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Evolution of chemical and isotopic composition of inorganic carbon in a complex semi-arid zone environment: Consequences for groundwater dating using radiocarbon

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Abstract

Estimating groundwater age is important for any groundwater resource assessment and radiocarbon (^{14}C) dating of dissolved inorganic carbon (DIC) can provide this information. In semi-arid zone (i.e. water-limited environments), there are a multitude of reasons why ^{14}C dating of groundwater and traditional correction models may not be directly transferable. Some include; (1) the complex hydrological responses of these systems that lead to a mixture of different ages in the aquifer(s), (2) the varied sources, origins and ages of organic matter in the unsaturated zone and (3) high evaporation rates. These all influence the evolution of DIC and are not easily accounted for in traditional correction models. In this study, we determined carbon isotope data for; DIC in water, carbonate minerals in the sediments, sediment organic matter, soil gas CO_2 from the unsaturated zone, and vegetation samples. The samples were collected after an extended drought, and again after a flood event, to capture the evolution of DIC after varying hydrological regimes. A graphical method (Han et al., 2012) was applied for interpretation of the carbon geochemical and isotopic data. Simple forward mass-balance modelling was carried out on key geochemical processes involving carbon and agreed well with observed data. High values of DIC and $\delta^{13}C_{DIC}$, and low $^{14}C_{DIC}$ could not be explained by a simple carbonate mineral–CO_2 gas dissolution process. Instead it is suggested that during extended drought, water–sediment interaction leads to ion exchange processes within the top ~10–20 m of the aquifer which promotes greater calcite dissolution in saline groundwater. This process was found to contribute more than half of the DIC, which is from a mostly 'dead' carbon source. DIC is also influenced by carbon exchange between DIC in water and carbonate minerals found in the top 2 m of the unsaturated zone. This process occurs because of repeated dissolution/precipitation of carbonate that is dependent on the water salinity driven by drought and periodic flooding conditions. This study shows that although ^{14}C cannot be directly applied as a dating tool in some circumstances, carbon geochemical/isotopic data can be useful in hydrological investigations related to identifying groundwater sources, mixing relations, recharge processes, geochemical evolution, and interaction with surface water.

Keywords: Radiocarbon; Carbon isotopes; Darling River; Groundwater; $CO_{2(g)}$; Unsaturated zone; Water–sediment reactions

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1. INTRODUCTION

Estimating groundwater age is important for any groundwater resource assessment as it provides information on groundwater replenishment rates, recognises palaeowaters, and can be used to calibrate groundwater flow models, which ultimately offer guidance on the sustainability of a groundwater resource. Radiocarbon (^{14}C with a half-life of 5730 ± 40 years) provides a useful tool for estimating the age of groundwater recharged on the ten thousand year time scale. Most groundwater dating studies measure the ^{14}C contents of the dissolved inorganic carbon (DIC) and fundamental assumptions are made when calculating an age. In order to calculate radiocarbon age it is essential to estimate the initial ^{14}C content ($^{14}C_0$) and this has direct impact on the results. The calculation of a ^{14}C groundwater 'age' still has many hydrochemical and hydrogeological challenges associated with its use (Tamers, 1975; Fontes and Garnier, 1979; Maloszewski and Zuber, 1991; Sanford, 1997; Plummer and Sprinkle, 2001; Gonfiantini and Zuppi, 2003;, amongst many others).

The commonly used adjustment models for $^{14}C_0$ in radiocarbon dating of groundwater are based on simple conceptualisation of certain geochemical processes. For example, where the HCO_3^- in water is a reaction product of dissolved CO_2 and carbonate minerals under closed-system conditions, the Tamers' model can be used (Tamers, 1975; Han and Plummer, 2013, 2016). Where carbonate dissolution is occurring under open-system conditions while carbon exchange between DIC and CO_2 gas from the unsaturated zone occurs, Mook's model (Mook, 1976, 1980) can be applied. In scenarios where carbonate dissolution takes place partly under open-system conditions in the unsaturated zone and partly under closed-system conditions in the aquifer, the IAEA model can be applied (Salem et al., 1980; Gonfiantini and Zuppi, 2003; Han and Plummer, 2016). For combined processes of the above and carbon exchange between DIC and carbonate minerals, the Eichinger (Eichinger, 1983) or Han and Plummer (Han and Plummer, 2013) model can be used.

There are a multitude of reasons why these correction methods cannot be directly transferred to semi-arid or water-limited environments. Firstly, contrasting recharge mechanisms from direct (rainfall) and indirect (i.e. river water) will influence the evolution of DIC in groundwater. These environments generally experience very low direct recharge from rainfall because evaporation rates far outweigh precipitation. And in some cases river recharge can provide a greater overall volume of groundwater recharge, however these events may not be predictable, being delivered on multi-annual timescales dependent on flow regimes of dryland rivers such as the Darling River (Meredith et al., 2015). These conditions can lead to groundwater age gradients forming within an aquifer and promote the development of a thick unsaturated zone (Wood et al., 2014). Tracing the evolution of DIC in such complex hydrological systems is challenging.

Secondly, because many of the correction models calculate $^{14}C_0$ by using an assumed $\delta^{13}C$ value of CO_2 gas in the unsaturated zone, in water-limited environments, this value has been found to be more variable than first realised. Soil $CO_{2(g)}$ in the unsaturated zone can be contributed from shallow and deep sources with varying ages (Walvoord et al., 2005; Carmi et al., 2009). Wood et al. (2014) modelled soil $CO_{2(g)}$ by varying recharge rates and water table depth in a water-limited environment in Australia. They identified how these variables influenced shallow and deep productions of soil $CO_{2(g)}$ in a thick unsaturated zone (30 m). This study did not calibrate these models with sediment analysis, therefore, questions still remain as to the soil $CO_{2(g)}$ source and the associated geochemical processes leading to DIC evolution. Organic carbon can also be sourced from vegetation which utilises both the C_3 (trees) and C_4 (grasses) photosynthetic pathways (Plummer and Sprinkle, 2001; Plummer and Glynn, 2013). This organic matter maybe *in situ* (either root zone material or soil organic matter (SOM) (Carmi et al., 2009)). Or it may be dissolved or colloidal organic matter being transported within the unsaturated zone. In all cases, organic matter can undergo microbial reprocessing in the unsaturated zone (Shen et al., 2015; Mattey et al., 2016) leading to varying sources of $CO_{2(g)}$. Therefore, measuring this soil $CO_{2(g)}$ source is crucial for radiocarbon studies in water-limited environments.

Furthermore, the high evaporation rates experienced in these regions promote the formation of soil carbonates. This is because they form in soils with a net water deficit (Cerling and Quade, 1993). The carbonate forms when the solution becomes supersaturated with carbonate due to an increase in the concentration of dissolved ions. The presence of carbonate minerals is likely to further hinder the simplistic use of radiocarbon corrections in the Australian setting. Cartwright et al. (2013) showed the degree of closed-system calcite dissolution in groundwater that was recently recharged by using $^{14}C_{DIC}$ and ^{3}H. This dual isotope approach is useful for groundwaters that contain measureable ^{3}H and can be used to identify mixing trends.

Finally and most importantly for this study, the commonly used ^{14}C correction models imply conceptually that a water sample is unmixed and of a single age. Very often, a groundwater sample is composed of a mixture of waters with distinctly different ages especially where river waters are the major source of recharge. The influence of this mixing can be extreme, for example, a palaeowater with an age greater than 1 Ma can be mixed with 1% of modern water, it will then appear to be less than 30 ka giving misleading age information (Han and Plummer, 2016). Therefore identifying this mixing and the geochemical processes that are influenced by the influx of this water with a different chemistry is important and hence the subject of this research.

The aims of this paper are: (1) to test, with measured data of carbon chemical and isotopic composition of DIC, whether the commonly held assumptions for carbon evolution within both the unsaturated and saturated zones of a groundwater system in a semi-arid zone climate hold true; (2) to show that mixed water samples can be recognised by analysing the chemical and isotopic composition of DIC, and (3) to present a method for resolving the abovementioned issues associated with interpreting DIC data in a water limited environment and in doing so define