Radiocarbon dating of groundwater

Radiocarbon or ^{14}C is a widely used tracer for groundwater movement for up to 30,000 years. ^{14}C can be used to estimate recharge rates and horizontal flow rates, vital to underpin decisions on sustainable extraction limits. Over the past decade, advances in analytical techniques have superseded the old cumbersome methods, and now sampling involves collection of just a few litres of water to make precise measurements.

Australia is a large flat continent and many large groundwater systems mimic the scale and topography of the landscape. This means groundwater systems such as those within the Murray Basin and Great Artesian Basin can be on a scale of thousands of square kilometers and flow paths are long and flow velocities small.

^{14}C, or radiocarbon, is the radioactive isotope of the element carbon and has a half-life of 5,730 years which makes it an ideal tracer for groundwater movement on the time scale of thousands of years. It is produced in the atmosphere and becomes part of the carbon cycle through uptake by plants and respiration and oxidation in the soil zone. Radiocarbon is well known as a dating tool of archeological artifacts but has also been the cornerstone for investigating groundwater flow for up to ~30,000 years.

How does the technique work?

Carbon dioxide in soil gas partially dissolves in soil water which then recharges the groundwater. The carbon contains small amounts of radiocarbon that occurs naturally in the atmosphere. If we can estimate the concentration of ^{14}C at the time of recharge, and measure the concentration at a well or spring, the ratio of these two concentrations informs us on the degree of change that has occurred due to radioactive decay, mixing, geochemical reactions or other processes. For example, in the simple case if we were to measure in the well a ^{14}C concentration of radiocarbon being half that of the ^{14}C concentration in the recharge area, this yields an apparent age of 5,730 years, which is one-half life of ^{14}C. While this could represent the time since recharge, the change could be for a range of other reasons discussed below.

In practice, estimating the starting concentration of ^{14}C is one of the difficult aspects of this technique: carbon dissolved in groundwater not only originates from the atmosphere where ^{14}C content is well known, but contains contributions of carbon that is ancient through dissolution of carbonate minerals or oxidation of old organic matter in the soil. While there are numerous ways to estimate this initial ^{14}C activity through measurements of chemistry and stable isotopes, it remains the major source of uncertainty for the application of ^{14}C in groundwater studies. If several ^{14}C measurements are used in a hydrogeological framework, such as along a hydraulic gradient in a confined system, we can estimate flow velocities or recharge rates. Also results for several depth profiles in unconfined groundwater systems can be converted to recharge rates using well construction information and simple analytical models.

While apparent ages are often assigned to the results, it is important to point out that these are averaged ages of the dissolved inorganic carbon and inferring anything on the groundwater system from these measurements needs to be done in a hydrogeological context. Nevertheless, the application of ^{14}C for understanding groundwater systems can provide transport information on time scales that is not available using conventional hydrological methods.

Applications

Radiocarbon has been used to study groundwater throughout the world since the early 1960s. Its first use in Australia was in studies of the Murray Basin, Perth Basin and Great Artesian Basin in the 1970s and since then several large groundwater systems have been investigated using radiocarbon as one of the most useful tools for hydrological information of water transport, namely to deduce horizontal flow rates or recharge rates.

CSIRO's Isotope Analysis Service supports the research projects of CSIRO and provides an effective and readily-accessible service for hydrology and environmental communities, including Government and private sectors, to obtain measurements of environmental isotopes and trace gases. The service undertakes approximately 3000 analyses each year for Australian and international clients. The results of these analyses guide informed natural resource management decisions.

HORIZONTAL VELOCITIES

The determination of horizontal velocities from groundwater tracers sheds light on the actual transport of the water mass that has happened historically rather than the present-day flow potential, which is determined by Darcy calculations. The example below is from the Tertiary confined aquifer system of the Dilwyn Formation of SE South Australia that shows how radiocarbon measurements can be used to derive internally consistent horizontal flow. Groundwater within the Tertiary sandstone aquifer shows a gentle head gradient from the higher elevation areas towards the sea approximately from east to west and north to south direction in the northern and southern part of the region respectively (see Figure 1a).

The concentration of radiocarbon from groundwater from two transects parallel to the head gradient are shown in Figure 1b. The radiocarbon concentration is lowest nearest the sea and increases towards the north and east to up to ~60%MC. The calculated groundwater velocities range from

LEFT **Figure 3. The Ti-Tree basin of central Australia is characterized by low topography and sparse spinifex and small native eucalyptus and acacia trees. The vegetation tends to be denser and taller near water courses.**

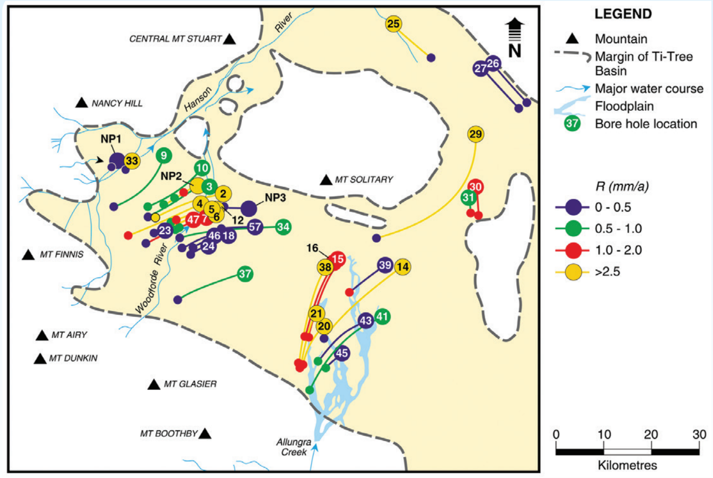
An example of ^{14}C in groundwater from central Australia

Radiocarbon is the cornerstone of groundwater assessment in the arid zone because very often these regions have low recharge rate and low hydraulic gradients and therefore groundwater that is in the time frame suitable for radiocarbon.

An example shown here is from about fifty ^{14}C determinations from wells collected from phreatic aquifers in the Ti-Tree basin located in the arid zone of Central Australia. The region is characterised by low topography, sparse vegetation (see Figure 3 above) and drainage courses that contain water only after annual monsoonal rains or even less frequent widespread floods. Rainfall shows high inter-annual variability averaging around 280 mm/yr and potential evapo-transpiration is >3,000 mm/yr. The source of recharge to the predominantly fresh groundwater resource in this region is unclear. While there is localised piezometric response to rainfall events, it is not self-evident that the resource is significantly replenished by these intermittent events.

The distribution of ^{14}C results cover the entire spectrum of the radiocarbon time scale as well as a handful of modern groundwater (i.e., groundwater containing radiocarbon from the atmospheric nuclear weapons testing). The distribution is partly caused by groundwater samples coming from different depth intervals below the water table. In other words they represent different components of water that have transited along various flow lines from the recharge zone to the well.

For each of the groundwater samples collected from discrete depth intervals one can estimate long-term recharge rates along inferred flow paths using a simple analytical model developed by Vogel (1967) that considers the depth of the screen interval from which the sample was taken and the total depth of the aquifer (Harrington *et al.* 2002; IAEA 2013). The recharge rates calculated from ^{14}C data collected at each of the wells (Figure 4) show that recharge rates are generally low, less than 2.5 mm/yr. Higher recharge rates are found in floodplain areas where significant floods are known to have occurred in the past. Relatively low recharge rates are found in water-courses on a 2-3 years time frame because these support deep-rooted vegetation that extract more water. In this study it was possible to derive initial "no decay" radiocarbon values from the $^{87}Sr/^{86}Sr$ isotopic ratio (Harrington & Herczeg 2003). It was possible to conclude from stable isotopes of water that recharge takes place mainly when the monthly amount of precipitation exceeds 150-200mm. And the recharge values from radiocarbon were confirmed by chloride mass balance (Harrington *et al.* 2002) and confirmed earlier studies by Calf *et al.* (1991). This emphasizes that radiocarbon should not be used alone but embedded in the concert of other tracers to derive a common system understanding. The spatial variability, and ability to integrate at least on specific flow paths adds important insights that are not possible from conventional hydrological techniques.



LEFT **Figure 4. Estimates of recharge rates for various flow paths determined from radiocarbon for the Ti Tree basin of central Australia (Harrington,1997).**

FURTHER READING AND LINKS

CSIRO: http://www.clw.csiro.au/services/isotope/

Rafter radiocarbon lab: http://www.gns.cri.nz/Home/Services/Laboratories-Facilities/Rafter-Radiocarbon-Laboratory

IAEA Book: Plummer, LN and Glynn, PD (2013): Radiocarbon dating of groundwater systems. In Ch. 4, A. Suckow, P. K. Aggarwal and L. J. Araguas-Araguas [eds], Isotope Methods for Dating Old Groundwater. International Atomic Energy Agency.

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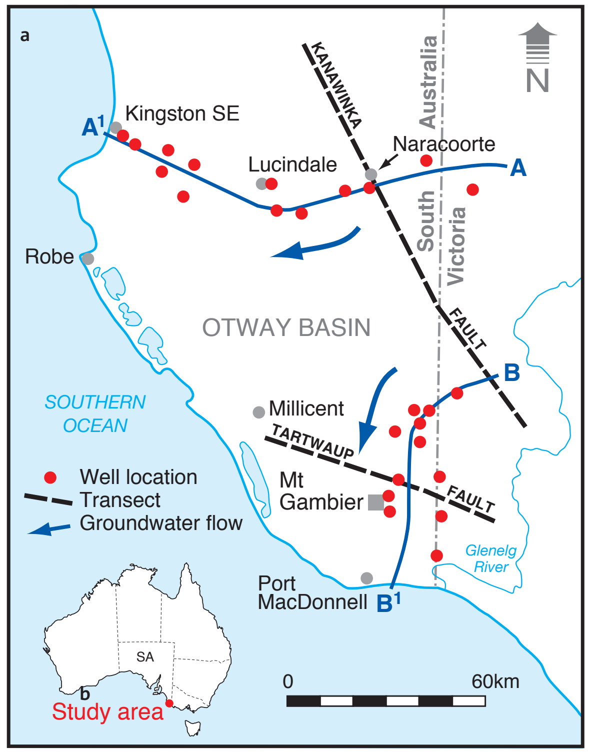
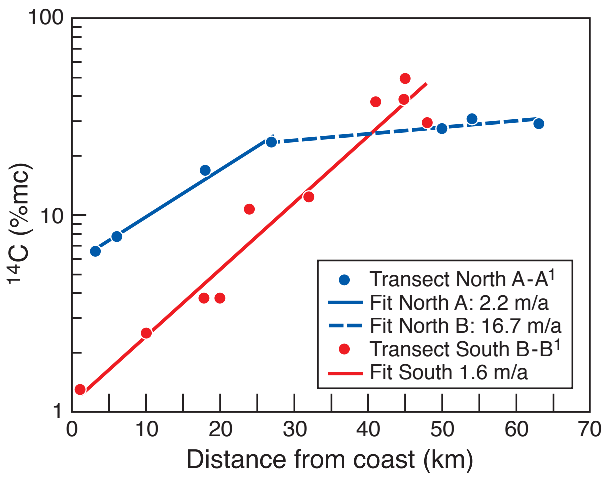
16 m yr^{-1} down to ~1.6 m yr^{-1}. The differences in flow velocities may reflect changes in the paleoclimate over the time scale of groundwater movement during the past 25 000 years as well as variability in aquifer conditions in different parts of the basin.

The results of such information are especially useful to test conceptual models that reveal the nature of how groundwater systems behave. In this example, the data (along with other tracers) provided information about the importance of recharge across the fault zones as well as travel time estimates that can constrain the rate of discharge. The data reinforces the notion of groundwater as a significant but slowly regenerating resource. Over long time frames it has been responding to changes in climate and sea level.





ABOVE **Figure 1. The top panel shows ^{14}C concentration in groundwater from the confined Tertiary sandstone aquifers of the Dilwyn Formation, SE South Australia. Groundwater flow is right to left and ^{14}C results on the lower panel allow deriving the groundwater velocities. Date from Love *et al.*, 1994. J. Hydrol., v. 153, 157-187.**

RECHARGE RATES

One of the perennial questions in groundwater resource evaluation is estimating the long-term recharge rate. A number of methods are applied in differing circumstances and each has their advantages and limitations. The main advantage of isotope methods such as radiocarbon is that they record the entire history over the last some thousand years of the groundwater flow system, while conventional hydraulic methods are biased towards the most recent hydrological regime.

A relatively simple approach for estimating recharge in phreatic or unconfined groundwater systems is to measure radiocarbon in water samples taken at different depth intervals. In an ideal world, the recharge would be constant across the landscape and radiocarbon in groundwater would decrease with depth at a rate dependent on the rate of recharge. While there are several assumptions and approximations, such as hydrological steady-state, uniform recharge rate across the land surface and relatively homogeneous aquifer physical properties, the method can be at best a reliable assessment of recharge and at worst an order of magnitude estimate. This is far better than an educated guess or to be left as an unconstrained parameter in a numerical groundwater model.

An example of a study from the western Victorian volcanic plains, shown in Figure 2, was done in a large generally flat region with layered system of fractured basalt in the 'highland' northern part of the area, abutting against weathered basalt on the plain overlying an unconsolidated Pliocene sand aquifer. The results of radiocarbon determination in wells with relatively short screen intervals show a wide distribution with depth which at first may appear disheartening. The various trends that would be expected for recharge rates ranging from 0.1 mm/yr to 3 mm/yr are also shown (assuming a best guess mean porosity of 20%). A closer look at the results reveal some generalisations: groundwater from the highland volcanics tend to show high ^{14}C values even at considerable depth that could be explained by recharge rates in the vicinity of 3 mm/yr. For the basaltic plains and some of the Pliocene sands ^{14}C in groundwater tends to decrease reaching 30-10%MC by about 30 m depth and is indicative of much lower vertical components of velocity between <0.1 – 0.4 mm/yr. This indicates two different modes of flow in this complex system with vertical velocity components that are considerably lower than recharge rates that had been previously assumed based on soil infiltration studies. While these trend lines can indicate recharge rates, they also can be caused by leakage between different parts of this layered aquifer system. The real advantage of radiotracers is that they can confirm or falsify conceptual models of flow and transport processes in groundwater systems on time scales that are not assessable with other means.

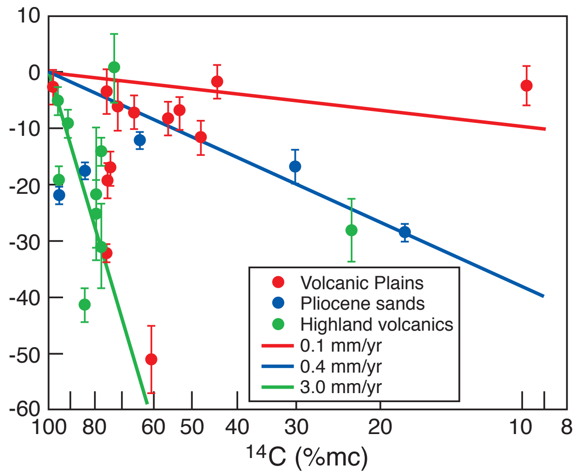
Advantages and limitations

Radiocarbon is the only readily available method for assessing groundwater movement between those waters with clear anthropogenic influence and up to 30,000 years. It therefore will keep its importance for estimating time scales of groundwater processes in large regional aquifer systems, particularly in the arid zone. Beyond the anthropogenic time scale (some centuries) it can be supplemented by ^{4}He (see separate fact sheet on noble gases). However, the study of groundwater systems on these long timescales always needs an interdisciplinary combination of all available information to confirm or falsify the possible conceptual scenarios. This implies the need to combine several tracers: Those covering shorter time scales than radiocarbon (like tritium, CFCs, SF_6, see separate fact sheets) will assess possible admixtures of young groundwater, may it due to sampling conditions like long well screens or due to gaps in confining aquitards that were supposed to be continuous. Those covering shorter time scales than radiocarbon (like tritium, CFCs, SF_6, see separate fact sheets) will assess possible admixtures of young groundwater. This may be due to sampling conditions like long well screens or due to gaps in confining aquitards. A comprehensive overview of methods to study old groundwater systems can be found in IAEA (2013).

One significant advantage in using radiocarbon is that dissolved inorganic carbon (DIC) is ubiquitous in groundwater and therefore virtually any water sample can be analyzed. Concentrations of DIC are usually sufficient such that only 1-5 liter of water is required for ^{14}C analysis using modern accelerator mass spectrometry techniques.

The main limitation or complicating feature is that inorganic carbon, including all the constituent isotope species, is not conservative. The effects of soil and aquifer chemical interactions between CO_2 gas, aqueous carbonate species and solid carbonates need to be evaluated using one of a number of chemical correction schemes. Invariably the starting point of ^{14}C concentration at the point it reaches the water table will be less than that in the equivalent overlying atmosphere due to dilution by very old ^{14}C-free carbon. Failing to take these interactions into account will result in an under-estimate of groundwater velocity. The correction schemes are not difficult but require some knowledge and intuition on the characteristics of the deep unsaturated zone to be able to make a confident assessment of the appropriate correction scheme to apply. This need not be a deterrent to using radiocarbon, but users should be aware that the transport of the carbon is not directly transferable to the transport of the water.

Most isotope laboratories will provide ^{14}C results to clients as percent modern carbon (%mc) notation along with an uncorrected (conventional) age. Because one cannot a priori convert this to a "corrected" 14C age or groundwater residence time without knowing the specific physical and chemical circumstances, the users are best placed to determine the appropriate correction schemes to estimate model ages.



LEFT **Figure 2. ^{14}C for groundwater from the western Victoria volcanic plains as a function of depth below the water table (unpublished data). The lines represent trends for various equally distributed recharge rates assuming 20% porosity.**

FAQs

Q: How are samples collected?

A: Water samples for radiocarbon analysis are collected in 1 – 5 L sealed glass or plastic containers and sent to the laboratory for further purification and analysis by accelerator mass spectrometry (AMS). The actual amount of water required depends on the dissolved inorganic carbon concentration and it is best to contact the CSIRO laboratory prior to sampling to find out how to determine this. The groundwater being sampled should have minimal contact with air. A pump rate of at least a few litres per minute will help ensure this. See **www.clw.csiro.au/services/isotope/** for more detailed sampling instructions.

Q: What additional information is necessary for interpretation?

A: It is always necessary to collect an additional 250 ml sample for full chemical analysis, including field pH and alkalinity, to assist with interpretation of the ^{14}C results. It is also strongly recommended to sample for tracers that assess young groundwater (CFCs, SF_6, tritium…) and for additional tracers for old groundwater (^{4}He, ^{36}Cl) to determine possible mixtures of different ages and to test the conceptual models needed for interpretation (IAEA 2013).

Q: How soon can I expect results?

A: The CSIRO laboratory prepares the sample for final analysis at The Australian National University (one of only two laboratories in Australia with AMS measurement facilities for ^{14}C). Results are usually completed within 2–3 months.

Q: How much does it cost?

A: For actual price information see the homepage of CSIRO Isotope analysis Service (IAS) **www.clw.csiro.au/services/isotope/** The client is responsible for analysis of field parameters such as temperature, pH and alkalinity as well as major ion analysis.

Q: Are there any alternative methods?

A: There are other isotope tracer methods that characterize younger water (tritium, CFCs, SF_6, ^{85}Kr, ^{39}Ar), a similar time range (^{4}He) or older water (^{36}Cl, ^{81}Kr). It is strongly recommended never to use ^{14}C alone but to always design an integrated study of the groundwater system including additional tracers (IAEA 2013). Some of these techniques are available from CSIRO-IAS, others require specialised sampling and analytical facilities available only in Europe and North America. Radiocarbon remains the cornerstone of investigating groundwater flow in the time scale up to 30,000 years.