.1$ for particle size 100 diameter, porosity 0.35, $CaCO_3$ content 15% and carbonate hardness of 3 m mole/litre. Even if this delay of 10% occurs one would not expect to observe it.

Reference

[1] K.O. Münnich et al., "Isotopes in Hydrology", p. 305
IAEA, Vienna (1967).

1.10 Discussion on the use of environmental isotopes in infiltration studies.

The first comment dealt with the horizontal groundwater movement. Because of the continuity requirement, one has to consider the horizontal movement of groundwater and the modification it would imply on the tritium and carbon-14 profiles. When the movement is slow, it does not distort much the profiles, as is probably the case in the aquifer studied: the hydraulic gradient is 2‰ and the groundwater velocity is estimated to be 20 m/yr.

A second comment pointed out that correction for the decay of tritium would improve the profiles presented in Fig. 19 and would lower tritium peaks. The method presented in the paper is based on the amount of tritium which goes to the groundwater rather than the identification of thermonuclear tritium pulses. The former approach is more conservative than the second, which uses the shape of the tritium profiles in the groundwater.

Similar profiles were observed also in two boreholes in the southern Vienna Basin. This suggests active recharge from above with high tritium content mixed with a horizontal contribution of groundwater flow that has a low tritium content. Although they give valuable information on the rate of recharge such studies are much more complicated than anticipated.

In ^{14}C measurements made in the U.S.A., in two wells 20 metres apart, one well going just below the water table, and the other considerably below, at about 25 metres, the ^{14}C data indicated the same age about 50% of the modern standard for both wells. When ^{13}C adjustments were made the ^{14}C of the shallow well came to 70% and the deeper one to 80% of the modern or more. This is rather a curious result as one expects younger water in the shallow well. Tritium results, however, confirmed the ^{14}C results. The tritium content of the water sample collected from the shallow well was 20 TU, and from the deeper one was 50 TU. This indicated that the area around the shallow well receives recharge much less readily than the area around the deeper well.

Fig. 23 shows that water at the water table has an appreciable carbonate content: this shows that solution has taken place in the non-saturated soil zone, a fact observed in other studies made in Germany also.

1.11 ENVIRONMENTAL TRITIUM IN SOIL MOISTURE AND GROUNDWATER IN DENMARK. Summary of the paper by Lars Jørgen Andersen.

Geography and Geology

The investigations took place in a representative area of Karup in the central part of Jutland Denmark (Fig. 25). Two wells were augered at localities with different geological and hydrological conditions. The first one Grønhøj no. 1 is in an unconfined aquifer of the outwashed sand and gravel of the last glaciation, which is the most common geological formation in the area. The land surface slopes slightly 1,2‰ to WSW and the depth to the groundwater is about 25 m below land surface. This well is located at the groundwater divide, the depth to water decreases toward a central stream which has a slope of about 1‰.

The second well is located near Engesvang in the southern part of the representative area, where the geological formations consist of the glacial drift, boulder clay from the Riss-glaciation and layers of meltwater sand. In the clay formation, a perched groundwater aquifer occurs from 5-10 m below land surface. Beneath this aquifer and the boulder clay is a water-table aquifer in the meltwater sand. The groundwater table here is about 25 m below land surface.

Drilling and sampling procedure

At two localities 6-inch wells were augered. Special care was taken to prevent water from entering the hole during drilling. The material was sampled every 20 cm and stored in sealed tin containers for later evaporation tests the weight of each sample was about 6 kg. Below the water table, water samples were taken by hammering a screen, half a meter down below the bottom of the hole, and pumping by compressed air. The groundwater was stored in glass bottles. The pumping was continued long enough before sample collection to obtain raw groundwater. The soil moisture from the unsaturated zone was later evaporated by distillation at 110 - 125°C. The samples were weighed before and after evaporation and the distilled water from the samples was weighted. The total loss in weight during the procedure averaged 1.8%. The water loss can probably be explained as a result of the effects of a vacuum water pump which was introduced in the procedure to accelerate distillation.

The volume of evaporated water varied from one sample to another depending on the moisture content, which varied from 150 - 1500 cm^3.

The number of samples, evaporated samples and analysed samples from each of the two wells are as follows:

NUMBER OF SAMPLES

	From the unsaturated zone			From the saturated zone	
	sampled	evaporated	analysed	sampled	analysed
Grønhøj no. 1	110	43	32	11	5
Engesvang	90	24	8	8	0

The tritium analysis has been made by the Danish Isotope Centre in Copenhagen by Mr. E. Mörck. The benzene method was used. The sensibility of this method is 10 TU and the standard error is ±5%. All the values of the tritium concentrations are given for December 1967.

The tritium profiles

The result of the tritium analysis is shown graphically on Figs. 26 and 27 together with a geological log and a moisture log. The moisture determinations were made by the neutron method.

No tritium determinations are available on precipitation samples from Danish stations during the previous years. Therefore, the values of Huddinge, Sweden, were adjusted with a factor of 0.85 and corrected for radioactive decay up to December 1967.

Values of precipitation at Grønhøj and estimated values of the difference between precipitation and evapotranspiration from January 1962 - March 1966 together with the above-mentioned adjusted tritium values from Huddinge are tabulated in Table I, and weighted average of tritium concentrations for the periods October - December, September-March and the year from February - February are tabulated in Table II. The low tritium content in the soil moisture below 18 m in the profile from Grønhøj may originate from precipitation from 1962 or earlier, and the three peaks may represent recharge from precipitation from the years 1963, 1964 and 1965. The low values in the upper two metres correspond to the precipitation values from October 1965 to March 1966.

If the calculated tritium concentrations for the precipitation at Grønhøj are correct, the tritium concentration of the soil moisture shows that the recharge may originate partly from precipitation in the summer time too. It can be seen from Tables I and II that the tritium concentrations of the precipitation from wintertime are too low during the years 1962 - 1965 to produce the registrated tritium content of the soil moisture. From Table I it can be seen that an excess in precipitation (the volume of precipitation minus the volume of evapotranspiration) normally exists in all months except June and July. This should also indicate that the possibilities of recharge to the groundwater or to the deeper parts of the unsaturated zone is possible during most of the year in the investigated area.

In the profile from Engesvang (Fig. 27) the low content of tritium in the unsaturated zone below the perched aquifer indicates that only small amounts of water infiltrate to this depth. This may be due to low hydraulic conductivity of the clay formation, but the relatively high moisture content of the clay beds should also prevent a faster movement of the front of the infiltrated water. If the measured content of 30 TU from the groundwater level is correct, it can be interpreted as a result of horizontal movements of groundwater and the origin of the tritium should be referred to as recharge outside the area of the perched groundwater aquifer.

The amount of the recharge

If it is assumed that all soil water successively will be replaced by the later infiltrated water it should be possible to determine the amount of recharge if the total amount of soil water and the time during which it has been infiltrated are known.

This should be the case at the well Grønhøj no. 1. From the moisture log the amount of the total stored water in the unsaturated zone can be calculated. A summation of soil moisture between ground surface and 18 m below ground surface gives a stored soil water volume of about 1600 mm.

In accordance with the above assumption, this volume should be equal to the recharge during the years 1962-1966 because the tritium profile shows that the recharge from 1962 has arrived to a depth of about 18 m below ground surface. The yearly amount of recharge as an average of these 4 years should be calculated to be about 400 mm.

The summation of excess of precipitation during the same period gives a value of about 1350 mm for the recharge. The deviation between these two values can be explained if the estimated values of the evapotranspiration are 400 mm per year but perhaps this value is too high and a value of 350 mm would be more realistic. This would increase the excess in precipitation with 200 mm and agreement of the two determinations would be achieved.

Conclusion

The investigations have shown that the soil moisture is well stratified in respect to tritium content and that a change in the content of tritium of the precipitation during a rather short time seems to be detectable in the soil moisture. It can be concluded that the summer precipitation also contributes to the recharge.

The tritium profile at Grønhøj shows that the infiltration rate in homogeneous formations is rather low (4-5 m/year) in spite of a rather high recharge (300 - 400 mm/year) and a low soil moisture content (about 10 vol.%). Tritium profiles in the unsaturated and saturated zones would give much more information about the hydrological properties if the input concentration of the recharge water was better known. This probably can be done by a continuous sampling of recharge water, just below the root zone by using tensiometres under vacuum.

1.12 Discussion on environmental tritium in soil moisture and groundwater in Denmark.

By means of γ-transmission methods in two drillholes, the high apparent speed of the moisture movement, compared to the actual movement of water is also observed in other experiments. After a heavy rain moisture seems to move very fast downwards. In summer the movement of moisture does not reach the groundwater table, it actually is sucked by the plant roots to be transpired and evaporated.

When the water content of the soil exceeds the specific retention of the soil, the downward movement starts. This movement is faster when the volume of the gravity water is larger. This type of movement is different from that taking place under saturated conditions where the response is almost immediate. In the case presented in the working paper the total porosity was 35% and the moisture content only 10 ~ 15% per volume.

Table I

Precipitation at Grønhøj, estimated values of excess ($P-E_v$) and corrected values of tritium content in precipitation at Huddinge 1962-66

	1966			1965			1964			1963			1962		
	P mm	$P-E_v$ mm	T_{corr} TU	P mm	$P-E_v$ mm	T_{corr} TU	P mm	$P-E_v$ mm	T_{corr} TU	P mm	$P-E_v$ mm	T_{corr} TU	P mm	$P-E_v$ mm	T_{corr} TU
December				92	87	158	120	115	269	14	9	487	32	27	192
November				54	39	157	44	29	221	144	129	698	29	14	258
October				44	14	99	43	13	291	100	70	693	42	12	136
September				68	21	296	71	24	471	51	4	1240	58	11	268
August				62	2	610	56	-4	1230	139	79	1805	143	73	315
July				104	34	539	98	28	970	59	-11	2690	57	-13	538
June				46	-15	858	93	32	1715	38	-23	2745	54	-7	576
May				34	-19	668	24	-29	1640	87	71	1815	96	43	574
April				70	32	265	37	-1	829	41	3	1730	36	20	590
March	56	40	213	20	4	328	7	-9	748	33	17	1050	39	23	420
February	56	51	204	23	18	313	14	9	675	8	3	710	57	52	472
January	32	32	196	74	74	303	50	50	617	8	8	368	60	60	276

Table II

Precipitation in mm and weighted average in tritium concentration TU, for the years 1962-1966

	1965		1964		1963		1962	
	mm	TU	mm	TU	mm	TU	mm	TU
October-December	190	145	207	263	258	690	113	172
September-March	346	188	375	310	323	770	167	262
February-February	733	350	625	825	720	950	592	410

2. ENVIRONMENTAL ISOTOPES IN SURFACE WATER AND GLACIOLOGICAL STUDIES

2.1 THE USE OF ENVIRONMENTAL ISOTOPES. PRECIPITATION - INFILTRATION - RUNOFF RELATIONS.

Summary of the paper by T. Dinçer

The use of environmental tracers in studying storage and water balance problems in surface and groundwater hydrology is possible only in cases where the tracer concentration in the input to the system is different from the output due to fractionation, radioactive decay and to mixing processes which occur during the storage and the transit of the water in the system. In precipitation - infiltration - runoff relations the difference between the short-term variations in the input concentrations and the almost constant tracer concentrations in the output can be used with advantage to separate the different components of the runoff and to estimate the actual input to the subsurface storage.

It is possible to separate the two basic components of the total runoff by using the equations

$$Q_T = Q_s + Q_g \qquad C_T Q_T = C_s Q_s + C_g Q_g \qquad (1, 2)$$

where Q_T is the total runoff, Q_s is the surface runoff and Q_g is the subsurface runoff, and C_s are the associated environmental tracer concentrations. Once the direct runoff is calculated, infiltration can be estimated from the difference of precipitation and the total runoff

$$I = P - Q_s \qquad (3)$$

The calculation of the infiltration by the subtraction of the total runoff from the precipitation which is used in routine hydrological studies is thus greatly improved, due to the fact that this latter method does not take into account the increase of the subsurface runoff in response to the increasing infiltration.

It is also possible to calculate the build-up of subsurface storage by using the relation

$$\Delta S = (I - Q_g)\Delta t \qquad (4)$$

and relate it to Q_g, thus developing a relation between the active storage and outflow from the storage.

The total subsurface storage volume can be determined using thermonuclear tritium content of the base flow in a given basin. This has been extensively discussed by A. Nir, and some practical applications have already been made. [1, 2]

In studying Precipitation - Infiltration - Runoff relations, a good sampling coverage of precipitation and of the streamflow is necessary. Samples of groundwater also could be helpful in choosing representative environmental isotope concentration values for the subsurface runoff. The frequency of sampling depends on the type of problem studied: in a rainflood study, hourly sampling could be necessary, whereas in a snowmelt runoff study daily sampling would be satisfactory.

2.2 Discussion

The present methods of studying the interaction of precipitation, surface water and groundwater are not adequate. Many of the routine methods are based on some assumptions rather than observations of the hydrologic phenomena. Concepts of surface flow, subsurface flow and interflow should be revised in the light of the results of the studies by environmental isotopes.

The study of river basins with environmental isotopes, especially with tritium gives surprising results and shows that only a small portion of water precipitated during the current year is carried out by the drainage system. A study of environmental isotopes made in a small mountain basin in northern Czechoslovakia [3] confirmed this fact. It was seen that less than half of the meltwater from the snow appeared in the runoff during the snowmelt season. The larger part of it infiltrated and reappeared mixed with water from the preceding and following years, two years later. Fig.28 gives the basic environmental isotope and hydrological data in graphical form.

References

[1] A. Nir, On the interpretation of tritium "age" measurements of groundwater. J. Geophys. Res. 69 (1964) No. 12 pp. 2589-95.

[2] T. Dinçer and G.H. Davis, Some considerations on tritium dating and the estimates of the tritium input functions. Memoires Vol. VIII. International Association of Hydrogeologists Congress of Istanbul, 1967 pp. 276-286.

[3] T. Dinçer et al., Tritium and oxygen-18 in snowmelt-runoff studies (to be published).

2.3 THE USE OF ENVIRONMENTAL ISOTOPES IN GLACIOLOGICAL STUDIES.

Summary of the contribution by W Dansgaard

Ten years ago Schoellander measured the age of the icebergs coming from glaciers,using the ^{14}C dating method and found suprisingly low ages; one was 3000 years old and ten others had ages of less than 1000 years. Recently we repeated the measurements using improved sample collection and extraction techniques. When the snow is accumulated in a glacier, some atmospheric air is trapped in the very fine bubbles which makes the ice appear white. Since the ice is practically impermeable, the measurement of the ^{14}C content of the air trapped in the ice is a good measure of the period when the air was trapped. To obtain 50 milligrams of carbon for analysis about 4 tons of ice are required.

Samples were collected from 15 icebergs. The ^{14}C analyses have not been made yet. but the silicon-32 content of the ice samples has been measured. In fact no silicon-32 has been found in these samples except in one. The measuring accuracy bein 0.01 dpm/ton, which is 30 times lower than the natural specific activity of silicon-32 in the ice, the ice samples should be at least 3000 years old as one would expect.

Fig. 29 shows the flow pattern of the ice in Greenland. The ice in the central part of the island moves right down to the bottom and then follows a course parallel to the land surface. Since the accumulation is 0.3 metres of ice per year and since the depth of the glacier is approximately 3000 m it must take more than 10,000 years for the ice to reach the bottom of the glacier and much more down to the coast.

In 1966, the Cold Region Research Establishment laboratories (CORE) in Hanover, New Hampshire, obtained cores of ice at Camp Century in Greenland down to a depth of 1400 m. The stable isotope variations of these samples were measured and provide an almost unique opportunity to study the past climatic conditions.

The surface velocity of the glacier where the samples were taken is 3.3 m/yr. This implies that all samples which were measured have their origin in the same area.

By studying the stable isotope variation in the core, which shows significant seasonal variations, it is possible to estimate the accumulation rate of the ice. The mean oxygen-18 content of the longer portions of the core, on the other hand, gives information about the mean atmospheric temperature at the time of deposition of the snow several thousand years ago.

The vertical stress in the glacier reduces the wave lengths of the stable isotope content of the ice. Therefore, the actual thickness is not necessarily the accumulation at the time of deposition.
A correction factor, which depends on the mode of flow of the ice is needed.

Owing to diffusion the amplitude of the seasonal variations is reduced in time. The diffusion coefficient of the ice at prevailing temperatures is 5×10^{-12} cm^2/sec. Although this value is extremely low, it stabilizes the seasonal variations in several thousand years.

In order to interpret the variations in wave lengths and amplitudes related to stable isotope content of ice layers, a proper flow model should be chosen. The generally accepted model conceived by Nye simply assumes a uniform vertical strain rate which is defined as the relative change of thickness of the annual layers per unit of time. This implies a flow model with uniform horizontal velocities along a vertical core until a few metres above the bedrock. This is a simple model, which would be suitable for an ideal plastic material. However it is known that the ice is not perfectly plastic.

The velocity profile can be approximated by horizontal velocities proportional to the distance from the bed up to some 400 metres from the bottom and between 400 - 1400 metres from the bottom constant velocity can be assumed. Based on these assumptions the vertical velocities can be calculated.

If a coordinate system moving with the same velocity as the ice is introduced and if a sheet of ice in this coordinate system is considered, the sheet of ice involving many periods of practically the same λ, it will be seen that there is a certain velocity in this moving system.

If the amplitude of oxygen-18 variations are plotted versus time or age of the ice layers, the amplitude will practically be zero in 12,000 years. This gives an indication how far back one can go in time to find the oxygen-18 variations in the ice.

At Camp Century the oxygen-18 variations were measured in function of the depth. It was found that some years had an accumulation of 0.17 metres, almost half of the mean accumulation rate.

2.4 Discussion

The determination of stable isotope variation in the past 10 - 20,000 years would be useful in other environmental isotope applications in hydrology. In many cases when the deuterium and oxygen-18 content of the groundwater samples in a given region are plotted against each other a scattering of data is observed, even though no altitude effect is expected. This scattering is probably due to the difference of mean ages of the samples. If the stable isotope variations in the past were known, it would be possible to interpret the groundwater data and even tell something about the recharge period.

A second point of interest is the analogy of the reduction of the amplitude of stable isotope variations in glaciers and in groundwater. In some aquifers, where the circulation is fast the stable isotope variation in the input is not completely lost in the output, especially that of springs. The comparison of the variation in the input and output is related to the turnover time of the system. In a study made in Cheju Island, South Korea, such variations were observed in the springs along the periphery of the island, indicating rather a fast circulation in the basalt aquifer feeding these springs [1]. On the other hand, in groundwater where the movement is slow, no stable isotope variations are observed.

Such interpretations may be misleading when there are mixtures of waters of different ages and origins. A change in the relative contribution of the components or sources of the water causes some variation in the stable isotope content in the outlet. However, this is also true for the other environmental isotope data, namely, tritium or carbon-14.

The changes that are observed in the mean annual stable isotope values could be due either to a real change or to the relative change of seasonal contributions or both. The phases, it was stated, were not equal as in a cosine function. The samples representing one year are covering the period since 1890. They show clearly the warming up of the climate in the twenties and also the cooling of the climate after the forties. To study these variations it is also necessary to measure the oscillation about the mean value. The curve in Fig. 30 shows the distribution between the summer and winter precipitation and thus gives much more information.

The core in Camp Century probably represents a few thousands of years of accumulation. Toward the bottom of the glacier the definition of the individual layers is impossible and it is not known how many years are represented. In the usual procedure 8 samples were analyzed for an annual layer, thus 80 samples give satisfactory information for a decade.

[1] Davis, G.H., et al. Geohydrologic interpretations of volcanic island from environmental isotopes.

3.1 SOME PRACTICAL CONSIDERATIONS IN ENVIRONMENTAL ISOTOPE APPLICATIONS IN HYDROLOGIC STUDIES.

Summary of the contribution by G.H. Davis

Research in application of environmental isotope techniques to hydrologic problems has been active and fertile over the past decade. The development of techniques for use of tritium, carbon-14 and more recently silicon-32 in groundwater dating and the broad spectrum of applications of deuterium and oxygen-18 in water problems has nearly all taken place during this period. However, the practical use of these techniques has generally not kept pace with the research and development. This is due, no doubt, in part to lack of communication between research scientists and people concerned with practical field problems, but also to the fact that water problems in the highly developed nations where the research is carried out, generally are greatly different in type and scope from water problems in the developing nations. For example, the main problems facing hydrologists in Northwestern Europe, a humid, industrialized area, are entirely different from the arid and semi-arid belts of Asia, Africa and South America.

Even the most sophisticated techniques for investigating underground waters give results that are crude in comparison with the simple technique of gauging flow in a surface stream with a current meter. Likewise, quantitative estimates of interrelations of surface and underground waters are subject to similar uncertainties because underground flow of some form plays an important role in nearly all flow systems. By the same token, underground flow does not lend itself to application of simple models because of the great complexity of the flow paths. For these reasons the subsurface environment deserves the special attention of isotope workers. The task is complex and difficult but the need is great for better tools.

The great value of environmental isotope applications to subsurface water problems lies in the fact that the isotopes of hydrogen and oxygen form part of the water molecule and therefore approach the requirement for the ideal tracer. Furthermore, the environmental isotopes, such as tritium, carbon-14, and silicon-32, are not subject to replenishment from underground sources. Used in combination, the stable isotopes ^{2}H, and ^{18}O offer the features of areal and seasonal variability in input (recharge) while the radioactive isotopes, ^{3}H, ^{14}C, and ^{32}Ci, have known variable inputs as well as characteristic radioactive decay rates after the water has been removed from contact with the atmosphere.

From the beginning of environmental isotope applications to underground waters much emphasis has been placed on using the property of radioactive decay to gauge velocity of flow. While this is indeed an important potential application, other equally valuable applications have tended to be overlooked. Furthermore, many attempts to arrive at subsurface flow rates have failed because of the use of oversimplified or erroneous models of the subsurface flow system. One example of this is the use of models assuming piston flow of water in groundwater systems despite a voluminous literature that demonstrates the importance of dispersion mixing in flow through porous media. Such oversimplifications have tended to discredit isotope work in the eyes of conventional hydrologists and many sound demonstrations of valid results will be needed to dispel this poor impression.

One particularly important aspect of application of environmental isotope techniques that has not received sufficient attention is their use in describing the subsurface environment. Unlike the physical scientist, who can design his experiment, the practising hydrologist is usually faced with a situtation where nature designed the experiment for him, then threw away the plans, and buried the equipment. The hydrologist can often draw broad qualitative conclusions as to direction and rate of flow from surface evidence, such as terrain features, geologic features, and surface waters. To quantify these concepts, however, generally requires expensive and detailed sampling of the subsurface environment by test drilling, laboratory analysis or core materials, pumping tests, chemical analyses of the water, and other indirect sampling procedures. Even with intensive investigation using these conventional methods, many questions cannot be resolved without the application of environmental isotopes. To cite but a few of the more important questions where even qualitative answers help to define the flow system model:

(a) Degree of stratification of subsurface waters.

(b) Whether or not infiltration from land surface is significant.

(c) Degree of confinement.

(d) Sources and seasonal distribution of recharge.

(e) Relative contributions to blends of waters having different travel times.

(f) General magnitude of underground storage as reflected by isotope variability in discharge.

(g) Hydraulic connection with lakes and swamps.

(h) Sources of contamination.

A good example of point (g) is the study of the Cheju island, an oceanic island which consists mainly of volcanic terrains similar to the Hawaiian volcanic formations, with apparently high permeability. In general one would have expected a large groundwater reservoir beneath the island, a fresh water lens floating over salt water, due to the difference of density of about 3% of the two fluids. However, the drilling which has been carried on by the Korean government was invariably unsuccessful in that when they found the water at all, it was saline. This led them to the conclusion that the fresh water lens was so thin that it would not be economic to consider the development of this resource. However, by periodic tritium and stable isotope sampling it was possible to show that the turnover time of the subsurface reservoir was substantial, on the order of about 9 yrs.

Using the combined environmental isotope approach, it is generally possible to greatly improve the model of the subsurface-flow regime. When a valid model has been developed, it is feasible to apply the property of radioactive decay to quantitative estimates of groundwater velocity and storage capacity.

It is evident that the approach described above requires the close collaboration of laboratory and field workers and a full spectrum of analytical facilities for adequate backup. Such a systematic, integrated technique has been applied with great success in recent years by IAEA in its field projects. A technique of special value is that used by IAEA of reconnaissance sampling of numerous sources for stable isotope analysis followed later by more time-consuming and expensive tritium and carbon-14 methods depending on what the stable isotope work reveals.

3.2 Discussion

An example of testing of hydrologic hypotheses with environmental isotopes was given by describing a study made by the U.S. Geological Survey in conjunction with the State of Texas. The problem was to determine the origin of some saline springs (30% sodium chloride) which were causing serious contamination to rivers to which they were tributary. This problem was solved with relatively little effort by studying the deuterium content of the springs and the precipitation originating from storms having various moisture origins.

The collection and storage of water samples for subsequent analysis would greatly help many studies of environmental isotopes in groundwater in the future. This especially applies to the thermonuclear tritium, which has a transient feature. The collection and storage of water samples from rivers springs and groundwater in general does not present problems and does not cost much. The analysis of these samples, whenever needed, could help to solve many hydrological problems, especially those related to aquifers with rapid circulation systems, such as karst and non-confined aquifers. A water sample represents a potential amount of information even before it is analysed. When samples are not available, it is not possible to obtain the information related to time, as there is continuous time variation in the thermonuclear tritium content of the water. Hydrological services of the countries should therefore, have a reasonable routine programme of water sampling. This is true also of the chemical analysis of the water. As to the storage of the samples, glass bottles with a screw cap and polyethylene gaskets would be adequate. The losses from such bottles would be about 10 mg/yr. They can be weighed with sensitive balances to see whether significant losses have taken place.

3.3 ON THE APPROACH TO HYDROLOGIC PROBLEMS.

Summary of the contribution by A. Nir

When using environmental isotope methods, hydrologists should first formulate a hypothesis or hypotheses concerning a given hydrologic problem. The second step is to figure out isotopic patterns that fit the different hypotheses. A few measurements of environmental isotope content of water in the system may then be sufficient to support one hypothesis and reject others. Before drilling a borehole, for example, geologists have some idea of the formations and the aquifers which can be tapped during the drilling based on surface geology, previous reports, or other sources of information. The isotope worker also should have the same type of knowledge· he should have at least a hypothesis before the sampling programme for environmental isotopes is undertaken. In fact, the extent and frequency of the sampling depends on the type of problem and the hypotheses that can logically be developed to study the problem.

In general, in areas where little is known about the hydrology, environmental isotope studies are of greatest value. In areas where hydrologic information is abundant, environmental isotope data is useful mainly to give additional confirmation to conditions already largely known.

As with some other relatively young scientific disciplines, in the application of environmental isotope techniques in hydrology, first the measurement technique was developed and then a considerable amount of data has been collected but adequate interpretation of much of the data is still lacking. Generally methods of interpretation develop and improve after initial data collection. The application of environmental isotopes in 1968 is still in the stage where reliable measurements and a large amount of data are available but these data contain a large amount of "noise" that needs to be eliminated. Better measurements are not enough to remove this noise; it is inherent in the measurements of hydrologic parameters. It would be useful for hydrologists to learn from other disciplines techniques used to filter the noise out of the significant information. These methods should be studied and tested experimentally first in areas where good hydrologic information is available; then they may be applied to other regions.

3.4 ON THE APPLICATION OF ENVIRONMENTAL ISOTOPE DATA IN GROUNDWATER RESOURCES DEVELOPMENT.

Summary of the contribution by Y. Harpaz

There are three phases in the water resources development engineering which can be defined as:

(a) Exploratory stage: In regions where no or little physical data (climate, geology, hydrology, etc.) are available, it is usual to start with a reconnaissance study to obtain some qualitative information concerning the availability of the water resources and on the possibility of their development for various uses, which are in general, water use for domestic purposes and for irrigation.

(b) The Development stage: This is the second stage where detailed investigations are made in order to make quantitative evaluation of the water resources in the region. This stage also involves the construction of the first facilities such as dams, and canals, for storage and distribution of water and explatory boreholes and wells for groundwater.

(c) The Operation and the Management stage: This stage is concerned with the optimal operation of the water resources in use. In this stage much more sophisticated quantitative methods are needed.

In all three stages environmental isotopes can be used profitably. The three basic components of a hydrologic system are the inflow, the outflow, and the system itself. The system has 2 kinds of properties· (1) "medium" and (2) "state" (or operational level) parameters. The first are storativity, permeability, transmissivity and the porosity of the system, which do not change with time but may have, and, indeed often do, have large variations from one point to another. The second type includes the instantaneous levels of a reservoir, and volume of storage, at a given time; they are not related to the medium.

It is useful furthermore, to classify the methods used in hydrologic studies in two basic groups called direct and indirect methods. Direct methods are those in which physical measurements can be made, such as water level measurements, determination of the porosity and permeability of the aquifer samples in the laboratory, measurement of the spring flow and so on. The indirect methods are those in which, for example, an estimate of the input is made by knowing the output and change of volume of the reservoir, or the reservoir characteristics are determined by comparing the input and the output.

In the exploratory stage of water resource development there is need to define the system, its boundaries and general characteristics. These evaluations are, in general, of qualitative nature they describe such characteristics as confinement of the aquifer, active recharge, or the dependability of the storage. In such descriptions environmental isotopes are useful in estimating the rate of circulation and recharge (tritium carbon-14), interrelation with surface water (deuterium, oxygen-18) and dependability of the storage (tritium, carbon-14).

In the second stage of water resource development, however, environmental isotopes can be an even more powerful tool. The answers should be quantitative and should complement conventional hydrologic techniques. In this case environmental isotopes help determine the input, the output, and the state parameters. At the end of this stage hydrologists develop a model which can be used in the operational stage to forecast the effect of various inputs and changes in the system.

In the second stage, also, it is possible to use environmental isotope tracers to estimate the mean residence time of the water in the system, the storage volumes, and to establish the water balance of the system using additional isotope balance equations. One of the most important applications is the use of stable isotopes to identify areas of recharge and areas of discharge not easily located by conventional hydrologic methods.

In the third stage the use of models is necessary to calculate the response of the system to natural and man-induced inputs. New state parameters, such as dispersivity and mixing which are not important at the earlier stages have to be considered at this stage. Stable isotopes and tritium can be very useful in this respect.

In the third stage also, hydrologists may use "mass models" in addition to an hydraulic model in which only the dynamics of the system is studied. Environmental isotope tracers along with artificial radioisotopes, can be useful in establishing and testing the mass models. A new parameter -- the tracer concentration -- is thus introduced in the study.

3.5 Discussion

During the discussion of the paper by Harpaz, it was stressed that the environmental isotope sampling should start at the earliest stage of water resource investigations. For a successful interpretation of the environmental isotope data, a long series of observations is necessary just as is true for other type of hydrological information. This is especially important when there are transient conditions in the mass flow and the environmental tracer input to the system.

3.6 UTILIZATION OF ENVIRONMENTAL ISOTOPE TECHNIQUES IN WATER RESOURCES INVESTIGATIONS AND DEVELOPMENT.

Summary of the paper by R. Ambroggi and D.J. Burdon

The paper reviews the urgent need for development of water resources and the rolè of national and international organizations in that development. After dealing with the problems of water-resources investigations and development, planning and management of environmental isotopes in hydrology is explained. It is pointed out that chemical methods (1) are still of major importance in studying the genesis of waters. These methods now should be supplemented by environmental isotope techniques.

In the part dealing with precipitation, surface water and underground water, the authors point out the usefulness of WMO/IAEA worldwide network of survey of environmental isotopes in precipitation. They further note the potential use of environmental isotopes in surface water studies. Concerning the groundwater, they state that the intangible occurrence of groundwater has led to neglect of this major resource by hydrologists. Now environmental isotopes offer a powerful tool for the investigation of this resource.

The authors then point to the collaboration of FAO and IAEA in several UN Special Fund projects which provide means for improving our understanding of both groundwater hydrology and the behaviour of the environmental isotopes in nature; this work will also improve the interpretation of the environmental isotopes in hydrology.

There is need for a continual dialogue and exchange of hypotheses between the field hydrologists, hydrogeologists and the physicists and other research workers. Some hypotheses put forward by the laboratory workers as a result of their analyses may readily be disproved by some related field evidence; likewise, other hypotheses may open up new lines of field investigations, which would otherwise be neglected. This active question-and-answer relation is most beneficial for the interpretation of the environmental isotopes because it requires the translation of the isotope data into the hydrological information.

The authors finally arrive at the following conclusions:

(i) The utilization of environmental isotope techniques in water resources investigation and development by FAO in collaboration with IAEA is a direct application of science and technology to the problems of the developing countries.

(ii) The use of environmental isotope techniques reduces the time taken to determine and evaluate water resources and so permits sound water resources development to take place at an earlier date. It thus helps to accelerate the use of water for irrigation and food production.

(iii) The use of environmental isotope techniques represents a collaboration between the field workers on water resources survey and development projects (mainly under the UNDP Special Fund) and the research workers who have made available such techniques for the use and benefit of the developing countries.

(iv) There is a need for a continuing and active dialogue between the field workers and the research workers; this interchange of problem and hypothesis must be strengthened to lead to even quicker and more fruitful solutions.

3.7 AN EXAMPLE OF THE COOPERATIVE WORK WITH FAO IN GROUNDWATER INVESTIGATIONS IN JORDAN. Summary of the paper by G.H. Davis

Fig. 31 shows the general layout of the project, a study of the groundwater resources in the high plateau and the southern desert of Jordan. The Dead Sea occupies a structural downdrop block, and is bordered on the east by a major fault. East of this fault line a very steep escarpment rises from about 400 m to more than 1000 m above sea level. In the high plateau, where the precipitation varies between 200 - 600 mm, the rainfall belt is very narrow and follows a north-south direction. The rest of the country receives less than 50 mm precipitation. The major input to groundwater, therefore, is along the escarpment where the precipitation is relatively high; it originates from moist air masses coming from the west.

Initially no environmental isotope data were being collected at precipitation stations in the project area. The first task, then, was to sample the precipitation at four stations in the rainfall belt (Irbid Amman, Rabba and Shobak). The precipitation increases in the north-south direction; however, there is also a marked decrease of altitude in that direction. It was expected, therefore, that the altitude effect would be counterbalanced by the amount effect. This has now been confirmed by the stable isotope data (Fig. 32).

The isotopic composition of the groundwater was found to vary slightly from one point to another. However, a common feature of these waters was the fact that on a $D - {}^{18}O$ diagram all points were found on the right side of the so-called mediterranean precipitation line defined by the precipitation in Israel and Jordan precipitation. (Fig. 33). Some of the groundwater samples were collected from springs, some from wells and test holes. The points representing these samples are clustered around the line with slope 8 and intercept 10, instead of the line representing the precipitation in Jordan and Israel. This illustrated that a single isotope is not enough to define a body of groundwater and that the isotopic composition of the groundwater samples do not necessarily fall on the line defined by the isotopic composition of the precipitation occurring in the presumed recharge area.

There are groundwater samples containing significant amounts of thermonuclear tritium. The carbon-14 content of the samples are about 80-85% of the modern, which also shows that the waters are modern and have an average residence or transit time of 10 ~ 20 years. On the other hand, there are samples with low tritium and carbon-14; these should be ancient waters. Carbon-14 dates were corrected using a modification of Pearson's method based on the $^{13}C/^{12}C$ ratios.

In the high plateau the aquifer consists of limestone where, it was assumed, recharge would occur readily. Oddly enough, however, the tritium content of the waters in this region is rather low. In the Jebel-Druz area on the other hand, groundwater samples are depleted with respect to stable isotopes as a result of the high elevation of the recharge area. Characteristically, in the hot springs, a marked shift in O-18 values was found.

These results, although difficult to interpret in some cases, yield valuable information on the groundwater system in Jordan. At specific locations information was obtained on the existence of modern recharge using tritium. There is no doubt that much of the water in the Southern Desert is of Pleistocene age as indicated by the carbon-14 contents. In the Azraq basin, which is heavily developed with shallow irrigation wells it was first assumed that recharge came from along the Eastern Jordan Valley escarpment moving rapidly toward the Azrag region. However the carbon-14 and stable isotope content of the waters indicate that they are at least thousands of years old and are related to recharge taking place in the arid zone rather than from the precipitation along the escarpment.

A major question in interpreting the stable isotope data is the significant shift toward the right of the points representing groundwaters with respect to the Jordan-Israel precipitation on the $D - {}^{18}O$ graph. No satisfactory answer has yet been found to this question.

3.8 Discussion

The pH of groundwaters can influence the oxygen-18 content of the samples collected. When pH is higher than 6, the possibility of exchange between a limestone aquifer and the water can be discarded.

The frequency of storms decreasing toward the east may be responsible for a different isotopic composition of the rainfall inland. Obviously such problems should be solved in connection with the study of the major storms in the region considered.

In the southern desert region old waters, probably of Pleistocene age, although depleted with respect to the modern groundwaters, are found on the same $D - {}^{18}O$ relation with modern waters. This relation is different from the line defined by the precipitation data obtained during recent years in Israel and Jordan. Evaporation could cause such a shift toward the right. However, such evaporation is different from that which occurs during the fall of the raindrops and is probably related to the evaporation taking place at the surface of the soil, prior to infiltration.

The interpretation of the stable isotope content of groundwater in relation to the stable isotope content of the precipitation contributing to the recharge is rather questionable; in a discussion of that several factors should be taken into account when interpreting these results.

An important point is the statistical nature of the variations of the stable isotope content of the precipitation. Time and areal isotopic variations should be studied separately. At a given station the stable isotope content of the precipitation depends largely on the isotopic composition of the water vapour from which the precipitation is derived plus such effects as the evaporation of the falling raindrops. There is, therefore, no reason to expect a definite relation between deuterium and oxygen-18. As the condensation occurs in equilibrium, i.e. in saturation conditions, the deuterium and oxygen-18 values of the precipitations that result from this vapour will lie on a line with a slope of 8.

The subsequent evaporation, which takes place during the fall of the raindrops, may change this slope somewhat, but in general, if the time averages of the deuterium and oxygen-18 content of the precipitation in a given region are plotted against each other, a slope of approximately 8 results.

The relation between deuterium and oxygen-18, however, might have different intercepts on the deuterium axis, i.e. excess deuterium values relative to the regional or global climatic changes. Such variations will make the comparison of the stable isotope content of the groundwaters with that of the precipitation difficult because the time averages represented by groundwater samples cover much longer periods than the stable isotope data of the precipitation.

In some cases carbon-14 ages are well correlated with the stable isotope content of the groundwater. In the Graz basin in Austria a remarkable relation (Fig. 34) was actually found, which indicates the influence of the paleotemperatures on the stable isotope content of the groundwaters. If the variations of paleotemperatures were known, stable isotopes, together with the chemical quality of water could give valuable information as to the age of water. Such information could be used in conjunction with the apparent carbon-14 ages and be useful in a way to adjust these apparent ages and bring them to the true time scale.

This approach, although theoretically acceptable, does not hold in regions such as Florida, where no significant variation in stable isotopes occurs in either modern or very old groundwaters, according to the deuterium and oxygen-18 data collected in carbon-14 studies in Florida. This can be explained by the geographic setting of Florida, a peninsula surrounded by oceanic waters. Recharge patterns of the past were similar to those of today. Most recharge occurs in summer by heavy thunderstorms and isotope fractionation takes place as a single stage Rayleigh process. A change in stable isotope content of the precipitation would occur only if different temperature and relative humidity conditions prevail over the oceans.

3.9 THE USE OF ENVIRONMENTAL ISOTOPES IN KARST HYDROLOGY
By B.R. Payne and T. Dinçer

3.9.1 Background

Karst formations are the most important aquifers in many regions of the world. Three special hydrologic features characterizing them are: the absence of a well-developed surface drainage network; a high infiltration capacity· and a concentrated subsurface flow pattern.

Several aspects of a karst aquifer system resemble a surface water system. For example, flow in the subsurface karst system is concentrated along major faults, solution channels and fractures, as flow in surface water is concentrated in surface streams. The high infiltration capacity of karst formations is evidenced by scarcity of surface drainage, the disappearance of large rivers into sinks, and large losses of water from lakes through sinks into the subsurface. The discharge of water from springs in large flows at the terminal ends of karst aquifer systems parallels the discharge of water by surface streams in a normal surface water system.

Finally, flow from a karst aquifer has the same two basic components as surface water. The first component which recedes quickly, is seasonal and is related to precipitation and the underground channel system. The relatively small storage capacity of these channels compares with channel storage of a surface system. The second component recedes slowly and indicates a large storage volume. It corresponds to base flow from a basin and comes from the multitude of minute fractures which make up the real storage capacity of a karst aquifer.

3.9.2 Interpretation of Environmental Tritium Data in Karst Groundwater

Separation of the two basic components in karst springs qualitatively may be possible through use of tritium. High tritium content during times of high flow and low tritium content during low flow periods indicate that the high-flow with high tritium content should come mostly from recent precipitation containing bomb-produced tritium. Low tritium content in the low "base" flow should come mostly from water that has been in storage (and in transit) since pre-bomb times. Pointing out these two facts with tritium is neither startling nor particularly interesting. Hydrologists have made this separation for many years by merely measuring discharge regularly, without resorting to elaborate laboratory analyses. The interest of the tritium data in karst hydrology consists essentially in estimating the mean residence or transit times in the karst and in estimating the size of the storage in the case where the outlet is a karst spring with a known discharge.

3.9.2.1 Transit time distribution function in karst systems

In an interpretation based on transient tracer input in a hydrologic system, the so-called transit or residence time distribution of the water becomes one of the most important elements to be determined. In studying karst hydrology with tritium -- which is particularly suited for such studies because karst hydrology has some characteristics of both surface- and ground-water systems — the determination of the transit time distribution is critical owing to the presence of thermonuclear tritium from precipitation.

First, assume that the transit time distribution at the outlet of a karst system, that is a spring, is similar to the transit time distribution of the surface runoff in a basin. This assumption is based on the following:

(a) Unlike the slow movement of a granular aquifer, the flow in a karst follows a concentrated pattern like surface flow with rather high velocities.

(b) Karst systems ordinarily have extensive recharge areas; this is evident from the large spring flows observed in such regions.

(c) Surface streams and karst systems are similar.

(d) Karst systems have a slow moving component similar to the subsurface runoff in river basins.

(e) Most of the large outlets of karst systems are found, in general, at or near the watershed borders. In many cases they are also situated close to recharge areas and include discharge that is circulated rather rapidly.

It is possible to consider the transit time distribution of water in a karst system as a two-dimensional distribution. The first dimension - time - results from the dispersion of water molecules starting from the same area of recharge; the second dimension - again time - results from the various distances water has to travel from widely separated recharge areas to the outlet of the system. In a confined aquifer, only the first dimension would be important. This two-dimensional transit time distribution function is, therefore, a rather flat distribution and its standard deviation is in the order of magnitude of its mean value.

3.9.2.2 Calculation of expected tritium content of the springs under different assumptions.

The interpretation of the tritium content of karst water is made according to the following steps:

(a) Estimate the tritium in the recharge either on a monthly or seasonal basis, depending on the climatic features of the region studied.

(b) Calculate the transit time distribution functions with different variances.

(c) Compare the expected tritium values obtained from the convolution integral with the actual tritium content of water samples collected from springs or groundwater

Although the approach is relatively simple, there are several problems related to the comparison of the expected and actual tritium content of water samples.

One of these problems arises when we consider the mixing of waters having essentially different mean transit times, i.e. the mixture of some recent karst water with the old karst water. In such a case, the relative tritium variation observed in a series of samples collected during a certain period of time will be similar to the variation which would be observed in a sample consisting only of recent waters containing thermonuclear tritium. Therefore, the absence of large time variation in tritium concentration in karst spring water indicates a single system.

3.9.2.3 Patterns of tritium variation in karst springs

Actual observations made in many karst springs have shown that as the tritium content of the water decreases, the time variation is also considerably reduced. The high tritium fallout of 1963-64 does not appear to have affected the tritium concentration of many karst springs. This can be explained by very flat transit time distribution in comparison to the mean transit time in the karst systems so far investigated, which fits the analogy of karst systems with surface waters.

Once a mean transit time has been determined using the above approach, it is possible to estimate storage in a karst aquifer if the discharges of the main springs are known. In a karst spring in southern Turkey with a constant discharge of approximately 10 m^3/sec, tritium levels never rose above 30 TU during the period 1963-68. Even without attempting to estimate the storage feeding this spring, one wonders what happened to the tritium going into the recharge in the early part of the thermonuclear period. If it is assumed that the tritium is still stored in the system, the average transit time should be at the order of 10 years or more. On the other hand, and in agreement with the approach explained in this paper, if it is assumed that tritium of thermonuclear origin exists in a small percentage in the samples collected between 1963 and 1968, again one has to agree that the storage should be at least 20 times the mean annual recharge in order to have such a dilution rate of the tritium input in 1963 and 1964, not to mention other years.

The above considerations show the uniqueness of tritium as a tool in karst hydrology. The interpretation of the tritium content of the karst springs based on the influence of large recharge areas on the transit time distribution — and other similarities with surface drainage networks — seems to be logical in the light of the results so far obtained. However, a few more years of monitoring the tritium content of karst springs will show definitely the basic hydrologic characteristics of karst regions.

3.9.3 Interpretation of Stable Isotopes

The stable isotope content of karst springs, and in general of water in karst regions, can be used to better define hydrologic boundaries in karst regions. The method gives unequivocal results when the interrelation of lakes formed in karst regions and the springs is studied. The existence of isotopically heavier water in a spring with a higher enrichment rate in oxygen-18 in comparison with deuterium, is the severest test for hypotheses which postulate the connection between a spring and a lake in an upland area.

Determination of subsurface karst basin boundaries by the stable isotope content of the groundwater and the spring water can often be used advantageously. It is possible to compare the stable isotope content of the karst water with the stable isotope content of the precipitation in the same region for the period when recharge to the karst system takes place. Also one can compare karst water samples from two different localities.

3.10 Discussion

A question was raised on the analogy between the transit time distribution function and the unit hydrograph concept. It was pointed out that the unit hydrograph does not correspond to the transit time distribution function. The time distribution of runoff is the result of the distribution of the distances of travel and of the transit time distribution of the flow originating from elementary areas forming the basin. Although the expressions used to describe the unit hydrograph and transit time distribution are similar, the unit hydrograph is merely the dynamic response function and does not take into accout the transport of the matter in the basin per se. Transit time function, on the contrary, is related to the distribution of the probability of the transit time (or residence time) of every individual molecule of water.

It was further pointed out that the analogy of the karst groundwater systems with the surface water systems would not hold, because there groundwater reservoirs are present in karst, while most surface water systems do not have large reservoirs.

Concerning the fit of the tritium data of springs with the theoretical curves based on the assumed transit time distribution functions it was stated that the time of observation was probably too short - only 4 years - to reach conclusive agreements.

The use of exponential transit or residence time distributions was suggested. This type of distribution holds for well mixed reservoirs. When the value of the parameter k in the equation giving the contribution of the n^{th} year in a well mixed reservoir

$$x_n = (1 - k)\, k^n$$

becomes large, this distribution tends to give results similar to those of the rectangular distribution.

The use of artificial tracers in conjunction with environmental tracers in this type of karst was discussed. When the tritium content of the spring waters indicate mean transit times on the order of decades, the use of artificial tracers cannot be recommended. An experiment made with artificial tritium in the region studied in Turkey was unsuccessful, because of the relatively slow movement of water in this type of karst terrain. There are some karst formations in Yugoslavia, Italy and Austria where artificial tracers have been used with success, but the tritium content of the waters in these regions also indicate that the transit time of water is of the order of days, or weeks.

It was pointed out that, when persistently low tritium values are found indicating long transit times, any type of transit time distribution function could be used to fit to the experimental data. In such cases the transit time distribution function would be flat, and, as the bulk of the tritium is provided by the years included in the thermonuclear period. these contributions would have approximately the same weight.

The delay of water in the unsaturated zone could also be considered to explain the rather low tritium content of the spring waters in the Antalya region. The percolation of water in such regions could take considerable time as the water table is probably relatively low compared to the earth surface.

3.11 CONSIDERATIONS ON THE GROUNDWATER MOVEMENT IN KARST FORMATION WITH REFERENCE TO TOTES GEBIRGE MASSIF IN AUSTRIA.

Summary of paper by J.G. Zötl

In karst massifs the joints are wider at the surface and at the border of the massif. At the core the joints are rather fine, and the water movement is relatively slower. Tracers injected some years ago were found in some galeries constructed in karst formations; however, tracers were found almost immediately in the springs at the borders of the massif.

In general. large solution caves are found at the base level of the karst reservoir. This base level changes with time, because of erosion. In Central Europe, for example, such caves are found high up in the massifs, such as at Dachstein in Austria. The base level changes not only by erosion, but also with the changes in the sea level. In the Pleistocene period (Würm) sea level was 100 meters lower than its present level: investigations made in Greece show that there are zones of high permeability lower than the present sea level. This should be taken into account when the storage in karst is studied and in interpreting the environmental isotope content of the water occurring in these regions.

In a karst massif the topographic basin does not, in general, correspond to the actual recharge area which is difficult to define, except perhaps in the case of isolated karst massifs. The tracer experiments made a few years ago in the karst massif of Totes Gebirge in the Central Alps shows the complexity of this situation. In these experiments the tracers injected at the central part of the massif were found in springs more than 30 km away from the point of injection. A curious fact is that the same tracer was found at a much later time in some springs which were much closer to the point of injection. So the tracer travelled in several directions but with very different velocities. Fig. 35 shows the outcome of these experiments and the tracer movement in the massif of Totes Gebirge.

3.12 Discussion

The tritium data obtained in a variety of karst springs shows that the conditions found in Totes Gebirge and other similar karst massifs cannot be generalized. In springs in the Southern Vienna Basin, for instance, different tritium levels ranging from the values found in simultaneous precipitation to concentrations lower than 100 TU were found. Almost all karst springs in Southern Turkey have tritium concentrations between 20 - 100 TU. This shows that the groundwater movement in karst can show large variations from one region to another. The use of the artificial tracers should, therefore, be recommended only in cases where the tritium content of the waters in the region is similar to that of precipitation at the time of sampling.

In Israel studies have shown that a karst aquifer can be studied in ways similar to those for granular aquifers. An analog model of a karst aquifer approximately 800 m deep was built using data on the permeability, effective porosity distribution which had been calculated previously from pumping tests. The results were satisfactory and proved that karst aquifers can be simulated by electrical analog models. Studies made by isotopes can be very useful to check the validity of such models.

A karst system is one in which the aquifer matrix reacts chemically with the water moving in it. This applies, with certain differences, to anhydrites, gypsums and essentially all the carbonates. Water reaches equilibrium with its container when all the carbon dioxide has been used up in the reaction. The time required to reach equilibrium is different for different rock species.

In a karst system turbulent flow can take place in contrast to the laminar flow which usually occurs in granular aquifers. Depending on the region the flow in a karst formation can be either turbulent or laminar. It is ordinarily turbulent near the exits of the system, but it may be turbulent also in the core of karst massifs. When a karst aquifer is confined, as it is the case in the karst aquifers in Israel, no or little turbulent flow should be expected. This makes the application of analog models appropriate as they are based on the similarity of Darcy Law and the flow of electrons under a hydraulic gradient and difference of potential, respectively.

4.1 COMMENTS ON "THE USE OF MATHEMATICAL MODELS IN INTERPRETING THE ENVIRONMENTAL ISOTOPE DATA".

Summary of the paper by A. Nir

4.1.1 Introduction

This working paper discusses the concepts and background information for using isotope date in geohydrology. This kind of review is necessary for evaluation of the present status of such work, to indicate gaps in our knowledge and to plan future work. This report does not include detailed mathematical formulations, as these are available in the references quoted; these should be consulted in detail before the actual discussion of the panel.

A discussion of interpretation of isotope data in hydrology is closely related to the general problem of models and interpretation methods in hydrology. Therefore this discussion will start with a brief survey of current interpretation of models in hydrology.

4.1.2 Current Methods in Hydrologic System Investigations

In the following discussion we use the terminology and definitions proposed by Amerocho and Hart (1964). They subdivide the major hydrological fields of study into physical hydrology and system investigations. Physical hydrology is concerned with well-defined physical components of the hydrologic cycle, such as evaporation, energy transfer, watershed hydraulics and others. The ultimate aim of this research is to understand the action of the basic physical components and their interactions, in order to combine them into a complete description of the hydrologic cycle. The system investigations approach is motivated by two main arguments: (a) the inadequacy of the knowledge now available and the knowledge likely to exist in the foreseeable future of the physical components and their interactions make the probability of a full synthesis of such a complex system very remote, (b) the success of the system approach in describing many features of the rainfall-runoff segment of the hydrologic cycle, and the significant advances in methodology of these techniques that we witness at present. The system investigations may be subdivided into parametric and stochastic methods. Parametric methods attempt to develop a completely deterministic description in terms of functional dependence between rainfall and runoff, considered as mass input and output to a hydrologic system. They are in turn subdivided into lumped and distributed systems and each of these may be linear or non-linear (Chow, 1967a).

Stochastic methods of system investigations comprise time series analysis, including Markov chains, stochastic system response analysis, and Monte Carlo methods.

The parametric approach, especially the distributed system synthesis may base its elements and their interconnections on certain analogies with the physical system. However, its usefulness in a descriptive or predictive role does not depend on these analogies. The above subdivision of hydrological research methods can be summarized in Table I:

Table I

Classification of hydrologic studies

Physical hydrology

1. Components of hydrologic cycle groundwater, unsaturated zone evaporation etc.
2. Energy transfer
3. Watershed hydraulics

System investigations

1. Parametric methods
   (a) Lumped-systems
      (i) Linear
      (ii) Non-linear
   (b) Distributed systems
      (i) Linear
      (ii) Non-linear
2. Stochastic methods
   (a) Time series, Markov chains
   (b) Stochastic system response functions
   (c) Monte-Carlo

A comprehensive summary of parametric and stochastic methods applied to hydrology is given in the proceedings of two recent symposia: Proc. Symposium on Analytical Methods in Hydrology (Symposium, 1967a) and Proc. International Hydrology Symposium, Fort Collins (Symposium, 1967b).

It seems that at present both approaches and their combinations fall short of the objectives of scientific hydrology, which can be defined, following Chow (1967b), as follows: Given initial and boundary conditions of hydrological, hydrogeological and hydrometeorological parameters, to forecast subsequent states of the hydrological system in both time and space. The physical system studies do not encompass yet fully many of its components and certainly not their multiple interactions. The parametric and stochastic methods can deal at best with description and prediction of existing systems in their stationary state but are unable to predict responses to changed conditions. Clearly the development of this subject requires incorporation of the physical knowledge in the system approach, so as to increase its capacity to deal with changing systems.

4.1.3 The Role of the Isotope Methods in Hydrological Models

The introduction of environmental isotope data into hydrological models may be better understood in view of the above presentation of general hydrological methodology. The initial work by Begemann and Libby [1957] attempted to interpret tritium data in terms of direct physical models - the one compartment mixing model in this case. The widespread objection to this interpretation was due to the specific physical assumption, which is not uniquely implied by the isotope data and the oversimplification to a one-parameter (mean residence time) mixing model. Another attempt of Brown [1961] was again of this nature - assumption of a physical model, again, the one-parameter mixing model. Re-evaluation of these and subsequent data of the Ottawa Valley led Eriksson [1963] to interpretation of the recharge area in terms of system analysis. This yielded a complete transit time distribution, i.e. much more information than the single mean residence time. The data were smoothed and renormalized to allow for fluctuations of the distribution function - some of the fluctuations possibly due to errors in measurement but some possibly due to non-steadiness of the hydrologic system. The same analysis mentions also the possible physical system providing the transit time distribution - in terms of fast runoff and a lake system, supplying a delayed response. From the point of view of method development, this was the most complete interpretation of isotope data, with the then available analytical tools. The presently available methods would allow this analysis to proceed further. Steady state assumptions would not be required. Use of a larger body of data could possibly allow the determination of the "Best" distribution in a stochastic sense, as shown by Eagleson [1966].

The concept of dating, as applied to tritium data by Libby and others, in the first years of application uses only the property of decay of tritium, assuming known and constant input concentration. It was based on two physical models: the piston flow and the one-compartment mixing models. The interpretation of dating data has been extended to two-parameter models by Nir [1964], the second parameter being the hydrodynamic dispersion, Dm. of a gaussian transit time distribution. This can, however, be generalized to a gaussian distribution due to stratification and recharge variations. Such an interpretation has been applied by Davis et al. [1967] to the Vienna Basin.

The use of a radioactive isotope as a dating tool can solve a one-parameter model or alternately reduce by one the number of unknown parameters of a multi-parameter model, as it provides only one "unit" of information in the form of one equation. [Nir, 1967]. But the solution depends on the type of model assumed, which determines the form of the equation to be solved.

Stable isotope data have been used mainly in physical hydrology: geographic origin of rainfall, amount of evaporation from surface bodies, ratio of actual mixing of defined water bodies are examples of such applications [IAEA, 1963]. This can be understood in view of relative constancy of stable isotope inputs and the difficulty of measurement of possible small fluctuations. Therefore average differences between different bodies of water were used rather than temporal fluctuations in one body.

This situation may, however, change with the accumulation of more data and improvements in instrumental precision. The role of isotope data in eliminating non-relevant information is not emphasized enough. It is often easier to state that certain waters cannot originate in a given area, cannot be of older recharge date or could not be in contact with older sources, than to indicate a definite way where they come from, or what is the date of origin. This information while negative in form of statement. in fact eliminates one or more alternative physical hypotheses. This elimination may save time and effort in the elucidation of the correct physical mechanism

4.1.4 The Role of Isotope Data in Future Developments

It may be safely assumed that environmental isotopes will continue to play a significant part in physical hydrology.

This may be inferred from the multitude of methods offered today to the experimenter studying atmosphere - surface water relations, evaporation, lake dynamics, infiltration, stratification etc. [IAEA, 1968] However, with the increasing emphasis on system analysis and stochastic approach, especially in catchment area investigations, there is a new field of application and in fact a new need for isotope data. Their importance may be seen in the following uses: [Nir, 1968].

(a) extension and amplification of hydrological data used in system analysis through isotope data.

(b) Formation of a connecting link between system analysis and physical hydrology: isotope data are often very sensitive to a specific physical model and may even suggest such a model.

(c) Preliminary information on a geohydrological system, where no hydrological data are available. Parametric or stochastic analysis of isotope data may give indication on deviations from steady state, stationary characteristics of the rainfall runoff, relations, type of distributions of transit times and, as mentioned in 4.1.6, even suggest a physical system. Such contribution is of major importance in investigation of underdeveloped areas where hydrological data may not be available and their collection more difficult and costly than that of isotope data.

4.1.5 Future Development of Isotope Methodology

If we accept the areas of future applications of the isotope data, there is a clear need to improve the interpretative tools at our disposal. Three stages can be indicated:

(a) Better theoretical understanding of the information-content of tracer data in system analysis, both parametric and stochastic.

(b) Investigation of specific models, by mathematical simulation as to their response to varied tracer inputs under steady state conditions - this will supply an extension of the theoretical studies, to situations not covered by the theory, due to limitations in mathematical methods.

(c) Test of theories on some representative basins.

All three stages can be pursued simultaneously as there is already some amount of knowledge in these areas. It would be of advantage to the rate of progress if theoretical hydrologists, with experience in recent stochastic system analysis, could be brought to cooperate actively in such research programs.

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4.2 Discussion

In some areas where the water movement is fast, such as in karst and basalt flows significant time variation of concentration in the environmental isotopes occurs at the outlet of such system. These variations in the case of a transient state - tritium for example - can be reproduced by a convolution integral assuming a convenient transit time distribution. In the case of stable isotopes there is a random stationary state created by the random selection of the precipitation contributing to the recharge. In sub-tropical regions, for example, the distribution of the months where the precipitation exceeds potential evaporation is almost random. In other regions, the input occurs at well defined periods of the year. However, the mean stable isotope content of the recharge water is subject to random fluctuations from one year to another as is the case for the volume of the annual recharge itself.

In regions where the mean transit time of the water is of the order of a few years, these variations of the stable content of the recharge are found in the outflow from the system, although considerably damped by the action of dispersion and mixing which takes place in the system. Such variations, if larger than the measuring accuracy are a sure sign of the relatively fast turnover rate of the system studied. It would be very desirable to relate the variance in the input and the output and determine a parameter related to the turnover time of the reservoir.

A second question was raised regarding use of the system analysis techniques for very slowly moving groundwater, where no time variation can be observed at the output and all original variation in the input is smoothed down by long transit times. It was stated that in theory this would be possible. However much of the resolution in such cases is lost by long-term integration and no information can be obtained, i.e. the signals are getting weak and the noise is relatively high.

It may be useful to apply the environmental isotope techniques to sub-systems, instead of to the large systems as a whole. Environmental isotope techniques, however, give the opportunity of locking into the large system and its different parts. When a lake is studied, for example, the residence time distribution of the water is perfectly exponential if there is instantaneous and complex mixing. Any deviation from this theoretical distribution would indicate incomplete mixing, which is a function of the temperature gradient in the lake, its depth etc. Therefore, when a reservoir of any type is studied, the output of the environmental isotopes can generally give good information, although it is not always quantitative.

4.3 ON THE CHARACTERISTICS OF RIVER BASINS.
Summary of the paper by E. Eriksson

4.3.1 Introduction [1]

Eriksson (1963) analyzes the characteristics of river basins from input - output data on tritium — Brown [2]— in the Ottawa River Basin. No model parameter assumption was made in this analysis, although steady state was assumed and the frequency distribution of transit times of the water through the basin was computed.

This paper discusses estimating transit time distributions in river basins from isotope data. As Nir points out, the estimates improve with the amount of data collected, provided sound procedures are adopted.

Eriksson's approach was to consider the mean concentration of tritium in river water as made up of a number of various fractions from previous years properly connected for radioactive decay. It is convenient to start with the year 1964. If the time ever since is divided into equal intervals we get for the first period

$$\gamma_1 = h_1 e^{-\frac{\lambda}{2}} . c_1$$

and the second

$$\gamma_2 = h_1 e^{-\frac{\lambda}{2}} c_1 + h_2 e^{-\lambda(1+\frac{1}{2})} c_1$$

etc. In these (γ) is the mean concentration of tritium in river water for the particular period in question, C is the mean concentration in the net amount of water added during the particular period and the exponential is simply the mean radioactive decay connection needed. In a more general form this can be written

$$\gamma_n = \sum_{j=1}^{n} h_j e^{-\lambda(j-\frac{1}{2})} C_{n+1-j} \qquad (1)$$

which is the formula corresponding to the so-called convolution integral used in hydrology. Equation (1) contains the tacit assumption that h_j i.e. the fractions of the precipitation (γ) intervals earlier is the same from year to year or in other words that the system is in a complete steady state. Rate of addition of water is constant, equalling the rate of runoff. Since this is hardly realistic we ought to consider the case where h_j is also a function of time i.e. depends on the specific interval under study. This additional restraint, which no longer involves any assumption of a steady state, can be indicated by an additional subscript, n, so that the equation reads:

$$\gamma_n = \sum_{j=1}^{n} h_{j,n} e^{-\lambda(j-\frac{1}{2})} C_{n+1-j} \qquad (2)$$

One could of course use this straight ahead in the computations but we can put but little confidence in the series of $h_{j,n}$:s so obtained. Sometimes an $h_{j,n}$ would turn out negative which is physically unrealistic.

We can, however define a mean $\bar{h}_j$ and a deviation from the mean, $h'_{j,n}$ so that $h_{j,n} = \bar{h}_j + h'_{j,n}$

By this definition $\sum_{j=1}^{n} h'_{j,n} = 0$ and $h'_{j,n}$ now becomes a stochastic variable with respect to n.

We can now rewrite the equation

$$\gamma_n = \sum_{j=1}^{n} \bar{h}_j e^{-\lambda(j-\frac{1}{2})} C_{n+1-j} + \sum_{j=1}^{n} h'_{j,n} e^{-\lambda(j-\frac{1}{2})} C_{n+1-j} \qquad (3)$$

The last term will, of course, oscillate around zero even if the $h'_{j,n}$:s are being weighted by the decay corrected tritium concentrations. We might put the second form on the righthand side equal to x_n where x_n is now defined as a stochastic variable. Then we get

$$\gamma_n = \sum_{j=1}^{n} \bar{h}_j e^{-\lambda(j-\frac{1}{2})} C_{n+1-j} + x_n$$

As the equation stands, the variance of x_n will determine the confidence intervals for our estimates of the $\bar{h}_j$:s. If the variance is large, the estimates of the $\bar{h}_j$:s will be poor and vice versa. We hence need an estimate of the variance of x_n.

In order to obtain an estimate of the variance of x_n it is necessary to terminate the series of $\bar{h}_j$:s at some suitable j-value, say k. If we divide the series into two parts we get:

$$\gamma_n = \sum_{j=1}^{k} \bar{h}_j e^{-\lambda(j-\frac{1}{2})} C_{n+1-j} + \sum_{j=k+1}^{n} \bar{h}_j e^{-\lambda(j-\frac{1}{2})} C_{n+1-j} + x_n \qquad (4)$$

where the second sum on the righthand side can be regarded as a residual, say R_n so that the equation reads:

$$\gamma_n = \sum_{j=1}^{k} \bar{h}_j e^{-\lambda(j-\frac{1}{2})} C_{n+1-j} + x_n + R_n \qquad (5\ )$$

We would further have the condition that $\sum_{j=1}^{n} \bar{h}_j \leq 1$. We could make the assumption that if the residual R_n contributes very little to γ_n, this part of the reservoir could be regarded as well mixed, i.e. h_j for $j > k$ would be written

$$a\, e^{-\alpha(k+2-j)}$$

It should further fit smoothly with the last h_j value of the first sum, i.e. $a = h_k$. Hence

$$R_n = \bar{h}_k \sum_{j=k+1}^{n} e^{-\alpha(k+2-j)-\lambda(j-\frac{1}{2})} C_{n+1-j}$$

This refinement is perhaps not needed since in general the error x_n would be larger than this residual. This means we may write

$$\gamma_n \cong \sum_{j=1}^{k} \bar{h}_j e^{-\lambda(j-\frac{1}{2})} c_{n+1-j} + x_n \qquad (6)$$

with the condition that

$$1 - \sum_{j=1}^{k} \bar{h}_j < \left[\frac{1}{n}\sum_{j=1}^{n} x_j^2\right]^{1/2} \qquad (7)$$

We observe that the variance of x_n consists of sums of weighted $h'_{j,n}$:s and the $h'_{j,n}$:s can be regarded as stochastical variables with a certain variance, say σ^2. The variance of x_n is, therfore, of the order of the variance of $h'_{j,n}$ times the square of the mean c_{n+1-j}. Since the latter will vary with n, the variance of x_n will also vary with n. We can standardize this by dividing by γ_n and write:

$$1 = \frac{1}{\gamma_n}\sum_{j=1}^{n} \bar{h}_j e^{-\lambda(j-\frac{1}{2})} c_{n+1-j} + \frac{x_n}{\gamma_n}$$

The best choice of the h_j:s would be obtained through the least squares procedure giving

$$D = \sum_{n=1}^{m}\left(\frac{x_n}{\gamma_n}\right)^2 = \sum_{n=1}^{m}\left[1 - \frac{1}{\gamma_n}\sum_{j=1}^{n} \bar{h}_j e^{-\lambda(j-\frac{1}{2})} c_{n+1-j}\right]^2$$

which is then differentiated with respect to the $\bar{h}_j$:s. These would have to be zero from which we would obtain the set of equations needed to solve for the h_j:s and compute the variance of

$$\frac{x_n}{\gamma_n}.$$

The latter would give an idea about the significance of the h_j:s.

The variance as $\frac{x_n}{\gamma_n}$ would now depend only on the variance of the $h'_{j,n}$:s, i.e. the deviations of h from the mean. This variance would depend to a considerable degree on the time interval chosen. If we chose a fraction of a year as our time interval, we will get the seasonal fluctuations in the $h'_{j,n}$:s which wn most cases would be large. This means that our error of the estimates of the $\bar{h}_j$:s would be large. In addition, many $\bar{h}_j$:s would be needed to cover a reasonable part of the transit time frequency distribution, so that there would not be so many degrees of freedom left. Chosing a year as the interval removes the seasonal variation from $h'_{j,n}$. Since no dependency can be expected in $h'_{j,n}$ from yearly means, we would expect this choice to be satisfactory. We lose, of course, the fine structure of the transit time frequency distribution but, on the other hand, we gain information because the estimated $\bar{h}_j$:s will contain less error.

So far we have had anough data to make an analysis in which proper error estimates are obtained. This will be possible in future also if adequate data are collected.

To compute transit time frequency distributions in river basins, yearly averages seem to be sufficient. Thus, it is inexpensive to obtain the data needed, especially if weighted monthly samples are lumped into representative yearly samples, before tritium analysis is made. This, at present, is the plan for the Scandinavian rivers which have been investigated since 1961.

4.4 Discussion

To apply this method one must determine the environmental isotope content of the input and the output. The frequency of the sampling for this is a function of the hydrologic characteristics of the basin. In large river basins the output concentrations do not have large variations and sampling is needed less frequently than in small basins to determine the tracer output of the system. However, representative sampling of the input (the precipitation over the basin) is usually difficult because the environmental isotope content of the precipitation has large seasonal variations. Especially for tritium, if the record for one particular month is missing or left out of a seasonal mean-value calculation of input, serious errors may result in the estimate of the input concentration.

The straightforward approach to this problem is to consider only the months when precipitation exceeds potential evaporation in the basin. This may work for surface waters, but the environmental isotope input to groundwater systems in river basins is related to a different period or season. Lysimeter data and some field experiments show that under the conditions prevalent in Central Europe, the spring precipitation is being evaporated in subsequent months and thus does not reach the saturated zone.

To identify variations in the source of river water, it is necessary to measure the tritium content throughout the year. Measurements of tritium content of the Saskatchewan river during 1963-64 showed wide fluctuations throughout the year; it was evident that the sources feeding the river changed with time. At certain periods subsurface inflow and at other times glacier and snowmelt were the most important contributors. The base flow had a low tritium content compared to that of meltwater, which reflected the high tritium content of current precipitation. Such variations are useful in understanding groundwater systems; an example of their use is a study in the Modry Dul basin, Czechoslovakia.

A question was asked whether future changes in the hydrological cycle would or would not significantly modify the environmental isotope inputs and relations. Such modifications could occur by the reforestation, artificial recharge of the aquifers, urbanization and the establishment of large surface reservoirs. Water stored in artificial surface reservoirs is considerably enriched with respect to the tritium and stable isotopes due to the molecular exchange of the reservoir waters with the atmospheric water vapour.

The question of change in the hydrologic regime is a general one when hydrologic time series such as runoff, sediment load of streams are studied. Especially when the changes are rapid there may be disruption in the time series. In that case, the analysis could be modified to treat them as transient phenomena to determine the new age distribution function.

5. LAKE WATER BALANCE STUDIES

5.1 LAKE WATER BALANCE STUDIES WITH ENVIRONMENTAL ISOTOPES

Summary of the contribution by T. Dincer

Stable isotope measurements of the lake waters made in various parts of the world have shown that lakes are considerably enriched with respect to stable isotopes compared to the precipitation, runoff and groundwaters in the same region.

In the steady-state conditions the isotopic composition of the inflow and lake waters is related to the inflow and evaporation by the simple equation

$$\frac{I}{E} = \frac{R_E - R_L}{R_I - R_L} \qquad (1)$$

where I and E are the rates of inflow and evaporation respectively, R_E the isotope ratio

$$\left(\frac{D}{H} \text{ or } \frac{^{18}O}{^{16}O}\right)$$

in the net water vapour flux from the lake, R_I the isotope ratio of the inflow and R_L the isotope ratio of the lake waters.

With a careful survey R_I and R_L can be estimated. However, the determination of R_E which is given by the following equation is much more difficult.

$$R_E = \frac{1}{K\,(1 - h)}\left(\frac{R_L}{\alpha} - h\,R_a\right) \qquad (2)$$

where R_a is the isotope ratio in the atmospheric water vapour over the lake, h the relative humidity calculated with respect to the water surface temperature, λ , the equilibrium fractionation factor and K, a factor taking into account the diffusion velocities of the various isotopic species of water and is not well known.

It seems to be possible however to bypass the difficulty of estimating K and measuring R_a by using lakes in the same region where the water balance is well known.

The stable isotope composition of the atmospheric water vapour can be estimated from the isotope balance of the lake with known water balance. For this estimation it is necessary to use a reasonable K value which is not necessarily the correct one. However, using the same value of K for evaluation of the stable isotopic composition of the net water vapour flux for the lake with unknown water balance will prevent large errors introduced by using an uncorrect K value.

Evaporation pans can possibly be used to estimate C_E for the lakes. At present, studies are being made in Neusiedler See in Austria to evaluate the usefulness of evaporation pans in lake isotope studies.

When the isotopic composition of the atmospheric water vapour is measured by sampling, it should be borne in mind that the selection of the location of the sampling point is not very important.

We can write

$$C_E = \frac{1}{K\,(1 - h)} \left[\frac{C_L}{\alpha} - (m\,h\,C_a + n\,h\,C_E) \right] \qquad (3)$$

where mh is the partial pressure of the water vapour from sources other than the lake and nh is the partial pressure of the water vapour produced by the lake. By solving this equation with respect to C_E and noting that

$Knh \cong nh$ the equation can be simplified to obtain

$$C_E \cong \frac{1}{K(1 - mh)} \left(\frac{C_L}{\alpha} - mh\,C_a\right) \qquad (4)$$

which is a good approximation even for relatively small values of m compared to unity in the case of deuterium.

Equation 4 shows that the water vapour produced by the lake has little influence on the isotopic composition of the water vapour at the point where the relative humidity is measured, regardless of the situation of this point with respect to the lake. It should be added however that this reasoning holds for lakes which do not have an influence in the environment as a major source of moisture.

5.2 Discussion

A question was raised on the validity of equation 4 showing the relative importance of the atmospheric moisture being contributed by the lake and by the other sources. This equation is an approximation and is valid where the contribution of the lake is a few percent in the case of oxygen-18, but is valid for much higher percentages for deuterium.

The isotope content of the lake water is by far the most important factor to determine. However when a sufficient number of samples which subsequently can be combined and repeatedly measured are collected the mean isotope content of the lake waters can be determined with desired accuracy.

Studies made in South Western France on six lakes having capacities 10 - 350 x 10^6 m^3 were reported. These studies which were made using environmental tritium, have shown the difficulty of applying tritium in lake water balance studies. The difficulty is due to the transient character of thermonuclear tritium.

Because there is no fractionation effect in the evapotranspiration process, the presence of swamps can be a complicating factor in lake studies. The water lost by evapotranspiration can be treated as other losses and cannot be easily separated from them.

6.1 ADJUSTMENT OF RADIOCARBON AGES OF GROUNDWATER BY MEANS OF $^{13}C/^{12}C$

Summary of the contribution by B.B. Hanshaw

The successful application of environmental isotope techniques in hydrology requires close cooperation between the isotope worker and the hydrologist. It is important to understand the problems that hydrologists are interested in solving. Ordinarily the basic problem for the hydrologist, as it is in all scientific fields, is the prediction: How will a hydrologic system respond to a given set of conditions? or what will happen if new conditions are introduced in the system. The purpose of the isotope worker,therefore, is to find ways of helping the hydrologist understand a system and predict its response.

In groundwater studies, hydrologists are interested in defining the boundaries and the aquifer characteristics such as the permeability distribution in the groundwater system. Telling the hydrologist the age of the water at a given point of the system may not be of much value to him. It is much more useful to identify the recharge and the discharge regions the interconnections between different surface and groundwater bodies and to give a reasonably accurate estimate of regional permeability of the aquifer.

One of the best uses of carbon-14 can be in estimating aquifer permeabilities. Darcy's formula states that the filter velocity is equal to permeability times the hydraulic gradient. The actual velocity of water in the aquifer is equal to filter velocity divided by the porosity. If the hydraulic gradient is known and if porosity can be estimated, it is possible to determine the regional permeability distribution using carbon-14 ages. Hydrologists are not interested in whether the water is 22.000 or 25.000 years old· therefore, the use of different age adjustment techniques is perhaps not as important as it looks to the laboratory worker. The raw C-14 data itself is already a valuable tool in groundwater studies for the hydrologist.

Most of the ^{14}C content picked up by groundwater in a recharge area comes from the soil-zone CO_2, derived principally from the oxidation of organic matter. Once the carbonate species and CO_2 from the zoil zone are incorporated in the groundwater system, two major problems, (1) the isotopic exchange of the dissolved carbonate species with the aquifer material and (2) the dissolution of the carbonate rocks by the free CO_2 available in the water, remain. Both are likely to add non-radiogenic carbon to the dissolved carbonate species in the water. The isotopic exchange is not significant in influencing the carbon-14 content of the groundwater. Recent studies by Rye of the US Geological Survey also bear on the isotopic exchange problem. Rye found that in calcite deposits 50 million years old, the dissolved CO_2 species were out of isotopic equilibrium with the solid phase.

One way to account for the dissolution of the carbonate rocks is based on the ^{13}C content of the dissolved carbonate species in water. The CO_2 which has been derived from the soil zone approximated by that of plant material, generally has a ^{13}C content $\delta^{13}C$ of $-25 \pm 2‰$ relative to the Peedee belemnite (PDB)standard. A major problem in finding a true "age" for groundwater is that the water generally dissolves non-radiogenic material, chiefly marine carbonate minerals with a $\delta^{13}C$ value of about zero. Solution of these minerals decreases the $^{14}C/^{12}C$ value, causing the ^{14}C age of the groundwater to appear older than it actually is. To adjust for the solution of carbonate minerals, we have had good results using a correction equation developed by Pearson (Pearson and White, 1967). This equation is:

$$^{14}C\%\ \text{mod.(adj.)} = \frac{\delta^{13}C_{soil} - \delta^{13}C_{ls}}{\delta^{13}C_{water} - \delta^{13}C_{ls}} \cdot {}^{14}C\%\ \text{mod.(lab)}$$

We believe that the age adjustment made using this equation is much more accurate than the one obtained simply by using the empirical approach of changing all laboratory ^{14}C determinations to reflect a postulated initial ^{14}C content of 85% of modern. Also, in more than a dozen (out of about 200 groundwater samples) that we analyzed, we found an initial ^{14}C% of greater than 85% with some as high as 98% of modern. Obviously, this empirical correction can be subject to considerable error.

The validity of the above adjustment equation is strengthened by tritium analysis in a recent study — one of a series of ^{14}C groundwater studies being conducted in various geologic terranes in the United States.

Field test of ^{13}C adjustment using tritium

Samples of groundwater from both recharge and confined portions of the limestone aquifer of central Florida were analyzed for carbon isotope and tritium content. Because tritium has a short half-life (12.26 years) compared to ^{14}C (5570 years), water in recharge areas should contain tritium whereas samples from farther down-gradient, in the non-recharge part of the system, should lack tritium and indicate old radiocarbon ages. Results of the study are given in Table 1 taken from Hanshaw and others (1968).

Table 1

Comparison of lab and adjusted ^{14}C ages using ^{13}C correction

Sample	Laboratory ^{14}C age	$^{13}C_{PDB}$‰	Adjusted ^{14}C age	TU
Weeki Wachee-11	3,800	-17.1	250	103 ± 10
Lecanto-5......	5,800	-14.4	800	36 ± 4
Lecanto-6......	5,350	-15.8	1,250	15 ± 2
Frostproof.....	21,800	-13.2	16,000	0.0 ± 1
Holopaw........	23,800	-14.9	19,200	0.7 ± 1
Arcadia........	35,500	- 13.3	29,800	0.0 ± 1
Ft. Pierce.....	31,000	- 5.8	------	0.1 ± 1
Palmdale.......	35,000	- 2.9	------	11.0 ± 2, 0.6 ± 1

The first three wells in Table 1 are in a recharge area and contain thermonuclear tritium. Weeki Wachee-11 had 103 T.U. in 1966; the average tritium content of rainfall in central Florida that year was 114 T.U. which indicates the sample was primarily post-1954 rainfall. The radiocarbon age of this samples is in agreement with tritium results when adjusted for solution of limestone by means of ^{13}C content. This shallow well is located almost exactly on the piezometric high and should contain only recent recharge. The two Lecanto samples are from wells farther down-gradient. They receive recharge both locally and by lateral flow from up-gradient recharge. Therefore, we would expect less tritium owing to mixing of recent rainfall with much older groundwater from up-gradient recharge. The next three wells in Table 1 are from the confined portion of the system, contain no measurable tritium, and produce very old water according to both columns of ^{14}C age.

The Ft. Pierce sample is an example of a situation where no correction is presently possible. The well produces slightly saline water (1300 mg/l TDS) of the sodium chloride type and doubtless represents mixing of potable groundwater with connate ocean water. Because the $\delta^{13}C$ ratio of sea water bicarbonate ion is zero, the result of mixing is to increase the ^{13}C content of the water. Also, when two solutions are mixed, local solution or precipitation of carbonate minerals could occur: this would change the ^{13}C content of the solution in an unknown way. Currently no way is known to adjust the age of such mixed samples if mineral solution or precipitation occurs. A further complication -- discussed in more detail in the next section -- in the Ft. Pierce well is the presence of H_2S gas.

Two samples for tritium analysis were taken at the Palmdale well. The analytical results point out the ease of sample contamination from atmospheric tritium. The well has an aerating tower to rid the water of H_2S prior to consumption. Apparently, several minutes contact with warm, humid air is sufficient to increase the tritium content of a water sample. A second sample for tritium analysis was taken before the water reached the aerating tower and essentially no tritium was found in this sample. The radiocarbon age was not adjusted for ^{13}C content because of the anomalously low $\delta^{13}C$ value. The cause of this low value is presently unknown.

Sulfate reduction

One reaction expressing sulfate reduction is: $SO_4^{-2} + 2CH_2O = H_2S + 2HCO_3^-$ or, in a petroliferous or more reducing environment: $SO_4^{-2} + CH_4 + H^+ = H_2S + HCO_3^- + H_2O$. Chemical changes such as those indicated by these equations, are observed in nature. Thus, in Florida and many other aquifer systems, sulfate commonly increases away from the recharge area. Generally, however its concentration levels off or decreases where H_2S occurs in the water. Likewise, HCO_3^- may increase in the area where H_2S is found. In order to correct for the production of dissolved carbonate species by sulfate reduction, we need to know the H_2S content; from it we may be able to calculate the amount of HCO_3^- produced. Also we need to know the $\delta^{13}C$ of the HCO_3^- produced. To calculate this the ^{13}C content of the bicarbonate precursor and the fractionation factor for the organic:bicarbonate reaction, must be known; these may be difficult to obtain. However, because the concentration of H_2S in most groundwater is commonly relatively low (on the order of 2 to 15 ppm), the sulfate reduction reaction may actually produce an insignificant additional amount of dissolved carbonate species and can, possibly, be ignored. It is possible that the activity of H_2S is buffered by some solid phase, perhaps pyrite. If so, the H_2S content is not a true measure of the HCO_3^- produced by sulfate reduction; perhaps the decrease in SO_4^{-2} or increase in HCO_3^- concentration (these would check each other) in the area of H_2S occurrence could be used to calculate the amount of HCO_3^- produced by the reaction. However, two problems remain: (1) lack of knowledge of the $\delta^{13}C$ of the HCO_3^- produced, and (2) the possibility of carbonate precipitation. Until the effects of the reduction reaction are better known, this should be considered a problem for further research.

$^{13}C/^{12}C$ fractionation during sampling

In order to use the adjustment equation, the measured $\delta^{13}C$ must be representative of the true value. Recent work has indicated that a serious discrepancy exists between $\delta^{13}C$ values obtained from $SrCO_3$ from a gas evolution method for collecting all the dissolved carbonate species and $\delta^{13}C$ values run on $SrCO_3$ obtained by means of direct precipitation. The results are given in Table 2.

Table 2

Comparison of ^{13}C obtained by gas evolution (G.E.) and direct precipitation (D.P.) techniques

Sample	$\delta^{13}C_{D.P.}$ −	$\delta^{13}C_{G.E.}$ =	$\delta^{13}C$
Weeki Wachee Spring	-13.40	-15.72	+2.32
Weeki Wachee-12	- 4.00	-10.62	+6.62
Yeehaw Junction	- 5.32	- 8.40	+3.08
Ft. Pierce	- 2.40	- 5.79	+3.39
Cocoa-12A	- 8.88	-11.69	+2.81
Clermont	- 9.99	-14.12	+4.13
Frostproof	- 8.80	-13.21	+4.41
Vero Beach	- 3.59	- 8.89	+5.30
Arcadia	- 8.05	-12.34	+4.29
Container Corporation	-10.38	-16.39	+6.01
Ft. Clinch	-10.40	-16.46	+6.06
Sether	-10.20	-15.79	+5.59
N.E. Florida Hospital	-10.04	-15.72	+5.60

It is obvious that a serious difference exists and that the ^{13}C results obtained from the D.P. method are invariably heavier than the ^{13}C results from the G.E. technique. The first nine sample pairs were not obtained at the same time nor in a necessarily totally comparable manner. Before the last four samples were taken, we had become aware of the problem and these were processed with great care. Samples were processed in a chemically identical manner. the results indicate the magnitude of the problem. An average discrepancy of 5.8 ± 0.2‰ occurs between the four pairs. In order to try to establish which technique gives the true $\delta^{13}C$ value an $NaHCO_3$ solution was prepared in the laboratory from reagent $NaHCO_3$ with known $\delta^{13}C$. The results are inconclusive:

Standard $NaHCO_3$, $\delta^{13}C$ = -11.4

$\delta^{13}C_{G.E.}$ = -12.8

$\delta^{13}C_{D.P.}$ = - 9.6

Apparently both methods give results which deviate from the true $\delta^{13}C$; G.E. gave light results, and the D.P. method gave too heavy value. ^{13}C fractionation during collection means that ^{14}C is most likely also fractionated. This is not a serious problem by itself in groundwater dating, but should be corrected if possible. However, the seriousness of the ^{13}C error shows up particularly in the use of the age adjustment equation. Further work to understand the reason for these deviations and to establish the best technique for obtaining samples of dissolved carbonate species for carbon isotope analysis is underway.

General hydrologic conclusions

With the help of the carbon-14 and tritium results and studies made independently by other workers using mineral saturation and temperatures, the area of major recharge of the aquifer has been extended considerably in comparison with the earlier assumptions based on the piezometric map only. The recharge area thus redefined has a broadly scattered carbon-14 age, total chemistry and other parameters. The total dissolved solids, for example do not show systematic variations nor does the distribution of chloride sulfate or calcium-magnesium ratio. However, from the region where the aquifer becomes confined toward the south, there are systematic variations with respect to carbon-14 content, which decreases gradually; downgradient the total dissolved solids increase in a similar way. Chloride continues to increase until it reaches a very high value along the coast.

Fig. 36 shows that in the area of major recharge the waters which are undersaturated are not right on the piezometric high. In the area where the aquiclude is thinner, low values for both calcite and dolomite saturation are found. The total dissolved solids show the same picture, i.e. the lowest values are not at the top of the piezometric high but in a different region, where actually large amounts of recharge are taking place. The carbon-14 ages agree with the chemistry of waters: the youngest ages are not found on the piezometric high but some distance downgradient, where probably recharge is more significant. However, if carbon-14 data are used without any hydrologic information, such as piezometric maps, they may lead to unacceptable results such as water flowing upgradient. It is important, therefore, to consider all the hydrologic, geologic, chemical and isotope data together in order to define a coherent hydrologic situation.

Figs 37 and 38 show the unadjusted and adjusted carbon-14 isochrones of the groundwater and how the age contours are moved by almost a half-life toward the recharge area when the adjustment is applied.

Table 3 shows the groundwater velocities calculated by carbon-14 ages compared with the velocities estimated by conventional techniques. The agreement is good both for corrected and uncorrected ages; the corrected ages are slightly more accurate. However considering the uncertainties in the estimates of the permeability, the difference is not significant. Permeability is a parameter which changes by several orders of magnitude in most aquifers so values that fall into the same order of magnitude can be considered compatible. This shows that the carbon-14 age adjustment using different techniques is not critical for practical hydrological work.

Table 3 Comparison of groundwater flow velocities from unadjusted and adjusted radiocarbon dates with hydrologic calculations. Velocity is in meters per year.

No.	Location	$V_{C^{14}}$	$V_{C^{14}}$(adjusted)	$V_{hydrologic}$
5	Polk City			
		8	13	10
2	Ft. Meade			
		2	4	7
7	Wauchula			
		12	6	5
1	Arcadia			
		-	5.5	-
6	Cleveland			
Between	5 and 7	4	8	9
Between	5 and 1	5	7	7
Between	5 and 6	7	9	7

6.2 Discussion

A question was asked about the source of CO_2 that increases the hardness of water along its course downgradient. The amount of CO_2 is not enough to increase, markedly, the bicarbonate content by dissolution. If an extra millimole of bicarbonate is to be added to water. one needs half a millimole of CO_2. The answer is that the CO_2 that originates from the soil zone reacts completely in the recharge area. Throughout the whole recharge area in the aquifer studied in Florida, waters are still undersaturated with respect to the calcite and continue to increase in saturation downgradient. These increments are not very large in many cases. It seems that there is still an "agressive" tendency in the water even beyond the recharge area and that it takes thousands of years for water to reach equilibrium with aquifer minerals. Unfortunately this cannot be duplicated by laboratory experiments.

If slightly acid water is passed through a column of calcite, no acid water is found at the bottom of the column even though the movement of water is very fast. This seems to show that the dissolution process is not slow. However it has been found in field experiments that unsaturation can extend for considerable distances.

Concerning the Pearson formula of adjustment of carbon-14 ages, it was stated that in some soils in arid and semi-arid regions limestone horizons are present at relatively shallow depths. In such cases considerable exchange can take place immediately after infiltration to the soil, before the water reaches the aquifer. Such a process makes the application of the Pearson's equation not valid.

In studies made in USSR, values of ^{13}C content were found to be -25‰ without exception in the soil air taken from depths 20-30 cm. In Germany, in similar experiments, similar results have been obtained, although the ^{13}C values were slightly lower — about -20 and -22‰. This shows that the value of -25‰ used in Pearson's formula is reasonable.

6.3 THE ^{14}C-WATER-AGE DETERMINATION by I Wendt.

The water-age determination by means of carbon-14 is based on the assumption that biogenic CO_2 (^{14}C activity = 100% compared with atmospheric CO_2 and $\delta^{13}C$ = -25‰) dissolves fossil carbonate (^{14}C = 0: $\delta^{13}C$ = 0) according to the equation

$$x\ CaCO_3 + (x + y)\ CO_2 \quad 2x\ HCO_3^- + y\ CO_2$$

The water therefore, has a certain concentration of HCO_3 and CO_2. In case this reaction represents a closed system, i.e. the total amount of CO_3 and CO_2 present before the reaction is equal to the amount of HCO_3 and CO_2 in solution after the reaction, the relative ^{14}C activity and the $\delta^{13}C$ value would be equal to the relative amount of biogenic carbon.

If, however, the $CaCO_3$ dissolution takes place above the groundwater table, the relative biogenic carbon content and, accordingly, the initial relative ^{14}C activity, is considerably higher than one would calculate from the HCO_3 and the CO_2 concentrations measured in the water sample. This is simply because part of the CO_2, which has exchanged with the dissolved carbon, remains in the pore volume of the soil.

The influence of this exchange has been investigated both theoretically and by means of model experiments in the laboratory. These investigations have proved that it is not possible to calculate the initial carbon-14 activity using the measured $\delta^{13}C$ value.

Based on these results, the groundwater recharge has been studied under natural conditions in large lysimeters of 4 m depth and 400 m^2 area. The three lysimeters were filled with predominantly sandy soil and were covered with grass, leaf-wood and pine-wood, respectively.

One can draw the following conclusions from the results obtained up to now:

6.3.1 The carbon-14 activity of the dissolved carbon increased from 1965 to 1968 slightly -- from about 90% modern to about 115% modern in all three lysimeters.

6.3.2 The carbon-14 activity and its time dependence is not equal in the three lysimeters.

6.3.3 The HCO_3 concentration changes within a few months, up to a factor of two.

6.3.4 The water is very soft and therefore contains only small CO_2 concentrations (compared with the HCO_3 concentration), but is still considerably higher than the theoretical equilibrium concentration.

6.3.5 The $\delta^{13}C$ values remain within the range from -15‰ to -18‰. The simple ^{13}C correction would yield ^{14}C activities of the biogenic CO_2 of 115 to 170‰ modern. If one corrects the measured ^{14}C activities using the chemical Q factor

$$\left(Q = \frac{\frac{1}{2}HCO_3 + CO_2}{HCO_3 + CO_2}\right)$$

one would obtain values of 150‰ modern to 200‰ modern. Such a difference between the two types of correction must be expected, in case the $CaCO_3$ dissolution takes place above the groundwater table.

The water collected at about 4 m depth is probably two to four years old. But because of the very pronounced change of the atmospheric carbon-14 activity during the last five years a correlation of carbon-14 activity of the water samples and the atmospheric CO_2 is possible only after a longer period of observation.

Repeated measurements of natural groundwaters show that most of the water sampling stations are constant in carbon-14 activity over several years, but some show changes with time.

An improvement of the carbon-14 method of water-age determination should include a check of the following assumptions:

a. Soil-CO_2 consists of pure modern CO_2:
^{14}C = 100% modern; $\delta^{13}C$ = -25‰

b. The carbonate in the soil is purely fossil:
^{14}C = 0; ^{13}C = 0

Assumption (a) seems to be proved at least partly. $\delta^{13}C$ values of soil-CO_2 already published and measurements made by the author, yielded ^{13}C = -25 ± 2‰. The ^{14}C activity of soil CO_2 taken from 20-30 cm depth at various places showed ^{14}C activities of 125% to 155% modern while the atmospheric CO_2 measured simultaneously yielded a constant value of 157 ± 1% modern.

6.4 Discussion

To take care of the process of dissolution taking place in the non-saturated zone the ^{13}C value of the biogenic carbon could be increased to, for example, -22‰ or even to -20‰. The work in the Floridan aquifer shows that the Pearson's adjustment formula is valid.

A question was raised also concerning the new method of adjustment. It was stated that the water moving in the unsaturated zone would still contain free CO_2 and by the time it reaches the water table it would still potentially dissolve carbonate from the soil. Conditions where such water is not actively dissolving calcite are rather unusual.

However, there is much more CO_2 present in the upper layers of the soil than finally is carried away by percolating water. Considerable amounts of CO_2 is active in some way or another in the solution process but is not finally dissolved in the water. The CO_2 concentration in the water drops very rapidly from the surface downward.

Concerning the time required for saturation of the water with respect to dissolved carbonate species the saturation is only a matter of days in laboratory experiments. However, in nature this does not happen and water is unsaturated with respect to dissolved carbonate species in many instances. Supersaturation and undersaturation are frequently observed, depending on the environment studied.

It was pointed out that the carbon contributed by the organic matter in the soil is not necessarily modern. A certain part could be as old as 2000 years, for example. However, it should be remembered that what matters in this case, is not the residence time, but the turnover time, i.e. mass divided by the flux; this is hardly more than 100 years. although a certain fraction of the carbon in the soil is very old. The contribution of this old carbon is negligible.

6.5 CARBON-14 STUDIES MADE BY THE INSTITUTE OF GEOLOGY OF THE AQUITAINE BASIN.

Summary of the contribution by P. Levêque

Studies of methodological nature have been made on three types of aquifers. The first, a non-confined aquifer, is situated in southern France on the left bank of the Rhône in the Craux plain. Tritium, carbon-14 and uranium were used together with the routine chemical analyses of water. The second aquifer is situated to the east and south-east of Paris, in a rather peculiar formation. The aquifer is confined in some places and non-confined in others; it is typically karstic at some places. The situation is complicated and the results of carbon-14 and tritium are both very interesting and useful. The third aquifer is the great sedimentary basin of Aquitaine. It is confined and has depths ranging between 100 and 550 meters.

The tritium content of the groundwater of the aquifer in the Craux plain has been measured and compared with the tritium content of the precipitation in the same region. The tritium concentration of the groundwater samples, which were about 250 T.U., indicated that the water was derived from precipitation that occurred three or four years ago, when the tritium content of the precipitation was high.

The carbon-14 results agreed with the tritium results. Eight samples, which were collected for carbon-14 analysis, showed ratios ranging from 86 to 300% of the modern carbon. The only carbon-13 result available is $^{13}C = -14.4‰$. The corrected carbon-14 age is found to be 260 ± 90 years.

6.6 Discussion

It was pointed out that in cases where carbon-13 values were more enriched than -12‰, the Pearson's corrections would not be applicable. Carbon-13 contents more enriched than -12‰ probably indicate water of volcanic origin. The carbon-13 content of waters in regions of active volcanism can be as high as 0‰ or even higher. Another possibility is the supersaturation where C-13 values as high as -10‰ can be observed. However, the temperature of waters of the Aquitaine Basin, which follow closely the geothermal gradient, indicate that the waters are not of volcanic origin.

If the C-13 content of the carbonate rocks or cement material in a sandstone aquifer is lower than ± 0‰ then the resulting carbon-13 content of the dissolved carbonates species will be too low, giving an apparently higher contribution to the biogenic carbon-13 and consequently making the water look older than it actually is. The carbon-13 content of an aquifer, or cement material, may also be different from one place to another. This makes it necessary to have a representative carbon-13 value of the aquifer by adequate sampling and measurement. The change of carbon-13 content of the limestone is not due to isotopic exchange. It is rather due to the solution and reprecipitation process.

6.7 ENVIRONMENTAL ISOTOPE INVESTIGATIONS IN THE GRAZ BASIN, AUSTRIA

Summary of the contribution by J.G. Zötl and G.L. Meyer

The tritium content of the samples collected in the deep artesian wells of the Graz basin was all below measuring level. The carbon-14 results indicated groundwater ages between 4000 and 25,000 years, showing that the groundwater movement in the aquifer studied is very slow. The raw carbon-14 ages were corrected by several methods which gave comparable results.

Because information on the aquifers tapped by the wells and their respective piezometric surfaces was lacking. no quantitative answers as to the velocity of the groundwater were obtained. This makes the deuterium and oxygen-18 content of the waters sampled even more critical. When oxygen-18 is plotted versus deuterium (Fig. 1) it is seen that all samples with relatively younger carbon-14 ages, i.e. less than 12,000 years, uncorrected, are found on the upper part of the diagram. This, of course, gives added confidence to the carbon-14 dating of the groundwater. The points representing groundwater samples do not fall on the modern precipitation line with the slope of 8 and deuterium excess of +10‰. Instead they all fall to the right of the line in similar fashion to those of Jordan and the Konya plain of Turkey. The isotopic changes that occur during the infiltration and percolation of the water into the soil may help explain the reason for this anomaly.

One plausible explanation of this condition is that there were changes in the paleozoic temperatures; during the past such changes would have influenced the isotopic composition of the precipitation and consequently of recharge as well. Also the chemistry of waters can help explain such situations; it should be investigated with the environmental isotope content of the groundwater. The variation in the stable isotope content of waters, in the case studied cannot be explained by the altitude effect as no large altitude differences can be expected in the recharge areas.

The carbon-13 values, which are around -10‰, should also be explained in order to have a satisfactory picture of the carbon-14 ages. The extracting of carbonates by different methods, i.e. gas evolution and precipitation from the water may cause the high carbon-13 values.

Although there are obvious difficulties in the interpretation of carbon-14 data, they are extremely useful. For example, the oldest waters were not found, as one would expect, near the center of the basin but at its borders. This may be significant in making estimates of the availability and the reliability of the groundwater resources in the Graz basin, where wqter supplies for dairy industries are important to the region's economy.

Whenever it is possible to check carbon-14 results by conventional hydrologic methods, excellent agreement has been found, but in regions where hydrologic information is not available or very sparse, one has to rely on the indications given by carbon-14 results only; quantitative results cannot be obtained.

The work in the Graz Basin is still in progress. In order to have a better interpretation of the environmental isotope data and especially of carbon-14 content of the groundwater, basic data collection such as streamflow measurements, piezometric elevation has started.

6.8 Discussion

Several persons expressed the opinion that the carbon-14 method had stood the test of several studies. There is no doubt that a powerful new hydrogeological tool is now available in the carbon-14 dating of water. However, it was also an unanimous opinion of the panel that some confusion reigned in the problems of exchange and adjustment of ages. The hydrologist in the field is not in a position to solve all these complicated problems and choose the right way of adjusting carbon-14 data. It was decided, therefore, that the panel make definite recommendations. The sub-group of the panel made the following recommendations, which were subsequently discussed by the whole panel and adopted:

6.9 RECOMMENDATIONS CONCERNING THE RADIOCARBON DATING OF GROUNDWATER

6.9.1 General Recommendations

6.9.1.1 It is the consensus of all the participants that radiocarbon dating of groundwater is a valid method and in most cases, when applied properly, it will give valuable new information about the aquifer system. This information is not available from other methods or available at least only after long and extensive investigation by routine hydrologic methods.

6.9.1.2 The carbon-14 method of dating applied to groundwater studies should be made more readily accessible to the field hydrologists. Most of the papers which cover the subject adequately and competently are scattered through a number of different publications that are not easily accessible for the practising hydrologist. A good survey paper covering the limitations and the advantages of the method, sampling procedures and interpretation of carbon-14 ages of groundwater should be prepared and published in a widely-read hydrologic journal.

6.9.2 A large number of studies indicate that molecular exchange of the water with the aquifer probably does not play a significant role in altering the carbon-14 content of groundwater. If considerable mass exchange did take place, the carbon-14 dating method could not work. The favourable comparison of flow rates and other aquifer characteristics estimated both from carbon-14 data and data obtained by standard hydrologic techniques indicates that this is not the case.

6.9.3 It is recommended that $\delta^{13}C$ standards be established and a limited intercomparison be carried out among the few laboratories.

6.9.4 Further investigations should be conducted for the comparison of gas evolution and precipitation methods of collecting the carbonates from the water sample.

ANNEX

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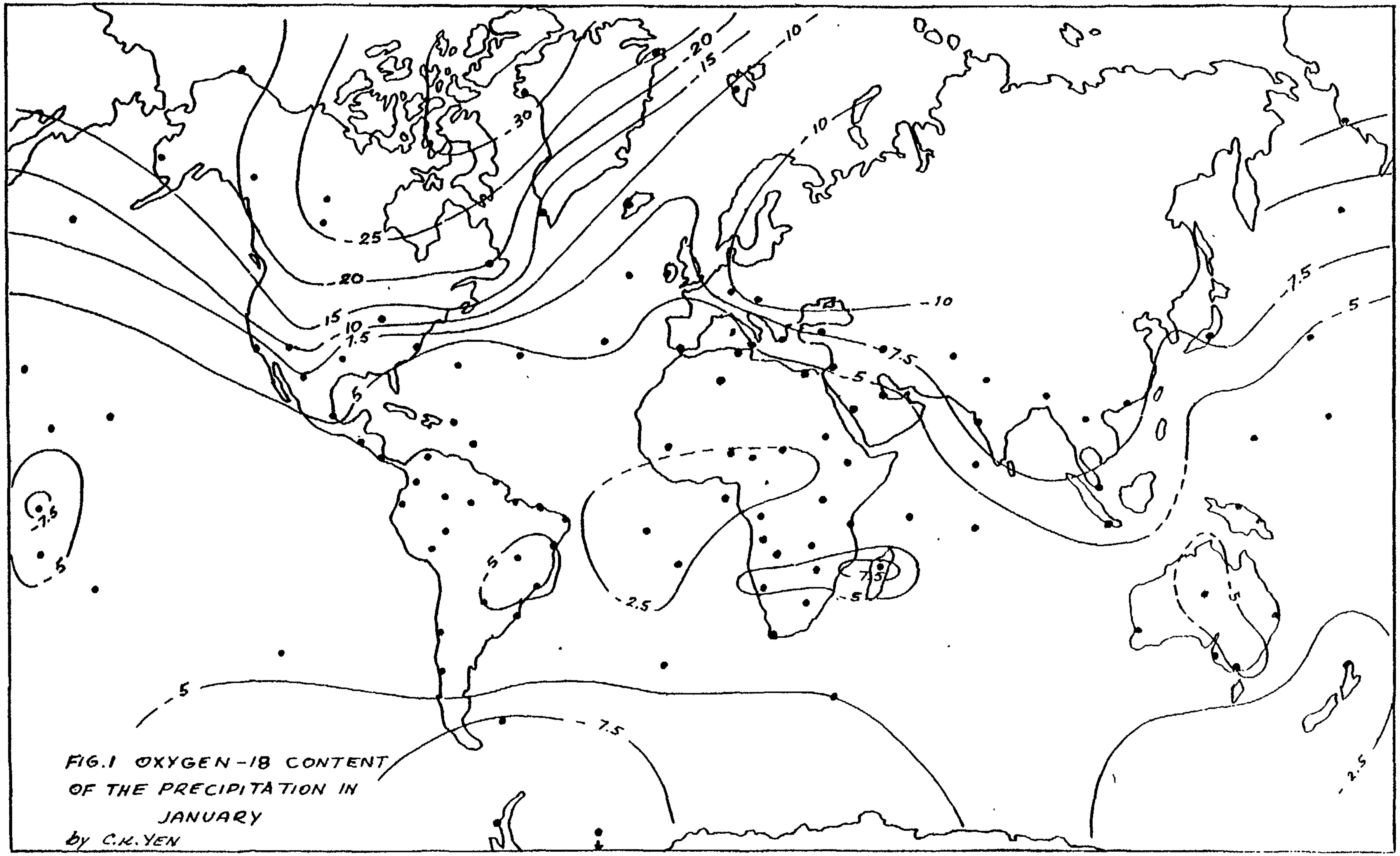


FIG. 1 OXYGEN-18 CONTENT OF THE PRECIPITATION IN JANUARY

by C.K. YEN

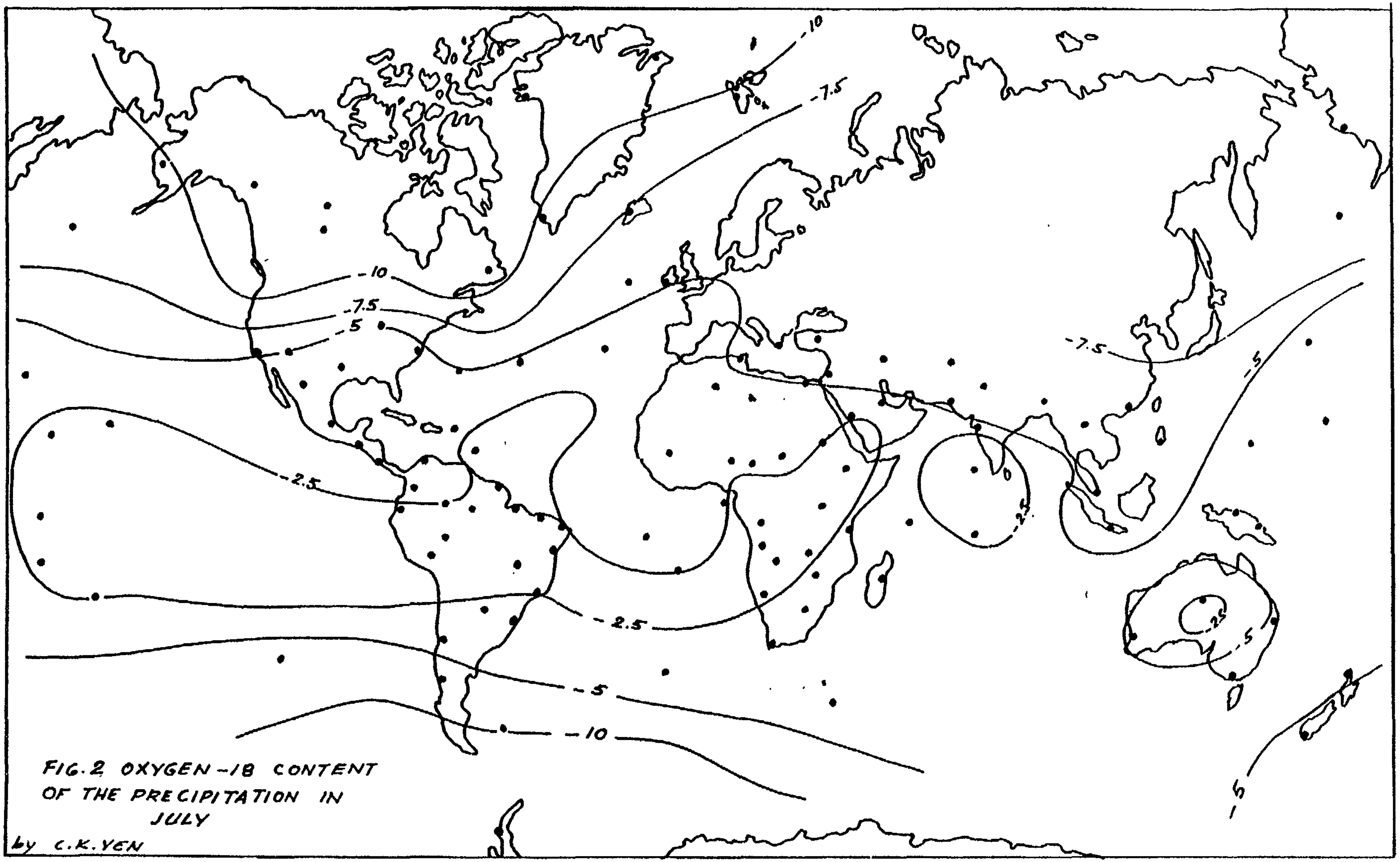


FIG. 2 OXYGEN-18 CONTENT OF THE PRECIPITATION IN JULY

by C.K. YEN

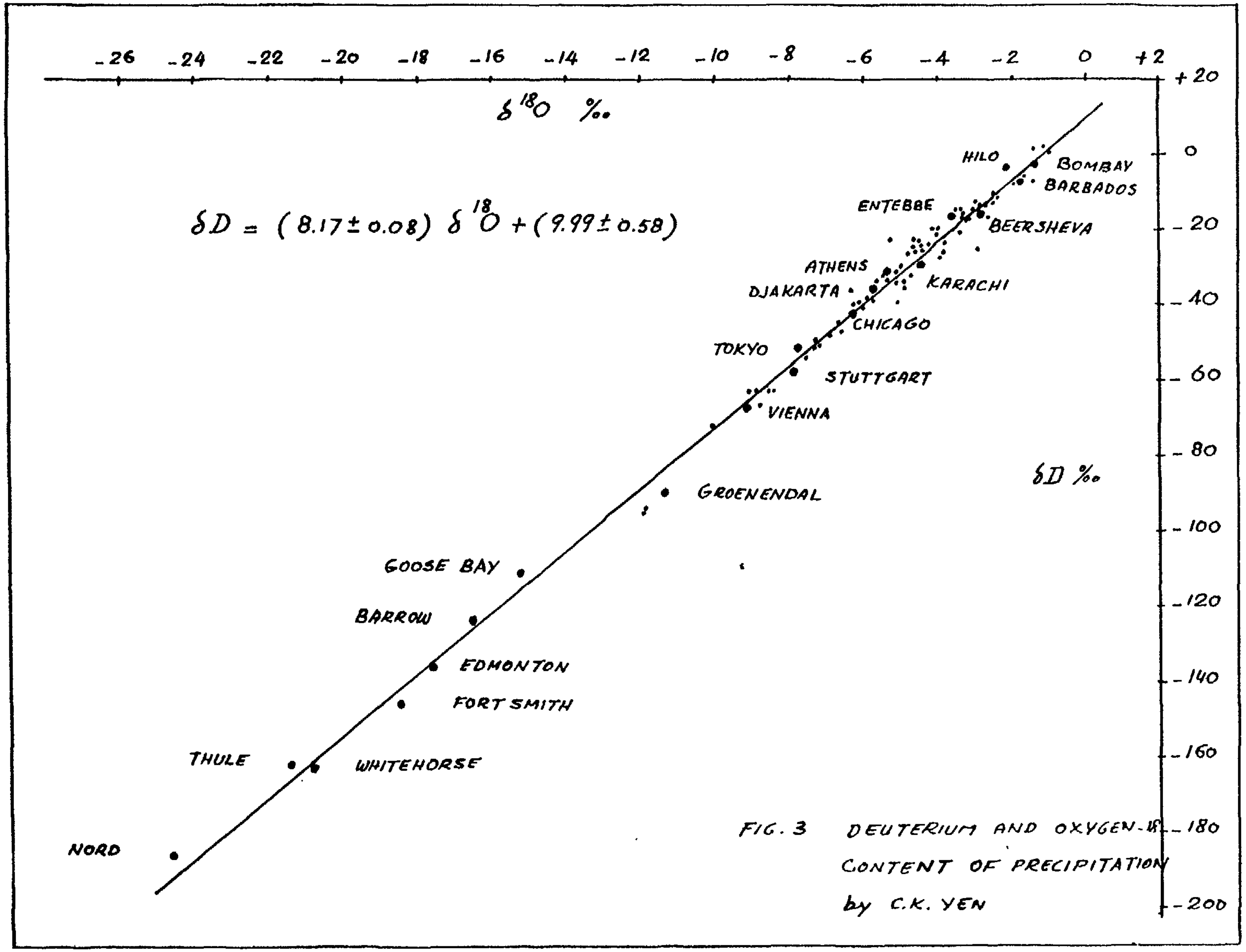


FIG. 3 DEUTERIUM AND OXYGEN-18 CONTENT OF PRECIPITATION by C.K. YEN

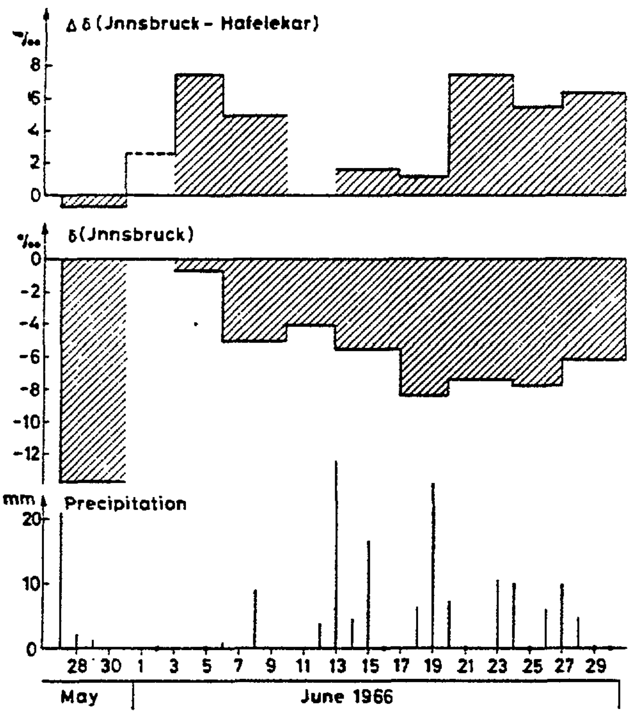


Fig. 4 Summer precipitation. Lower section: Amounts of precipitation at Innsbruck. Mid section: Mean $\delta(O^{18})$ of precipitation at Innsbruck. Upper section: Mean $\delta(O^{18})$ difference, $\Delta\delta$, between Innsbruck and Hafelekar.

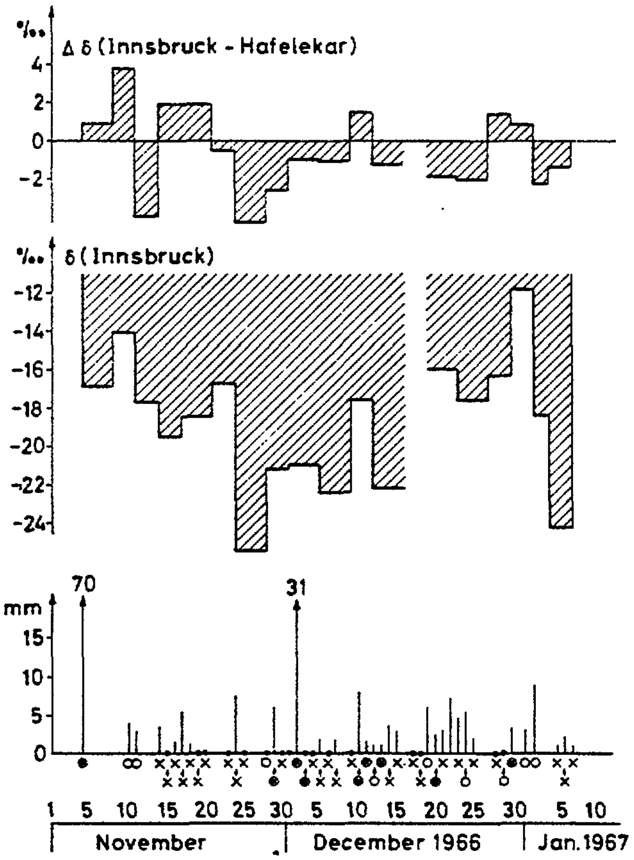


Fig. 5 Winter precipitation (cp. Fig. 1).

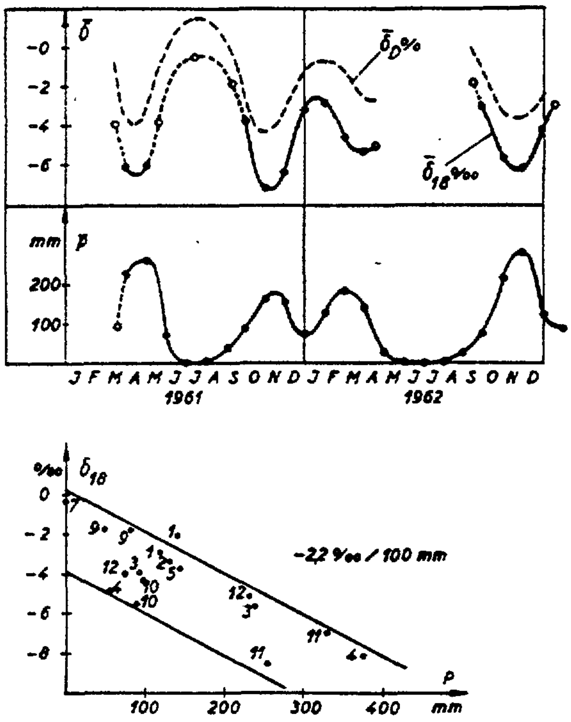


FIG. 6 Amount effect at Binza (Leopoldville), Congo.

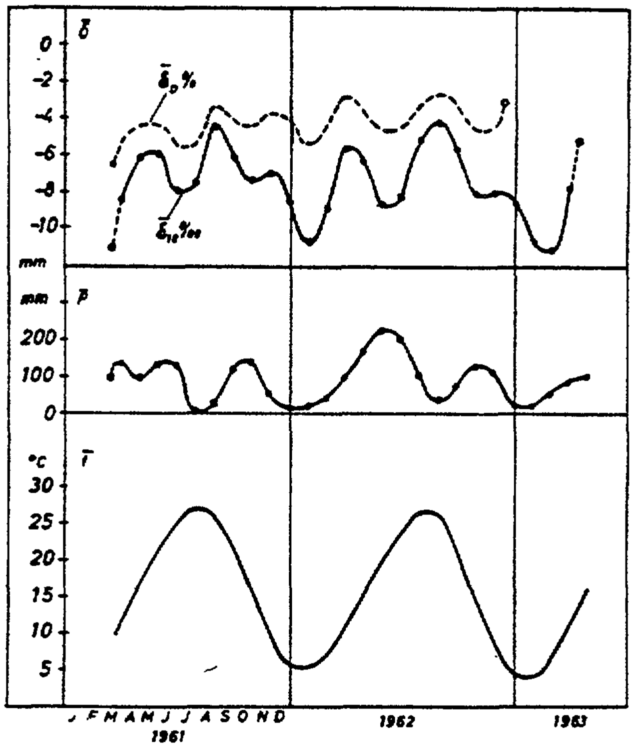


FIG. 7. Combined temperature effect and amount effect at Tokyo. Upper section: $\bar{\delta}$ = mean δ of two neighbouring months. Mid section: $\bar{p}$ = the corresponding amount of precipitation. Lower section: The corresponding mean air temperature at surface.

FIG. 8 DEUTERIUM CONTENT OF SURFACE WATERS IN CANADA

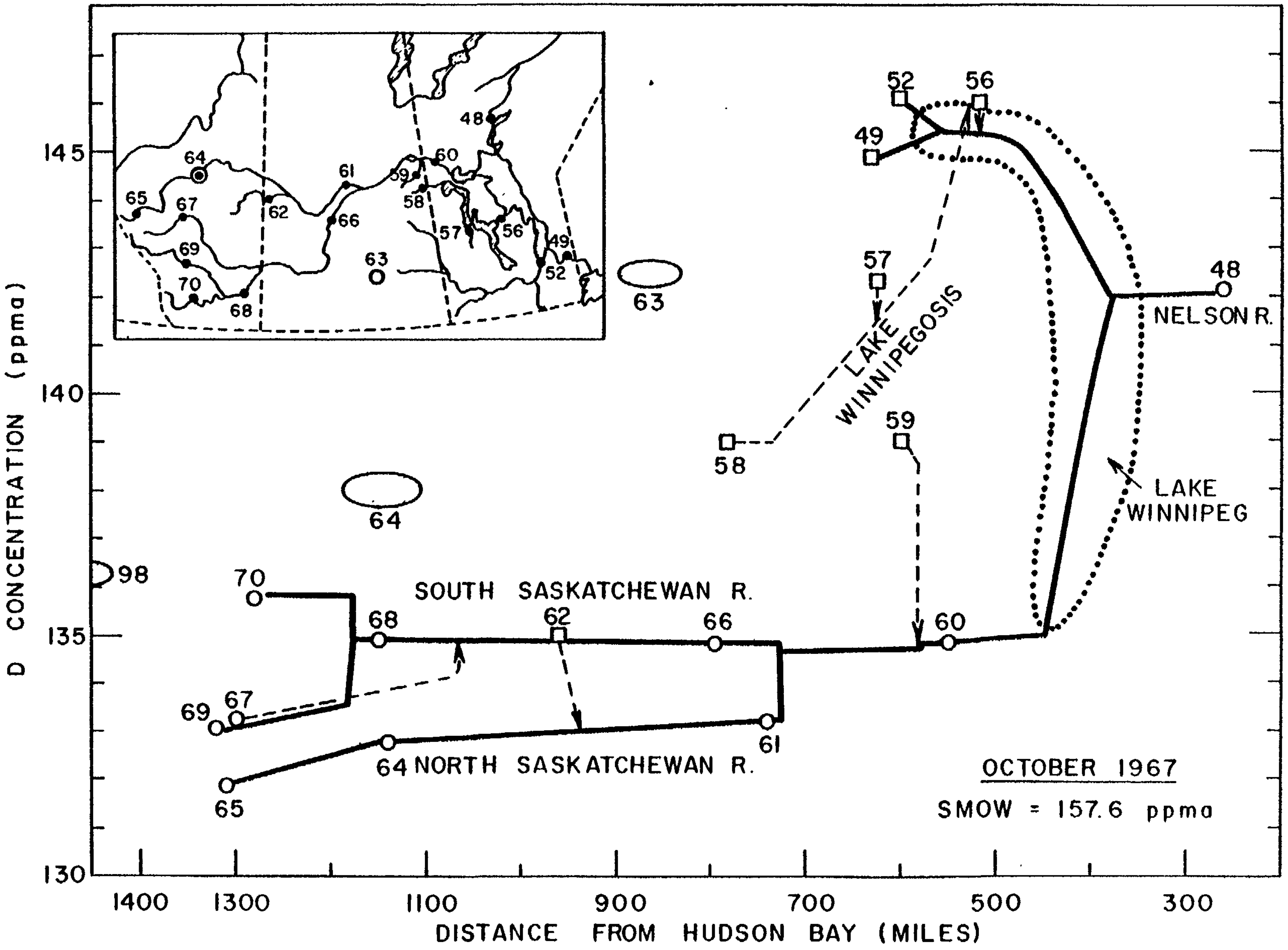


FIG. 9. DEUTERIUM CONCENTRATIONS ALONG THE SASKATCHEWAN - WINNIPEG - NELSON SYSTEM

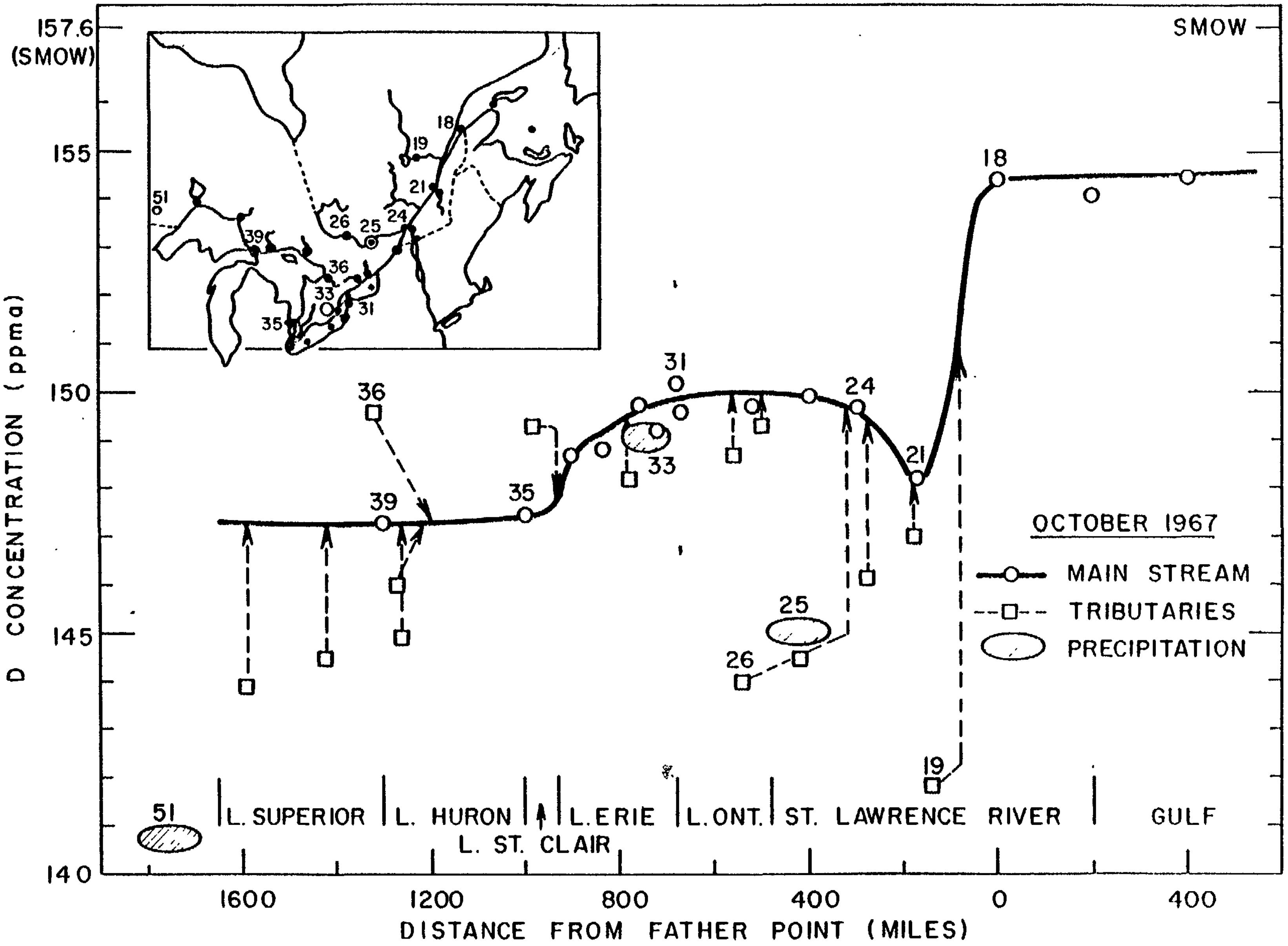


FIG.10 DEUTERIUM CONCENTRATIONS ALONG THE GREAT LAKES - ST. LAWRENCE SYSTEM

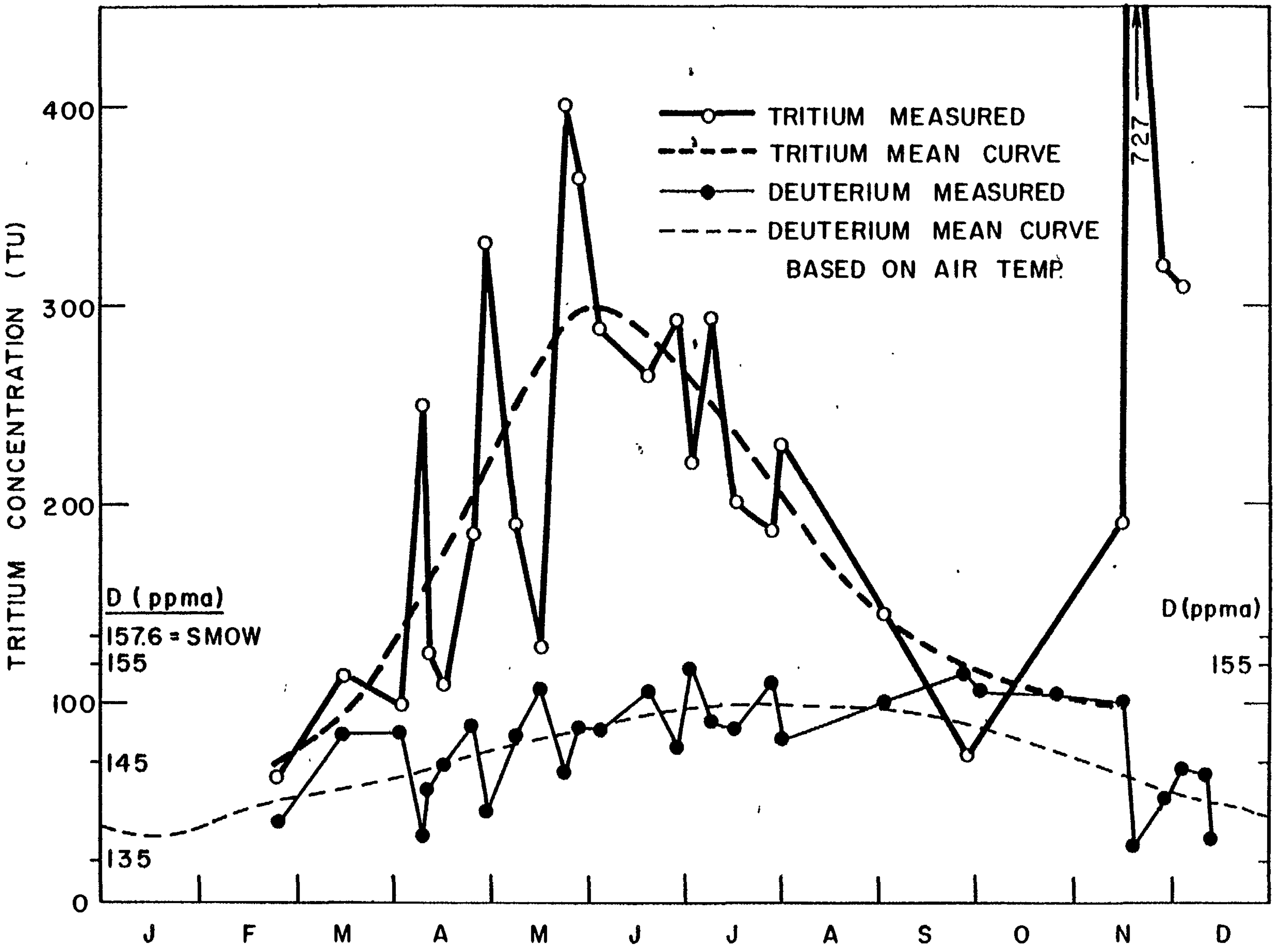


FIG. 11 TRITIUM AND DEUTERIUM IN OTTAWA PPTN
1961

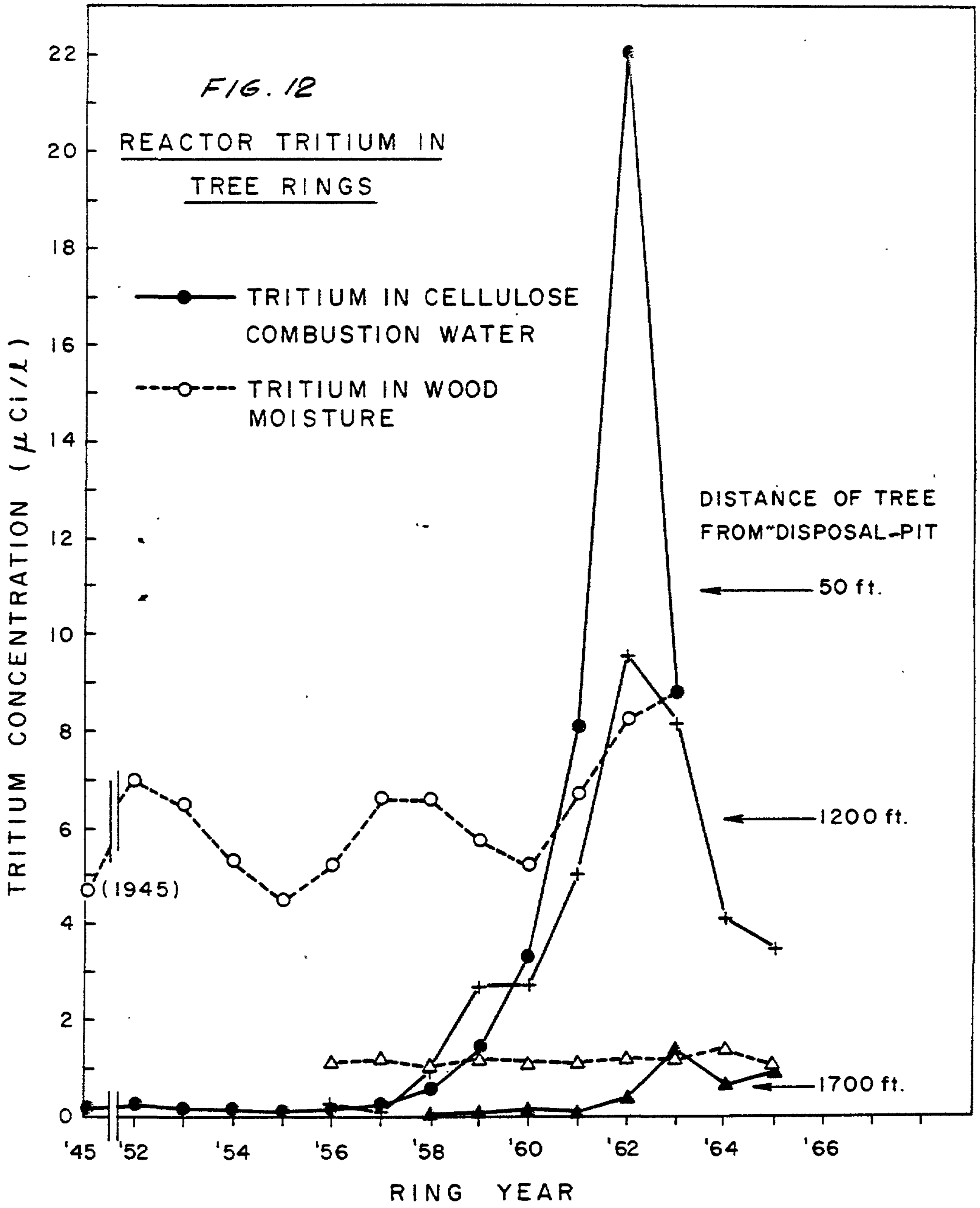


FIG. 12

REACTOR TRITIUM IN TREE RINGS

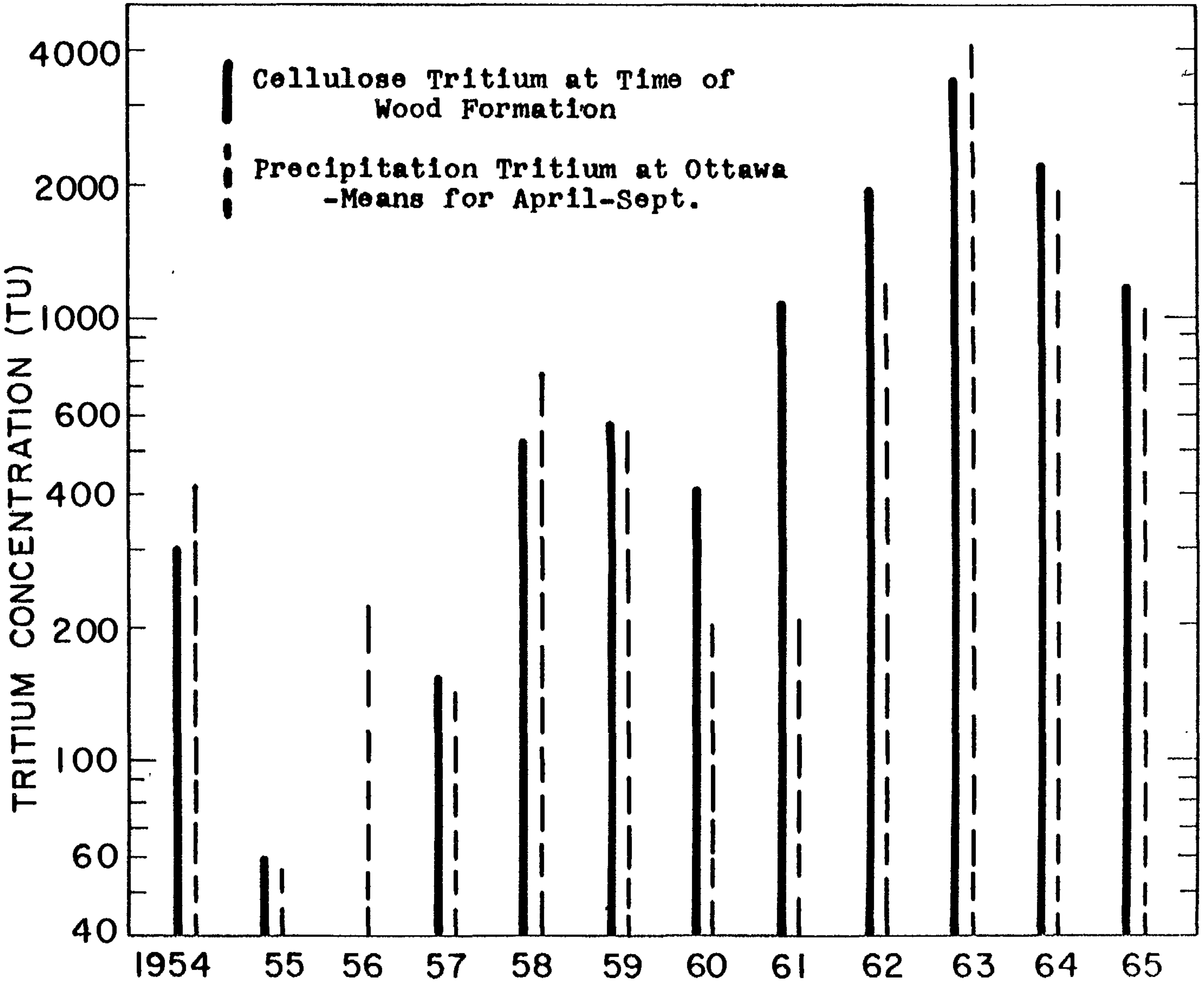


FIG. 13 TRITIUM IN TREE RINGS AND PRECIPITATION AT DEEP RIVER

FIG.14 STATIONS COOPERATING IN THE IAEA/WMO ISOTOPES-IN-WATER NETWORK INCLUDING THOSE RECOMMENDED FOR ADDITION

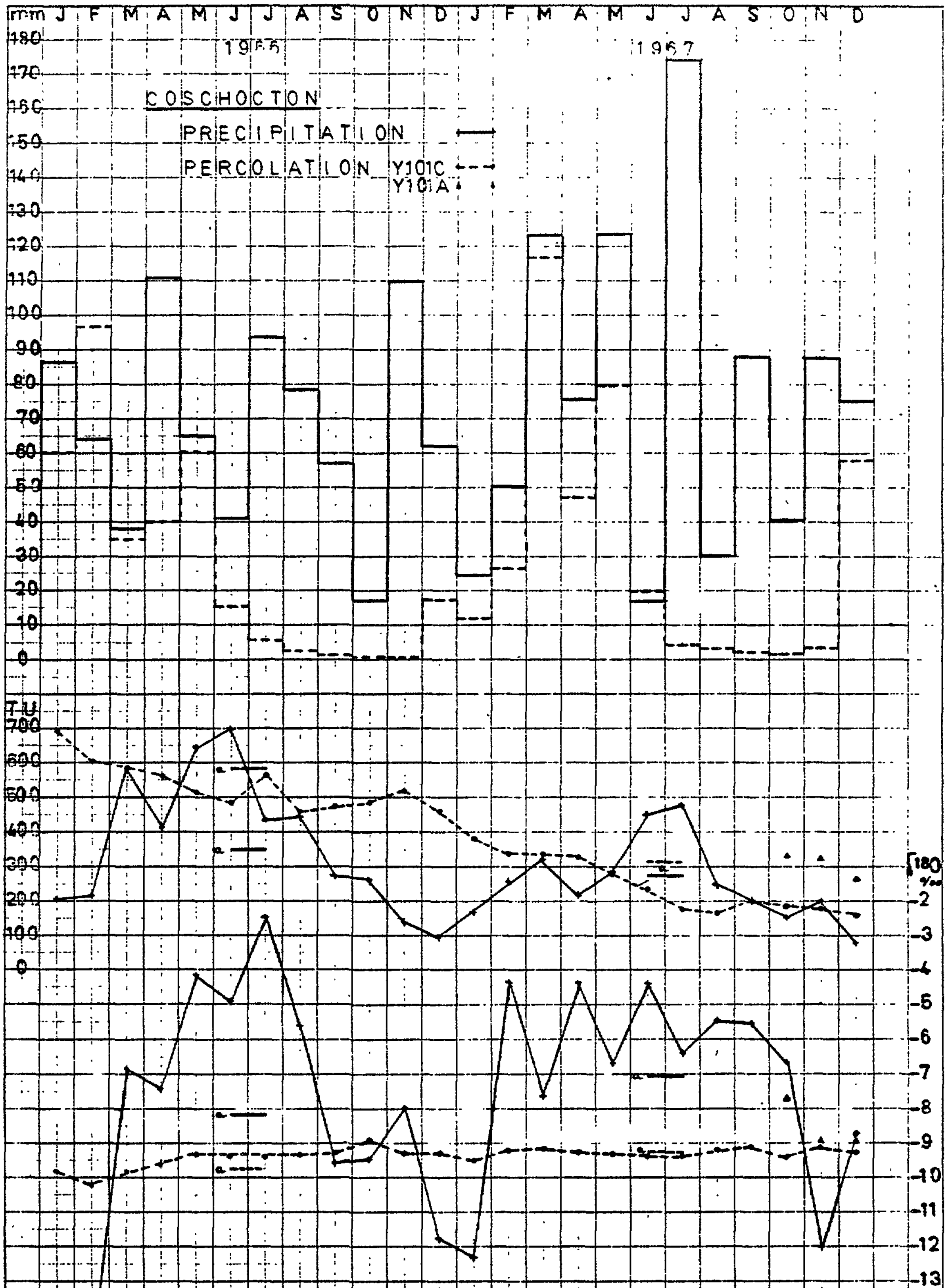

mm
J F M A M J J A S O N D J F M A M J J A S O N D
1966
1967
COSCHOCTON
PRECIPITATION
PERCOLATION Y101C
Y101A
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
TU
700
600
500
400
300
200
100
0
180 ‰
-2
-3
-4
-5
-6
-7
-8
-9
-10
-11
-12
-13
-14
-15

FIG. 15

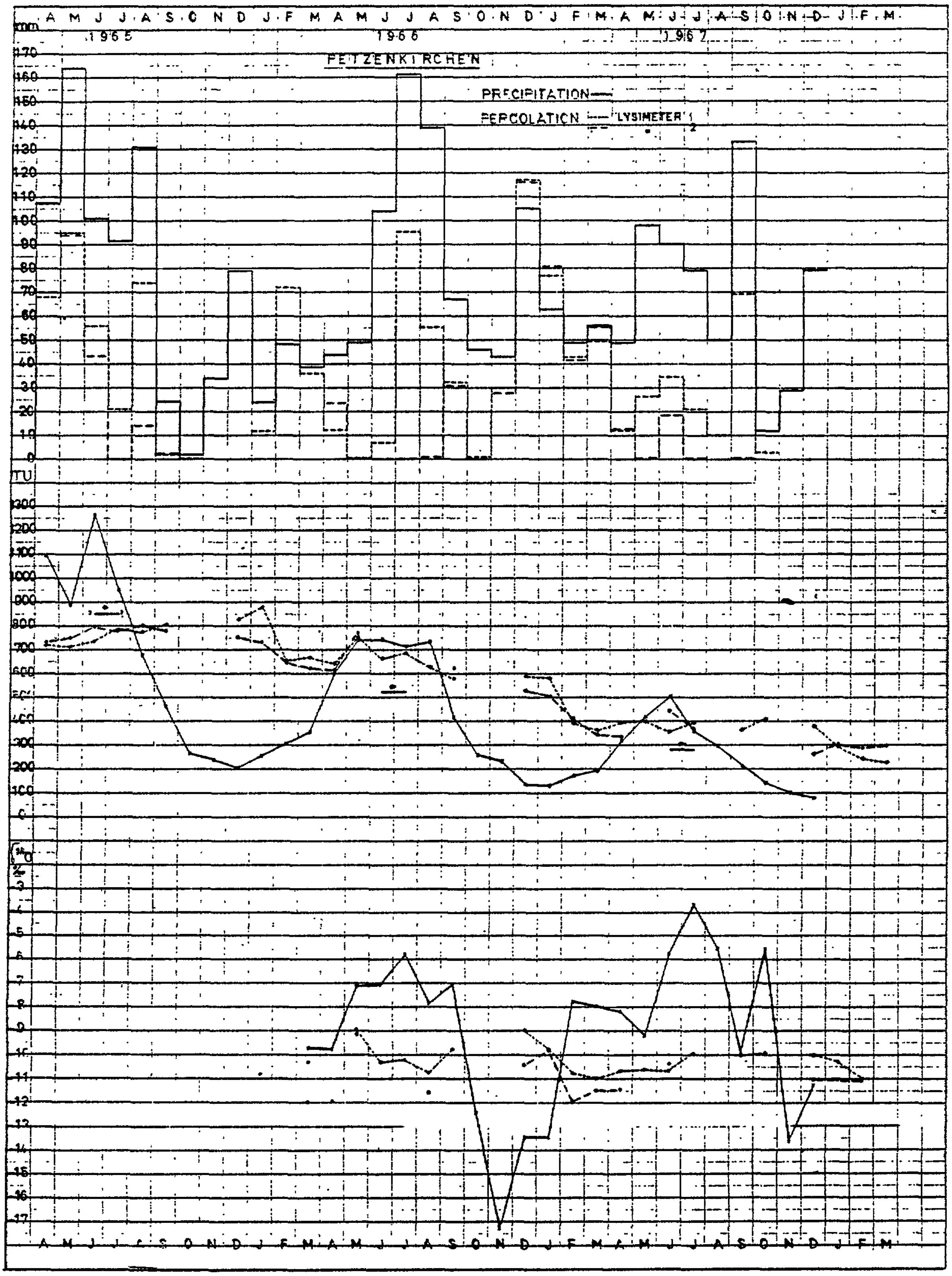

A M J J A S O N D J F M A M J J A S O N D J F M A M J J A S O N D J F M
mm
1965
1966
1967
PETZENKIRCHEN
PRECIPITATION
PERCOLATION
LYSIMETER 1
2
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
TU
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
δ18O
‰
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
A M J J A S O N D J F M A M J J A S O N D J F M A M J J A S O N D J F M

FIG. 16

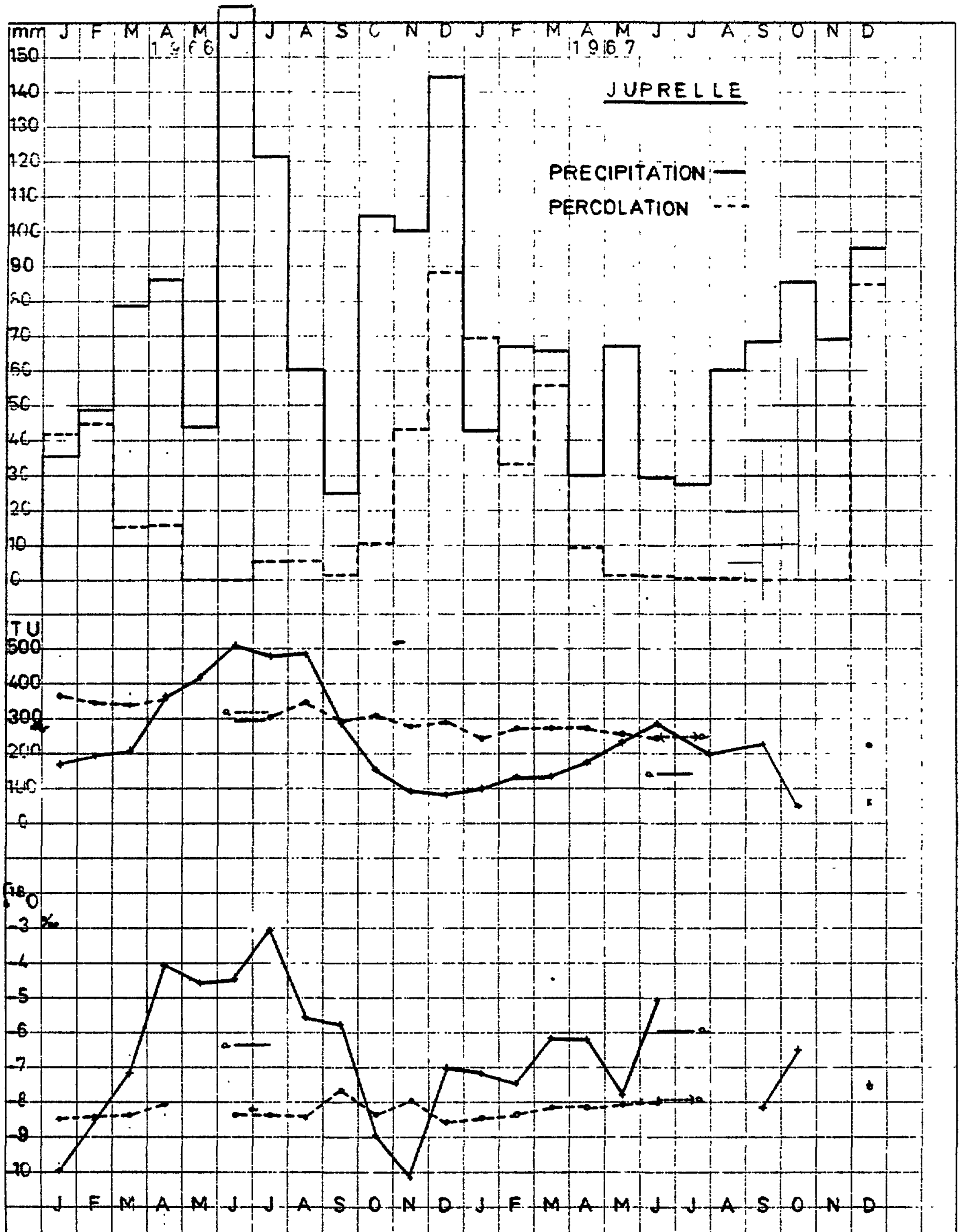

mm
J F M A M J J A S O N D J F M A M J J A S O N D
1966
1967
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
JUPRELLE
PRECIPITATION
PERCOLATION
TU
500
400
300
200
100
0
δ18O
0
-3 ‰
-4
-5
-6
-7
-8
-9
-10

FIG. 17

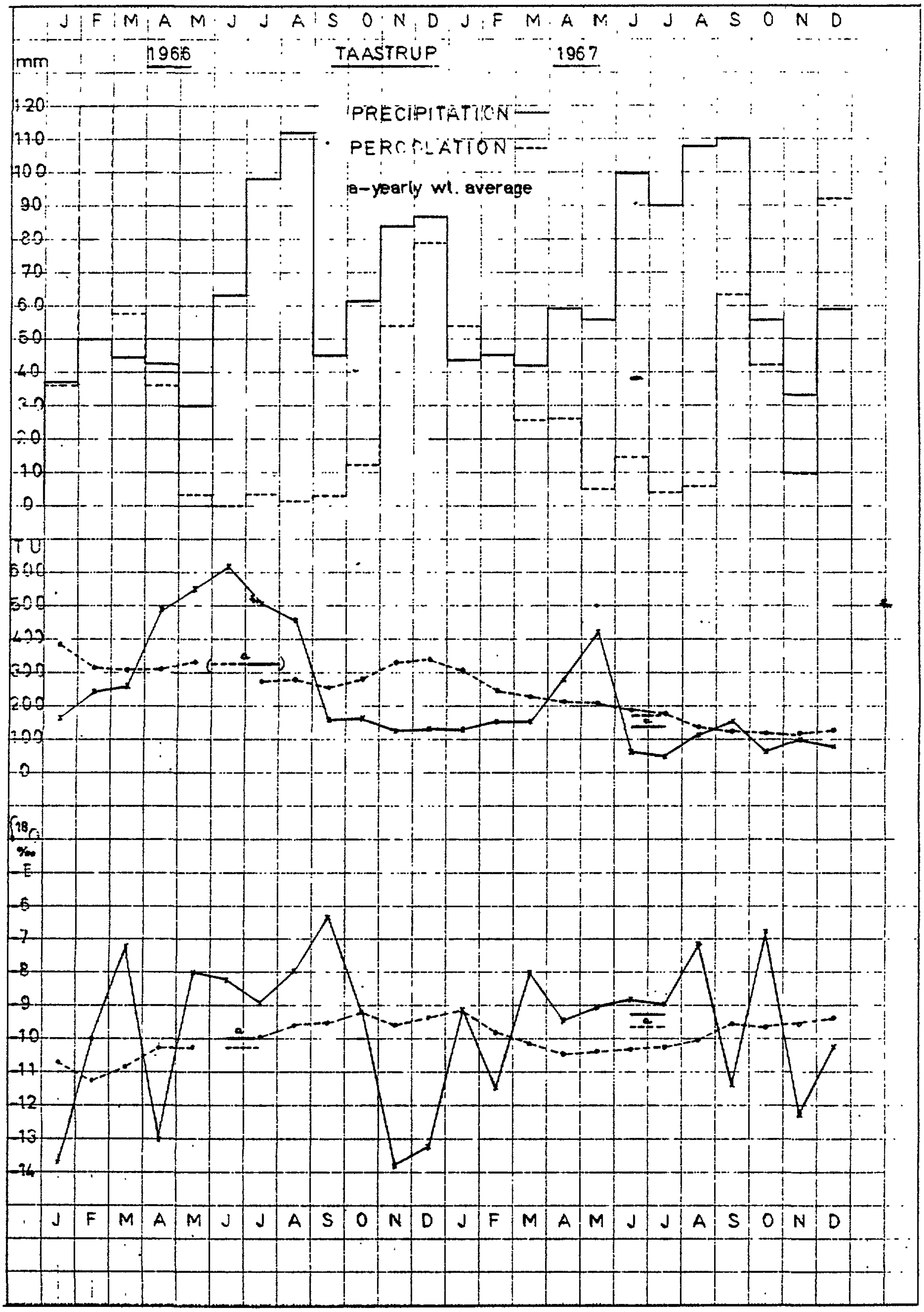

J F M A M J J A S O N D J F M A M J J A S O N D
mm
1966
TAASTRUP
1967
120
110
100
90
80
70
60
50
40
30
20
10
0
PRECIPITATION
PERCOLATION
a–yearly wt. average
TU
600
500
400
300
200
100
0
a
δ18O
‰
E
-6
-7
-8
-9
-10
-11
-12
-13
-14
J F M A M J J A S O N D J F M A M J J A S O N D

FIG. 18

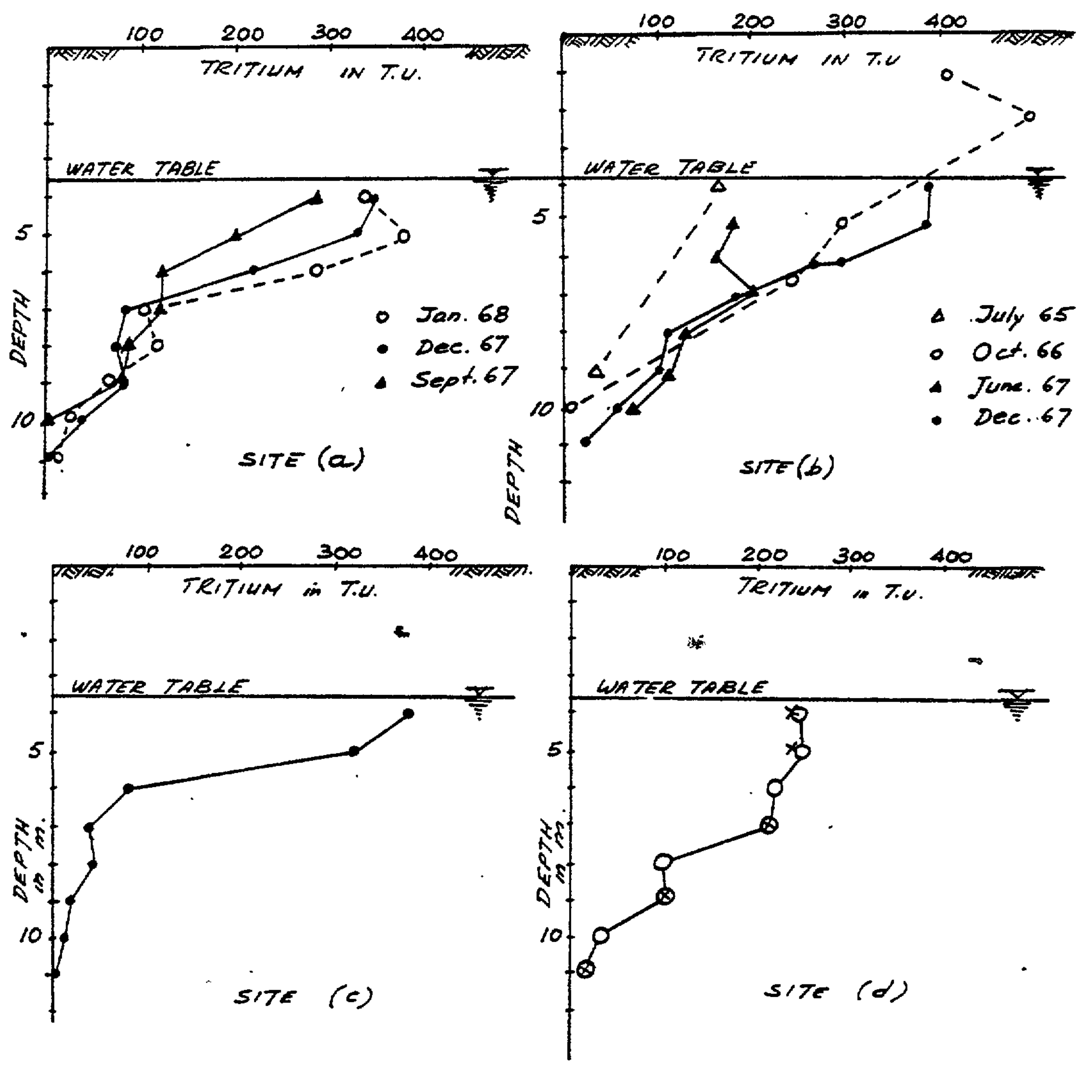


FIG. 19 TRITIUM CONCENTRATIONS IN GROUNDWATER IN THE RHINE VALLEY (SANDHAUSEN NEAR HEIDELBERG)

VALUES MARKED -x- in (d) WERE TAKEN FROM 60 LITRE SAMPLES AS A CHECK ON POSSIBLE VERTICAL MIXING DURING SAMPLING.

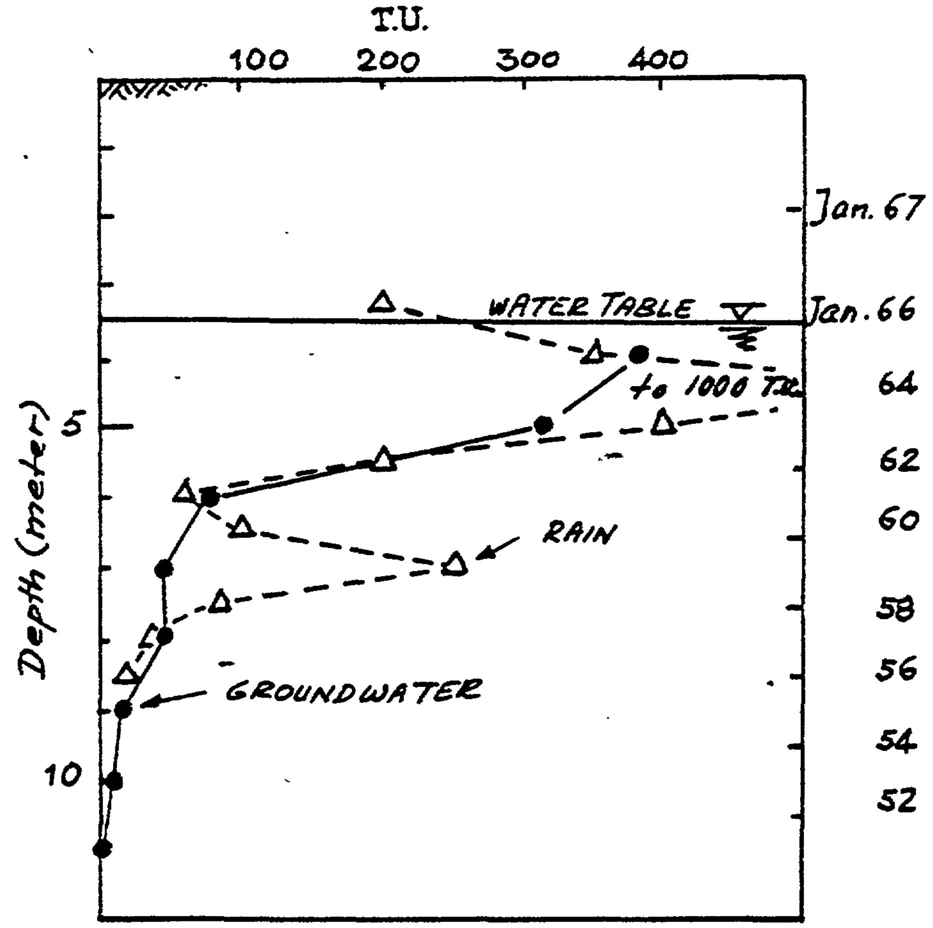


FIG. 20 COMPARAISON OF TRITIUM CONCENTRATION IN RAIN BEING PROJECTED INTO THE AQUIFER (RECHARGE 170 mm/year) WITH TRITIUM DEPTH PROFILE FROM FIG. 19 (c). NO CORRECTION WAS MADE FOR DECAY.

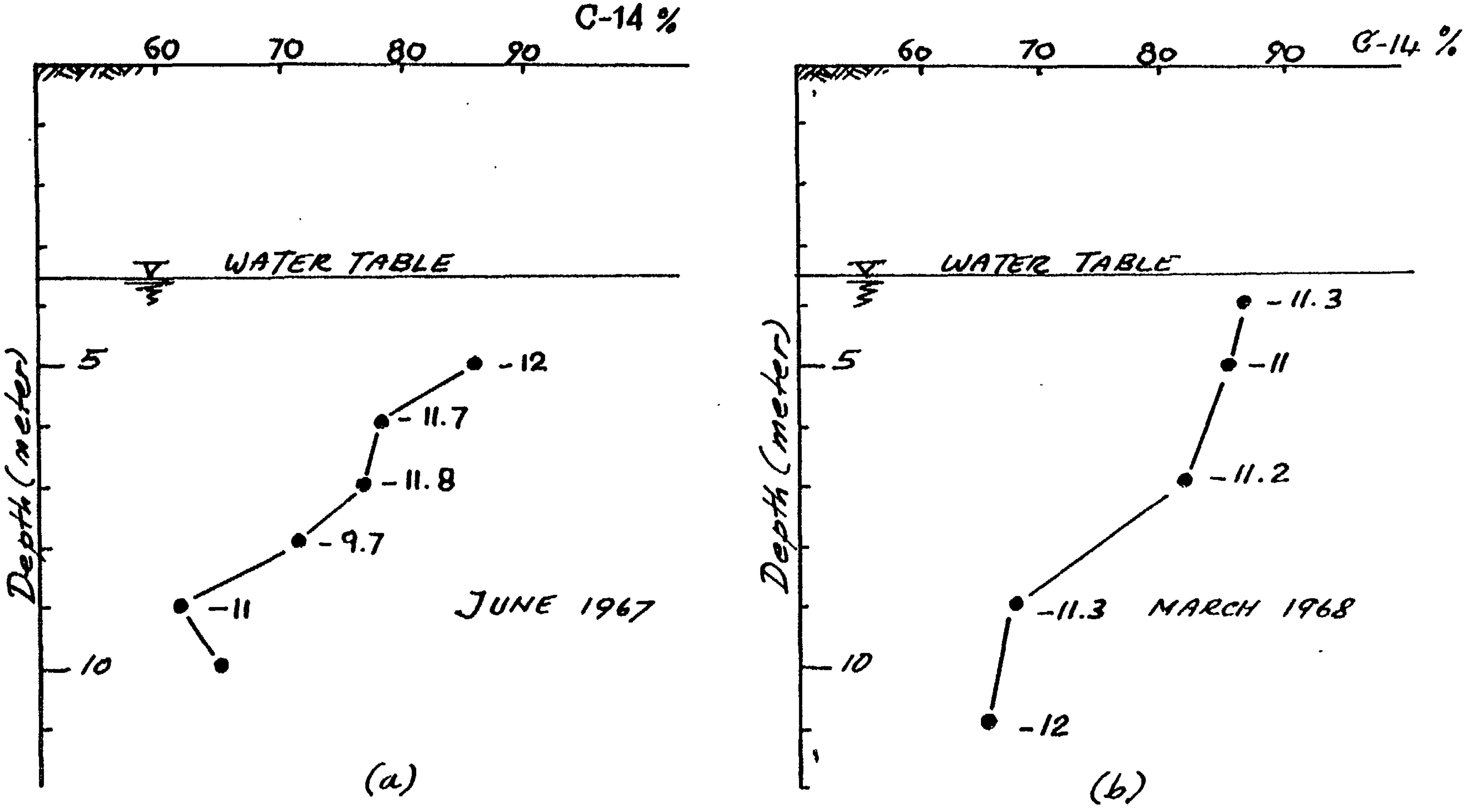


FIG. 21 ^{14}C CONCENTRATION IN GROUNDWATER IN SANDHAUSEN. THE NUMERICAL VALUES GIVE ^{13}C CONCENTRATION IN ‰ OF PDB. THE CORRESPONDING TRITIUM CONCENTRATIONS ARE SHOWN IN FIG 19 (a) and (d).

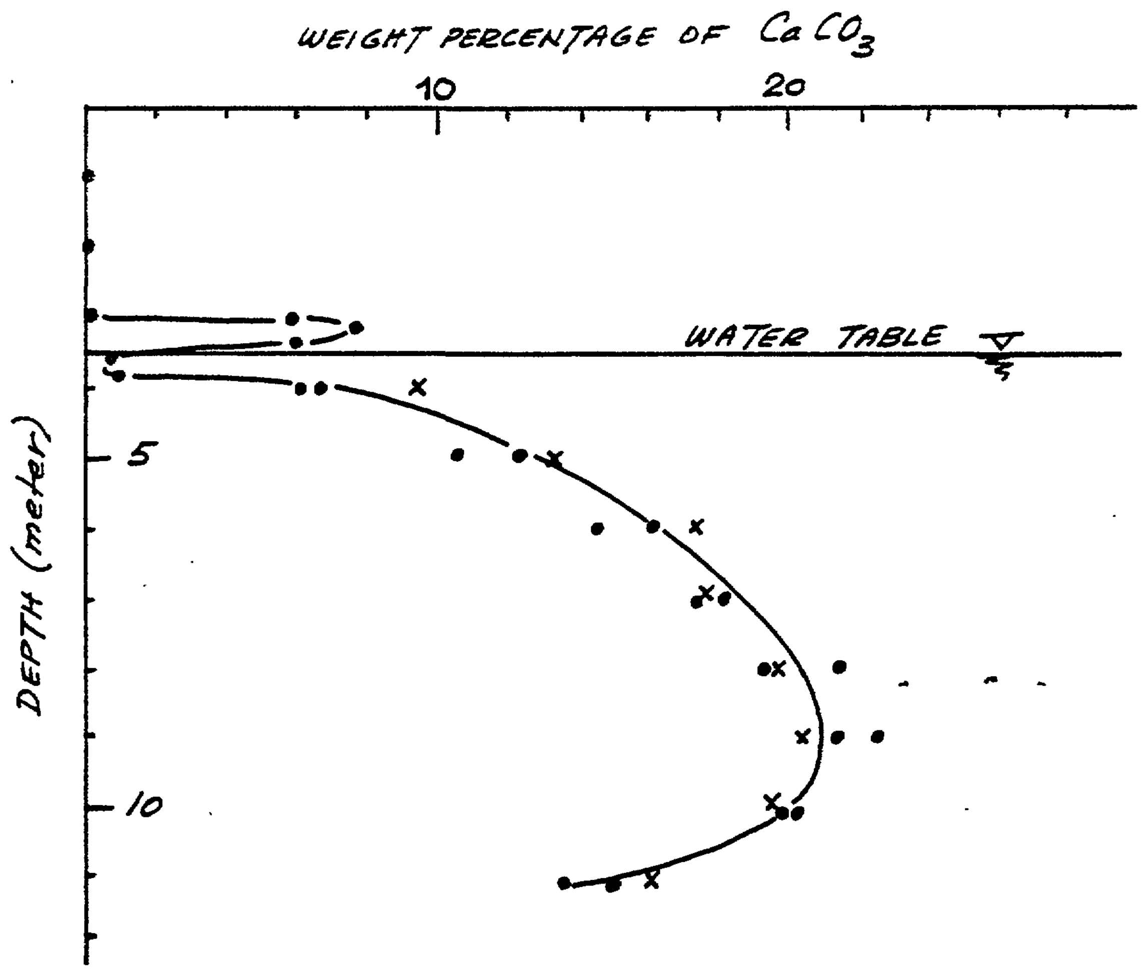


FIG. 22 $CaCO_3$ CONTENT OF AQUIFER MATERIAL AT DIFFERENT DEPTHS FOR THE SAMPLING SITES IND SANDHAUSEN. SAMPLES BELOW THE WATER TABLE WERE SUCKED THROUGH THE FILTER DURING SAMPLING OF WATER. THEREFORE THEY REPRESENT ONLY THE FINE GRAINED FRACTION OF THE MATERIAL.

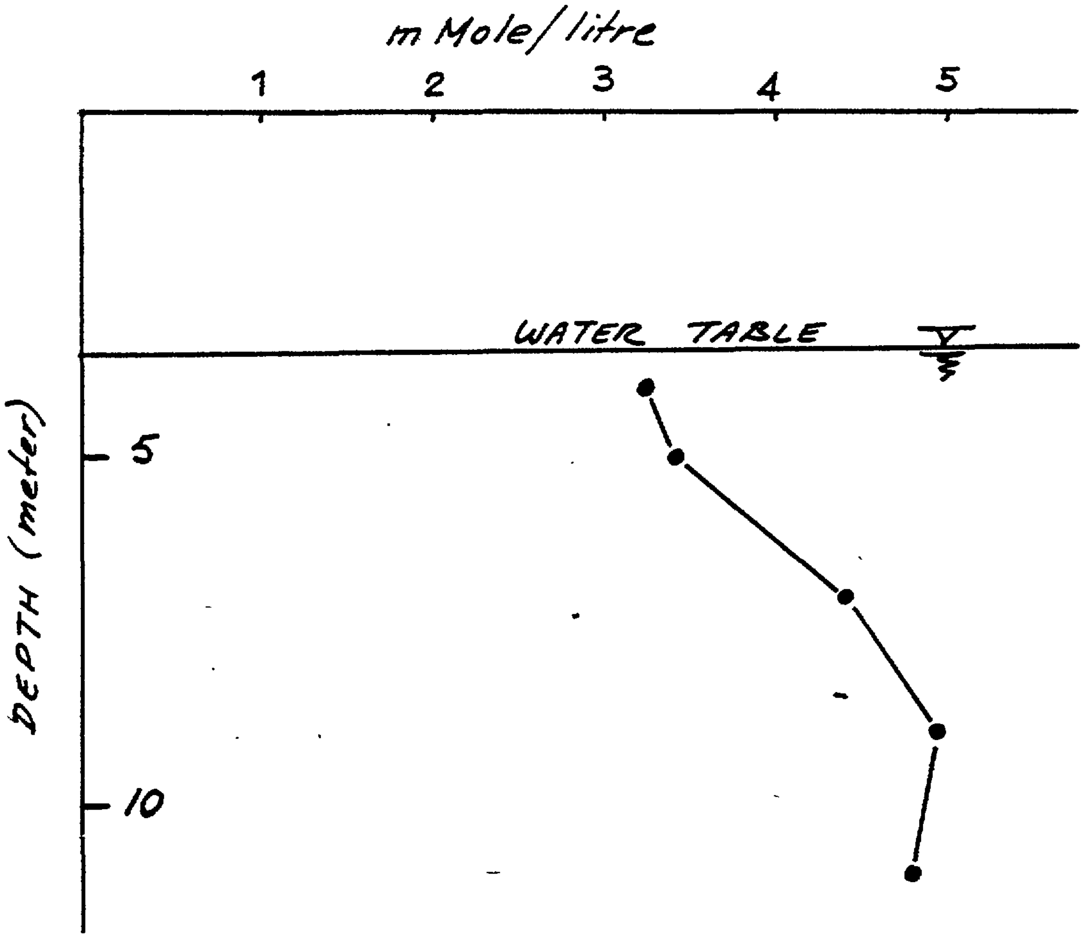


FIG. 23 TOTAL CARBONATE CONTENT OF GROUNDWATER IN SANDHAUSEN SEE ALSO FIG. 22

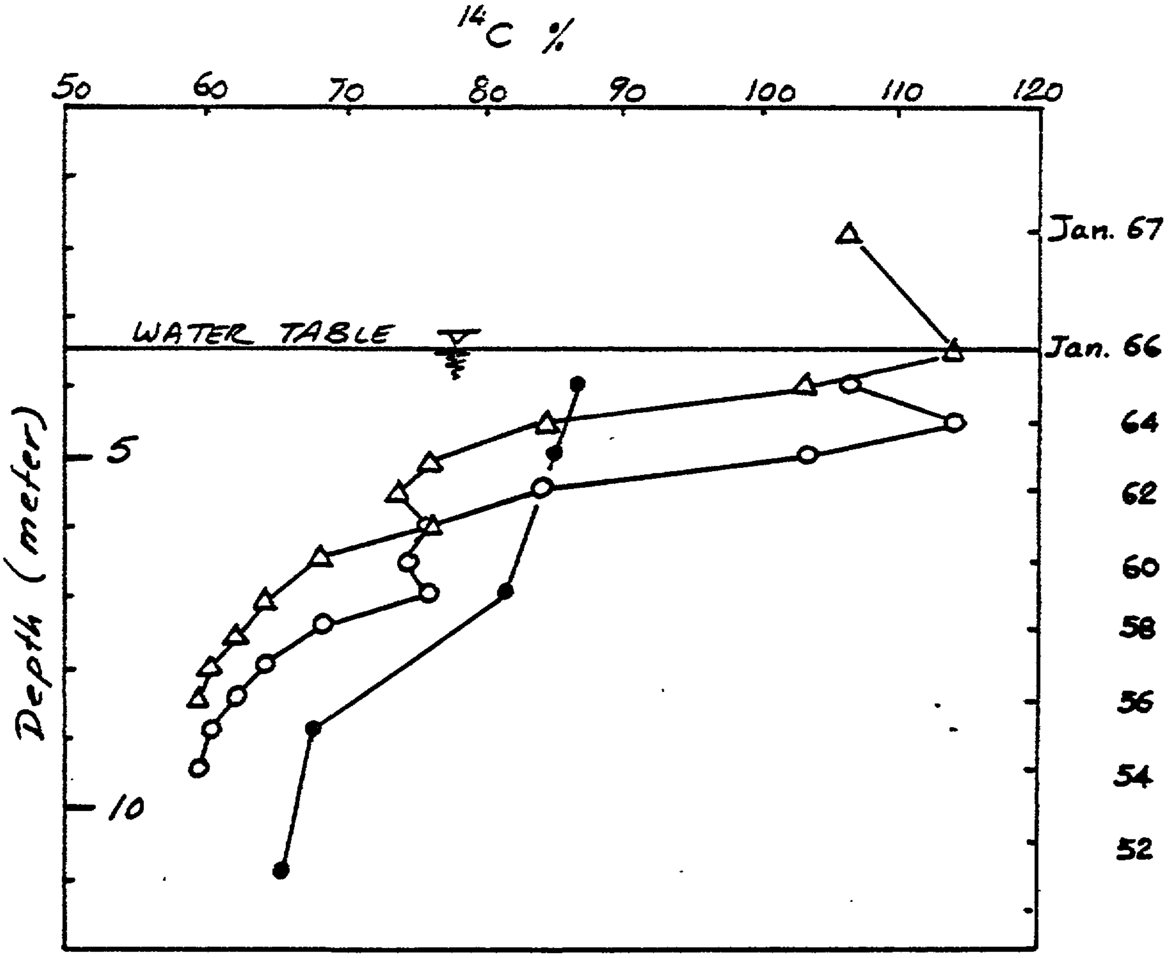


FIG. 24 PROJECTION OF ATMOSPHERIC ^{14}C INTO THE GROUNDWATER WITH (-Δ-) AND WITHOUT (-o-) A DELAY OF 2 YEARS IN THE BIOSPHERE. THE VALUES ARE BASED ON A PREBOMB ^{14}C CONCENTRATION IN GROUNDWATER OF 60%. THE ^{14}C PROFILE OF FIG. 21 (b) IS SHOWN FOR COMPARAISON (-•-)

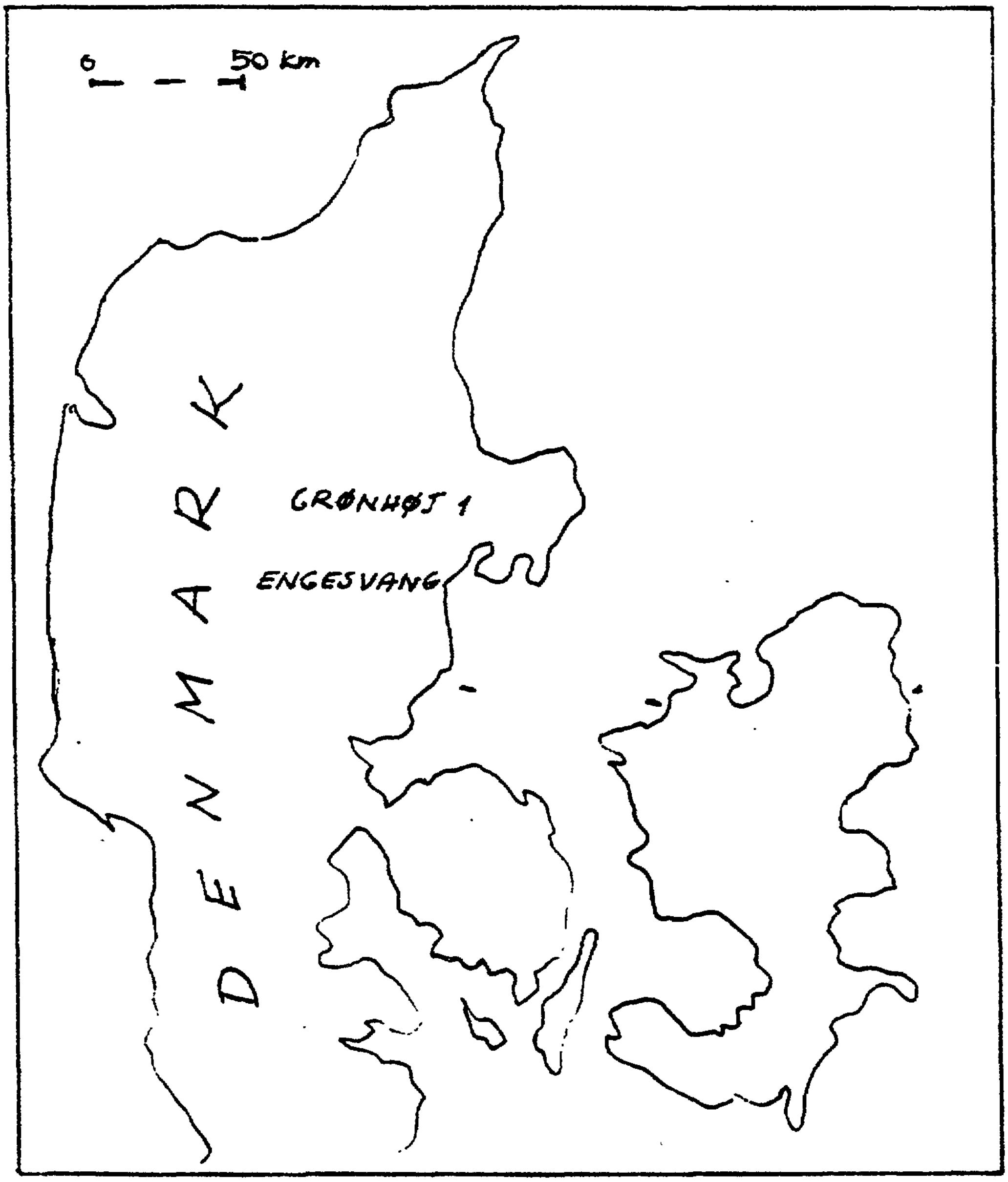
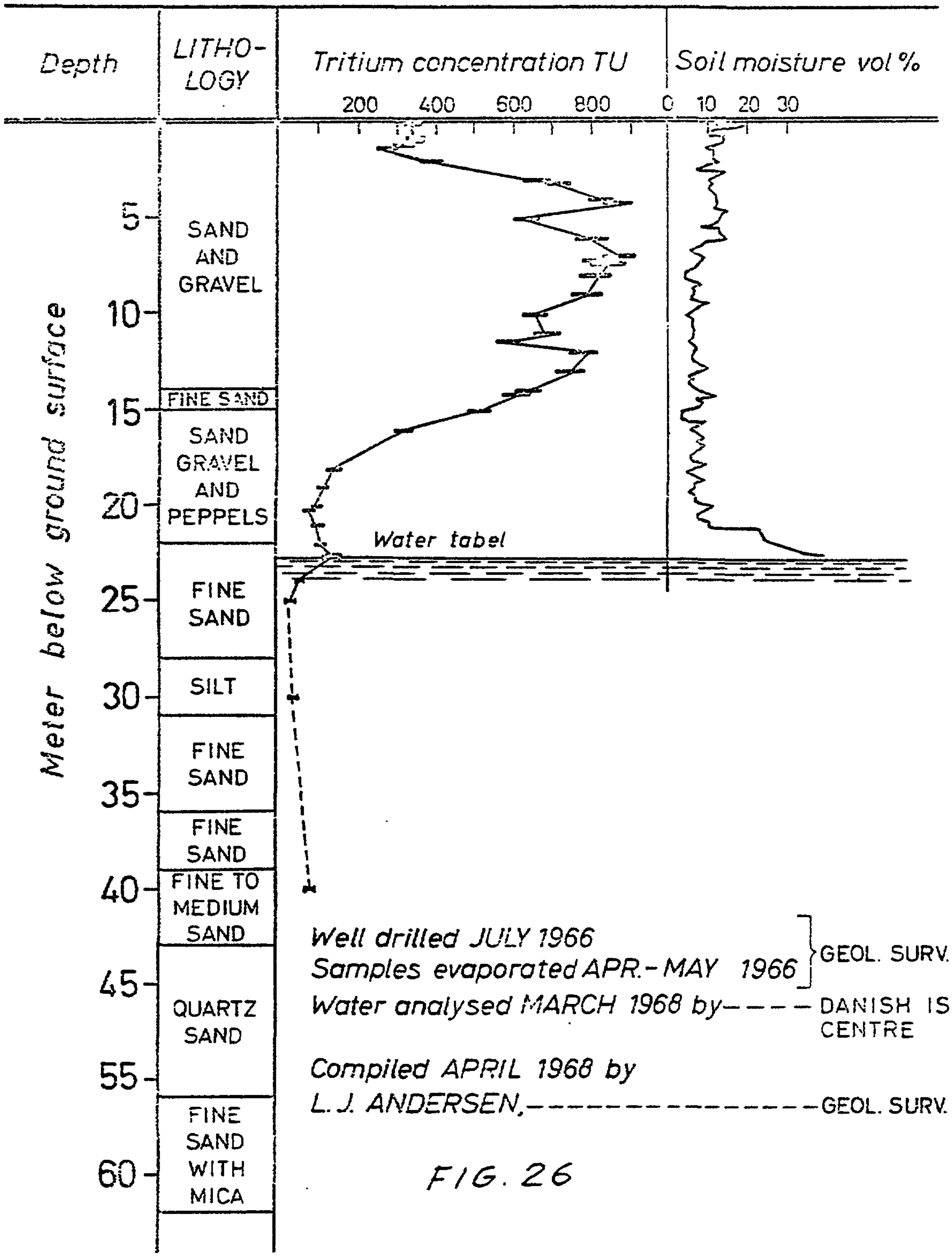


FIG. 25 LOCATION OF TRITIUM PROFILE STUDIES

Well GRØNHØJ No 1 D.G.U. file nr. 66.664

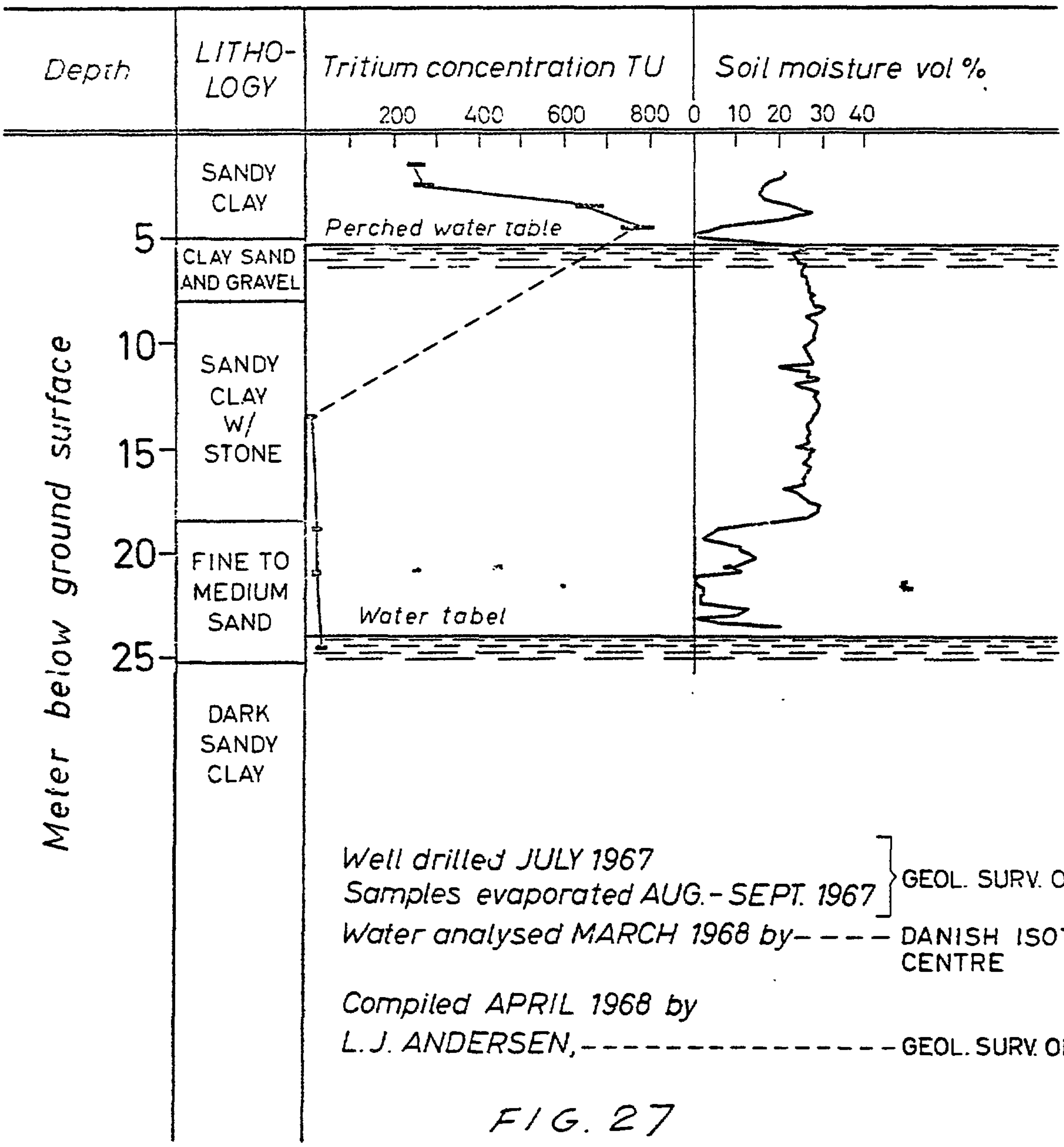


Well drilled JULY 1966 }
Samples evaporated APR.-MAY 1966 } GEOL. SURV. OF DENMARK
Water analysed MARCH 1968 by---- DANISH ISOTOPE CENTRE

Compiled APRIL 1968 by
L. J. ANDERSEN,--------------GEOL. SURV. OF DENMARK

FIG. 26

Well near ENGESVANG D.G.U. file no. 86.913



Well drilled JULY 1967
Samples evaporated AUG.-SEPT. 1967 } GEOL. SURV. OF DENMARK
Water analysed MARCH 1968 by---- DANISH ISOTOPE CENTRE

Compiled APRIL 1968 by
L. J. ANDERSEN,---------------- GEOL. SURV. OF DENMARK

FIG. 27

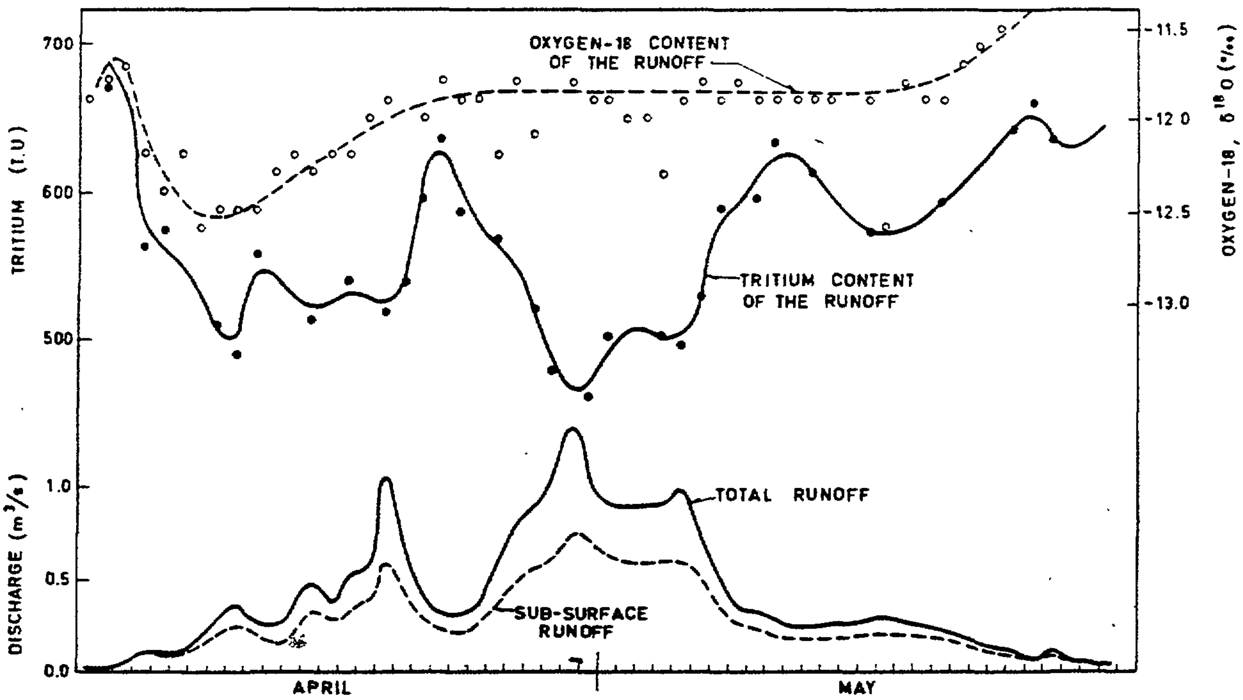


FIG.28 Streamflow hydrograph, tritium and ^{18}O content of the runoff during snowmelt season 1965-66 in Modry Dul basin. The sub-surface runoff is estimated by using the relation given in Fig.2. (V.2)

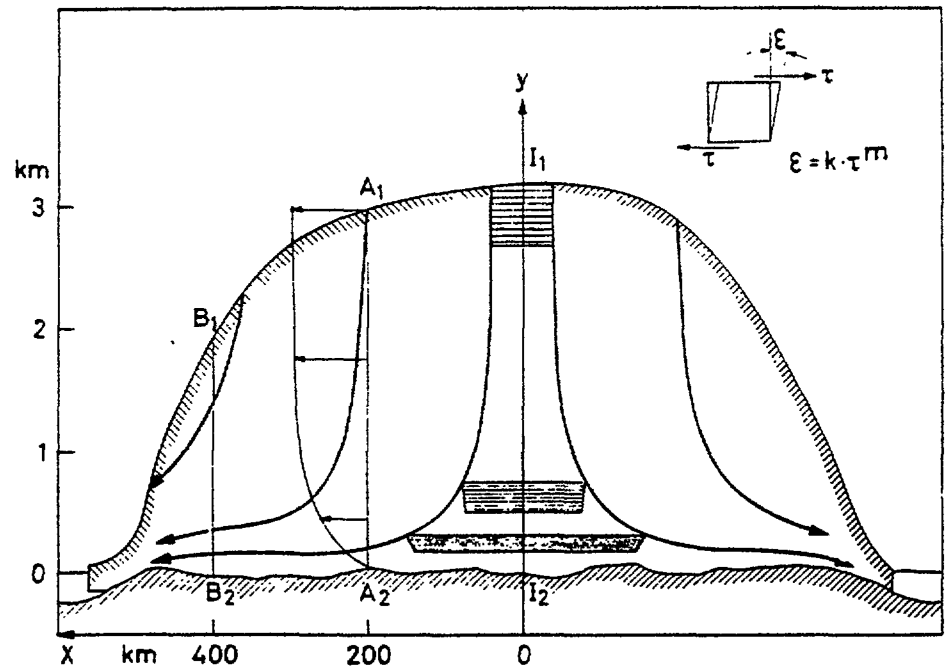


FIG.29 Cross-section of a glacier.

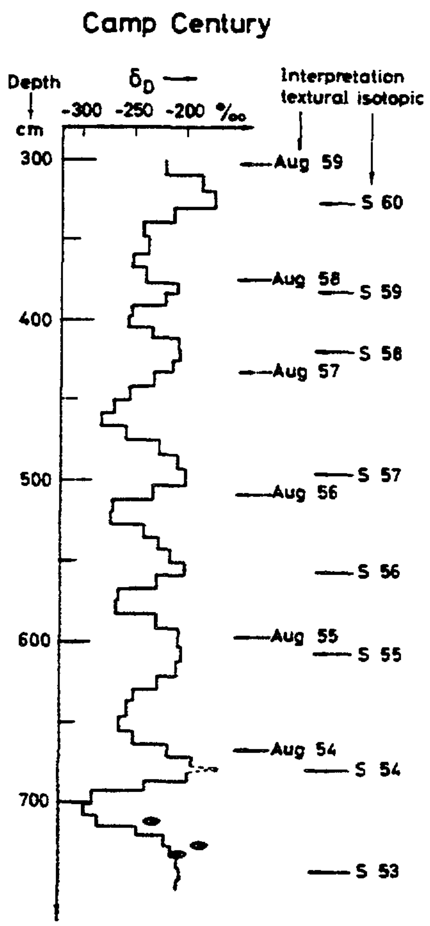


FIG.30 Deuterium profile of a glacier.

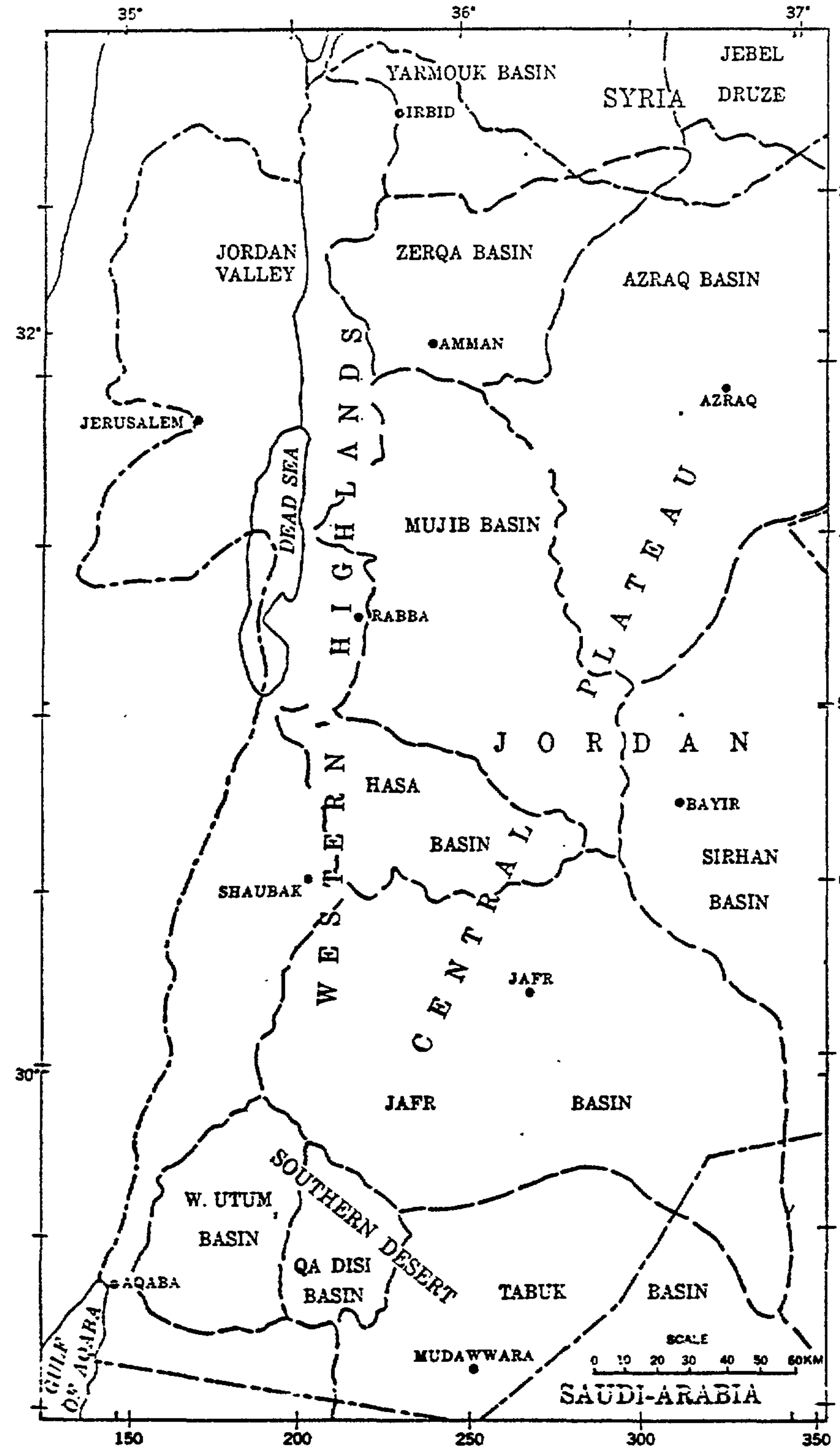


Figure 31 - Major topographic features and drainage basins of Jordan. Numbers along bottom and right margins are coordinates for Jordan kilometer grid system.

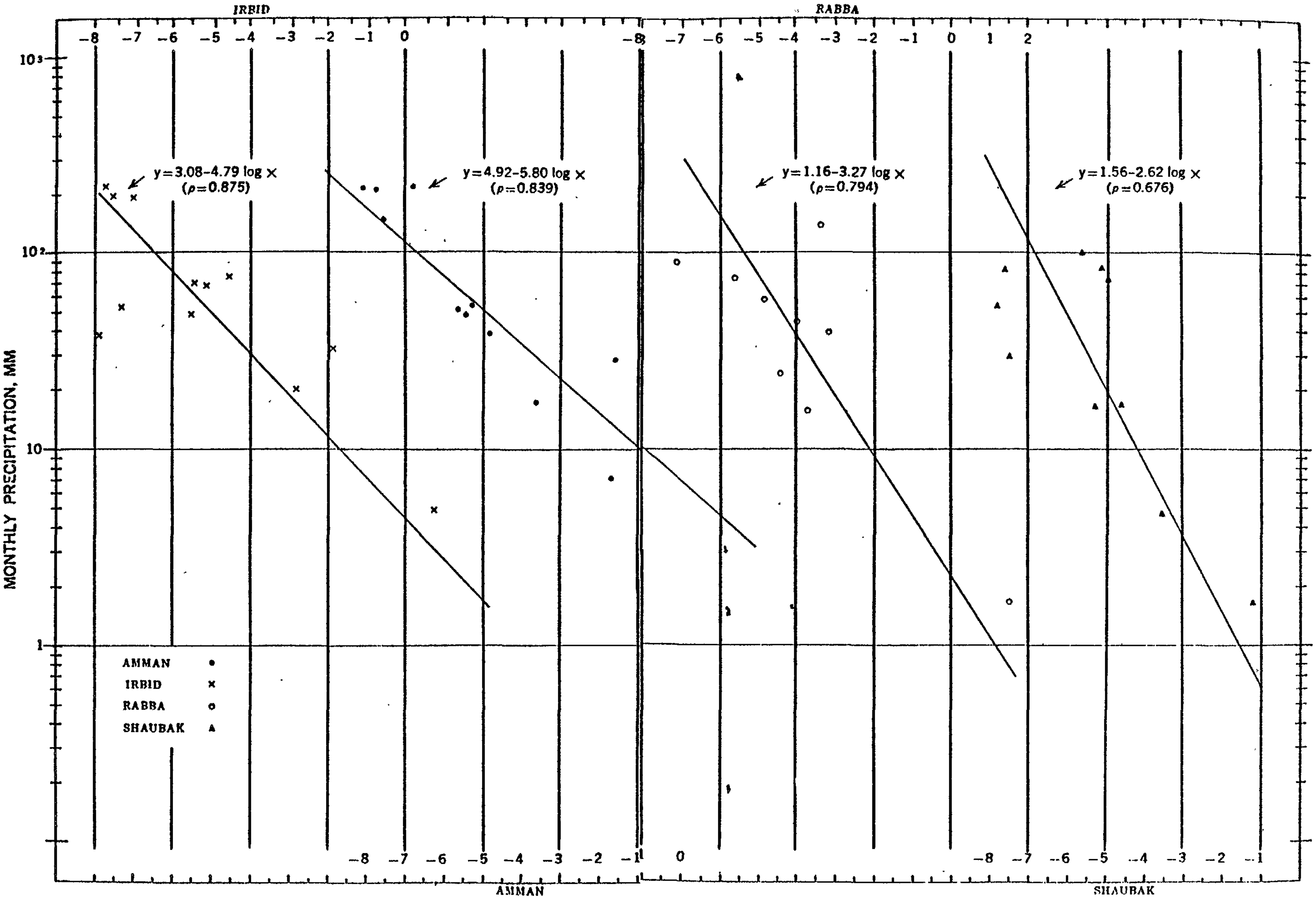


Figure 32 Monthly precipitation amount vs. ^{18}O content

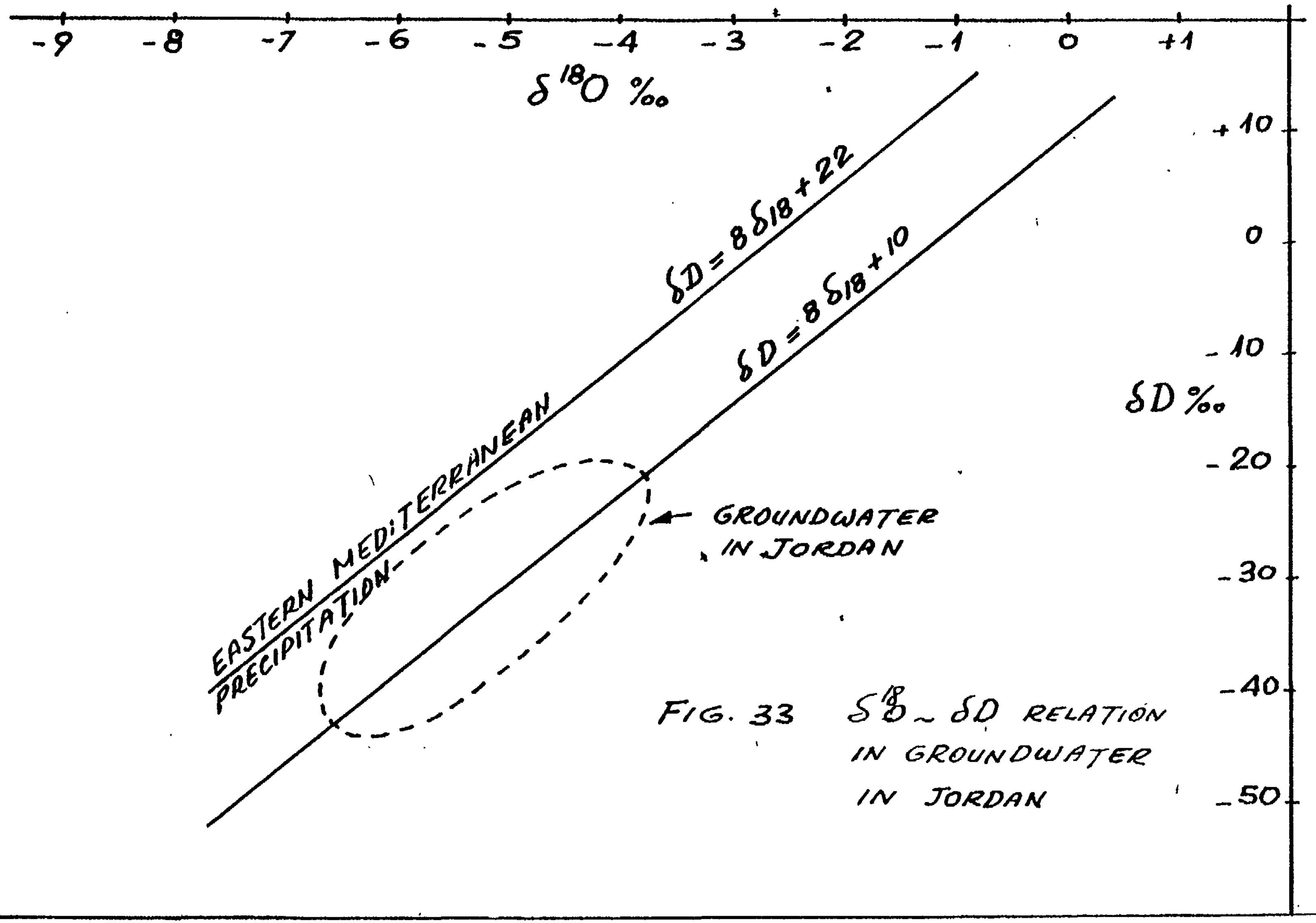


FIG. 33 $\delta^{18}O \sim \delta D$ RELATION IN GROUNDWATER IN JORDAN

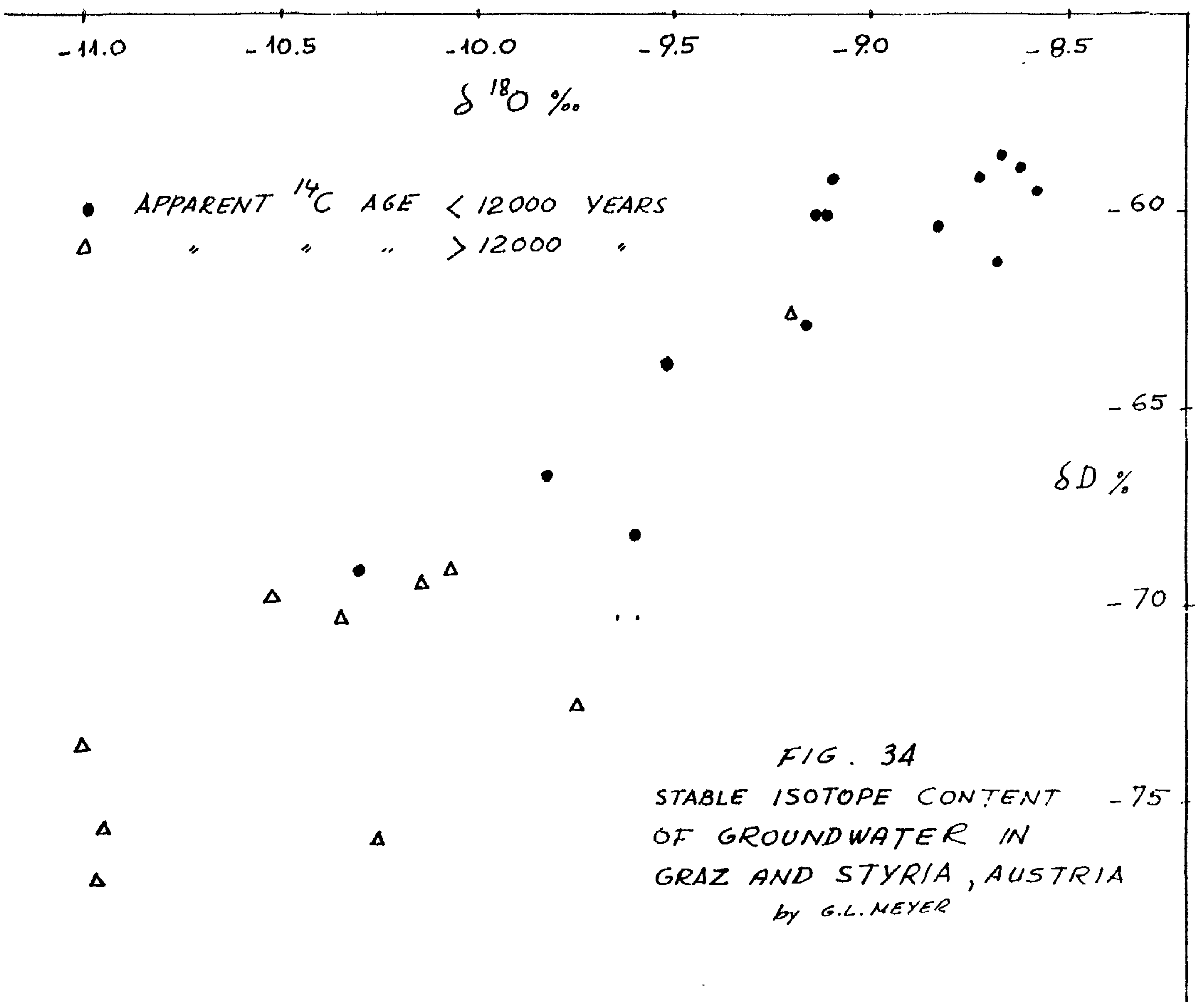
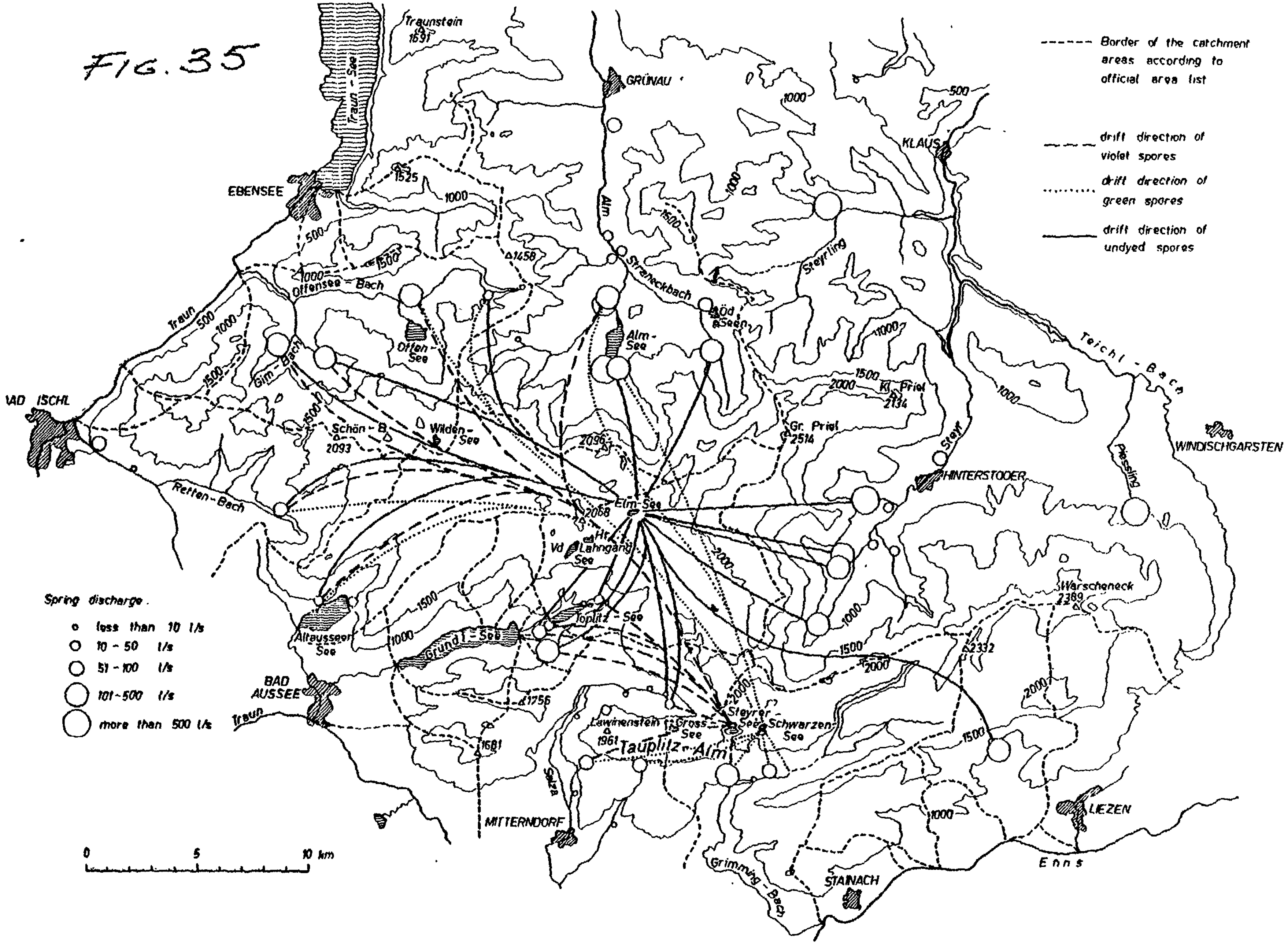


FIG. 34

STABLE ISOTOPE CONTENT OF GROUNDWATER IN GRAZ AND STYRIA, AUSTRIA

by G.L. MEYER

FIG. 35


Border of the catchment areas according to official area list
drift direction of violet spores
drift direction of green spores
drift direction of undyed spores
Spring discharge.
less than 10 l/s
10 - 50 l/s
51 - 100 l/s
101-500 l/s
more than 500 l/s
0
5
10 km
Traunstein
1691
Traun - See
GRÜNAU
KLAUS
EBENSEE
1525
1000
500
1500
Alm
Straneckbach
Öd Seen
Steyrling
Offensee - Bach
Offen See
Alm- See
Traun
Gim - Bach
AD ISCHL
Schön - B.
2093
Wilden- See
2096
Gr. Priel
2514
Kl. Priel
2134
2000
Teichl - Bach
WINDISCHGARSTEN
Steyr
HINTERSTODER
Piessling
Retten-Bach
Elm-See
2068
Hr. Lahngang
Vd. Lahngang See
Toplitz - See
Altausseer See
Grundl - See
BAD AUSSEE
Traun
1756
1681
Warscheneck
2389
2332
Lawinenstein
1961
Gross See
Steyrer - See
Schwarzen - See
Tauplitz - Alm
Salza
MITTERNDORF
Grimming - Bach
STAINACH
LIEZEN
Enns
1458

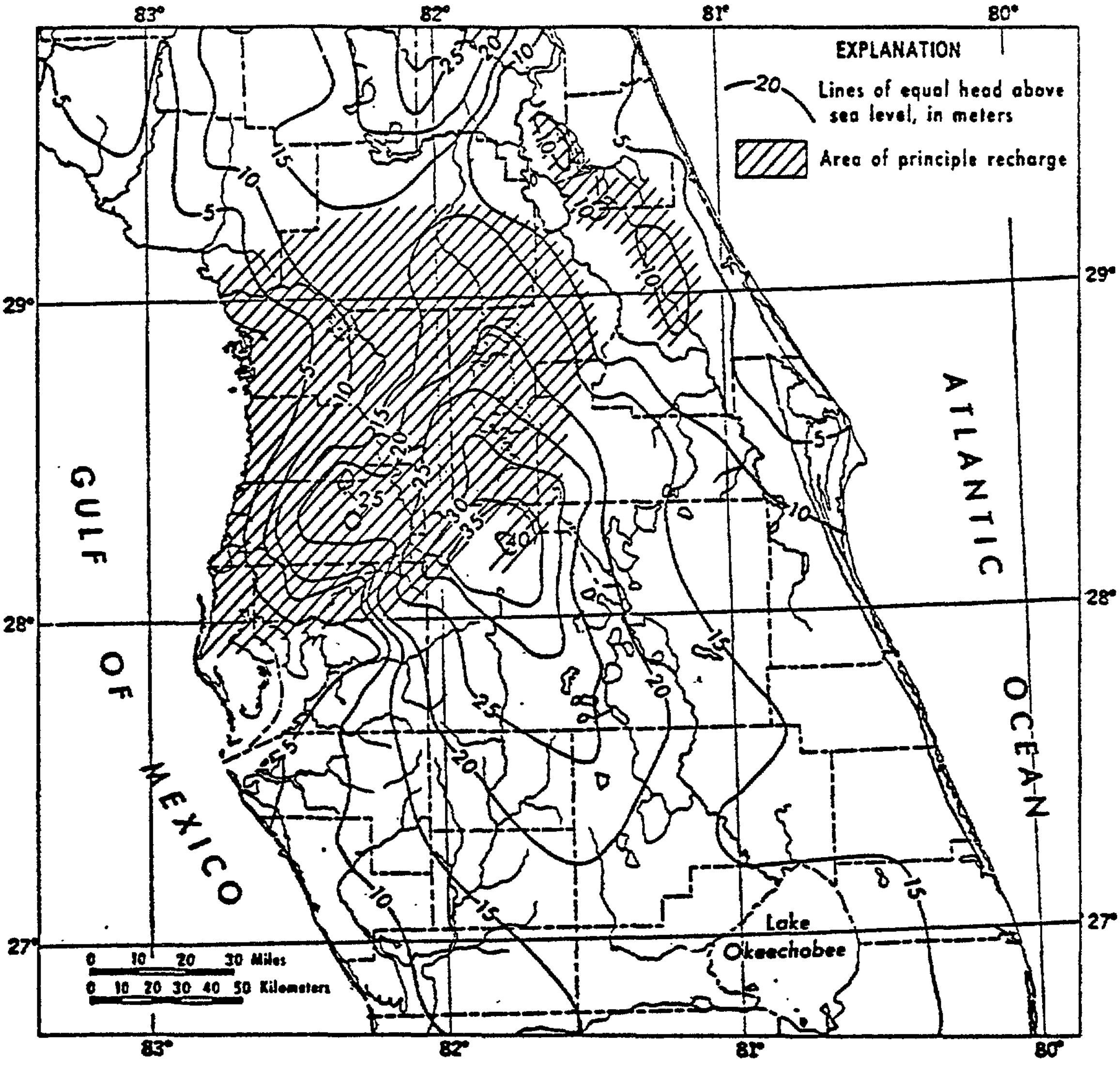


Figure 36 Potentiometric surface of the principal artesian limestone aquifer in central Florida showing areas of principal recharge.

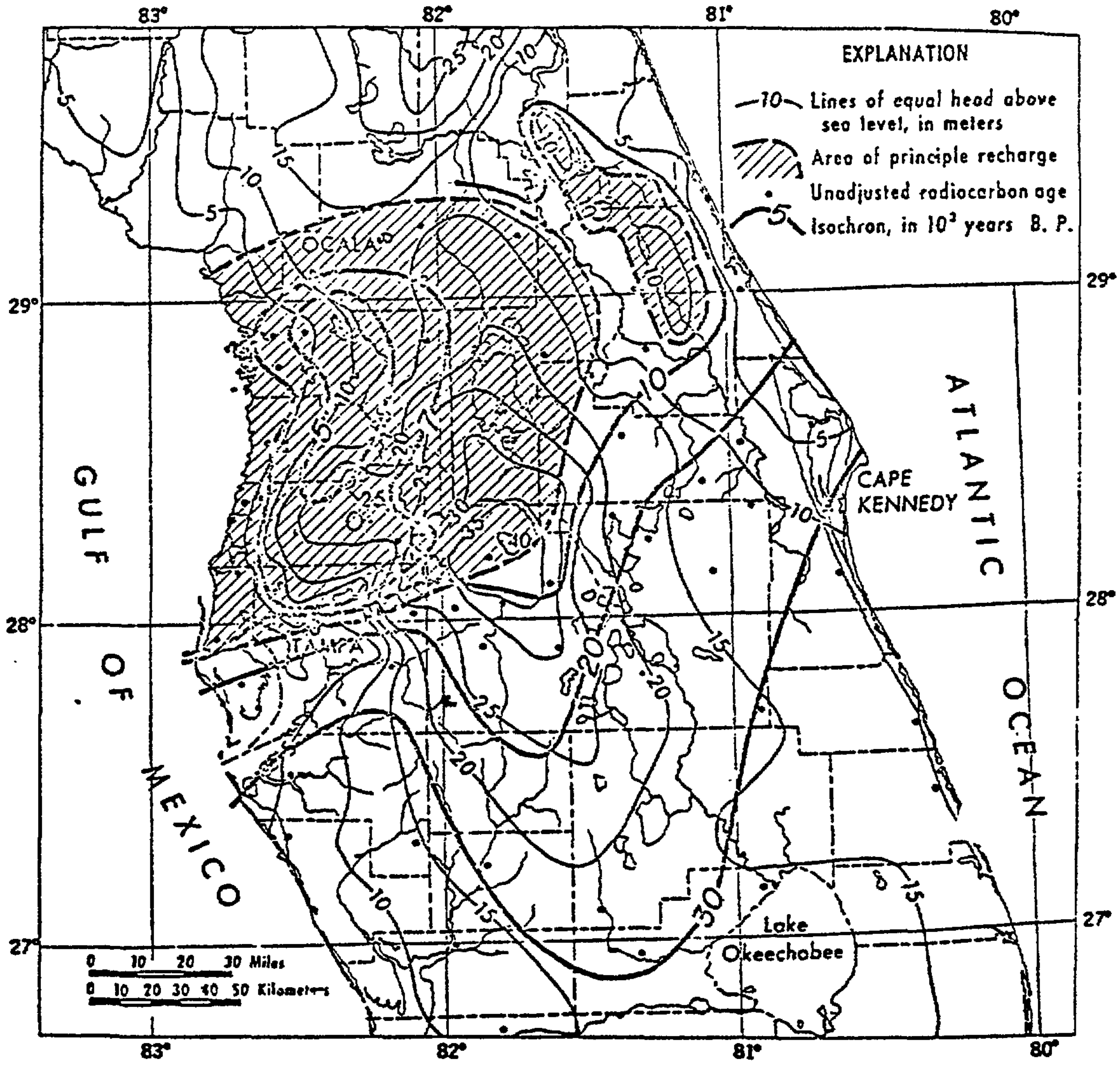


Figure 37 Potentiometric map of principal artesian aquifer in central Florida showing unadjusted hydroisochrons from Carbon-14 dating of dissolved carbonate species in ground water.

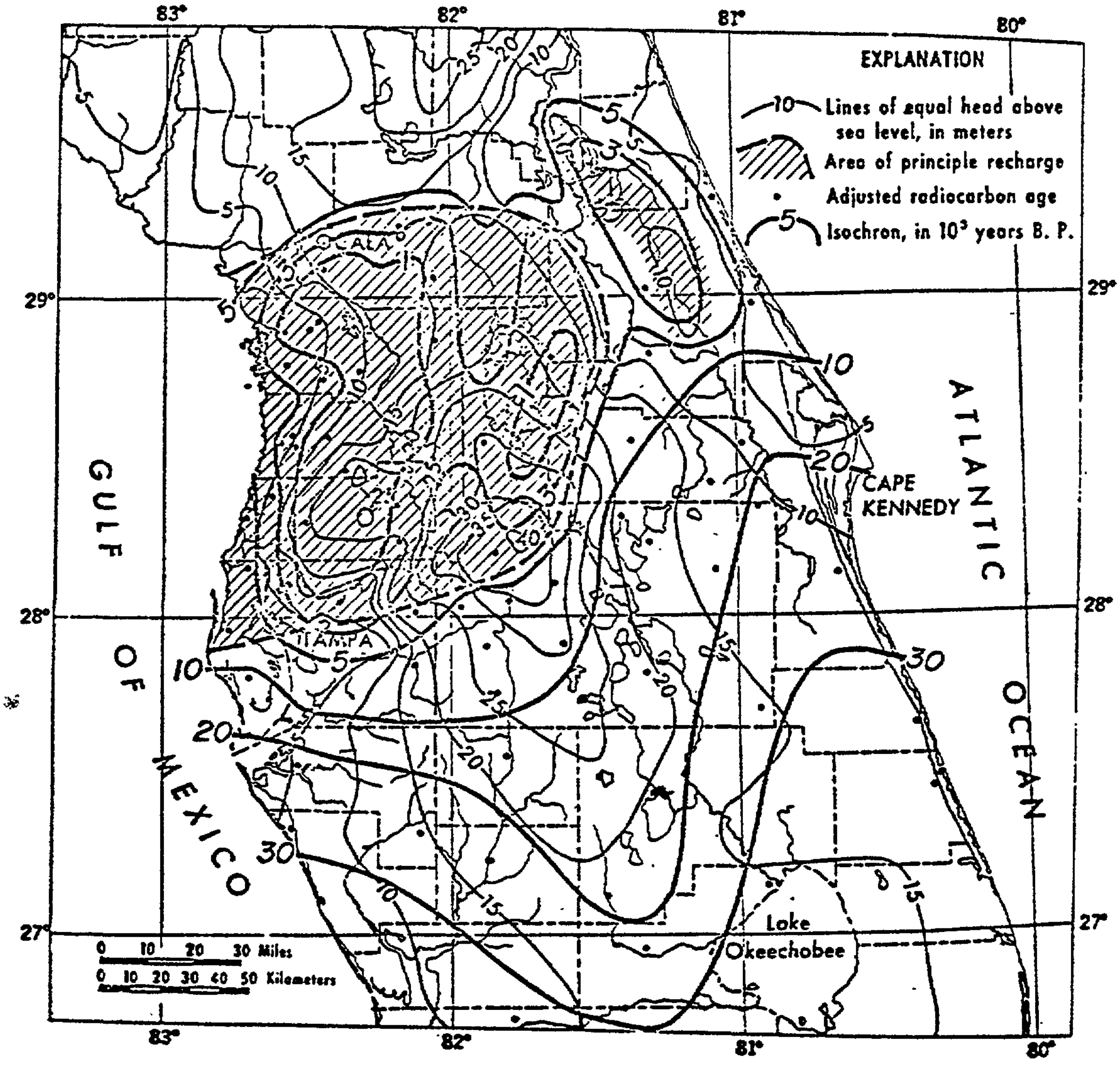


Figure 38 Potentiometric map of principal artesian aquifer in central Florida showing adjusted hydroisochrons. Carbon-14 age of dissolved carbonate solution is corrected for limestone solution by means of C^{13}/C^{12} ratios.