



## Carbon-14 in streams as a tracer of discharging groundwater



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### SUMMARY

Quantification of the volume of groundwater discharge to streams, and the source aquifer of that discharge, is required to adequately manage the impacts of groundwater use on stream ecosystems. This has been achieved through longitudinal surveys of gaseous tracers, but their effectiveness can be limited by rapid equilibration between the stream and the atmosphere. Here we develop the use of carbon-14 in dissolved inorganic carbon (DIC) in a stream as a tracer of groundwater discharge. A controlled equilibration experiment was conducted, during which groundwater with an initial  $^{14}\text{C}$  activity of 5.5 pMC was allowed to equilibrate with the atmosphere over 72 days. The effective transfer velocity for  $^{14}\text{C}$  was measured as  $0.013\text{ m d}^{-1}$ . The method was then tested at an artificial groundwater discharge location, where the effective transfer velocity was measured as  $0.025\text{ m d}^{-1}$ . In these simple systems, the ratio of the effective  $^{14}\text{C}$  transfer velocity to the  $\text{CO}_2$  gas transfer velocity is a function of pH, and proportional to the fraction of DIC present as  $\text{CO}_2$ . The method was then applied along a reach of the Daly River, Australia, where groundwater discharge is known to occur. A decrease of 7 pMC was observed across the major spring discharge zone, with subsequent equilibration with the atmosphere occurring over at least tens of kilometres. This allowed for the effective transfer velocity to be estimated at between  $0.09$  and  $0.15\text{ m d}^{-1}$ , and for the  $^{14}\text{C}$  activity of groundwater discharge to be estimated at between 60 and 66 pMC. The equilibration of  $^{14}\text{C}$  in stream DIC is in the order of 10 times slower than for gas tracers, which may allow for the detection of smaller groundwater discharge fluxes than is possible with gas tracers. If the total groundwater discharge flux is known, measurements of  $^{14}\text{C}$  in stream DIC can also be used to infer the  $^{14}\text{C}$  activity of discharging groundwater. This method may be a useful alternative to direct groundwater sampling, particularly in remote basins with few groundwater wells.

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### 1. Introduction

Knowledge of the source of groundwater discharging to streams is important for understanding the potential risks of stream depletion due to groundwater abstraction, or surface water contamination. Often groundwater discharge to streams originates from multiple aquifers, and has a range of aquifer residence times. By measuring multiple age indicators along a stream, each sensitive to a different range of groundwater residence times, it is theoretically possible to identify groundwater contributions of differing ages. Previous studies have quantified groundwater discharge to streams using radon-222 ( $^{222}\text{Rn}$ ), which is sensitive to groundwater discharge with residence times longer than a few days (Cook

et al., 2003, 2006; Gardner et al., 2011). Groundwater discharge with residence times less than 100 years has been detected using chlorofluorocarbons (CFCs),  $\text{SF}_6$ , tritium ( $^3\text{H}$ ), or the ratio of tritium to helium-3 ( $^3\text{H}/^3\text{He}$ ) (Cook et al., 2003, 2006; Smerdon et al., 2012; Stolp et al., 2010). The only groundwater age tracer that has been used to specifically quantify old groundwater discharge is terrigenic helium-4 (Gardner et al., 2011; Smerdon et al., 2012). Helium-4 ( $^4\text{He}$ ) can be used to measure groundwater residence times greater than 100 years, but is most sensitive to much longer residence times ( $\geq 10,000$  years) (Cook and Herczeg, 2000).

A potential limitation of dissolved gases as tracers of groundwater discharge to streams is that they degas rapidly to the atmosphere, and so the tracer concentration is most sensitive to the groundwater discharge flux close to the sampling location. The rate of equilibration with the atmosphere therefore provides a limit on the sampling resolution required to detect groundwater discharge, with faster equilibration requiring finer sampling resolution (Cook,

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2012). For carbon-14 ( $^{14}\text{C}$ ), the process of equilibration is driven by  $\text{CO}_2$  exchange across the air–water interface, and is effectively buffered by the other dissolved inorganic carbon species in solution. The rate of equilibration of  $^{14}\text{C}$  is therefore likely to be much slower than the rate of equilibration of  $\text{CO}_2$ , and other gas tracers. While a number of studies have investigated gas transfer rates for  $\text{CO}_2$ , the rate of  $^{14}\text{C}$  equilibration between total dissolved inorganic carbon (TDIC) and the atmosphere has not previously been quantified.

If discharge of groundwater induces a detectable change in  $^{14}\text{C}$  activity of dissolved inorganic carbon (DIC – used interchangeably with TDIC) along a stream reach, this can be used to quantify groundwater discharge from a source aquifer with known  $^{14}\text{C}$  activity. Alternatively, if the quantity of groundwater discharge is known, changes in stream  $^{14}\text{C}$  activity can be used to infer the  $^{14}\text{C}$  activity of groundwater discharging into the stream. Given the relative ease of sampling surface waters, this could provide a useful technique for estimating groundwater  $^{14}\text{C}$  activity in the absence of direct groundwater samples.

While many studies have measured the carbon-13 ( $^{13}\text{C}$ ) signatures of stream DIC (Aucour et al., 1999; Doctor et al., 2008; Hagedorn and Cartwright, 2010; Hélie et al., 2002; Mayorga et al., 2005), and  $\delta^{13}\text{C}$  has been used as a tracer of groundwater discharge (Meredith and Kuzara, 2012), there are few published studies that have measured the  $^{14}\text{C}$  activity of DIC in streams. Those studies that have measured  $^{14}\text{C}$  in stream DIC were focussed on quantifying carbon fluxes associated with stream ecosystems (Raymond et al., 2004; Raymond and Hopkinson, 2003) and the efflux of  $\text{CO}_2$  from streams to the atmosphere (Mayorga et al., 2005). As far as we are aware, this is the first study to apply  $^{14}\text{C}$  as a tracer of groundwater discharge to streams. Furthermore, we believe that this is the first study to measure the rate of equilibration of  $^{14}\text{C}$  in TDIC in groundwater exposed to the atmosphere.

The aims of this paper are twofold. Firstly, we test the hypothesis that  $^{14}\text{C}$  activity of dissolved inorganic carbon in a stream can be used to detect groundwater discharge to a stream, with a much lower sampling resolution than is required for other dissolved gas tracers. Additionally, we test the hypothesis that changes in stream  $^{14}\text{C}$  activity across a groundwater discharge zone can be used to infer the  $^{14}\text{C}$  activity of the discharging groundwater.

In order to test these hypotheses, a controlled equilibration experiment is presented during which rates of carbon isotope equilibration between old (approximately 30 ka) groundwater and the atmosphere were measured. Next, the rate of carbon isotope equilibration is measured in a naturally ephemeral creek channel receiving artificial groundwater discharge. Finally, the application of  $^{14}\text{C}$  as a tracer of groundwater discharge to streams is demonstrated in the Daly River in northern Australia. The Daly River was chosen as the test site because there are discrete spring (groundwater) discharge zones that have previously been mapped, and because previous studies suggest that the total carbon pool is dominated by dissolved inorganic carbon at the time of sampling (dry season, baseflow conditions) (Robson et al., 2010; Tickell, 2011).

## 2. Theory

### 2.1. Isotopic equilibration mechanisms

Conceptually, we begin with a stream containing dissolved inorganic carbon that is in chemical and isotopic equilibrium with the atmosphere. Suppose that groundwater with a different DIC concentration and  $^{14}\text{C}$  activity then enters the stream at a discrete location. We assume that at the location of groundwater discharge, the isotopic composition of the stream is determined by the mixing

fractions of TDIC in groundwater and surface water. Downstream of the location of groundwater discharge, there are two processes that can drive carbon isotopic re-equilibration between the stream and atmosphere; chemical exchange and isotopic exchange (Broecker et al., 1980; Broecker and Walton, 1959).

#### 2.1.1. Chemical exchange

Carbon cycling in stream systems is complex, and may involve reactions between inorganic and organic carbon, dissolution or precipitation of particulate carbon, and  $\text{CO}_2$  production or consumption (Aucour et al., 1999; Hagedorn and Cartwright, 2010; Hélie et al., 2002; Raymond and Bauer, 2001b). In the current study, in-stream DOC was expected to be small relative to DIC, and so we did not explicitly account for DIC production through mineralization of dissolved organic carbon (DOC) or particulate organic carbon (POC). The validity of this approach is discussed in Section 5. In other stream systems with high DOC concentrations, or rapid mineralization rates, this source of DIC may need to be explicitly included in the carbon isotopic mass balance.

In our analysis, we assume that the dominant process driving carbon isotopic equilibration downstream of a groundwater discharge zone is the exchange of  $\text{CO}_2$  between the stream and the atmosphere. Groundwater typically has high levels of dissolved  $\text{CO}_2$  that will degas to the atmosphere through gas exchange upon discharge to a river. This degassing of  $\text{CO}_2$  causes an increase in pH, which shifts the distribution of carbonate species in the TDIC pool (Appelo and Postma, 2005). There is a fractionation effect associated with this  $\text{CO}_2$  exchange because of the different molecular weights of  $^{12}\text{CO}_2$ ,  $^{13}\text{CO}_2$  and  $^{14}\text{CO}_2$ . As the  $\text{CO}_2$  degasses, this fractionation causes an enrichment of the carbon isotopic signature of TDIC in the stream (Choi et al., 1998; Doctor et al., 2008).

The  $\text{CO}_2$  exchange flux is driven by the degree of disequilibrium from the atmosphere, with the rate of change in  $\text{CO}_2$  concentration in a volume,  $V$  ( $\text{L}^3$ ), of water with surface area,  $A$  ( $\text{L}^2$ ), given by;

$$\frac{\partial \text{CO}_2}{\partial t} = k_{\text{CO}_2} \frac{A}{V} (\text{CO}_{2\text{eq}} - \text{CO}_2) \quad (1)$$

where  $\text{CO}_2$  is the concentration of dissolved  $\text{CO}_2$  in solution ( $\text{M L}^{-3}$ ),  $\text{CO}_{2\text{eq}}$  is the concentration of dissolved  $\text{CO}_2$  in equilibrium with the atmospheric  $\text{CO}_2$  partial pressure ( $\text{M L}^{-3}$ ),  $t$  is time (T), and  $k_{\text{CO}_2}$  is the gas transfer velocity ( $\text{L T}^{-1}$ ). This gas transfer velocity is a function of the diffusion coefficient of  $\text{CO}_2$  and the turbulence in the boundary layer at the air–water interface (Genereux and Hemond, 1992; Raymond and Cole, 2001). Equations in the form of Eq. (1) can also be written for each carbon isotopologue of  $\text{CO}_2$ , however, because  $^{12}\text{C}$  is much more abundant than  $^{13}\text{C}$  or  $^{14}\text{C}$ , chemical exchange will be dominated by  $^{12}\text{CO}_2$ .

The enrichment caused by fractionation during  $\text{CO}_2$  degassing can be simulated as a Rayleigh distillation process (Hendy, 1971), described by;

$$\delta \cong \varepsilon_T \ln(f) + \delta_0 \quad (2)$$

where  $\delta$  is the carbon isotopic composition of the remaining solution,  $\delta_0$  is the initial carbon isotopic composition,  $f$  is the fraction of dissolved inorganic carbon remaining in solution, and  $\varepsilon_T$  is the total enrichment factor (Clark and Fritz, 1997). This enrichment factor is expressed relative to  $\text{HCO}_3^-$ , which dominates the dissolved carbon species in the pH range of natural waters (6.5–8.5). In this open system, where degassed  $\text{CO}_2$  is continuously removed from the system,  $\varepsilon_T$  will be the sum of an equilibrium enrichment,  $\varepsilon_{\text{g-HCO}_3^-}$ , due to the different solubilities of each isotopologue of  $\text{CO}_2$ , and a kinetic enrichment,  $\varepsilon_k$ , driven by the different gas transfer velocities of each isotopologue (Zhang et al., 1995), such that  $\varepsilon_T = \varepsilon_{\text{g-HCO}_3^-} + \varepsilon_k$ .

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