Evolution of chemical and isotopic composition of inorganic carbon in the unsaturated and saturated zones of a semi-arid zone environment.

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Estimating groundwater age is important for any groundwater resource assessment and radiocarbon (^{14}C) dating can provide this information. However a thorough investigation of the water in the soil-plant-atmosphere continuum leading to the evolution of dissolved inorganic carbon (DIC) in groundwater is required for interpretation in a water-limited environment. In this study we trace the evolution of DIC through the unsaturated and saturated zones after prolonged drought and post-flooding of a major river system, the Darling River. In doing so, we quantified the contribution of carbon from various processes influencing the ^{14}C content of DIC in groundwater. None of the simple ^{14}C adjustment models could be applied for age estimation. Therefore, we used a combination of a graphical method and mass-balance calculations. It was found that the saline groundwaters evolved via carbon exchange between DIC- carbon dioxide gas ($CO_{2(g)}$) in the unsaturated zone and DIC-carbonate minerals in the saturated zone with water-sediment reactions driving ion exchange on clay minerals facilitating carbonate dissolution. This study shows the problems associated with using radiocarbon dating in a semi-arid zone or water-limited environment and the required carbon measurements needed to reduce this uncertainty.