VALIDITY OF RADIOCARBON DATES ON GROUND WATER

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Abstract. Carbonate species, dissolved in appreciable quantities in all ground waters, can be extracted and used for radiocarbon dating. The material is mainly of biogenic origin, but contains some bicarbonate produced from limestone. This causes a dilution of the radiocarbon activity of the total carbonate species in the water and a correction is necessary in order to determine absolute radiocarbon ages, i.e., the time since the waters went underground.

Three methods of evaluating the limestone contributions are examined critically: carbonate species ratios, carbon-13 variations, and concurrent tritium measurements. All possess uncertainties. The largest errors occur in the carbon-13 procedure, due to the wide natural fluctuation of the stable isotope content in plants and the occurrence of isotope effects in the soil air-water carbon dioxide exchange. Comparisons of the limestone dilution correction techniques show that they produce analogous results in actual aquifer studies, but with small differences in the calculated radiocarbon ages. The reasons for these inconsistencies have not yet been unequivocally established. Two problems are: the possibility of irreversible exchange of the ground water dissolved carbonate species with limestone in the aquifer matrix, and the significance of exchange of carbon dioxide in the water with that of the soil air in the surface layer of the catchment zone. Experiments are suggested that could resolve these questions.

1. Introduction

The purpose of radiocarbon dating of ground water is to determine when the water went underground. Radioanalysis of the carbonate species (carbonates, bicarbonates, and dissolved carbon dioxide) present in all ground waters can provide information on the recharge of underground deposits as well as flow directions and rates. These methods are valid for limits of 5 yr to 60000 yr.

Surface water and rainfall infiltrating into the ground contain small amounts of carbon dioxide extracted from the air. Leaving the atmosphere, the water comes in contact with the soil air, where the partial pressure of carbon dioxide is considerably higher. This gas is the result of plant root respiration and, to a smaller extent, plant decay in the first metre or two of depth below the surface. Ground water carbonate species (principally bicarbonate and dissolved carbon dioxide) concentrations increase here due to the removal of water in large quantities by plant roots. The reaction of the dissolved carbon dioxide with limestone to form bicarbonate begins and continues throughout the regions of the aquifer where the mineral is present.

The initial work on the use of carbonate species as material for radiocarbon dating of ground water was described by Münnich (1957). It was shown that the radiocarbon concentrations were diluted by the reaction of the dissolved carbon dioxide with limestone to form bicarbonate,

$$CO_2 + CaCO_3 + H_2O \rightarrow 2HCO_3^- + Ca^{++}.$$

The amount of dissolving calcium and magnesium carbonate, virtually radiocarbon-free, can be monitored by observing the bicarbonate buildup in the water. Half of the concentration of that carbonate species originated from the limestone and the other

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half from the dissolved carbon dioxide, which possessed the radiocarbon concentration of contemporary plants. Calcium carbonate being highly insoluble, carbon from this source enters into solution through the above reaction. Its final concentration would not exceed the original amount of carbon dioxide present. Therefore, the dilution of the radiocarbon initially dissolved in the ground water would be limited to a maximum of 50%. This would produce a radiocarbon dating error of one carbon-14 half-life (5730 yr) in the measured date, no matter how old the sample is (Godwin, 1962). Münnich showed that a correction for the limestone dilution of the total radiocarbon of the carbonate species could be effected by comparing the relative amounts of bicarbonate and dissolved carbon dioxide present.

Other reactions whereby bicarbonate could be produced or limestone dissolved were demonstrated by Vogel and Ehhalt (1963). The weathering of silicate materials

$$CaAl_2(SiO_4)_2 + 2CO_2 + H_2O \rightarrow Ca^{++} + 2HCO_3^- + Al_2O_3 + SiO_2$$

and the reaction of plant debris humic acids are possibilities,

$$\begin{aligned} &CaCO_3 + 2H^+ \rightarrow Ca^{++} + CO_2 + H_2O, \\ &2CaCO_3 + 2H^+ \rightarrow 2Ca^{++} + 2HCO_3^- . \end{aligned}$$

However, it was shown that the silicate reaction should be very slow and the humic acid concentrations generally too small for these reactions to be significant contributors to the dissolved carbonate species in most ground waters.

The Heidelberg Laboratory introduced the use of the stable carbon-13 isotope as a method for the correction of ground water carbonate species for limestone dilution (Brinkmann *et al.*, 1959). This procedure was based on the fact that limestone, in addition to containing essentially no radiocarbon, has a carbon-13 content different from that of plants and the atmosphere. It is, on the average, 2% richer in this isotope than the average for plants and 0.8% richer that atmospheric carbon dioxide.

The standard way of presenting carbon-13 concentrations is in the form of a ratio of the deviation from an accepted standard to that reference (Craig, 1953). The standard used is commonly Craig's limestone (denoted PDB) with a defined *relative carbon-13 content* (denoted δC^{13}) of 0.00‰ (per thousand). These deviations are calcaluated according to the formula

$$\delta C^{13} = \frac{C^{13}/C^{12}_{\text{sample}} - C^{13}/C^{12}_{\text{standard}}}{C^{13}/C^{12}_{\text{standard}}} \cdot 1000\,‰ .$$

This expression for carbon-13 concentrations in terms of differences from a standard takes advantage of the precision of the special mass spectrometers equipped for natural isotope concentrations measurements. On this basis, plants would have carbon-13 contents with an average of approximately −20‰ and atmospheric carbon dioxide of the order of −8‰, the negative signs indicating that both the plants and carbon dioxide in the air have lower carbon-13 concentrations than limestone. The precision of the measurements can be ±0.1‰, but the actual normal variation of the concentrations of the materials in nature show variations orders of magnitude greater than this, as much as ±12‰ for plants, as will be described in Section 3.2.

Differences in carbon-13 content can be employed to estimate the contribution of dissolved carbonate species derived originally from limestone. For example, bicarbonate in ground water showing a carbon-13 content of −10‰ would indicate the probability that half of the carbon came from limestone and that a correction of 5730 yr, added to the apparent radiocarbon date, would give the true age of the water.

Another technique for limestone dilution correction, using an exponential model, has been introduced (Geyh, 1972b). The comparisons of radiocarbon and tritium contents in several samples from the same catchment area over the period of a year provides a means of determining the initial radiocarbon content of the dissolved carbon dioxide, as well as residence times and seasons of recharge. The method appears promising, but must be studied under a variety of conditions before its reliabiliy can be established. There is still the question of the relative ambiguity of the interpretation of tritium concentrations in ground waters, compared to radiocarbon. Tritium contamination of rain due to the testing of atmospheric thermonuclear devices was considerably more severe than radiocarbon, reaching values of as much as 1000 times normal in the northern temperate zone peak year of 1963 (Münnich and Roether, 1967). Radiocarbon, on the other hand, was never more than twice normal (Nydal *et al.*, 1971). The possibility of minimal amounts of younger water infiltrating into the sampled ground waters means that individual measurements cannot lead to any definite conclusions. Large numbers of samples must be examined in order to obtain distributions of tritium values that would support unambiguous interpretations.

Radiocarbon dating of ground water is obviously not reliable in zones susceptible to the addition of magmatic carbon dioxide or that originating from oil or lignite deposits. The occurrence of this error factor can be seen in abnormally large carbonate species concentrations (Tamers *et al.*, 1968; Scharpenseel and Tamers, 1970). Actually, the possibility of the oxidation of organic matter in either the aquifer matrix or the water itself is minimal, due to the slow reaction rates at usual ground water temperatures and the low solubility of oxygen in water. Oxygen concentration is the order of 1/100 of that of bicarbonate in ground water. Humic matter out of the aeration zone in ordinary soils is known to decay very slowly, with residence times of the order of thousands of years (Scharpenseel and Pietig, 1969a). However, the possibility exists that the oxidation of organic matter in aquifers could slowly proceed through a coupled sulfate reduction reaction (Custodio, 1967) or the action of anerobic bacteria (Matthess *et al.*, 1969). Whether possibilities of this sort occur fast enough to be of significance relative to the half-life or radiocarbon are not known; it would be most prudent to avoid using the radiocarbon dating method for the study of the few aquifers with important organic carbon deposits.

In addition to the question of the validity of the correction for limestone dilution, radiocarbon dates of ground water are also challenged on the possibility of exchange reactions between dissolved carbonate species and the calcium carbonate of limestone particles present in aquifers. A reversible ion exchange probably does exist on selected sites on exposed surfaces, but the effect would not change either the isotopic composition of the dissolved carbonate species or the chemical compositions once an equilibrium state had been reached. This would also be the case of exchange between the dissolved carbon dioxide and the gas present in the soil air. The irreversible effect of water-soil carbon dioxide exchange should be limited to the topmost levels of soil. It is here that the soil air would be renewed. In all other regions of the aquifer this reversible exchange would produce no net change in the solution composition after equilibrium had been established.

2. Exchange Possibilities of Dissolved Carbonate Species

2.1. IRREVERSIBLE EXCHANGE-DISSOLVED CARBONATE SPECIES WITH LIMESTONE

The validity of radiocarbon dates on ground water depends on the absence of significant amounts of irreversible exchange between the dissolved carbonate species and limestone particles in the aquifer matrix. Reversible ion exchange would produce no net alteration of the solution composition, but could result in a decreased velocity of the carbonate species ions with respect to the water flow. The reversible exchange would be a surface phenomenon, whereas irreversible phenomena taking place after aquifer equilibrium had been established would imply solid state diffusion of the surface ions into the interior of the calcium carbonate crystals. Other limestone molecules or ions that previously were inside the rock would have to diffuse outwards to the surface. This type of mixing in solids at ordinary temperatures is known to be an extremely slow process. In the absence of rapid diffusion, any exchange between the dissolved carbonate species would be reversible and would not affect the radiocarbon concentration of the dissolved carbonate species of the ground water.

The possibility of exchange has been examined in laboratory models. Samos (1949) applied artificial tracers to the investigation of the exchange of dissolved carbonate ions with solid carbonate. Even under the varying conditions of his experiments, no significant amount of irreversible exchange was observed. Anderson (1969), in careful studies of surface diffusion into calcite crystals, proved that even at relatively high temperatures (50 °C) less than 3% irreversible exchange could occur in 10^7 yr. Haul and Stein (1955) thoroughly studied the irreversible exchange caused by the diffusion of carbon dioxide into calcite crystals. The room temperature diffusion coefficient was found to be 10^{-43} cm^2 s^{-1} and a lattice diffusion activation energy of 2.4×10^5 J/mol (58 kcal/mol). This would exclude significant diffusion losses in less than 10^5 yr. All these periods are much longer than the limits of radiocarbon dating.

Also pertinent would be the results of an oxygen-18 isotopic paleo-temperature study by Emiliani (1956). He found no postdepositional isotopic exchange in Oligocene and Miocene pelagic foraminifera samples. Irreversible exchange would have resulted in enrichment of oxygen-18. But the isotopic compositions were not in equilibrium with the modern low temperature surrounding water, indicating that diffusion was slow enough to prevent irreversible exchanges even in millions of yr.

There have been investigations using artificial carbon-14 and tritium as tracers on fine powders of calcium carbonate, obtained either by extensive grinding of limestone (Münnich *et al.*, 1967; Thilo and Münnich, 1970) or precipitation from solution (Wendt *et al.*, 1967). Despite the excellence of these studies, artificial conditions, such as the fresh exposure of surfaces and the microscopic particle sizes, present an uncertainty in the significance of the results with respect to their pertinence to the conditions existing in natural aquifers. Thilo and Münnich point out this aspect in their work and emphasize that more stable limestone surfaces would be expected in nature. The diffusion study of dissolved carbonates into the artificial calcite particles gives a coefficient of diffusion of 10^{-28} cm^2 s^{-1}, which is orders of magnitude less than that observed by Haul and Stein (1955) for actual calcite crystals. The ready exchange of oxygen-18 in the recently precipitated calcium carbonate is contrasted to the absence of irreversible exchange noted by Emiliani (1956) in non-artificial situation.

The only natural system studied with tracers was a loess column (Thilo and Münnich, 1970), but here the observed exchange should be with the major clay constituent and not necessarily with the traces of carbonate present. There would also be mechanical problems with the percolation of water through the fine particles of this type of soil.

In the natural environment, gross limestone particles, much larger than those used in the artificial material studies, have been subjected to at least thousands of years of attack by flowing ground water. They would be expected to have become desensitized through the development of relatively inactive surfaces. This is in agreement with the observation that, despite ages of thousands of yr (Tamers, 1967a), several aquifers show deep ground waters with important amounts of dissolved carbon dioxide that had not yet reacted with the limestone of the deposit to produce bicarbonate. Work on extensive areas of the Floridian artesian aquifer (Back and Hanshaw, 1971) showed that the deposits of Tertiary calcite and dolomite take 4000 yr and 15000 yr, respectively, to reach equilibrium with the flowing ground water. The reaction of the dissolution of limestone by carbon dioxide should be much faster than the irreversible exchange between the dissolved carbonate species ions and the interior of the solid calcium carbonate particles. If the conditions were not such as to permit the limestone-carbon dioxide reaction to approach completion, the dissolved ion-solid limestone exchange should be negligible here.

It is indispensable that exchange experiments to be conducted on whole natural limestone particles, in order to be applicable to the problem of the validity of radiocarbon dates on ground water and ion exchange reactions in nature. Chemists working on surface studies, such as heterogeneous catalysis or absorption kinetics investigations, are thoroughly familiar with the universal phenomenon of desensitization of materials as they are subjected to even the most dilute solutions. They are, likewise, cognizant of the ready production of additional ion exchange sites by artificially exposing fresh surfaces in crystaline matrices.

The comparison of tritium and radiocarbon contents in natural sytems could be used to provide information on the possibility of irreversible losses due to the diffusion of originally dissolved carbonate species into the limestone particles (Münnich and Roether, 1963). The downward movement of tritium in the aquifer would indicate a value for the recharge rate. This permits the estimation of the carbon-14 transport into the aquifer, which is compared to the measured depth distribution of radiocarbon in the ground water. In an experiment of this type, Thilo and Münnich (1970) studied tritium and radiocarbon in a homogeneous shallow aquifer near Heidelberg. The results in this completely natural system showed no evidence of a delay in the transport of the carbon-14 of the dissolved carbonate species compared to that of the tritium of the water. There was no observation of any carbon-14 losses due to irreversible carbonate exchange.

2.2. Irreversible exchange-dissolved carbonate species with soil air carbon dioxide

The effect of a possible irreversible exchange of the dissolved carbonate species with limestone would occasion radiocarbon dates on ground water that are falsely old, even after the usual correction for limestone dilution. There is another uncertainty, however, that would result in ground water radiocarbon dates being incorrect in the sense that the calculated values, after limestone dilution correction, would be younger than the real age of the water. This would be due to an exchange that would take place between the solution carbonate species and the soil air (Münnich, 1957; Vogel and Ehhalt, 1963; Wendt *et al.*, 1967). The dissolved carbon dioxide and bicarbonate, whose radiocarbon content has already been diluted by limestone reaction, can exchange with an excess of undiluted carbon dioxide in the soil air. In principle, the dissolved carbonate species could revert to 100% modern specific radiocarbon activity, but still retain their approximate chemical composition.

There is some uncertainty whether the consequence of exchange with the soil air carbon dioxide is significant. Any exchange would tend to lower the radiocarbon concentration of the carbon dioxide of the soil air and, in this way, nullify the net effect of further exchanges. A ready renewal of the soil air by mixing with the atmosphere (in a period of a month or two) would have to occur if this cancelling out would not obviate the entire problem.

The soil air-atmosphere mixing is prevalent in the uppermost layers of soil and would be due, principally, to changing atmospheric pressures. These variations are generally less than 1% at any given location. The atmospheric pressure variation effect on the renewal of the soil air would depend on the depth of the unsaturated soil zone, the permeability of the material, and the rapidity of the rhythm of pressure variations. For example, assuming an infinite permeability and prolonged pressure changes, at a ground water level 20 m below the surface, pressure fluctuations of $\pm\frac{1}{2}\%$ would cause a zone of soil air-atmosphere mixing at only the top 10 cm level.

Wendt *et al.* (1967) have made an important analysis of the effect of temperature on isotopic exchange processes between the dissolved carbonate species and calcium carbonate. Their finding of exchange with freshly precipitated solid material illustrates a limiting case, but experiments must still be performed to determine whether the phenomenon would take place to a significant extent on the large old limestone rocks that had been washed by ground water for thousands and millions of years. Nevertheless, this work illustrates the possible equilibrium disruption that could be a source of error in radiocarbon dating studies of ground water. Especially interesting is the finding that the potential precipitation and redissolution processes influence the carbon-14 and carbon-13 problems differently. They conclude that the carbon-13 correction for limestone dilution would be unreliable, due to this consideration alone. More experiments to study the possibilities suggested, particularly with natural limestone particles, will have to be carried out.

The key uncertainty in these problems is where the actual soil air-atmosphere mixing depth is significant. Lerman (1972a), in a carbon-13 study of soil air carbon dioxide, failed to find evidence of exchange with the atmosphere at 20 cm depths. This series of measurements supports the assumption of the limitation of atmospheric renewal of soil air carbon dioxide. The 10 to 20 cm surface level is small compared to a 1 or 2 m plant root zone, where the major quantities of carbon dioxide are absorbed into the ground water, and the very much larger distances (tens of metres and even kilometres) where the carbon dioxide actually completes its reaction with limestone to produce the radiocarbon dilution. This would substantially reduce the possibility of a large error in the case where limestone dilution was corrected by the carbonate species ratio method. An exchange between the carbon dioxides in the soil and in the ground water would not be significant if it occurred before the main limestone-dilution reaction had started. This effect, of the order of 1‰, would be negligible for the carbonate species ratio correction method, but would be very serious in the carbon-13 technique. An isotope effect here of even ½‰ would introduce a large error, despite its occurrence before the principal limestone dilution reactions. The results of Wendt *et al.* (1967) show the uncertainties that would occur in the attempt to use carbon-13 as a quantitative tool in limestone dilution correction of radiocarbon dates on ground water.

Emrich *et al.* (1970) have determined various carbon-13 isotope fractionations that would occur. Further evidence against the possibility of deep soil air-atmosphere mixing would be the observation in a large variety of regions and climates of long (hundreds and thousands of years) residence times of decaying plant matter a few decimetres under the surface (Scharpenseel *et al.*, 1968; Mückenhausen *et al.*, 1968; Scharpenseel and Pietig, 1969b; Scharpenseel, 1970; Herrera and Tamers, 1971; Geyh *et al.*, 1971; Scharpenseel, 1972). This must be due to a lack of soil air-atmosphere mixing, since it was shown that dead plant materials on the surface are largely decomposed to carbon dioxide in a year or two (Führ and Sauerbeck, 1968; Oberländer and Roth, 1968; Oberländer and Roth, 1972).

The carbon dioxide of the soil air, which is the principal source of biogenic radiocarbon for the ground water carbonate species, is mostly produced by the respiration of plant roots (Lerman, 1972a). If, as discussed above, the zone of extensive, rapid soil air-atmosphere mixing is only the top 10 or 20 cm of well packed ground, it is pertinent to consider what percentage of plant roots lie at this depth. Actually, both the vertical and horizontal growth of plant roots vary enormously, depending on both the local climate and the particular plant (see Epstein, 1973, for a general discussion). Ninety-nine percent of the root system of the common, dry environment, locoweed is below 10 cm from the surface, whereas roots of the prickly-pear cactus are 99% within 10 cm of the surface. Other examples, corn roots and apple tree roots are more than 90% below 10 cm, but many grasses have their root system near the surface.

The question of the importance of the exchange of dissolved carbonate species of ground water with carbon dioxide in the soil air has not yet been unequivocally resolved. It is pertinent to the problem of the accuracy of the limestone dilution correction methods; the errors from this source must be added to the determinant errors of any of the correction procedures. However, unlike the problem of the possibility of the irreversible exchange of ground water, dissolved carbonate species with soil air is limited and could not produce gross errors in radiocarbon dates on ground water. Nor, generally, could it change the interpretation of radiocarbon data for a thoroughly studied aquifer in the case when the carbonate species ratios were used for the limestone dilution correction. The possible errors with the carbon-13 technique would be much larger.

3. Limestone Dilution Correction

3.1. DISSOLVED CARBONATE SPECIES CONCENTRATION VARIATIONS

As initially suggested by Münnich (1957), the relative amounts of the dissolved carbonate species can give an indication of the limestone contribution. The dissolving of limestone depends on a reaction with carbon dioxide to form bicarbonate. The contribution of limestone to the total amount of dissolved carbonate species will be equal, on a molar basis, to one half of the bicarbonate concentration and the biogenic carbon will have supplied the other half of the bicarbonate, plus all of the dissolved carbon dioxide present as such in the ground water.

Geyh and Wendt (1965) expressed the relative contribution of plant carbon in the carbonate species as

$$q = \frac{[\mathrm{CO_2}] + \frac{1}{2}[\mathrm{HCO_3^-}]}{[\mathrm{CO_2}] + [\mathrm{HCO_3^-}]},$$

with the correction to the measured radiocarbon content

$$\mathrm{C}^{14}_{\text{corrected}} = q \cdot \mathrm{C}^{14}_{\text{measured}}.$$

The experimental technique consists of measuring, in the field, both the carbon dioxide and bicarbonate contents of the ground water samples, the former with a pH determination on water recently removed from the well and the latter with a calibrated sulfuric acid titration to a pH 4.3 end point. The radiocarbon age of the ground water would then be calculated using the corrected activity in the usual exponential decay equation

$$\mathrm{C}^{14}_{\text{corrected}}/\mathrm{C}^{14}_{\text{modern std.}} = e^{-\lambda t},$$

where λ is the decay constant of carbon-14 and t is the age of the sample, i.e., how long it has been underground.

There is a critical importance to carrying out the chemical analyses rapidly. If the samples are taken back to the laboratory for measurement, changed values are inevitably obtained. This is due to the rapid release of carbon dioxide from the extracted specimens. The bulk samples for the carbonate species extraction, must be tightly enclosed to avoid this loss. The carbon dioxide escape causes an isotope effect that leads to spurious carbon-13 values. Stable isotope studies on ground water are relevant only when strict precautions have been taken to eliminate the possibility of this source of error (Mook, 1970).

The validity of the bicarbonate analysis has been verified, but that of field pH measurements, leading to reliable carbon dioxide concentrations, is more difficult. The author has used a measurement of the total carbonate species as a substitute for carbon dioxide analysis. The concentration of the component of the carbonate species was obtained from the difference of the bicarbonate concentration and the total carbonate species present (Tamers, 1967a). After acidification of the ground water and nitrogen sweeping of 24 hours, a quantitative collection of the carbon dioxide of the total carbonate species is obtained. This serves as an analysis technique for total carbonate species and the collection of the sample for radiocarbon analysis. In this procedure, it is essential to have leak-proof connections on the top of the drum during

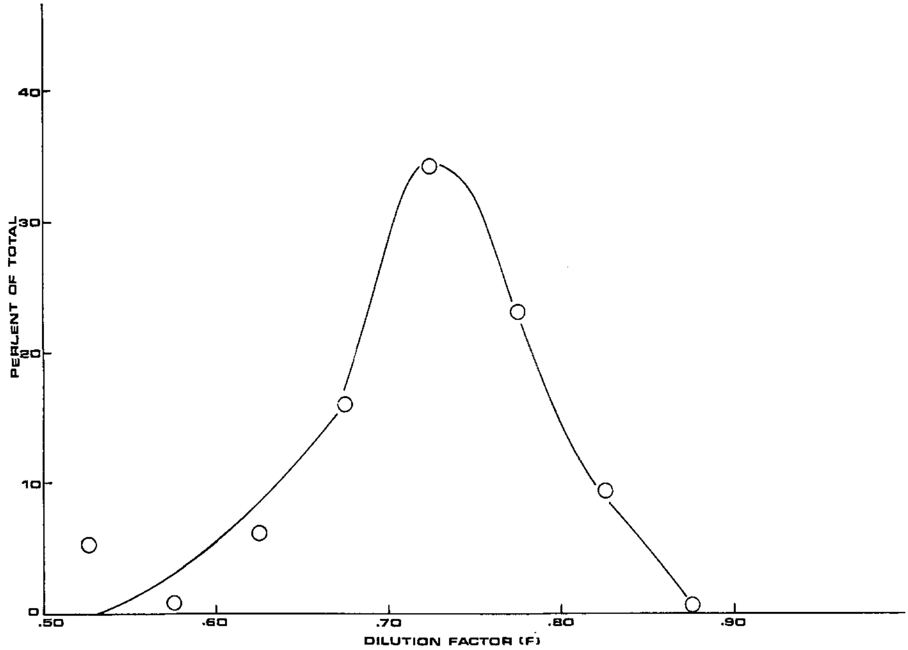

Fig. 1. Distribution of the limestone dilution correction factor, *F*, calculated from the carbonate species concentrations of ninety ground water specimens (Tamers, 1967a; Tamers, 1966; Tamers and Thielen, 1966; Tamers, 1969).

the transportation to the laboratory, as well as during the extraction. The use of the total carbonates instead of carbon dioxide would modify the previous equation to

$$F = \frac{[C_{\mathrm{total}}] - \frac{1}{2}[HCO_3^-]}{[C_{\mathrm{total}}]} = q,$$

where F is the fraction of carbon in the dissolved carbonate species coming from plant materials. Figure 1 illustrates the range of values observed in several aquifers where the chemical analyses were carried out under optimum conditions.

The validity of this limestone dilution correction method depends on the extent of the soil air-dissolved carbonates species exchange and the irreversible limestone exchange described in the previous section. In addition, Geyh (1970) has shown that limestone in topsoil is often not radiocarbon-free. He argues that this is due to precipitation of carbonates from water during the summer, with consequent dissolving in the winter when the major rainfall infiltration into the ground water aquifer takes place. There are questions, however, as to the form of the radiocarbon containing deposit on the surface limestone and whether the phenomenon also exists in the deep lying limestone of the aquifer matrix. If the precipitated deposits are a reversal of the limestone dilution equation, an error would be introduced. The evolved carbon dioxide would have a lowered radiocarbon content and the deposit would be calcium carbonate, whose subsequent reaction with new carbon dioxide would produce dissolved bicarbonate that had more than half the modern radiocarbon content. This produces an effect in both the carbonate species and carbon-13 limestone dilution correction methods. However, the errors would be limited.

An equation that would illustrate the situation was given by Tamers (1967a):

$$C^{14}_{\mathrm{measured}} e^{\lambda t} = F \cdot C^{14}_{\mathrm{modern}} + (1 - F) \cdot C^{14}_{\mathrm{limestone}},$$

where the right hand side of the relation equals the original radiocarbon content of the zero age, limestone diluted, dissolved carbonate species. The fraction of the radiocarbon of the carbonate species that came from limestone, $(1-F)C^{14}_{\mathrm{limestone}}$, might not be zero and the actual correction for limestone dilution would be less than had been assumed previously. For example, with a measured value of $F = 0.70$ and $C^{14}_{\mathrm{limestone}} =$ 10% modern, the radiocarbon dating sample would show $C^{14}_{\mathrm{measured}} = 73\%$ modern ($C^{14}_{\mathrm{modern}} = 100\%$ modern in the case of no aritficial atmospheric contamination) as the zero age radiocarbon concentration. If the limestone activity were ignored a value of 70% modern would be obtained. To illustrate the extent of the error from this source, in the case of a $C^{14}_{\mathrm{measured}} = 50\%$ modern, the age of the sample without cognizance of the limestone activity would have been calculated to be 2790 yr, while it would be 3130 yr with the limestone activity taken into account, an error of 340 yr or 11%. If the radiocarbon in the limestone is present as calcium bicarbonate instead of calcium carbonate, a smaller net error would be introduced into the limestone dilution correction.

Nevertheless, the question remains as to whether the limestone radiocarbon is limited to only the surface layers. It is probably considerably less in the deeper zones.

Therefore, the error illustrated above would be smaller than that shown and the effect would be negligible. It will be necessary to extend Geyh's important contribution to the study of the possibility of radiocarbon in limestone particles deep in the aquifers in order to settle the problem of the total possible error from this source.

In order to take into account the possibility of the various conceivable errors, it has been suggested (Tamers, 1967a) that the limestone dilution corrected ground water age equation

$$t = -(1/\lambda)\ln\left(C^{14}_{\text{measured}}/C^{14}_{\text{modern}}\right) + (1/\lambda)\ln F,$$

be modified to

$$t = -(1/\lambda)\ln\left(C^{14}_{\text{measured}}/C^{14}_{\text{modern}}\right) + (\tfrac{3}{4}\lambda)/\ln F \pm (\tfrac{1}{4}\lambda)/\ln F.$$

In this case the positive sign for the last term would take into account any apparent aging of the sample by irreversible limestone dilution. The negative sign would compensate for cases of significant amounts or radiocarbon activity in the limestone dilutant, irreversible soil air-atmosphere exchange, or any carbon dioxide that escaped during the sampling. These would cause chemical analyses for the total carbon to be falsely low. The limit of the positive error would be the case where none of these is significant. As explained, there is reason to believe that all of these potential sources of errors are not large.

3.2. NATURAL CARBON-13 VARIATIONS

The use of the naturally occurring stable isotope, carbon-13, has been proposed for the estimation of limestone dilution of the radiocarbon content of ground waters (Vogel, 1959; Brinkman *et al.*, 1960; Vogel and Ehhalt, 1963; Geyh and Wendt, 1965). Table I summarizes various concentrations found in nature.

TABLE I

Usual δC^{13} variations in nature (all values relative to the PDB standard)

Limestone	+2.8 to −2.8‰	(Craig, 1953)
Atmospheric carbon dioxide	−6.6 to −7.4‰	(Craig, 1953)
Plant material, Calvin cycle	−20 to −36‰	(Craig, 1953) (Wickman, 1952) (Lowdon and Dyck, 1974) (Troughton, 1972)
Plant material, Hatch-Slack cycle	−9 to −18‰	(Bender, 1968) (Lowdon and Dyck, 1974) (Stuiver and Deevey, 1962) (Hall, 1967) (Tauber, 1967) (Troughton, 1972)
Ground Water dissolved carbonate species	+9 to −20‰	(See Mook (1970) for a summary of this situation).

The wide fluctuations of the carbon-13 content of plant material are striking. It is now well established that there are at least two photosynthetic pathways which produce different degrees of isotope effects from the carbon dioxide of the atmosphere (Hatch and Slack, 1966; Bender, 1968; Smith and Epstein, 1971; Volk and Jackson, 1972). The carbon isotope effect in plants is related to the ratio of rates of photosynthesis to photorespiration. The higher the ratios, the smaller the isotope effects. There are also pronounced variations with the age of the plant (Salin and Homann, 1971) and seasonal changes (Lowdon and Dyck, 1974). Photosynthesis of plants proceeds along certain cycles. That known as the *Calvin cycle* predominates, while the *Hatch-Slack cycle* is not uncommon. Although the latter has been considered effective only for tropical climates, the cycle does include plants such as corn, crabgrass, and millet, which are prevalent in temperate zones.

Figure 2 illustrates the sources of variations of carbon-13 and carbon-14 in ground water carbonate species. Possible isotope effects in the handling of the sampling operation are included. In particular, care must be taken when the water is removed from the well to minimize the escape of dissolved carbon dioxide. This would result in the lowering of the carbon-13 content of carbonate species. The figure also gives examples of mixtures of effects, illustrating the virtually complete spectra of carbon-13 values that can be obtained.

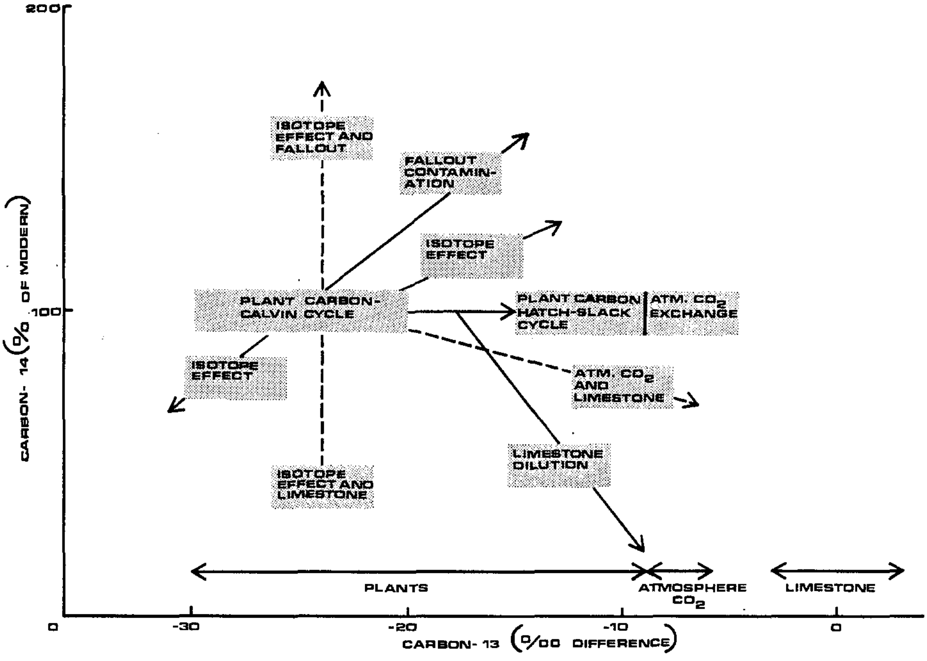

Fig. 2. Natural distributions of carbon-14 and carbon-13 in plants, limestone, atmospheric carbon dioxide and ground water carbonates. The dotted lines illustrate combinations of effects.

The use of carbon-13 to correct ground water radiocarbon dates can be expressed by the equation (Tamers, 1967a)

$$\delta C^{13}_{\text{measured}} = F\cdot\delta C^{13}_{\text{plants}} + (1-F)\,\delta C^{13}_{\text{limestone}}\,,$$

which is similar to that described for carbon-14. However, the exponential factor for radioactive decay is absent because carbon-13 is stable. F is the fraction of the carbon of the dissolved carbonate species that came from plant materials. It is seen from the similarity between the carbon-13 and carbon-14 equations that comparisons can be made to examine the validity of the carbonate species ratios method of limestone dilution correction. That is to say, it would be of interest to determine whether the limestone dilution corrected carbon-13 values come close to reproducing the natural distribution for plant carbon isotopes. Only systems where great care was taken to insure correct analyses of carbon dioxide and bicarbonate are applicable to this treatment. Such measurements must be carried out at the well site.

The findings from three aquifers are shown in Figures 3, 4 and 5. Data in a study by Geyh and Wendt (1965) on a Niedersachsen water deposit have a similar distribution. It is seen that the corrected carbon-13 values approach the Calvin cycle plant carbon-13 distributions, but are inevitably on the higher side. The reasons for this are possibly a small contribution of atmospheric carbon dioxide in the dissolved ground water carbonates and/or the existence of plants following the Hatch-Slack photosynthesis

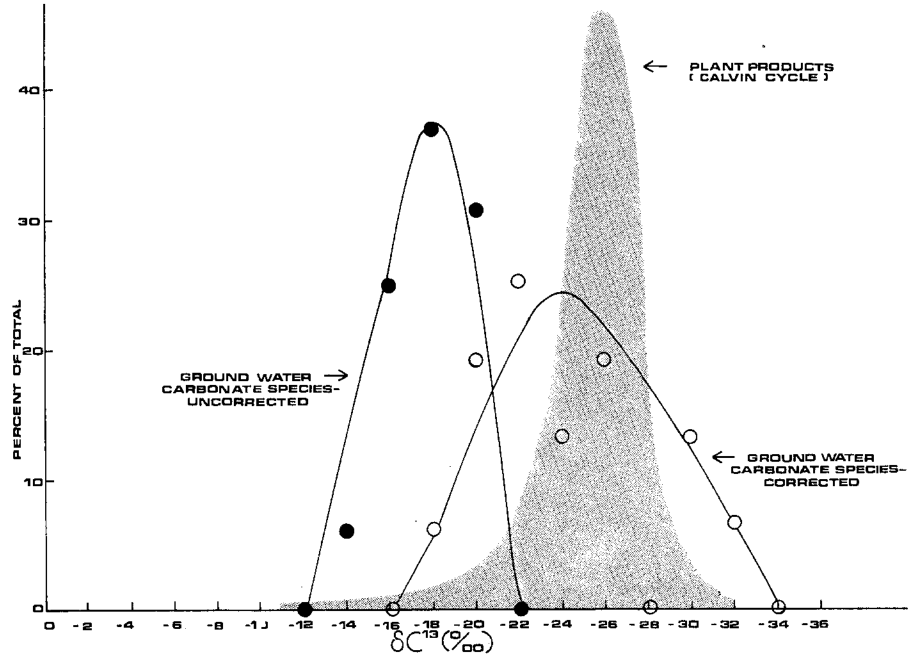

Fig. 3. Comparison of $\delta C^{13}_{\text{measured}}$ and $\delta C^{13}_{\text{corrected}}$ with the known values of Calvin cycle plants. Water samples from Maracaibo, Venezuela. Correction by the carbonate species method (Tamers, 1967a).

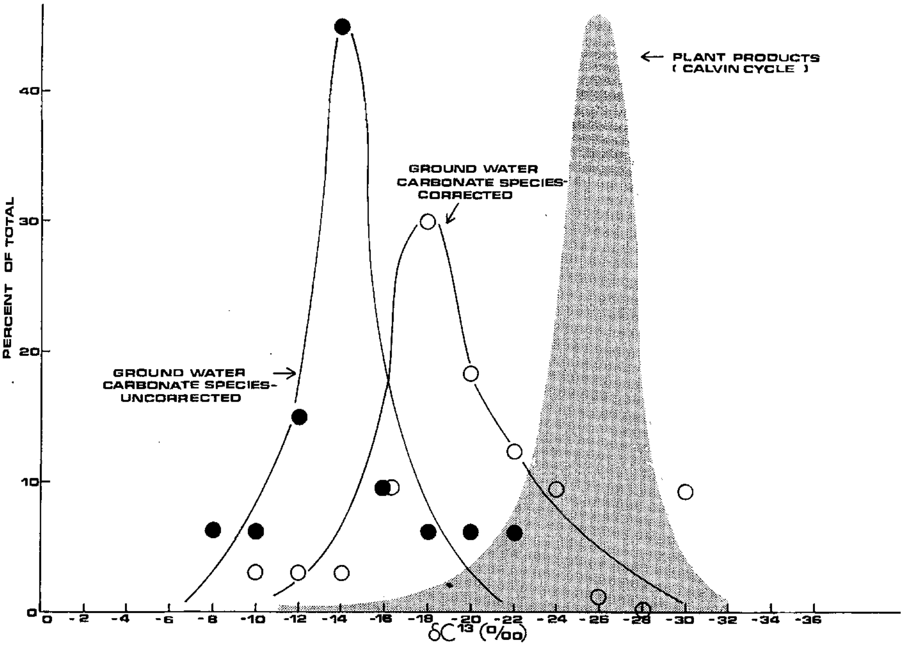

Fig. 4. Comparison of $\delta C^{13}_{\text{measured}}$ and $\delta C^{13}_{\text{corrected}}$ with the known values of Calvin cycle plants. Water samples from Coro, Venezuela. Correction by the carbonate species method (Tamers, 1966).

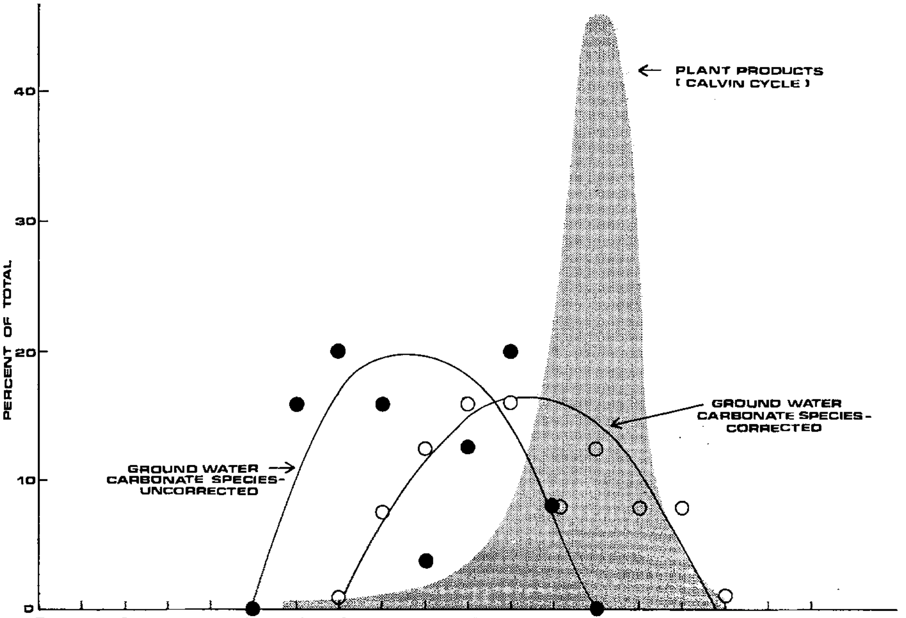

Fig. 5. Comparison of $\delta C^{13}_{\text{measured}}$ and $\delta C^{13}_{\text{corrected}}$ with the known values of Calvin cycle plants. Water samples from the basin surrounding the Lake of Velencia, Venezuela. Correction by the carbonate species method (Tamers and Thielen, 1966).

cycle. Nevertheless, the closeness of the corrected carbon-13 values to the natural distribution of plant carbon isotopes indicates that irreversible limestone exchange does not occur to a noticeable extent. Finally, if the carbonate species ratio equation is capable of correcting the stable carbon-13 concentrations, it must also be useable for the estimation of limestone dilution for radiocarbon dating of ground water.

If the only important ground water dilution reaction is that of the carbon dioxide attack of limestone, natural values of carbon-13 in the dissolved carbonate species should not usually be higher than about $-10‰$ (in the case of a Calvin-cycle plant cover), since a maximum of 50% of the total solution carbon could have come from limestone. Nevertheless, values higher than this have been observed, for example, by Conrod and Fontes (1972), Lerman (1967), and Mook (1970). This is explained as due to isotopic exchange with the unsaturated zone carbon dioxide (Vogel, 1959; Wendt *et al.*, 1967). The process should be strongly temperature sensitive (Mook, 1972).

Another explanation of the occasional, high, ground water carbon-13 values would be the introduction of an isotope effect during the sampling operation. If the dissolved carbonate species originally in the sample are not collected quantitatively, a change in the isotopic composition of the sample could occur. An isotope effect of 1 or $\frac{1}{2}\%$, sufficient to explain the anomalous values, would be possible if a significant portion of the dissolved carbon dioxide gas escaped from the extracted water before the carbonate species could be precipitated. A further source of high carbon-13 ground water values would lie in the above-average content of the soil air in certain localities (Lerman, 1972a; Rightmire and Hanshaw, 1973). This would originate from non-Calvin cycle vegetation.

Analyses of soil air covered by Calvin-cycle plants did show the expected $\delta C^{13}_{\text{soil air}}$ of about $-25‰$ (Galimov, 1966), with the absence of a noticeable isotope effect in the process of plant respiration. However, Lerman (1972b) observed that the carbon-13 content of the soil air carbon dioxide is considerably higher for cover with plants following other types of cycles. He showed that the prevalence of these plant types are not limited to arid zones, as previously assumed. Photosynthetic cycles are taxonomic and not environmental adaptations. Mazor *et al.* (1974), likewise observed large δC^{13} variations in ground water carbonates from Kalahari, Africa. They conclude that the stable isotope measurements cannot be employed for radiocarbon dilution corrections.

The natural variations observed for the carbon-13 content of plants and limestone cause extensive uncertainties in its use for the limestone dilution correction of ground water carbonate species. The fraction of the ground water dissolved carbon coming from plants would be calculated by a rearrangement of the preceding equation to

$$F = (\delta C^{13}_{\text{measured}} - \delta C^{13}_{\text{limestone}})/(\delta C^{13}_{\text{plants}} - \delta C^{13}_{\text{limestone}}).$$

As an example, ignoring the possibility of Hatch-Slack cycle contributions and also atmospheric carbon dioxide, and taking only the most probably values of Calvin cycle plants,

$$\delta C^{13}_{\text{plants}} = -25 \pm 5‰,$$

$$\delta C^{13}_{\text{limestone}} = 0 \pm 3\text{‰}.$$

Also, let

$$\delta C^{13}_{\text{measured}} = -\ 17.5 \pm 0.1\text{‰}.$$

This results in a correction factor, $F = 0.70 \pm 0.20$, i.e., between 50% and 90% of the disssolved carbonate species is of plant origin. Actually, the uncertainty is larger than this. $\delta C^{13}_{\text{limestone}}$ values, for example, as low as -20‰ have been observed (Winograd and Farlekas, 1974). Likewise, the error given for $\delta C^{13}_{\text{plants}}$ represents only the most predominant values. Scharpenseel (1974) has recently found concentrations in soil plant material varying from -33.2‰ to -18.6‰.

To continue the example, let us consider the case of a ground water sample with $C^{14}_{\text{measured}} = 50 \pm 0\%$ modern. With the above $F = 0.70 \pm 0.20$, the limestone dilution corrected age would be 2790 ± 2430 yr. The sample is between 360 and 5220 yr old. The extent of the errors here make the carbon-13 correction method useless, despite the fact that only the normal variations were taken into account and other sources of errors were not included.

In order to employ the carbon-13 method to obtain for ground water carbonates the correction for limestone dilution, it would be necessary to make a thorough preliminary study of the distribution of carbon-13 in plants of the aquifer recharge area, including seasonal variations. The values for limestone particles throughout the deposit will also have to be studied. If there is any significant presence of Hatch-Slack cycle plants, the quantitative applicability of carbon-13 to the ground water investigation is dubious. Studies must also be carried out to decide whether the pre-historic climatic variations might have effected the plant photosynthetic characteristics for the older samples.

Carbon-13 provides a potentially important tool for quantitative studies of ground water dating. However, large numbers of samples from both the aquifer matrix material and the plant cover must be analysed to elucidate the degree of variation of the isotope in each particular situation. There is no justification for quoting only the usual determinant error, ±0.1‰, in the high precision mass spectrometric measurements. An estimation of indeterminant errors must also be included in order to clearly define the total uncertainties in the corrected radiocarbon age of ground water.

In the most optimistic case it could be imagined that

$$\delta C^{13}_{\text{plants}} = -\ 25 \pm 3\text{‰},$$
$$\delta C^{13}_{\text{limestone}} = 0 \pm 0\text{‰},$$

and, taking as an example,

$$\delta C^{13}_{\text{measured}} = -\ 17.5 \pm 0.1\text{‰}.$$

The $\delta C^{13}_{\text{plants}}$ uncertainty quoted is only the known seasonal variations (Lowdon and Dyck, 1974). Here, the calculation would lead to $F = 0.70 \pm 0.14$. In the case of a sample with $C^{14}_{\text{measured}} = 50 \pm 0\%$ modern, the limestone-dilution corrected age would be 2790 ± 1680 yr. The sample would be between 1110 and 4470 yr old. These errors are still substantial and there remains the question of whether the carbon-13 correction was worthwhile even in this hypothetical case. Nevertheless, the carbon-13 measurements always do serve the purpose of monitoring against the occurrence of an unexpected situation, such as the entrance of magmatic carbon dioxide, that would affect the radiocarbon dating. The analyses shown in Figures 2, 3 and 4 illustrate this use of carbon-13. Employed in this way, the stable isotope can be useful in a qualitative sense in radiocarbon dating studies of subterranean water.

3.3. RADIOCARBON- TRITIUM VARIATIONS AND THE EXPONENTIAL MODEL

An exponential model for an empirical estimation of the initial carbon-14 concentrations in contemporary age ground waters was outlined by Eriksson (1962). Ground water is treated as a mixture of different age components whose concentrations decrease exponentially with their ages. The reciprocal of the isotopically determined age of the youngest constituent water is defined as the *mean residence time* (MRT). Since tritium is not affected by the uncertainties of limestone or soil air exchange, it has been applied to the estimation of the real age of recent infiltrating ground water (Münnich and Roether, 1963; Münnich *et al.*, 1967; Scharpenseel and Pietig, 1969b; Geyh and Mairhofer, 1970; Geyh, 1972a; Geyh, 1972b; Scharpenseel *et al.*, 1973; Scharpenseel and Ohling, 1974).

Geyh *et al.* (1971), describe the case of recharge and discharge of a spring, that has been in a steady state condition over a long period and whose ground water is thoroughly mixed, with the general equation

$$B_n = (1-x)^{n-i} B_{1950} e^{-(n-i)} + x \sum_{i}^{n} q a_i (1-x)^{n-i} e^{-(n-i)},$$

where $i = 1950$, B_n is the content of the particular isotope measured (tritium in this case) during the yr n (with A.D. as + and B.C. as −), and x is the fraction of the ground water recharged each yr; it is the reciprocal of the mean residence time. B_{1950} is the content in 1950, the standard reference yr. The exponential terms take into account radioactive decay. qa_i is the annual isotopic input function (in the case of carbon-14, a_i is the mean isotopic concentration of atmospheric carbon dioxide). This has been thoroughly studied by several laboratories in various parts of the world (Tamers, 1967b; Lal, 1965; Nydal and Lövseth, 1970; Fairhall and Young, 1970; Nydal *et al.*, 1971). Tritium variations are also well known (see, for example, Münnich *et al.*, 1967).

Geyh (1972b) has found tritium in recent ground waters to be applicable to the previous equation in the study of ground water radiocarbon variations. He introduces a supplementary factor which accounts for the seasonal differences in the tritium content of precipitation. Using multiple samples in which both radiocarbon and tritium are measured, values for q and MRT are obtained, permitting the solution of the equation for the exponential model.

Seasonal variations of natural deuterium and oxygen-18 have also been investigated for the determination of q (Siegenthaler *et al.*, 1970). These stable isotopes were compared to tritium concentrations of various waters. Long term measurements are needed to obtain meaningful results.

Geyh's laboratory in Hannover has taken the lead in the application of the exponential model to ground water dating and large numbers of measurements have been made (Geyh, 1972b; Geyh, 1973; Geyh and Michel, 1974; Geyh, 1974). It is important to recognize differing continential effects of the tritium and radiocarbon input functions in various localities and to use data pertinent to the region being studied. For example, there are large differences between the northern and southern hemispheres and from the temperate to the tropical zones. The extent of the seasonal variations are, likewise, widely variable.

Using tables of weighted tritium contents of precipitation for the periods September to March (the winter season) and January to December (the entire year) for central Europe, and radiocarbon contents of atmospheric carbon dioxide of the atmosphere at the same times, it is possible to arrive at estimates of the mean residence time and q values of ground waters. In these studies, various possibilities of MRT (tritium) and MRT (carbon-14) are obtained, and the comparison of the two sets of data allows a choice to be made of the most reasonable value.

Geyh (1972a) has found from sampling in central Europe and Brazil (Geyh and Kreysing, 1973) that the q values obtained using the exponential model are approximately 15% larger than those obtained from measurements of the carbonate species concentrations. After an extensive sampling program, he was able to establish initial radiocarbon dilution values of q based on the geology of the catchment area. His ranges are 0.65–0.75, 0.75–0.90, and 0.90–1.00 for regions of karst, limey sediments such as loess, and crystalline rocks, respectively. Nevertheless, there are other aquifers where the exponential model q values are in agreement with those obtained by carbonate species chemical analyses for F. The modern waters of Barquisimeto, Venezuela, a karst aquifer, show an average F value of 0.68 (Tamers, 1969), which is exactly the same as that obtained by Geyh (1972a) for exponential model treatment of the karst region of Swabia. A preliminary exponential model analysis of tritium and radiocarbon contents of the Barquisimeto ground waters is being undertaken (Geyh and Tamers, 1974). Another limestone containing deposit, the Biscayne aquifer of South Florida, showed an average F value of 0.67 (Tamers *et al.*, 1975), again in complete agreement with the exponential model of Geyh.

The Geyh model certainly merits further study and might be in closer agreement with the carbonate species concentrations method than previously thought. The reason for the initial disagreement is not clear. Geyh considers the possibility of exchange with limestone, but, as explained previously, this should not be irreversible. Any error due to irreversible exchange with the carbon dioxide of the soil air would produce a disagreement in the direction opposite from that observed. The interpretation of the ground water as a mixture of different age components is certainly closer to the truth than the previous methods that implied a single age for each sample.

There remain some questions on the relative precision of the method, particularly with respect to the effect of the large variations in the tritium fallout from nuclear weapon testing. The atmospheric contamination of carbon-14 was limited, whereas tritium contents of rain varied extremely. Studies by the exponential method probably should involve large numbers of samples in order to average out these fluctuations. The method is also limited to the treatment of samples less than about 50 yr old. This restricts the technique to the study of the radiocarbon dilution of the catchment areas, where the ground waters are still young. The initial radiocarbon content of ground water is, of course, interesting in itself and reliable values for this can be used to investigate the precision of limestone dilution corrections from various other methods. Nevertheless, in most cases the limestone dilution process does proceed throughout the aquifer and the correction for samples no longer of modern age, away from the water bearing outcrop zone, must still be determined or estimated by another method.

Despite these limitations, Geyh's exponential method of ground water radiocarbon age treatment is considered to be one of the most promising fields for further investigation. It will probably be of considerable value in the determination of the accuracy and precision finally assigned to radiocarbon dates on ground water.

4. Summary

The accuracies of the various methods of correcting radiocarbon dates on ground water carbonate species for limestone dilution are major questions at this time. Confidence in each procedure has been examined from theoretical considerations and by comparing the results obtained by applying different methods to the same samples.

The limestone correction techniques are in limited disagreement, although none point to large inaccuracies in the others. The carbonate species ratios, done under optimum well site analysis circumstances, do not correct the limestone diluted carbon-13 values back to the known distribution of Calvin cycle plant material carbon-13. The reasons for this are uncertain, but it has been suggested that there is a significant contribution of Hatch-Slack cycle plants in the regions studied and there could exist an exchange of soil air carbon dioxide with the total ground water carbonate species, causing an isotope effect, especially significant in the interpretation of the stable isotope concentrations.

If the Hatch-Slack cycle plants are present in significant quantities, the natural variations of carbon-13 in plant materials will be so large that the use of this isotope as a quantitative tool in ground water dating is controversial. The plant cover of catchment areas for aquifers being studied must be thoroughly sampled to determine the natural distribution of the stable isotope. Studies will be necessary, also, to outline the variations that can be expected with changing climatic conditions, especially in the cases of aquifers containing old waters. Although the determinant errors involved in the laboratory measurement of carbon-13 ratios are very small, the indeterminant errors, arising from extensive natural variations, make the carbon-13 limestone dilution correction method for ground water radiocarbon dates the technique that presently shows the largest uncertainties. Unless studies of natural variations in catchment area plants are carried out, the use of the stable isotope should be limited to qualitative interpretations, i.e., to verify the absence of magmatic or petroleum carbon dioxide additions to the water.

The validity of the carbonate species ratio method of limestone dilution correction is supported by the approximate correction of carbon-13 concentrations to the normal range of plant materials. Due to the large natural variations of the stable isotope, this evidence can only be semi-quantitative. The chemical analyses of bicarbonate and dissolved carbon dioxide (or total carbon) must be carried out with great caution at the sampling site, moments after the ground water has been extracted. The escape of carbon dioxide from ground water samples is rapid, as can be seen by measuring the pH value of recently extracted specimens for a period of only a few minutes following the water extraction. The carbon dioxide is put into the ground water at a soil air partial pressure orders of magnitude higher than that of the atmosphere. This is the principal cause of the release of the carbon dioxide from the solution when it is brought up to the air. Also, sampling carried out in the warmer months and daytime usually mean higher atmospheric temperatures than the temperature of the ground waters, further leading to the release of carbon dioxide. The quantitative analysis errors here can be very large. Bicarbonate concentrations, likewise, will show errors if the sample is brought back to the laboratory for analysis.

If the carbon dioxide or total carbon analyses are wrong (too low), an isotope effect in an eventual carbon-13 measurement can be expected. The concentration of that stable isotope in the carbonate species remaining in the ground water sample will be high. In order to avoid carbon-13 isotope enrichments, the ground water carbonate species must be fixed immediately upon obtaining the specimens. Even tightly enclosed bottles brought back to the laboratory for chemical analyses show radically changed values compared to well site measurements of dissolved carbon dioxide.

The reasons for the disagreements between some of the comparisons of the limestone dilution exponential model corrections and the carbonate species ratio results are not clear. Exchange with aquifer matrix limestone would produce a shift in the observed direction, but there is some reason to believe that an irreversible effect should not be large. This point remains an important question. There are also other aquifers where the exponential model and carbonate species results, as well as carbon-13, are in agreement.

Further investigations should be made of the exponential model with numerous aquifers studied. Extensive sampling should be undertaken in order to evaluate the accuracy of the results. The reliability of the method was not yet been established, but it appears promising. These studies should be combined with the highest quality carbonate species chemical analyses and carbon-13 measurements, where the avoidance of an isotope effect during the sampling has been assured. The extent of the possible occurrence of ambiguities in the tritium data interpretation due to variations in the contents of this fallout product in individual rains should be examined.

Isotope exchange studies must be carried out on whole, natural limestone particles from a variety of locations using artificial isotopes in both carbon dioxide and bicarbonate. The rocks should be from the infiltration and saturation zone of aquifers whose ground water is being dated with radio-carbon. This would be an investigation of the possibility of irreversible exchange over the period of a year or two, a length of time sufficient to provide indications of the probability of this happening to a significant extent in hundreds of years. The experiments should have analyses good to $\pm 0.1\%$ and must involve a kinetic study during the period in order to permit reasonable extrapolations to much longer periods.

An investigation of the carbon-14 content of limestone particles underground and in aquifers would be of interest. The contents found in surface materials are significant to the validity of radiocarbon dates on ground water, but the extent of the error from this source will depend on how far the phenomenon persists underground, where the majority of the dissolved carbon dioxide reacts with limestone. The study would provide another indication of the extent of irreversible exchange. Only whole particles well underground, both within and out of the root zone, should be examined.

A thorough study is needed of the depth in the soil at which significant (in less than 3 months) exchange between the carbon dioxide of the soil air and the atmosphere has taken place. This should be conducted in various types of undisturbed soils, under a variety of temperature and atmospheric pressure fluctuations, and with different plant covers. Large numbers of measurements will be necessary, using artificial carbon-14 traced carbon dioxide.

The gross validity of radiocarbon dates on ground water is now undisputed; however, there is considerable disagreement on the usefulness of the three methods of correcting for limestone dilution. Further experiments performed under conditions closely approaching the natural systems will be able to determine the extent of possible irreversible exchanges that would contribute uncertainties to the absolute ages calculated for individual ground water samples.

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Note: I.A.E.A. = International Atomic Energy Agency

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