



## **Understanding the carbon cycle in a Late Quaternary-age limestone aquifer system using radiocarbon of dissolved inorganic and organic carbon**

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Estimating groundwater residence time is critical for our understanding of hydrogeological systems, for groundwater resource assessments and for the sustainable management of groundwater resources. Due to its capacity to date groundwater up to 30 thousand years old, as well as the ubiquitous nature of dissolved carbon (as organic and inorganic forms) in groundwater,  $^{14}\text{C}$  is the most widely used radiogenic dating technique in regional aquifers. However, the geochemistry of carbon in groundwater systems includes interaction with the atmosphere, biosphere and geosphere, which results in multiple sources and sinks of carbon that vary in time and space. Identifying these sources of carbon and processes relating to its release or removal is important for understanding the evolution of the groundwater and essential for residence time calculations. This study investigates both the inorganic and organic facets of the carbon cycle in groundwaters throughout a freshwater lens and mixing zone of a carbonate island aquifer and identifies the sources of carbon that contribute to the groundwater system. Groundwater samples were collected from shallow (5-20 m) groundwater wells on a small carbonate Island in Western Australia in September 2014 and analysed for major and minor ions, stable water isotopes (SWIs:  $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$ ),  $^3\text{H}$ ,  $^{14}\text{C}$  and  $^{13}\text{C}$  carbon isotope values of both DIC and DOC, and  $^3\text{H}$ . The composition of groundwater DOC was investigated by Liquid Chromatography-Organic Carbon Detection (LC-OCD) analysis. The presence of  $^3\text{H}$  (0.12 to 1.35 TU) in most samples indicates that groundwaters on the Island are modern, however the measured  $^{14}\text{C}$  DIC values (8.4 to 97.2 pmc) suggest that most samples are significantly older due to carbonate dissolution and recrystallisation reactions that are identified and quantified in this work.  $^{14}\text{C}$  DOC values (46.6 to 105.6 pMC) were higher than  $^{14}\text{C}$  DIC values and were well correlated with  $^3\text{H}$  values, however deeper groundwaters had lower  $^{14}\text{C}$  DOC values than expected. LC-OCD chromatography of these groundwaters were found to contain higher concentrations of humic substances, that are most likely attributed to the presence of paleosol horizons at depth in the limestone, which are a common feature in aeolianite deposits along the Western coast of Australia and are related to Quaternary sea level change. The paleosols likely contribute old organic matter to the deeper groundwaters, which may explain the lower  $^{14}\text{C}$  DOC values. This study has shown that a combined approach that utilises both DIC and DOC tracers, as well as  $^3\text{H}$ , is required to identify the sources and evolution of carbon in a groundwater system, as well as the processes that effect the application of  $^{14}\text{C}$  dating to groundwaters within a carbonate aquifer.