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RADIOCARBON DATING OF GROUND WATER - PRACTICAL APPLICATIONS -

Radiocarbon dating of ground water is used in combination with the primary measurements of classical hydrological and chemical analyses. Radiocarbon dating will produce the best results when it involves multiple measurements or sequential sampling. The most useful data come from these comparisons and not from absolute ages. In the case of multiple measurements, the apparent ages of the ground water taken from pumps that are at varying distances from the aquifer outcrop could be a means of verifying flow rate and also indicate situations of over-pumping. In the case of sequential sampling of an individual well every six or twelve months, any changes in the apparent age of the water are plotted versus time. In particular, if the age of the water is getting younger with time, it would usually be due to a drawing-down of the more shallow water layers. Radiocarbon dating has the potential of giving advance notice of impending contamination by surface layer waters.

WHAT IS RADIOCARBON DATING?

High-energy particles coming from outer space, the cosmic radiation, cause nuclear transformations in the atoms of the earth's atmosphere. Radiocarbon (carbon 14 or C14 or ^{14}C) is produced by the reaction of cosmic radiation secondary neutrons with nitrogen in our air. This naturally occurring radioactivity exists in all living matter that is in contact with the earth's atmosphere – plants, the animals that eat the plants, and the animals that eat the animals that eat the plants. These living entities, while they are alive, will have the same radiocarbon content as the earth's atmosphere.

However, for dead objects or materials removed from equilibrium with the atmosphere, it was demonstrated that the original contents of radiocarbon decreased exponentially in a predictable relationship with time. The half-life of radiocarbon is approximately 5568 years, a number used by all radiocarbon dating laboratories by international convention. This means that a sample would lose 50% of its concentration of the isotope each time a period of 5568 years passed. That is to say, after this amount of time the specific activity of radiocarbon-containing substances (disintegrations per minute per gram of carbon) would be half that of a modern sample, one fourth after 11140 years (two half-lives), an eighth after 16700 years (three half-lives), etc. The radiocarbon age is the time that has passed since the sample was removed from equilibrium with the atmosphere either by death of plants or animals or with non-living entities like ground water, a physical movement outside of contact with the air.

Radiocarbon dates from organic materials can often be calibrated using historically known-age samples and those from tree-ring counting. The dates are reported as years AD or BC. However, this type of calibration is not applicable to ground water dating. Here, the dates are reported as years BP, which is used to stand for Before Present, but now signifies years before 1950 AD.



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In principle, radiocarbon dating is not usable for samples less than 280 BP. However, laboratories can distinguish excess radiocarbon contents from large-scale thermonuclear device atmospheric testing, which began in 1953. In many cases, the shape of the fallout curve can be used to date recent events [1], i.e. samples from ten to fifty years old. This is often useful in ground water studies.

RADIOCARBON DATING OF GROUND WATER

Radiocarbon dating of ground water can give indications as to when the water was taken out of contact with the atmosphere, i.e. when it went underground. However, there are uncertainties present in calculating the percentage of carbonate species that originated from living plants in the aquifer outcrop and the atmosphere as opposed to that added by ancient carbonaceous deposits in the aquifer matrix. For this reason, radiocarbon dating of ground water is most useful when repeated sampling occurs. In this case, obtaining absolute ages with their attendant uncertainties are not the primary numbers used in site interpretations. The uncorrected apparent ages are the primary numbers; they are used to compare with other apparent ages in the study. This will largely obviate the correction uncertainty. In all cases, the most useful data will come from these comparisons and not from absolute ages. Also, the uncorrected apparent ages can be interpreted as maximum ages, i.e. the real age of the ground water is equal to or less than the apparent age.

By extracting the carbonates of the water for radiocarbon dating, the measurements can provide information on the recharge of underground deposits as well as flow directions and rates. This is valid for samples from 10 years old to 40,000 years old.

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 vegetation (root-respiration) generated carbon dioxide is much higher. The radiocarbon content of these sources is the so-called “modern” level and is used for the reference in the age calculations. On average, from twenty to more than sixty wells are sampled in an aquifer. Less than ten wells is not a suitable study; in this case, interpretation of the ages will often be ambiguous.

In the case of aquifers containing fossil carbon, such as peat or brown coal, radiocarbon dating can give ambiguous results and these aquifers should not be studied with this dating technique. Water obtained from surface springs can provide useful apparent “ages”, but there is inevitably a problem with the carbon dilution correction because a large isotope effect can be generated when the carbon dioxide under pressure in the water readily bubbles out. In that case, a “best estimated age” cannot be calculated.



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RADIOCARBON AGE CALCULATION

The basic radiocarbon age determination calculation is as follows:

$$t = - 8035 \ln (\delta C14_{\text{final}} / \delta C14_{\text{initial}})$$

t = the radiocarbon age of the sample

8035 = the decay constant of radiocarbon, i.e., the half-life divided by ln 2. A half-life of 5568 years for carbon 14 is used, as per international convention

ln = the natural logarithm

$\delta C14_{\text{final}}$ = the measured net radiocarbon content of the sample

$\delta C14_{\text{initial}}$ = the net radiocarbon content of the modern standard

The results of radiocarbon dating of ground water are presented as three items:

1. The “apparent age” gives the simple measurement age of the ground water, from the above formula, before the carbon dilution correction would be applied. This apparent age is used as the reference value in sequential sampling studies. Since the carbon dilution correction is in only one direction, making the age younger, the apparent or reference age should be taken as a maximum age of the ground water sample.
2. The carbon-13 value is used for the estimation of the carbon dilution factor, leading to a corrected age or “best estimate age.”
3. The “best estimate age” is that age obtained after the carbon dilution correction. It should not be used for further calculations or quantitative interpretations since the veracity of the carbon dilution correction cannot be verified. The best estimate age is only intended to present easily visualized results. The apparent age is the best reference and is used for all comparison studies.

FOSSIL CARBON DILUTION IN GROUND WATER

The dissolved carbon dioxide can pick up further carbon by chemical reactions with the aquifer matrix materials. The matrix materials produce a dilution of the original radiocarbon content. It is important to note that the effect of this dilution by matrix materials is in only one direction – it will make the apparent radiocarbon dates older than they would be otherwise. Therefore, the



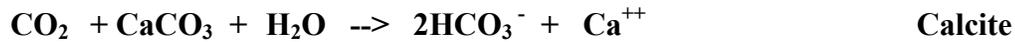
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apparent ages of the ground water can be taken as maximum ages.

The most common equations of matrix dilution would be with limestone or caliche:



It can be seen that the fossil carbon of the calcite or dolomite in the aquifer would be contributing half of the bicarbonate ions. These reactions usually do not go to completion, but in that case exactly half of the DIC in the water would be derived from the fossil source. This would result in a correction of 5568 years to the age calculation (see formula below).

However, there are a number of other possibilities for the dilution of the original “modern” carbon with “ancient” carbon (from matrix material that was formed more than 40,000 years ago) [2][3][4][5][6][7][8][9]. Corrections must be made for this when estimating the true age of the water. In most cases, it would be for the above-described equations.

Other models for ground water carbonate species correction include the Methanogenesis Model, the Dedolomitization Model, and the Silicate Dissolution Model [8]. Choosing which model is closest to a description of the aquifer would depend on the chemical characteristics of the water studied. However, the uncertainties are such that aquifers that have fossil carbon lenses [9], those with low redox states (methane production) or high sulfate concentrations (hydrogen sulfide production) must be treated with special caution [10]. This is due to severe carbon-13 ratio disturbances making difficult any correction for fossil carbonate dilution. The chemical analyses of ground water would identify these types of aquifers.

Corrections for limestone dilution described by the above calcite and dolomite equations can be made with two techniques [3]. These involve the use of carbon-13 (a naturally occurring stable isotope of carbon) or analyses of the amounts of bicarbonate present with respect to concentration of the total dissolved inorganic carbon (DIC) in the water. Carbon-13 contents are measured routinely in all samples for ground water dating. It can also be measured in the root zone of the outcrop vegetation and the aquifer limestone or caliche that diluted the original radiocarbon content.

The following equation gives the carbon-13 correction factor for limestone dilution:

$$F \cdot \delta C13_{\text{initial}} + (1 - F) \cdot \delta C13_{\text{limestone}} = \delta C13_{\text{final}}$$

F = the fraction of dissolved carbonates that originated from living plant decay or from carbon dioxide in the atmosphere

$\delta C13_{\text{initial}}$ = the relative amount of carbon-13 in the pre-dilution carbonate species

$\delta C13_{\text{limestone}}$ = the carbon-13 content of the aquifer carbonate matrix

$\delta C13_{\text{final}}$ = the carbon-13 content of the sample to be dated

The following equation shows the carbonate species correction factor for limestone dilution:

$$F = ([C_{\text{Total}}] - 2 [HCO_3^-]) / [C_{\text{Total}}]$$

F = the fraction of dissolved carbonates that originated from living plant decay or from carbon dioxide in the atmosphere.

$[C_{\text{Total}}]$ = the total DIC concentration expressed in equivalents/liter

$[HCO_3^-]$ = the bicarbonate concentration expressed in equivalents/liter

In effecting either of the approaches for the dilution correction, the measured ratio of the sample to the modern standard radiocarbon activities is divided by F; this is done before the radiocarbon age calculation is carried out. The carbon-13 technique is most commonly used and is the situation that has been extensively studied. Unless the chemical analyses of the ground water indicate low redox situations (as seen with hydrogen sulfide or methane production), that equation would be applied to the observed radiocarbon ratios.

There are some indications using other types of tracers that the “limestone dilution” correction is approximately valid, at least in the few aquifers studied [3][4][8]. Nevertheless, the validity of the correction in other aquifers is unknown. Therefore, special caution should prevail before using the technique for “best estimate” dating.

PRACTICAL APPLICATIONS OF RADIOCARBON DATING OF GROUND WATER

In majority of cases, the measured radiocarbon contents of ground water produce values that are less than “modern.” This is due to two factors:

- (1) the above-discussed dilution with fossil aquifer matrix materials, and
- (2) the water has taken time to arrive at the sampled well from the outcrop and the original radiocarbon content has decreased by radioactive decay.



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As discussed above, it is possible to estimate the contribution from the first item, which often remains approximately constant in many aquifers.

Eliminating the dilution factor, the decrease in the original radiocarbon content would potentially allow an apparent age of the water to be calculated. That is, the time that has passed since the original water entered the aquifer on its trip to the final destination or the residence time. This assumes that the natural aquifer ground water flow is not being seriously disturbed, for example, by over-pumping. An indication of that unfortunate situation would be seen in the non-uniform rate of increase of the radiocarbon ages of extracted ground water as a function of distance from the outcrop. In many instances, the presence of younger-than-expected ages would show which wells are being over-pumped. In order to identify this over-pumping situation, a number of wells at varying distances from the outcrop would be sampled for radiocarbon apparent age. Plotting of the obtained ages versus outcrop distance could show any over-exploitation instances for individual wells.

The comparison of the apparent ages in individual wells as a function of time is especially interesting from the point of view of practical applications. It would be important to establish as soon as possible a program of sequential sampling (every six or twelve months) of each well. The comparison of the apparent radiocarbon ages over time is the most useful of all procedures. This technique was used in a study carried out in a fast-flowing aquifer in Venezuela [1]. It was shown that sequential sampling over a period of only three years gave significantly more useful information than was obtained by the initial sampling.

RELATIVE RADIOCARBON AGES BASED ON DISTANCE FROM THE AQUIFER OUTCROP

The use of radiocarbon dating of ground water is best when apparent ages of various wells (an average of ten to sixty wells per study) can be compared with respect to distance from the outcrop [11].

The simplest situation is where the apparent radiocarbon ages of wells in different distances and locations from the aquifer outcrop increase with distance as the ground water slowly flows towards its outlet. In this case, the number of years difference between wells divided by that distance would give the flow rate of the water. Using the known porosity and extent of the aquifer, the amount of water flowing past each well could be calculated. From this, the sustainable yield would be apparent. However, the results would be clearly anomalous in the case of over-exploitation of the aquifer.

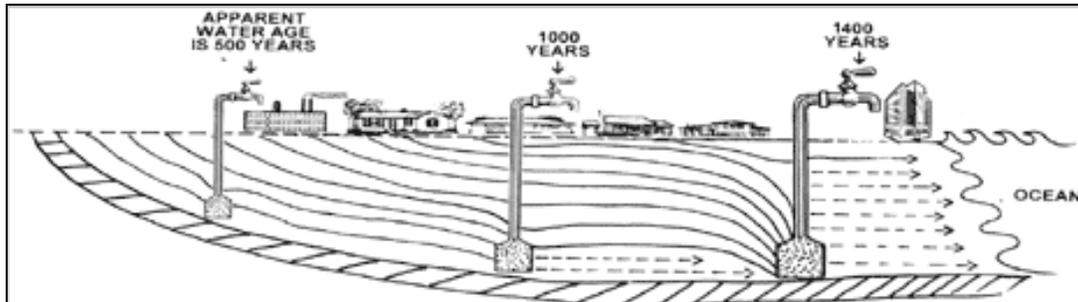


Figure 1: Radiocarbon ages of ground water as a function of distance from the aquifer's outcrop. This illustrative case shows laminar ground water flow curves with three pumping rates located at different distances from the outcrop limit. The last well is over-pumping and drawing water down from shallow levels.

The hypothetical situation of **Figure 1** illustrates a simple problem.

Here, the first well on the left side is small and only takes water from the lowest levels, which are fed by the maximum distance of the outcrop area. The second well, with a medium production rate, is not only taking water from the deepest level but also from levels slightly above. The large capacity third well, on the far right in the figure, is over-pumping. In addition to taking water from several layers in the deepest third of the aquifer, over-production is taking some water from the more shallow layers of the aquifer but still not from the surface above it. Nevertheless, the situation of this high-capacity third well is precarious since the figure illustrates that it is approaching the pumping of water that infiltrated from a developed area. Radiocarbon dating clearly shows here that a potentially serious problem is developing.

As the situation with the third well deteriorates, part of its source water will eventually come from an inhabited area. The water department running the well would immediately see this from routine monitoring, when serious chemical and biological changes in the water occur. However, it would be very useful to know in advance of this potential situation before the disaster happens. Radiocarbon dating would enable the problem to be identified early so that corrective steps could be taken.

CHANGING RADIOCARBON AGES FROM THE SAME WELL SAMPLED ANNUALLY

The use of the radiocarbon dating method is best with annual or biannual sampling of individual wells [1]. The values obtained would be compared to those of previous years. The most desirable situation is when the radiocarbon ages of sequentially sampled waters (every six or twelve months) from a particular well remain the same over the years.

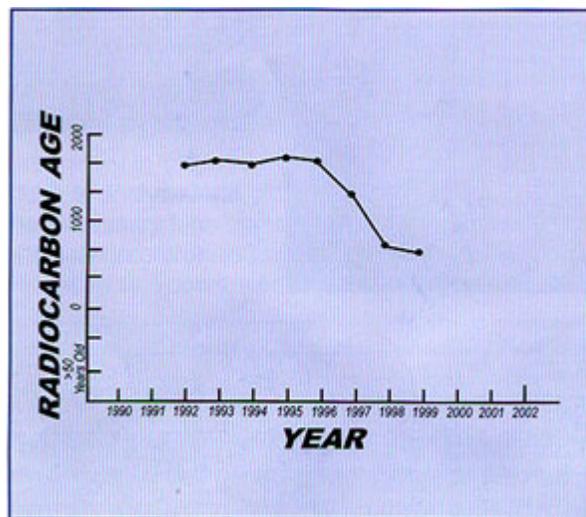


Figure 2: Radiocarbon ages of ground water of an individual well sampled annually. In this illustrative case, a new pumping system was initiated at this well in 1995, substantially increasing the pumping rate in this area. The radiocarbon dating will have to be continued to see if there is an indication of increasing shallow water down-draft or if the curve flattens out before the surface water starts intruding.

Figure 2 illustrates a case where sampling began in 1992 and gave same age results for a number of years. The pumping was moderate and indicated a sustainable yield. However, the ground water extracted from this well began showing younger and younger radiocarbon ages. This change, which happened in the illustration in 1995, correlated with the introduction of high-capacity pumping which was too large for water flow rate. The over-production resulted in water drawn from more shallow levels, which had younger apparent ages. The shape of the curve would have to be carefully monitored. If the radiocarbon ages of extracted water eventually flattened out, it might be possible to continue the present exploitation rate. However, if the radiocarbon ages keep falling, the production rate would have to be decreased to avoid the ultimate drawing of water from the surface.



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It is imperative that the initial sampling begin as soon as possible so that the baseline values can be established. Radiocarbon dating of ground water is less useful after well contamination has occurred. In the previous example, Figure 1, it would have been very interesting to have known the values of radiocarbon ages obtained from a moderate-sized well operating in the position that is now occupied by the large capacity well (right-hand side in the figure). This information can only now be obtained by drastically cutting down on the extraction rate of this well and allowing time for the aquifer to recover. This would probably take years and would not be realistically feasible undertaking in a production field.

SAMPLING PROCEDURES

There are two techniques used in radiocarbon dating:

- (1) the radiometric technique for normal size samples, which counts the beta radiation coming from a prepared material, and
- (2) the AMS (Accelerator Mass Spectrometry) technique, which is suited for very small amounts of samples.

Beta Analytic Inc. uses the AMS technique.

For ground water dating, the AMS technique is most common due to the reduced physical labor for the collection of the sample in the field and, afterwards, the laboratory. With a sample sent for AMS dating, we need one liter of the well water. A standard wide-mouth plastic bottle available in all chemical supply firms is generally used. Please note that the persons sampling the well or working in the laboratory should not be wearing luminous watches - this can cause tritium contamination.

TRITIUM DATING

Tritium (H-3) dating of ground water is sometimes used as ancillary data for the radiocarbon dating study. It is less successful than radiocarbon dating for two reasons:

- (1) the half-life of tritium is merely 12 years (versus approximately 5568 years for radiocarbon), meaning that only young ground water would show measurable values, and
- (2) the contamination of the atmosphere with nuclear testing fallout tritium was extensive, reaching thousands of times the normal amount, resulting in a serious ambiguity.

In general, the only unambiguous finding would be zero tritium; this would mean that the water is more than 100 years old and there is no infiltration from the surface or shallow levels. Most



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other results would have multiple interpretations and, therefore be of limited use in hydrological studies.

CARBON-13

This stable isotope of carbon is used in correcting radiocarbon dates, as shown previously. In ground water dating, this carbon-13 measurement is used to produce “best estimate” ages. It has been shown [3] that the limestone dilution correction using relative bicarbonate and total DIC chemical analyses will approximately correct the measured carbon-13 values back to reasonable initial carbon-13 values. This permits an enhanced confidence in the validity of the limestone dilution correction of the apparent ages.

Carbon-13 values are expressed as deviations from a standard, PDB limestone, which is taken as 0.00 o/oo (per mil) [12]. The $\delta C13_{final}$ values measured for ground water carbonates ($\delta C13_{final}$) generally vary between -4 and -25 o/oo. This means that the amount of carbon-13 found in the ground water carbonate is less than that in the limestone standard. In order to use the carbon-13 correction described above, values for the $\delta C13_{limestone}$ and $\delta C13_{initial}$ are also needed, i.e. the values in the aquifer matrix and the plant cover at the outcrop. If these are not known, the value of 0 o/oo is used for the limestone and values of -12 or -22 o/oo are used, respectively, if the outcrop cover is known to be grass (C4 plants) or if the cover is of temperate climate, non-grass vegetation (C3 plants).

A major difficulty with carbon-13 values is that they are particularly susceptible to isotope effect during the sampling procedure. This is especially serious in ground water studies where the water is often supersaturated underground and carbon dioxide starts bubbling out after it is released to the surface. The sampling bottle lid should be securely tightened to prevent further carbon dioxide loss.

CHEMICAL AND HYDROGEOLOGICAL DATA

Standard chemical analyses and hydrogeological investigations are the primary tool for ground water studies [13]. They are indispensable in the final interpretation of radiocarbon dates on ground water, which is used to give supplementary information useful in interpreting the results of the hydrogeological and chemical findings.

All discussions of the radiocarbon ages must be made in conjunction with these primary analyses data and any significant changes in these values observed over several years of measurements. Documentation of the changes in the chemical compositions of the waters over time as well as a thorough description of the hydrogeology of the aquifer are important for the practical interpretation of the radiocarbon dates.



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CONCLUSION

It is reasonable to anticipate that the next global crisis will be fresh water [14]. The previous international crisis was energy, especially oil supply. This commodity, oil, has many alternative materials that could take its place if necessary. However, there is nothing that can replace fresh water. A crisis on dividing up the dwindling supplies of water will be of catastrophic proportions. The increasing world populations will guarantee outbreaks of serious problems.

Radiocarbon dating of ground water has the potential to give information to predict situations of over-exploitation of aquifers. This would allow time to reverse the over-pumping before the appearance of surface contamination in the wells. The procedure of sequential sampling, radiocarbon ages versus time, would give the best results. Also good would be multiple sampling of a well field so that a comparison could be made of radiocarbon ages versus distance from the outcrop limit; this could show instances of over-pumping of specific wells.

Water system engineers and technicians often must make multi-million dollar decisions. They will use classical hydrological and chemical data as their primary tools. Radiocarbon dating of ground water can provide supplementary information. However, there are uncertainties in all types of data interpretation. But the uncertainties in interpreting hydrologic and chemical data are different from that of radiocarbon dating. If all of these techniques point to the same conclusion, a strong recommendation for action can be made. If there is a difference, investigation of the origin of this might prevent a disastrously wrong multi-million dollar decision. For this reason, radiocarbon dating of ground water should be routinely used for all aquifers.

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