RESEARCH ARTICLE

Key Points:
- Environmental tracer approaches to estimate surface water—groundwater exchange fluxes depend on appropriate characterization of end-members
- Extent of mixing of exchanging porewater and groundwater prior to discharge will affect choice of end-members
- Although absolute fluxes cannot always be determined, both porewater and groundwater fluxes can be constrained by tracer methods

Correspondence to:
P. G. Cook,
peter.cook@flinders.edu.au

Quantifying Surface Water, Porewater, and Groundwater Interactions Using Tracers: Tracer Fluxes, Water Fluxes, and End-member Concentrations

Peter G. Cook[1,2] , **Valentí Rodellas[3]** , **and Thomas C. Stieglitz[3,4]**

[1]National Centre for Groundwater Research and Training (NCGRT), School of the Environment, Flinders University, Adelaide, SA, Australia, [2]Aix-Marseille Université, IMéRA, Marseille, France, [3]CEREGE, Aix-Marseille Université, CNRS, IRD, INRA, Coll France, CEREGE, Aix-en-Provence, France, [4]Centre for Tropical Water and Aquatic Ecosystem Research, James Cook University, Townsville, QLD, Australia

Abstract Tracer approaches to estimate both *porewater exchange* (the cycling of water between surface water and sediments, with zero net water flux) and *groundwater inflow* (the net flow of terrestrially derived groundwater into surface water) are commonly based on solute mass balances. However, this requires appropriate characterization of tracer end-member concentrations in exchanging or discharging water. Where either porewater exchange or groundwater inflow to surface water occur in isolation, then the water flux is easily estimated from the net tracer flux if the end-member is appropriately chosen. However, in most natural systems porewater exchange and groundwater inflow will occur concurrently. Our analysis shows that if groundwater inflow (Q_g) and porewater exchange (Q_p) mix completely before discharging to surface water, then the combined water flux ($Q_g + Q_p$) can be approximated by dividing the combined tracer flux by the difference between the porewater and surface water concentrations, ($c_p - c$). If Q_g and Q_p do not mix prior to discharge, then ($Q_g + Q_p$) can only be constrained by minimum and maximum values. The minimum value is obtained by dividing the net tracer flux by the groundwater concentration, and the maximum is obtained by dividing by ($c_p - c$). Dividing by the groundwater concentration gives a maximum value for Q_g. If porewater exchange and groundwater outflow occur concurrently, then dividing the net tracer flux by ($c_p - c$) will provide a minimum value for Q_p. Use of multiple tracers, and spatial and temporal replication should provide a more complete picture of exchange processes and the extent of subsurface mixing.

1. Introduction

Interactions between surface water, porewater, and groundwater have been the focus of hydrological research for many decades. Flow of subsurface water into a river can be classified into (i) groundwater that discharges to the river having originally recharged the aquifer some distance from the river, and (ii) water that originated within the river itself and that entered the aquifer for a period of time before later returning to the river. The latter (usually referred to as hyporheic exchange) is important for a range of biogeochemical processes and can exert an important influence on river water quality, while the former influences both river water quantity and quality (Boulton et al., 1998). Similarly, flow of subsurface waters to marine and coastal environments can be classified into (i) net discharge of terrestrially derived groundwater, which usually has a relatively low salinity, and (ii) an exchange between surface water and subsurface porewaters without a net water flux in either direction, induced by wave and tidal processes (sometimes referred to as seawater recirculation; Santos et al., 2009, 2012). Similar processes also occur in freshwater lacustrine environments (e.g., Rosenberry et al., 2013; Taniguchi & Fukuo, 1996).

Quantifying the magnitudes of all of these interactions represents a major challenge. Environmental tracers are increasingly used for quantifying rates of seawater recirculation in estuarine, coastal, and marine environments (Cai et al., 2014; Santos et al., 2014; Rodellas et al., 2017), rates of hyporheic exchange in rivers (Bourke et al., 2014; Frei & Gilfedder, 2015), and net flows of terrestrial-derived groundwater to rivers, lakes, and to the ocean (Cook et al., 2006; Garcia-Solsona et al., 2010; Krabbenhoft et al., 1990). Seawater recirculation and hyporheic exchange fluxes usually are measured with radioactive tracers which are produced from

decay of parent isotopes within the geological matrix. For these tracers, concentrations within the subsurface will always be higher than concentrations within surface water, and so porewater exchange creates a net tracer flux into surface water, even though the net water flux is zero. The tracer flux is determined either from a surface water mass balance, or from porewater profiles. Both radon and radium have been used to estimate seawater recirculation and hyporheic exchange (Bourke et al., 2014; Cable & Martin, 2008; Cai et al., 2014; Lamontagne & Cook, 2007; Rodellas et al., 2017; Stieglitz et al., 2013). Numerous tracers have been used as part of surface water balances to calculate net groundwater inflows to surface water, including ^{2}H, ^{18}O, helium, ion chemistry, and radioactive tracers (Cook et al., 2006; Krabbenhoft et al., 1990; Oxtobee & Novakowski, 2002). Temperature has also been used for quantifying exchange fluxes (e.g., Loheide & Gorelick, 2006; Martin et al., 2006), but it is not discussed in this paper because the processes affecting subsurface temperatures are very different to those affecting dissolved solutes.

Converting the tracer flux to a water flux requires dividing by the tracer end-member concentration. Characterization of the end-member concentration is thus a critical component of tracer-derived estimates of porewater and groundwater fluxes. Issues related to the selection of end-members for determining groundwater and porewater fluxes from tracer mass balances have received significant attention in the literature. However, most of these studies have examined the impact of uncertainty and temporal variation in end-members on estimates of groundwater inflow or porewater exchange (e.g., Cerdà-Domènech et al., 2017; Genereux et al., 1993; Gonneea et al., 2013). None have considered how the existence of both porewater exchange and groundwater inflow affects the choice of end-members, and how the choice of end-members affects the estimated fluxes. Most previous studies have focused on the flux of interest (i.e., groundwater inflow, hyporheic exchange, or seawater recirculation), and either not explicitly considered a possible contribution from the other flux (e.g., Cook et al., 2003; Schmidt et al., 2009; Wu et al., 2004), or argued that the contribution of the other flux is small (e.g., Beck et al., 2007; Bourke et al., 2014; Trezzi et al., 2016). Other studies have claimed that their approach measures the combined porewater and groundwater flux, but without necessarily demonstrating that this is the case (e.g., Moore et al., 2008; Rodellas et al., 2017). Very few studies have explicitly evaluated both porewater and groundwater fluxes (Charette et al., 2013; Rodellas et al., 2017; Stieglitz et al., 2013). In this paper, issues related to the definition of appropriate end-member concentrations for estimating porewater exchange and groundwater fluxes using tracer approaches are explicitly examined with the aid of simple mixing models. Based on these simple models we provide advice on end-members that should be used for calculation of both groundwater and porewater exchange fluxes.

2. Terminology

The terminology surrounding surface water—porewater exchange, seawater recirculation, hyporheic exchange, and groundwater discharge can be confusing, and also differs between the different disciplines which are involved in these studies (chiefly, marine and hydrologic communities) (Wilson et al., 2016). In this paper, we use the term *porewater exchange* to refer to the cycling of water between surface water and sediments, with zero net water flux; this includes both seawater recirculation in coastal and marine environments and hyporheic exchange in rivers. The term *groundwater inflow* is used for the net discharge of terrestrially derived groundwater into surface water, while *groundwater outflow* is used for surface water that enters the subsurface and does not subsequently flow back into the surface water. As we wish to discriminate between porewater exchange and groundwater inflow, we deliberately avoid the term *submarine groundwater discharge* (SGD), which is often defined to include both porewater exchange and groundwater inflow (Burnett et al., 2003).

We also distinguish between two different groups of tracers. The first group (which we simply refer to as *radiometric tracers*) comprises those tracers that are produced from radioactive decay of parent isotopes within the subsurface and which are themselves radioactive (e.g., ^{222}Rn, Ra isotopes). Porewater concentrations of these tracers will be greater than surface water concentrations, and their concentration profiles in porewater can be used to determine exchange fluxes (e.g., Cable & Martin, 2008; Cai et al., 2014). The second group of tracers (*conservative tracers*) are those which are neither produced nor degraded within the subsurface. This would include many dissolved ions (particularly chloride), but also ^{2}H and ^{18}O. We consider only environmental tracers, which are those that are naturally present within the environment.

3. Models of Groundwater, Porewater, and Surface Water Exchange

In river systems, porewater exchange is often conceptualized in terms of discrete zones of upwelling and downwelling, which can be relatively stable in time and space (Savant et al., 1987). According to this model, groundwater inflows will be concentrated immediately upstream and downstream of areas of porewater exchange (Cardenas & Wilson, 2007). A similar conceptualization can be applied in marine systems, where the driving forces of porewater exchange produce discrete and stable zones of upwelling and downwelling. If porewaters do not mix, but rather porewater exchange comprises flow paths with different lengths and subsurface residence times, then the porewater concentrations are likely to be highly spatially variable, depending on the travel time along the particular subsurface flow path. Considering all such flow paths, the net flux of a radiometric tracer into surface water (F; M L^{-2} T^{-1}) might be expressed

$$F = Q_g c_g + \sum_t q_p(t)\left[\left(\frac{\gamma}{\lambda} - c\right)\left(1 - e^{-\lambda t}\right)\right],$$ (1)

where $q_p(t)$ is the flux of porewater having subsurface residence time t (L T^{-1}), Q_g is the water flux due to groundwater inflow (L T^{-1}), c_g is the groundwater inflow concentration (M L^{-3}), γ is the tracer production rate in the subsurface (M L^{-3} T^{-1}), λ is the decay rate (T^{-1}), and c is the surface water concentration (M L^{-3}). The term in square brackets is the difference between the concentration entering at the start of a surface water flow path (c), and the concentration that ultimately discharges back into the surface water $\left(\frac{\gamma}{\lambda} - \left(\frac{\gamma}{\lambda} - c\right)e^{-\lambda t}\right)$, and the summation is across all such porewater exchange flow paths. Fluxes Q_g and $q_p(t)$ are calculated as average values across the system, and so they are already normalized by their respective contributing areas. (Although porewater fluxes occur in both directions, values of $q_p(t)$ in (1) are positive.) However, if only the tracer flux, F, is measured, then estimation of the water flux from this tracer flux would require a much more detailed understanding of the discharge patterns than is usually available, and/or extensive sampling over the discharge area. Simply dividing F by c_g will overestimate the groundwater flux (Q_g) and neglect the contribution of porewater exchange (q_p).

Equation (1) assumes that groundwater and porewater exchange flow paths do not mix and can be discretely sampled. In reality, some degree of mixing will occur due to hydrodynamic dispersion, and this will be enhanced if the locations of upwelling and downwelling zones change through time. Some degree of mixing will also be created by the process of sampling. In the following sections, we examine four scenarios: the first where only groundwater inflow occurs (Figure 1a), and the second where only porewater exchange occurs (Figure 1b), but porewater is completely mixed. The third scenario is where both porewater exchange and groundwater inflow occur and porewater exchange is completely mixed, but does not mix with discharging groundwater (Figure 1c). The fourth scenario is where groundwater and porewater mix in the subsurface, before discharging to the surface water (Figure 1d). Derivations supporting our analysis are presented in Appendix A. In each case, we use a simple conceptualization of water exchange between the surface water and a subsurface layer of constant thickness that is well-mixed, and thus assume complete mixing of porewater exchange flow paths. Similar models have been previously used in studies of porewater exchange in rivers and coastal lakes (Bourke et al., 2014; Cook et al., 2006; Morrice et al., 1997; Stieglitz et al., 2013). Although this model does not represent the complexity of porewater exchange processes, it is useful for demonstrating a number of issues. Many of these issues would remain with more complex conceptualizations. Although we are primarily interested in quantifying groundwater and porewater inflows, how groundwater outflow from surface water affects end-member concentrations is also discussed. Some of the issues related to end-member determination for models (a) and (b) have been discussed in previous studies, but are briefly discussed here in the interests of completeness.

3.1. Groundwater Inflow Without Porewater Exchange

We initially suppose that groundwater flow represents the only source of tracer flux to surface water from sediments. If the advective flux of groundwater dominates the diffusive flux (or if the diffusive flux is separately quantified, and subtracted from the tracer flux), then the groundwater flux can be determined by dividing the tracer flux by the tracer concentration in discharging groundwater:

$$Q_g = \frac{F}{c_g}.$$ (2)

The groundwater concentration end-member is either estimated by measuring the tracer concentration in groundwater from near-shore or near-bank piezometers or wells (Cartwright et al., 2011; Charette et al.,
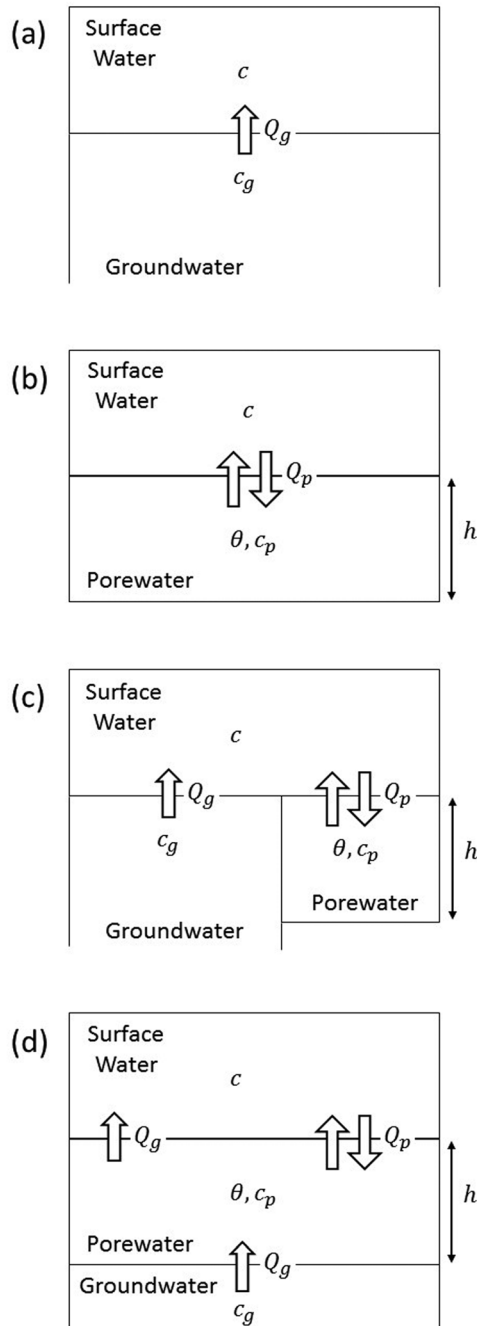
Figure 1. Different conceptual models for surface water-groundwater interaction. (a) Groundwater inflow only. (b) Porewater exchange only, that is completely mixed. (c) Groundwater inflow and porewater exchange both occur, but do not mix. (d) Groundwater inflow mixes with exchanging porewater, before entering the surface water. Q_g and Q_p are the rates of groundwater inflow and porewater exchange, respectively (L T^{-1}), c, c_p, and c_g are concentrations in surface water, porewater, and groundwater (M L^{-3}), h (L) is the thickness of the perfectly mixed subsurface layer, and θ is the porosity. Fluxes Q_g and Q_p are calculated as average values across the system, and so they are already normalized by their respective contributing areas. Groundwater outflows, in which the direction of exchange with the groundwater is reversed, are also considered.

2013; McCallum et al., 2012; Tovar-Sánchez et al., 2014) or measuring the tracer concentration in groundwater actually discharging to surface water, usually through seepage meters or springs (Cook et al, 2003; Moore, 2006; Stieglitz et al., 2013). In the case of radiometric tracers, it is also possible to perform sediment equilibration experiments to estimate the tracer concentration in equilibrium with sediments (Burnett & Dulaiova, 2003; Dimova et al., 2013). Since available piezometers are often located tens of meters or more from the surface water, sampling these to determine end-members requires that the tracer concentration is representative of discharging groundwaters (i.e., no further tracer additions or removals). This can be problematic for short-lived radioactive tracers (e.g., Rn, [224]Ra, and [223]Ra), as the concentration of groundwater inflow will reflect the composition of the sediments that the water is exposed to a few days prior to discharging to surface waters (Schmidt et al., 2009). Measurement of end-member concentrations distant from the surface water can also be problematic for ionic tracers if other processes (e.g., evapotranspiration by riparian vegetation) result in concentration changes between the sampling point and the point of groundwater inflow.

Representativeness of end-member concentrations is another issue that needs careful consideration, and several studies have found large spatial variability in groundwater end-member concentrations, which can contribute to a large uncertainty in water fluxes (see summary in Cook, 2013). Groundwater inflow rates can also be highly spatially variable (Cey et al., 1998; Kennedy et al., 2009). Where both groundwater inflow rate and concentration vary, then the end-member concentration used in equation (2) should be the flux weighted mean groundwater concentration. This is difficult to determine without detailed spatial mapping of groundwater inflow rate and inflow concentration.

3.2. Porewater Exchange Without Net Groundwater Inflow or Outflow

We now suppose that porewater exchange is the only process whereby surface water and subsurface water exchange. In the case of conservative tracers, the concentration within the subsurface will simply be equal to the surface water concentration, and there will be no net tracer flux, thus preventing the application of these tracers to estimate porewater exchange. For radiometric tracers, porewater exchange will result in a net tracer flux, as concentrations of these tracers in porewater should exceed those in surface water. In this case, the water flux is obtained by dividing the tracer flux by the end-member concentration. In fact, since we usually measure a net tracer flux, then the water flux is obtained by dividing by the difference in tracer concentration between the porewater and the overlying surface water:

$$Q_p = \frac{F}{(c_p - c)}, \qquad (3)$$

where F (M L^{-2} T^{-1}) is the net tracer flux, Q_p (L T^{-1}) is the total porewater flux (which occurs in both directions), and c_p (M L^{-3}) is the porewater tracer concentration. The problem arises because c_p is not a constant, as it depends on the residence time of porewater within the sediments (i.e., c_p will be a function of Q_p). This implies that the water flux is not proportional to the tracer flux. Four different approaches have been used for estimating c_p:

1. Assuming c_p is equal to the concentration in ambient groundwater (e.g., Burnett & Dimova, 2012; Stieglitz et al., 2013; Tait et al., 2017).
2. Performing sediment equilibration experiments for radiometric tracers, and assuming that the tracer concentration in equilibrium with sediments equals c_p (e.g., Baudron et al., 2015).
3. Directly measuring the tracer concentration in porewater, usually within a meter of the sediment-water interface (e.g., Cable & Martin, 2008; Garcia-Orellana et al., 2014; Lamontagne & Cook, 2007; Rodellas et al., 2017). Where porewater concentration profiles are obtained, then it is common to use the shallowest measured porewater concentration, usually at 0.1–0.2 m depth (e.g., Cable & Martin, 2008; Martin et al., 2007).
4. Using seepage meters to collect samples of porewater that is actually flowing into the surface water (Michael et al., 2011).

It is clear that the concentration of porewater that is discharging to the surface water (c_p) is the concentration immediately below the sediment-water interface, and this concentration should be used in equation (2). Approaches (1) and (2) are not appropriate for short timescale recirculation processes as groundwater will have a different chemical signature to porewater, and accumulation and decay rates of radiometric tracers are unlikely to be in equilibrium within the porewater. The use of seepage meters allows direct measurement of the tracer concentration in exchanging porewater, but their installation may alter fluxes across the sediment-water interface, and thus also the tracer concentration (Smith et al., 2009).

Porewater profiles for radiometric tracers inevitably display tracer concentrations that increase with depth, with the greatest gradients occurring at the shallowest depths. Cook et al. (2018) showed that the depth at which porewater end-member concentration should be measured depended upon the chosen hydrodynamic dispersivity. Hydrodynamic dispersivity is a modeling parameter used to describe the scale length of mixing due to subsurface heterogeneity, and has been shown to increase with the scale of observation. For solute transport over a distance of 0.5–1.0 m (the typical depth of porewater profiles), the hydrodynamic dispersivity is approximately 0.005 m (Gelhar et al., 1992), which implies that the end-member concentration needs to be measured within 0.01 m of the sediment surface (the depth is twice the hydrodynamic dispersivity; Shanahan & Harleman, 1984). Collecting porewater at such shallow depths is possible, but the volume of water that can be reliably sampled is very small (Harvey & Fuller, 1998; Harvey et al., 2013) which can complicate analysis of some of the radiometric tracers. In the example presented by Cook et al. (2018), if the concentration at 0.05–0.1 m was used in equation (3) rather than that at 0.01 m, then the water flux would be underestimated by a factor of between 4 and 10.

Rather than directly measuring the end-member concentration, it is also possible to relate the tracer flux to the water flux by assuming either a value for the mean residence time of the porewater (t_p) or the volume of the mixing zone, $h\theta$ (e.g., Cook et al., 2006; Stieglitz et al., 2013; Webster et al., 1994). If porewater exchange is driven by tidal processes, for example, then a mean value for t_p can perhaps be estimated and used to estimate the water flux (Webster et al., 1994). However, for other driving forces, such as wave action or river flows, the residence time would need to be independently determined. h is similarly difficult to constrain and small errors in estimation of h can result in very large errors in the water flux (Figure 2). Without independent measurement of c_p, it may only be possible to define a minimum value for Q_p (the actual flux will be equal to this minimum value when the porewater residence time is long; equation (A5) in Appendix A). This also allows calculation of a minimum value for the volume of the mixing zone (from rearrangement of equation (A3); Bourke et al., 2014).
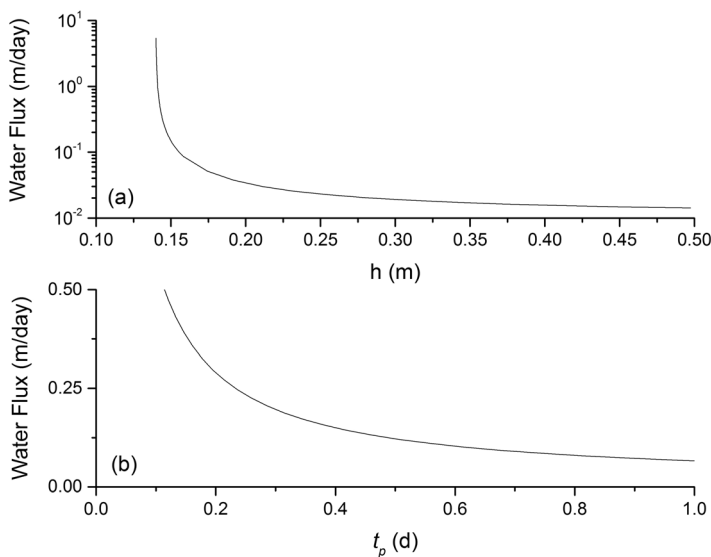
Figure 2. Estimated pore water flux, based on a measured net radon flux of $F = 50$ Bq m^{-2} d^{-1}, and assuming a single perfectly mixed reservoir. (a) Estimated water flux based on different assumed values of mixing zone depth, h. (b) Estimated water flux based on different assumed values of mixing zone mean residence time. Other model parameters are $c = 30$ Bq m^{-3}, $\gamma = 900$ Bq m^{-3} d^{-1}, and $\theta = 0.4$.

3.3. Porewater Exchange and Groundwater Inflow/Outflow as Discrete Pathways

If porewater exchange and groundwater inflow occur as discrete pathways, then the relationship between tracer flux and water flux will

depend on whether the tracer flux is measured for the entire surface water system (e.g., using a tracer mass balance), or at a point (e.g., using porewater profiles). If the tracer flux is measured based on a surface water balance, then the total net tracer flux is equal to

$$F = Q_g c_g + Q_p (c_p - c). \tag{4}$$

In this case, estimation of the water flux is difficult. For radiometric tracers, dividing the tracer flux by $(c_p - c)$ will overestimate the total water flux $(Q_g + Q_p)$, whereas dividing by c_g will underestimate the total water flux, as usually $(c_p - c) < c_g$. Notice also that if porewater exchange occurs but all the tracer flux is incorrectly assumed to be driven by groundwater inflows, dividing F by c_g will overestimate the groundwater flux (Q_g). For conservative tracers, dividing the tracer flux by c_g will provide an exact estimate of the groundwater flux (see equations (A6)–(A11), in Appendix A). If groundwater outflow occurs, then the net tracer flux is

$$F = Q_p (c_p - c) - Q_l c, \tag{5}$$

where Q_l is the groundwater outflow (L T^{-1}), and so dividing the total net tracer flux by $(c_p - c)$ will underestimate the porewater flux, Q_p (equations A12, A13).

When the tracer flux is measured using porewater profiles, the estimated flux will only capture the mechanism (i.e., porewater exchange or groundwater inflow) occurring at that given point. The water fluxes at each given point will be estimated by dividing by porewater or groundwater concentrations (in the porewater exchange and groundwater inflow zones, respectively), as described in sections 3.1 and 3.2. An estimation of the total water flux will thus require including sites that cover all the mechanisms and an appropriate estimation of the relative areas of porewater exchange and groundwater inflow and/or outflow zones.

3.4. Porewater Exchange and Groundwater Inflow Mix Prior to Discharge
If groundwater inflow mixes with exchanging porewater before entering surface water, then this mixing will influence the concentration at the sediment-water interface. The mass balance of the mixing zone can be expressed

$$Q_p c + Q_g c_g + \gamma h \theta = Q_p c_p + Q_g c_p + \lambda h \theta c_p, \tag{6}$$

where h (L) is the depth of the subsurface mixing zone, γ is the production rate within the subsurface (M T^{-1} L^{-3}), λ is the radioactive decay rate (T^{-1}), θ is the subsurface porosity, and other parameters are as previously defined (Figure 1d). The net tracer flux into the surface water is

$$F = Q_g c_p + Q_p (c_p - c). \tag{7}$$

Dividing by $(c_p - c)$ and substituting for c_p using (6) and rearranging then gives

$$\left(\frac{F}{c_p - c} - \frac{\lambda h \theta}{\varepsilon} \right) \frac{\varepsilon}{\varepsilon + 1} \leq Q_p + Q_g \leq \frac{F}{c_p - c}, \tag{8}$$

where $\varepsilon = \frac{c_g}{c} - 1$ (see equations (A15)–(A20) in Appendix A). Thus, for large values of $\frac{c_g}{c}$ (and hence also of ε), the total water flux can be approximated by dividing the net tracer flux by $(c_p - c)$. Although this approximation will overestimate the total water flux, the degree of overestimation will be small (notice that these overestimates will be less than if porewater and groundwater inflow do not mix prior to discharging to surface water; compare equations (A8) and (A17).) Of course, if $c_p \gg c$, then dividing the tracer flux by c_p rather than $(c_p - c)$ also provides a reasonable approximation of the water flux. Dividing F by c_g will overestimate Q_g, but the overestimation will be less than in the scenario where porewater and groundwater inflow do not mix prior to discharge (compare equations (A10) and (A22)). Of course, measurement of groundwater end-member concentrations must be made beyond the zone influenced by porewater exchange. For river systems, bank storage exchange can create mixing zones between groundwater and river water that can extend for many tens of meters (McCallum et al., 2010; Welch et al., 2013), and so measurements of groundwater end-members need to be made at greater distance. For conservative tracers, although porewater exchange alone will not create a tracer flux into the surface water, if groundwater and exchanging porewater interact, then concentrations within the porewater will still be affected by the porewater exchange flux, and so porewater concentrations can provide information on this flux (see equations (A17)–(A23) in

the Appendix A).The approaches described above for estimating water fluxes thus apply for conservative as well as radiometric tracers. If groundwater outflow occurs rather than groundwater inflow, dividing the total flux by $(c_p - c)$ will underestimate Q_p, and the degree of underestimation can potentially be large (see equations (A24)–(A26)).

3.5. Comparison Between Porewater Mixing and Flow Path Models

If porewater exchange occurs along discrete flow paths that do not mix, then c_p will be highly spatially variable, reflecting differences in subsurface residence times of the flow paths. In the case of a single flow path, the subsurface travel time is given by (A4), and so the concentration at the discharge point will be

$$c'_p = \frac{\gamma}{\lambda} - \left(\frac{\gamma}{\lambda} - c \right) e^{\frac{-h\theta\lambda}{Q_p}}. \tag{9}$$

In contrast, for the porewater mixing model (Figure 1b), the concentration of porewater is related to model parameters by

$$c_p = \frac{Q_p c + \gamma h\theta}{Q_p + \lambda h\theta}, \tag{10}$$

(see A1 in Appendix A for derivation). Minimum and maximum values of the ratio of c_p to c'_p are difficult to evaluate analytically, but it can be numerically shown that c_p/c'_p lies between 0.75 and 1.0. Since the porewater flux is proportional to $(c_p - c)$, the difference between calculated tracer fluxes from the two conceptualizations will be less than 25%, irrespective of the number of flow paths. However, this assumes that the value of c_p used by the mixing model is the mean (flux-weighted) concentration in porewater discharge. Clearly, collection of numerous samples to estimate the variability of porewater concentrations is recommended. Ultimately, this is likely to prove to be one of the limitations of the tracer approach.

4. Discussion

Where either porewater exchange or groundwater inflow to surface water occur in isolation, then the water flux is easily estimated by dividing the net tracer flux by an appropriately chosen end-member concentration. In the case of porewater exchange, this means measuring the tracer concentration within a few centimeters of the surface water-porewater interface. In the case of groundwater inflow, it means measuring the tracer concentration in samples representative of groundwater actually discharging to the system (i.e., after the tracer has undergone all geochemical transformations). However, when both porewater exchange and groundwater inflow occur, absolute estimation of fluxes is more difficult (Table 1). Dividing the net tracer flux by the difference between the porewater and surface water concentration $(c_p - c)$ will provide a maximum value for the combined flux $(Q_p + Q_g)$ (assuming that the tracer concentration in groundwater is higher than in porewater fluids, as is commonly the case). Dividing the net tracer flux by the groundwater

Table 1
Methods for Determination of Water Fluxes for Different Conceptual Models

Conceptual model	Tracer flux	Water flux estimation
Tracer flux only due to Q_g	$F = Q_g c_g$	$Q_g = \frac{F}{c_g}$
Tracer flux only due to Q_p[a]	$F = Q_p(c_p - c)$	$Q_p = \frac{F}{c_p - c}$
Both Q_g and Q_p contribute to tracer flux, but do not mix prior to discharge[a]	$F = Q_g c_g + Q_p(c_p - c)$	$\frac{F}{c_g} < Q_g + Q_p < \frac{F}{c_p - c}$
		$Q_g \leq \frac{F}{c_g}$
Both Q_l and Q_p contribute to tracer flux, but do not mix prior to discharge[a]	$F = Q_p(c_p - c) - Q_l c$	$Q_p > \frac{F}{c_p - c}$
Both Q_g and Q_p contribute to tracer flux and mix prior to discharge	$F = Q_g c_g + Q_p(c_p - c)$	$Q_g + Q_p \approx \frac{F}{c_p - c}$
		$Q_g \leq \frac{F}{c_g}$
Both Q_l and Q_p contribute to tracer flux and mix prior to discharge	$F = Q_p(c_p - c) - Q_l c$	$Q_p > \frac{F}{c_p - c}$

[a]For conservative tracers $c_p = c$, and so there is no tracer flux due to porewater exchange.

concentration will provide a maximum value for the groundwater flux (Q_g). In both cases, the maximum value will be closer to the actual flux, if porewater exchange and groundwater inflow completely mix prior to discharge. If porewater exchange and groundwater outflow occur concurrently, then dividing the net tracer flux by ($c_p − c$) will provide a minimum value for Q_p, which will be closer to the true value if porewater exchange and groundwater outflow occur as discrete processes and do not mix in the subsurface.

In most natural systems, both porewater exchange and groundwater exchange will occur, and estimation of exchange fluxes is considerably simplified if ancillary data can indicate that one of these contributions is small and can be neglected. Thus, some previous studies have argued that porewater exchange is negligible in comparison with groundwater inputs, based on low permeability of ocean or lake sediments, and thus assumed that the tracer flux is entirely due to groundwater inflow (e.g., Beck et al., 2007). Bourke et al. (2014) demonstrated the absence of groundwater inflow to a river based on comparison of groundwater and river levels, and hence used radon concentrations to estimate the porewater exchange flux. Some authors have argued that because radium sorbs to aquifer material at low salinities, it will not be influenced by inflow of entirely fresh groundwater and so in marine environments it is most sensitive to porewater exchange (e.g., Tait et al., 2017). Although this might be the case if fresh groundwater and porewater exchange represent discrete pathways (Figure 1c), it may be problematic where groundwater mixes with porewater exchange before discharging to surface water (Figure 1d). For most marine environments, groundwater discharges to the sea as brackish water (even in karstic springs; e.g., Garcia-Solsona et al., 2010) and thus concentrations of radium in groundwater (and thus groundwater fluxes) are not negligible (Rodellas et al., 2015; Cho & Kim, 2016). Our analysis does not consider the implications of mixing of water masses on radium sorption and desorption. If porewater exchange and groundwater have different salinities and mix in the subsurface prior to entering the surface water, then the relationship between radium flux and water flux becomes more complex, and the simple relationships developed in this paper cannot be applied. The effect of salinity on radium sorption remains a major unresolved issue in the many studies using radium as a tracer for these exchange processes.

A number of coastal zone studies acknowledge that porewater exchange and groundwater flows are not easily discriminated, and thus define the term *submarine groundwater discharge* (SGD) to comprise both sources (Burnett et al., 2003). However, to estimate this combined flux, they often divide the tracer flux by the groundwater concentration (e.g., McCoy et al., 2007; Swarzenski et al., 2007). Because the tracer concentration in porewater exchange usually will be much lower than the groundwater concentration, this approach will generally greatly underestimate the total subsurface water flux. As shown here, if the tracer flux is divided by ($c_p − c$), then the combined flux will be overestimated, and the degree of overestimation will depend upon the extent of subsurface mixing between groundwater inflow and porewater exchange and the difference between c_p and c_g.

A possible approach for discriminating between porewater and groundwater fluxes is based on either temporal or spatial variations of fluxes. Yu et al. (2013) assumed that the tracer flux due to porewater exchange is constant along a river, but that groundwater inflow varies spatially. They then assume that the smallest tracer flux along the river is equal to the tracer flux from porewater exchange, and that higher tracer fluxes in other river reaches must be due to groundwater inflow. Similarly, if groundwater inflow is constant in time and porewater exchange varies (perhaps due to variations in wind speed, in the case of a lake or estuary), then it might be possible to discriminate between porewater and groundwater fluxes based on temporal variation in the total flux. Others have tried to combine different tracers to differentiate porewater and groundwater fluxes (e.g., Colbert & Hammond, 2008; Stieglitz et al., 2013; Rodellas et al., 2017). The combination of radon and a conservative tracer such as chloride would appear to have potential, particularly in riverine settings.

Some of the problems in estimating water flux also apply if the water flux is then used to determine nutrient fluxes to surface water, or inputs of other solutes (e.g., trace metals). A number of studies have estimated nutrient discharge to surface water by multiplying the tracer-derived water flux (from both porewater exchange and groundwater flow) by the nutrient concentration in the end-member (e.g., Charette & Buesseler, 2004; Hwang et al., 2016; Santos et al., 2008; Tovar-Sánchez et al., 2014). Aside from the discussed uncertainties associated with the tracer-derived estimates of groundwater and porewater fluxes, it is often difficult to determine the most representative nutrient concentration in the end-member, since most of the dissolved compounds display nonconservative behavior due to biogeochemical transformations

occurring in the subsurface, and reaction rates can vary over small spatial scales (Santos et al., 2008; Slomp & Van Cappellen, 2004). Some studies have directly used the concentration in groundwater (e.g., measured from coastal wells) as the nutrient end-member (e.g., McCutchan et al., 2003; Tait et al., 2017). This will over-estimate the mean nutrient concentration in total water exchange (and thus the nutrient flux to surface water) if the nutrient concentration in fresh groundwater is greater than in recirculated porewater (e.g., Weinstein et al., 2011). Even when porewater concentrations are used, such samples are usually collected from between 0.2 and 1 m depth (Charette, 2007; Santos et al., 2008; Rodellas et al., 2014), and so the nutrient concentration in exchanging porewater may still be in error, due to the potential for biogeochemical transformations at shallower depths (Kennedy et al., 2009). If porewater and groundwater mix prior to discharge, then a better approach is to measure the nutrient concentration in very shallow porewater samples or from seepage meters (e.g., Gilmore et al., 2016). This should represent nutrient concentrations discharged after all biogeochemical processes have occurred, and also integrate the relative importance of porewater and groundwater sources. Of course, the concentration of nutrients in seawater needs to be subtracted from the porewater concentration, to determine the net nutrient flux.

Although the mixing models presented in this paper are idealized, they nevertheless are useful for demonstrating some of the complexities of estimating surface water-groundwater exchanges. Whether or not porewater and groundwater mix prior to discharge will depend on the nature of the surface water—groundwater system. The existence of discrete pathways for groundwater inflow is more likely in karstic or fractured rock systems. However, even in the absence of such geological heterogeneities, groundwater inflow to lakes and coastal waters tends to concentrate near the shoreline (Bokuniewicz, 2001; Genereux & Bandopadhyay, 2001; Pfannkuch & Winter, 1984), and so some separation between areas dominated by groundwater inflow and those dominated by porewater exchange will often occur (Michael et al., 2011). Mixing between groundwater inflow and porewater exchange is more likely when porewater exchange is driven by changes in surface water level (e.g., driven by tides, seiches, and wave action; Rosenberry et al., 2013) than under conditions of stable surface water level and stable bed forms, when zones of upwelling and downwelling are also likely to be stable (e.g., Savant et al., 1987). However, neither the flow path nor complete mixing model are likely to occur in reality, and the true situation probably lies somewhere in between these extremes. One of the key limitations of both of these models is that they assume that both groundwater inflow and porewater exchange are constant in time, which is not commonly the case. In river systems, changes in surface water levels give rise to bank storage exchange fluxes, which can be directed either towards or away from the river. Similarly, temporal changes in water levels in lakes and lagoons can be introduced by winds and tidal processes. The time of sampling can thus influence the exchange flux that is calculated, and sampling at different times is recommended in these systems.

5. Conclusions

Groundwater inflow and porewater exchange between surface water and underlying sediments can be estimated from tracer mass balances, although determining water fluxes from tracer fluxes requires careful selection of tracer end-member concentrations. The most appropriate method for determining these end-members will depend upon both the nature of the tracers and the nature of water exchange. If both porewater exchange and groundwater inflow occur, and mix prior to discharge, then the total water flux (porewater exchange plus groundwater inflow) usually can be approximated by dividing the tracer flux by the difference between the porewater and surface water concentration. If porewater exchange and groundwater inflow occur without mixing prior to discharge then the total water flux can only be constrained by minimum and maximum values. In both cases, maximum estimates of Q_g can also be separately determined. If river loss mixes with porewater prior to discharge, the minimum values of Q_p can be derived. Use of multiple tracers, and spatial and temporal replication should provide a more complete picture of exchange processes.

Appendix A

A1. Mixing Model for Porewater Exchange Without Groundwater Inflow or Outflow

In the case of a simple subsurface reservoir with constant volume that is perfectly mixed, the mass balance for a radiometric tracer only subject to porewater exchange is given by

$$Q_p c + \gamma h\theta = Q_p c_p + \lambda h\theta c_p, \tag{A1}$$

where Q_p (L T^{-1}) is the water flux (both into and out of the subsurface); c_p and c (M L^{-3}) are the tracer concentrations within the subsurface and within the surface water, respectively; h (L) is the depth of the subsurface mixing zone; γ is the production rate within the subsurface (M T^{-1} L^{-3}); λ is the radioactive decay rate (T^{-1}); and θ is the subsurface porosity. The left-hand side of equation (A1) represents the addition of tracer to the subsurface and the right-hand side represents the losses, which must balance the inputs at steady state. The net tracer flux (F; M L^{-2} T^{-1}) from the subsurface into the surface water is then

$$F = Q_p(c_p - c). \tag{A2}$$

We can calculate the relationship between water flux and tracer flux by solving (A1) and (A2) simultaneously (by elimination of c_p).

$$F = Q_p\left(\frac{\gamma h\theta - \lambda h\theta c}{Q_p + \lambda h\theta}\right) \tag{A3}$$

Thus, if we know the residence time of porewater (t_p), then we can use the relationship between mean residence time and Q_p:

$$t_p = \frac{h\theta}{Q_p}, \tag{A4}$$

to develop a relationship between F, Q_p, and t_p:

$$F = Q_p\left(\frac{\gamma - \lambda c}{t_p^{-1} + \lambda}\right). \tag{A5}$$

Notice that for conservative tracers $\gamma = \lambda = 0$ and so $c_p = c$, implying that there is no net tracer flux ($F = 0$).

A2. Porewater Exchange and Groundwater Inflow as Discrete Pathways
Suppose that porewater exchange and groundwater inflow occur as discrete pathways, but porewater is internally well-mixed. The mass balance of the porewater mixing zone is simply given by (A1). The net tracer flux into the surface water is

$$F = Q_p(c_p - c) + Q_g c_g \tag{A6}$$

and so

$$\frac{F}{c_p - c} = Q_p + Q_g \frac{c_g}{c_p - c}. \tag{A7}$$

Since the residence time of groundwater in the subsurface is long, radiometric tracers with short half-lives will usually be at secular equilibrium, so that $c_g = \gamma/\lambda$. Substituting for c_p using (A1) and for γ using $\gamma = \lambda c_g$ then gives

$$\frac{F}{c_p - c} = Q_p + Q_g\left(\frac{c_g}{c_g - c}\right)\left(\frac{Q_p + \lambda h\theta}{\lambda h\theta}\right) > Q_p + Q_g. \tag{A8}$$

Similarly

$$\frac{F}{c_g} = Q_g + Q_p \frac{c_p - c}{c_g} \tag{A9}$$

and thus,

$$\frac{F}{c_g} = Q_g + Q_p \frac{\lambda h\theta}{Q_p + \lambda h\theta} \frac{c_g - c}{c_g}, \tag{A10}$$

so

$$Q_g \leq \frac{F}{c_g} < Q_g + Q_p. \tag{A11}$$

The equality in (A11) occurs for conservative tracers, for which $\gamma = \lambda = 0$.

A3. Porewater Exchange and Groundwater Outflow as Discrete Pathways

Suppose that porewater exchange and groundwater outflow occur as discrete pathways, but porewater is internally well-mixed. The mass balance of the porewater mixing zone is given by (A1). The net tracer flux into the surface water is

$$F = Q_p(c_p - c) - Q_l c, \tag{A12}$$

where Q_l (L T^{-1}) is the rate of groundwater outflow. Thus,

$$\frac{F}{c_p - c} = Q_p - Q_l \frac{c}{c_p - c} < Q_p. \tag{A13}$$

A4. Porewater Exchange Mixes With Groundwater Inflow

If both porewater exchange and groundwater inflow mix before discharging to surface water, then the mass balance of the mixing zone can be expressed

$$Q_p c + Q_g c_g + \gamma h \theta = Q_p c_p + Q_g c_p + \lambda h \theta c_p. \tag{A14}$$

The net tracer flux into the surface water is

$$F = Q_p(c_p - c) + Q_g c_p \tag{A15}$$

and so

$$\frac{F}{c_p - c} = Q_p + Q_g \frac{c_p}{c_p - c}. \tag{A16}$$

Substituting for c_p using (A14) and recognizing that $\gamma = c_g \lambda$ gives

$$\frac{F}{c_p - c} = Q_p + Q_g \frac{c_g}{c_g - c} \frac{Q_p \frac{c}{c_g} + Q_g + \lambda h \theta}{Q_g + \lambda h \theta} \geq Q_p + Q_g. \tag{A17}$$

We can also rewrite (A17) as

$$\frac{F}{c_p - c} = (Q_p + Q_g)\left(1 + \frac{Q_g c}{Q_g(c_g - c) + \gamma h \theta - \lambda h \theta c}\right) + \frac{\lambda h \theta Q_g c}{Q_g(c_g - c) + \gamma h \theta - \lambda h \theta c}. \tag{A18}$$

Thus (assuming $\gamma > \lambda c$), we get

$$Q_p + Q_g \leq \frac{F}{c_p - c} \leq (Q_p + Q_g)\left(1 + \frac{1}{\varepsilon}\right) + \frac{\lambda h \theta}{\varepsilon} \tag{A19}$$

and so

$$\left(\frac{F}{c_p - c} - \frac{\lambda h \theta}{\varepsilon}\right)\frac{\varepsilon}{\varepsilon + 1} \leq Q_p + Q_g \leq \frac{F}{c_p - c}. \tag{A20}$$

where $\varepsilon = \frac{c_g}{c} - 1$. Thus for large values of $\frac{c_g}{c}$ (and hence also of ε), $Q_p + Q_g$ is reasonably well constrained.

Dividing F by c_g gives

$$\frac{F}{c_g} = Q_p \frac{c_p - c}{c_g} + Q_g \frac{c_p}{c_g}. \tag{A21}$$

Substituting for c_p using (A14) and using $\gamma = c_g \lambda$ then gives

$$\frac{F}{c_g} = Q_g + Q_p \frac{\lambda h \theta}{Q_p + Q_g + \lambda h \theta} \frac{c_g - c}{c_g} \tag{A22}$$

and hence,

$$Q_g \leq \frac{F}{c_g} < Q_g + Q_p. \tag{A23}$$

A5. Porewater Exchange Mixes With Groundwater Outflow

If a net groundwater flow occurs from the surface water to the groundwater, and porewater exchange and groundwater outflow completely mix within the porewater zone, then the mass balance of the mixing zone can be expressed

$$Q_p c + Q_l c + \gamma h\theta = Q_p c_p + Q_l c_p + \lambda h\theta c_p, \tag{A24}$$

where Q_l (L T^{-1}) is the rate of groundwater outflow. The net tracer flux into the surface water is

$$F = Q_p(c_p - c) - Q_l c \tag{A25}$$

and so,

$$\frac{F}{c_p - c} = Q_p - Q_l \frac{c}{c_p - c} = Q_p - Q_l \left(\frac{c}{c_g - c}\right)\left(\frac{Q_p + Q_l + \lambda h\theta}{\lambda h\theta}\right) < Q_p. \tag{A26}$$

References

Baudron, P., Cockenpot, S., Lopez-Castejon, F., Radakovitch, O., Gilabert, J., Mayer, A., et al. (2015). Combining radon, short-lived radium isotopes and hydrodynamic modeling to assess submarine groundwater discharge from an anthropized semiarid watershed to a Mediterranean lagoon (Mar Menor, SE Spain). *Journal of Hydrology*, *525*, 55–71. https://doi.org/10.1016/j.jhydrol.2015.03.015

Beck, A. J., Rapaglia, J. P., Cochran, J. K., & Bokuniewicz, H. J. (2007). Radium mass-balance in Jamaica Bay, NY: Evidence for a substantial flux of submarine groundwater. *Marine Chemistry*, *106*(3–4), 419–441. https://doi.org/10.1016/j.marchem.2007.03.008

Bokuniewicz, H. (2001). Toward a coastal ground-water typology. *Journal of Sea Research*, *46*(2), 99–108. https://doi.org/10.1016/S1385-1101(01)00074-0

Boulton, A. J., Findlay, S., Marmonier, P., Stanley, E. H., & Valett, H. M. (1998). The functional significance of the hyporheic zone in streams and rivers. *Annual Review of Ecology and Systematics*, *29*, 59–81.

Bourke, S. A., Cook, P. G., Shanafield, M., Dogramaci, S., & Clark, J. F. (2014). Characterisation of hyporheic exchange in a losing stream using radon-222. *Journal of Hydrology*, *519*, 94–105. https://doi.org/10.1016/j.jhydrol.2014.06.057

Burnett, W. C., Bokuniewicz, H., Huettel, M., Moore, W. S., & Taniguchi, M. (2003). Groundwater and pore water inputs to the coastal zone. *Biogeochemistry*, *66*(1/2), 3–33. https://doi.org/10.1023/B:BIOG.0000006066.21240.53

Burnett, W. C., & Dimova, N. (2012). A radon-based mass balance model for assessing groundwater inflows to lakes. In M. Taniguchi & T. Shiraiwa (Eds.), *The dilemma of boundaries* (pp. 55–66). Tokyo, Japan: Springer.

Burnett, W. C., & Dulaiova, H. (2003). Estimating the dynamics of groundwater input into the coastal zone via continuous radon-222 measurements. *Journal of Environmental Radioactivity*, *69*(1–2), 21–35. https://doi.org/10.1016/S0265-931X(03)00084-5

Cable, J. E., & Martin, J. B. (2008). In situ evaluation of nearshore marine and fresh pore water transport into Flamengo Bay, Brazil. *Estuarine, Coastal and Shelf Science*, *76*(3), 473–483. https://doi.org/10.1016/j.ecss.2007.07.045

Cai, P., Shi, X., Moore, W. S., Peng, S., Wang, G., & Dai, M. (2014). 224Ra:228Th disequilibrium in coastal sediments: Implications for solute transfer across the sediment–water interface. *Geochimica et Cosmochimica Acta*, *125*, 68–84. https://doi.org/10.1016/j.gca.2013.09.029

Cardenas, M. B., & Wilson, J. L. (2007). Exchange across a sediment-water interface with ambient groundwater discharge. *Journal of Hydrology*, *346*, 69–80.

Cartwright, I., Hofmann, H., Sirianos, M. A., Weaver, T. R., & Simmons, C. T. (2011). Geochemical and 222Rn constraints on baseflow to the Murray River, Australia, and timescales for the decay of low-salinity groundwater lenses. *Journal of Hydrology*, *405*(3–4), 333–343. https://doi.org/10.1016/j.jhydrol.2011.05.030

Cerdà-Domènech, M., Rodellas, V., Folch, A., & Garcia-Orellana, J. (2017). Constraining the temporal variations of Ra isotopes and Rn in the groundwater end-member: Implications for derived SGD estimates. *Science of the Total Environment*, *595*, 849–857. https://doi.org/10.1016/j.scitotenv.2017.03.005

Cey, E. E., Rudolph, D. L., Parkin, G. W., & Aravena, R. (1998). Quantifying groundwater discharge to a small perennial stream in southern Ontario, Canada. *Journal of Hydrology*, *210*(1–4), 21–37. https://doi.org/10.1016/S0022-1694(98)00172-3

Charette, M. A. (2007). Hydrologic forcing of submarine groundwater discharge: Insight from a seasonal study of radium isotopes in a groundwater-dominated salt marsh estuary. *Limnology and Oceanography: Methods*, *52*(1), 230–239.

Charette, M. A., & Buesseler, K. O. (2004). Submarine groundwater discharge of nutrients and copper to an urban subestuary of Chesapeake Bay (Elizabeth River). *Limnology and Oceanography: Methods*, *49*(2), 376–385.

Charette, M. A., Henderson, P. B., Breier, C. F., & Liu, Q. (2013). Submarine groundwater discharge in a river-dominated Florida estuary. *Marine Chemistry*, *156*, 3–17. https://doi.org/10.1016/j.marchem.2013.04.001

Cho, H.-M., & Kim, G. (2016). Determining groundwater Ra end-member values for the estimation of the magnitude of submarine groundwater discharge using Ra isotope tracers. *Geophysical Research Letters*, *43*, 3865–3871. https://doi.org/10.1002/2016GL068805

Colbert, S. L., & Hammond, D. E. (2008). Shoreline and seafloor fluxes of water and short-lived Ra isotopes to surface water of San Pedro Bay, CA. *Marine Chemistry*, *108*(1–2), 1–17. https://doi.org/10.1016/j.marchem.2007.09.004

Cook, P. G. (2013). Estimating groundwater discharge to rivers from river chemistry surveys. *Hydrological Processes*, *27*(25), 3694–3707. https://doi.org/10.1002/hyp.9493

Cook, P. G., Favreau, G., Dighton, J. C., & Tickell, S. (2003). Determining natural groundwater influx to a tropical river using radon, chlorofluorocarbons and ionic environmental tracers. *Journal of Hydrology*, *277*(1–2), 74–88. https://doi.org/10.1016/S0022-1694(03)00087-8

Cook, P. G., Lamontagne, S., Berhane, D., & Clark, J. F. (2006). Quantifying groundwater discharge to Cockburn River, southeastern Australia, using dissolved gas tracers 222 Rn and SF 6. *Water Resources Research*, *42*, W10411. https://doi.org/10.1029/2006WR004921

Cook, P. G., Rodellas, V., Andrisoa, A., & Stieglitz, T. C. (2018). Exchange across the sediment-water interface quantified from porewater tracer profiles. *Journal of Hydrology*, https://doi.org/10.1016/j.jhydrol.2018.02.070, in press.

Dimova, N. T., Burnett, W. C., Chanton, J. P., & Corbett, J. E. (2013). Application of radon-222 to investigate groundwater discharge into small shallow lakes. *Journal of Hydrology*, *486*, 112–122. https://doi.org/10.1016/j.jhydrol.2013.01.043

Frei, S., & Gilfedder, B. S. (2015). FINIFLUX: An implicit finite element model for quantification of groundwater fluxes and hyporheic exchange in streams and rivers using radon. *Water Resources Research*, *51*, 6776–6786. https://doi.org/10.1002/2015WR017212

Garcia-Orellana, J., Cochran, J. K., Bokuniewicz, H., Daniel, J. W. R., Rodellas, V., & Heilbrun, C. (2014). Evaluation of ^{224}Ra as a tracer for submarine groundwater discharge in Long Island Sound (NY). *Geochimica et Cosmochimica Acta*, *141*, 314–330. https://doi.org/10.1016/j.gca.2014.05.009

Genereux, D. P., Hemond, H. F., & Mulholland, P. J. (1993). Use of radon-222 and calcium as tracers in a three-end-member mixing model for streamflow generation on the West Fork of Walker Branch Watershed. *Journal of Hydrology*, *142*, 167–211. https://doi.org/10.1016/0022-1694(93)90010-7

Garcia-Solsona, E., Garcia-Orellana, J., Masqué, P., Rodellas, V., Mejías, M., Ballesteros, B., et al. (2010). Groundwater and nutrient discharge through karstic coastal springs (Castelló, Spain). *Biogeosciences*, *7*(9), 2625–2638. https://doi.org/10.5194/bg-7-2625-2010

Gelhar, L. W., Welty, C., & Rehfeldt, K. R. (1992). A critical review of data on field-scale dispersion in aquifers. *Water Resources Research*, *28*(7), 1955–1974. https://doi.org/10.1029/92WR00607

Genereux, D., & Bandopadhyay, I. (2001). Numerical investigation of lake bed seepage patterns: Effects of porous medium and lake properties. *Journal of Hydrology*, *241*(3–4), 286–303. https://doi.org/10.1016/S0022-1694(00)00380-2

Gilmore, T. E., Genereux, D. P., Solomon, D. K., Solder, J. E., Kimball, B. A., Mitasova, H., et al. (2016). Quantifying the fate of agricultural nitrogen in an unconfined aquifer: Stream-based observations at three measurement scales. *Water Resources Research*, *52*, 1961–1983. https://doi.org/10.1002/2015WR017599

Gonneea, M. E., Mulligan, A. E., & Charette, M. A. (2013). Seasonal cycles in radium and barium within a subterranean estuary: Implications for groundwater derived chemical fluxes to surface waters. *Geochimica et Cosmochimica Acta*, *119*, 164–177. https://doi.org/10.1016/j.gca.2013.05.034

Harvey, J. W., Böhlke, J. K., Voytek, M. A., Scott, D., & Tobias, C. R. (2013). Hyporheic zone denitrification: Controls on effective reaction depth and contribution to whole-stream mass balance. *Water Resources Research*, *49*, 6298–6316. https://doi.org/10.1002/wrcr.20492

Harvey, J. W., & Fuller, C. C. (1998). Effect of enhanced manganese oxidation in the hyporheic zone on basin-scale geochemical mass balance. *Water Resources Research*, *34*(4), 623–636. https://doi.org/10.1029/97WR03606

Hwang, D.-W., Lee, I.-S., Choi, M., & Kim, T.-H. (2016). Estimating the input of submarine groundwater discharge (SGD) and SGD-derived nutrients in Geoje Bay, Korea using 222Rn-Si mass balance model. *Marine Pollution Bulletin*, *110*(1), 119–126. https://doi.org/10.1016/j.marpolbul.2016.06.073

Kennedy, C. D., Genereux, D. P., Corbett, D. R., & Mitasova, H. (2009). Spatial and temporal dynamics of coupled groundwater and nitrogen fluxes through a streambed in an agricultural watershed. *Water Resources Research*, *45*, W09401. https://doi.org/10.1029/2008WR007397

Krabbenhoft, D. P., Bowser, C. J., Anderson, M. P., & Valley, J. W. (1990). Estimating groundwater exchange with lakes: 1. The stable isotope mass balance method. *Water Resources Research*, *26*(10), 2445–2453. https://doi.org/10.1029/WR026i010p02445

Lamontagne, S., & Cook, P. G. (2007). Estimation of hyporheic water residence time in situ using 222 Rn disequilibrium. *Limnology and Oceanography: Methods*, *5*(11), 407–416. https://doi.org/10.4319/lom.2007.5.407

Loheide, S. P., & Gorelick, S. M. (2006). Quantifying stream-aquifer interactions through the analysis of remotely sensed thermographic profiles and in situ temperature histories. *Environmental Science and Technology*, *40*, 3336–3341. https://doi.org/10.1021/ES0522074

Martin, J. B., Cable, J. E., Jaeger, J., Hartl, K., & Smith, C. G. (2006). Thermal and chemical evidence for rapid water exchange across the sediment-water interface by bioirrigation in the Indian River Lagoon, Florida. *Limnology and Oceanography: Methods*, *51*(3), 1332–1341.

Martin, J. B., Cable, J. E., Smith, C., Roy, M., & Cherrier, J. (2007). Magnitudes of submarine groundwater discharge from marine and terrestrial sources: Indian River Lagoon, Florida. *Water Resources Research*, *43*, W05440. https://doi.org/10.1029/2006WR005266

McCallum, J. L., Cook, P. G., Berhane, D., Rumpf, C., & McMahon, G. (2012). Quantifying groundwater flows to streams using differential flow gaugings and water chemistry. *Journal of Hydrology*, *416–417*, 118–132.

McCallum, J. L., Cook, P. G., Brunner, P., & Berhane, D. (2010). Solute dynamics during bank storage flows and implications for chemical base flow separation. *Water Resources Research*, *46*, W07541. https://doi.org/10.1029/2009WR008539

McCoy, C. A., Corbett, D. R., Cable, J. E., & Spruill, R. K. (2007). Hydrogeological characterization of southeast coastal plain aquifers and groundwater discharge to Onslow Bay, North Carolina (USA). *Journal of Hydrology*, *339*(3–4), 159–171. https://doi.org/10.1016/j.jhydrol.2007.03.008

McCutchan, J. H., Saunders, J. F., Pribyl, A. L., & Lewis, W. M. (2003). Open-channel estimation of denitrification. *Limnology and Oceanography: Methods*, *1*(1), 74–81. https://doi.org/10.4319/lom.2003.1.74

Michael, H. A., Charette, M. A., & Harvey, C. F. (2011). Patterns and variability of groundwater flow and radium activity at the coast: A case study from Waquoit Bay, Massachusetts. *Marine Chemistry*, *127*(1–4), 100–114. https://doi.org/10.1016/j.marchem.2011.08.001

Moore, W. S. (2006). Radium isotopes as tracers of submarine groundwater discharge in Sicily. *Continental Shelf Research*, *26*(7), 852–861. https://doi.org/10.1016/j.csr.2005.12.004

Moore, W. S., Sarmiento, J. L., & Key, R. M. (2008). Submarine groundwater discharge revealed by 228Ra distribution in the upper Atlantic Ocean. *Nature Geoscience*, *1*(5), 309–311.

Morrice, J. A., Valett, H. M., Dahm, C. N., & Campana, M. E. (1997). Alluvial characteristics, groundwater-surface water exchange and hydrological retention in headwater streams. *Hydrological Processes*, *11*(3), 253–267.

Oxtobee, J. P., & Novakowski, K. (2002). A field investigation of groundwater/surface water interaction in a fractured bedrock environment. *Journal of Hydrology*, *269*(3–4), 169–193. https://doi.org/10.1016/S0022-1694(02)00213-5

Pfannkuch, H. O., & Winter, T. C. (1984). Effect of anisotropy and groundwater system geometry on seepage through lakebeds. *Journal of Hydrology*, *75*(1–4), 213–237. https://doi.org/10.1016/0022-1694(84)90051-9

Rodellas, V., Garcia-Orellana, J., Masqué, P., Feldman, M., & Weinstein, Y. (2015). Submarine groundwater discharge as a major source of nutrients to the Mediterranean Sea. *Proceedings of the National Academy of Sciences of the United States of America*, *112*(13), 3926–3930. https://doi.org/10.1073/pnas.1419049112

Rodellas, V., Garcia-Orellana, J., Trezzi, G., Masqué, P., Stieglitz, T. C., Bokuniewicz, H., et al. (2017). Using the radium quartet to quantify submarine groundwater discharge and porewater exchange. *Geochimica et Cosmochimica Acta*, *196*, https://doi.org/10.1016/j.gca.2016.09.016

Rodellas, V., Garcia-Orellana, J., Tovar-Sánchez, A., Basterretxea, G., López-Garcia, J. M., Sánchez-Quiles, D., et al. (2014). Submarine ground-water discharge as a source of nutrients and trace metals in a Mediterranean Bay (Palma Beach, Balearic Islands). *Marine Chemistry*, *160*, 56–66. https://doi.org/10.1016/j.marchem.2014.01.007

Rosenberry, D. O., Sheibley, R. W., Cox, S. E., Simonds, F. W., & Naftz, D. L. (2013). Temporal variability of exchange between groundwater and surface water based on high-frequency direct measurements of seepage at the sediment-water interface. *Water Resources Research*, *49*, 2975–2986. https://doi.org/10.1002/wrcr.20198

Santos, I. R., Burnett, W. C., Chanton, J., Dimova, N., & Peterson, R. N. (2009). Land or ocean? Assessing the driving forces of submarine groundwater discharge at a coastal site in the Gulf of Mexico. *Journal of Geophysical Research*, *114*, C04012. https://doi.org/10.1029/2008JC005038

Santos, I. R., Burnett, W. C., Chanton, J., Mwashote, B., Suryaputra, I. G. N. A., & Dittmar, T. (2008). Nutrient biogeochemistry in a Gulf of Mexico subterranean estuary and groundwater-derived fluxes to the coastal ocean. *Limnology and Oceanography: Methods*, *53*(2), 705–718.

Santos, I. R., Eyre, B. D., & Huettel, M. (2012). The driving forces of porewater and groundwater flow in permeable coastal sediments: A review. *Estuarine, and Coastal Shelf Science*, *98*, 1–15. https://doi.org/10.1016/j.ecss.2011.10.024

Santos, I. R., Bryan, K. R., Pilditch, C. A., & Tait, D. R. (2014). Influence of porewater exchange on nutrient dynamics in two New Zealand estuarine intertidal flats. *Marine Chemistry*, *167*, 57–70. https://doi.org/10.1016/j.marchem.2014.04.006

Savant, S. A., Reible, D. D., & Thibodeaux, L. J. (1987). Convective transport within stable river sediments. *Water Resources Research*, *23*(9), 1763–1768. https://doi.org/10.1029/WR023i009p01763

Schmidt, A., Stringer, C. E., Haferkorn, U., & Schubert, M. (2009). Quantification of groundwater discharge into lakes using radon-222 as naturally occurring tracer. *Environmental Geology*, *56*(5), 855–863. https://doi.org/10.1007/s00254-008-1186-3

Shanahan, P., & Harleman, D. R. F. (1984). Transport in lake water quality modeling. *Journal of Environmental Engineering*, *110*(1), 42–57. https://doi.org/10.1061/(ASCE)0733-9372(1984)110:1(42)

Slomp, C. P., & Van Cappellen, P. (2004). Nutrient inputs to the coastal ocean through submarine groundwater discharge: Controls and potential impact. *Journal of Hydrology*, *295*(1–4), 64–86. https://doi.org/10.1016/j.jhydrol.2004.02.018

Smith, A. J., Herne, D. E., & Turner, J. V. (2009). Wave effects on submarine groundwater seepage measurement. *Advances in Water Resources*, *32*(6), 820–833. https://doi.org/10.1016/j.advwatres.2009.02.003

Stieglitz, T. C., van Beek, P., Souhaut, M., & Cook, P. G. (2013). Karstic groundwater discharge and seawater recirculation through sediments in shallow coastal Mediterranean lagoons, determined from water, salt and radon budgets. *Marine Chemistry*, *156*, 73–84. https://doi.org/10.1016/j.marchem.2013.05.005

Swarzenski, P. W., Simonds, F. W., Paulson, A. J., Kruse, S., & Chris, R. (2007). Geochemical and geophysical examination of submarine groundwater discharge and associated nutrient loading estimates into Lynch Cove, Hood Canal, WA. *Environmental Science and Technology*, *41*, 7022–7029. https://doi.org/10.1021/ES070881A

Tait, D. R., Maher, D. T., Sanders, C. J., & Santos, I. R. (2017). Radium-derived porewater exchange and dissolved N and P fluxes in mangroves. *Geochimica et Cosmochimica Acta*, *200*, 295–309. https://doi.org/10.1016/j.gca.2016.12.024

Taniguchi, M., & Fukuo, Y. (1996). An effect of seiche on groundwater seepage rate into Lake Biwa, Japan. *Water Resources Research*, *32*(2), 333–338.

Tovar-Sánchez, A., Basterretxea, G., Rodellas, V., Sánchez-Quiles, D., García-Orellana, J., Masqué, P., et al. (2014). Contribution of groundwater discharge to the coastal dissolved nutrients and trace metal concentrations in Majorca Island: Karstic vs detrital systems. *Environmental Science and Technology*, *48*(20), 11819–11827. https://doi.org/10.1021/es502958t

Trezzi, G., Garcia-Orellana, J., Santos-Echeandia, J., Rodellas, V., Garcia-Solsona, E., Garcia-Fernandez, G., et al. (2016). The influence of a metal-enriched mining waste deposit on submarine groundwater discharge to the coastal sea. *Marine Chemistry*, *178*, 35–45.

Webster, I. T., Hancock, G. J., & Murray, A. S. (1994). Use of radium isotopes to examine pore-water exchange in an estuary. *Limnology and Oceanography*, *39*(8), 1917–1927.

Weinstein, Y., Yechieli, Y., Shalem, Y., Burnett, W. C., Swarzenski, P. W., & Herut, B. (2011). What is the role of fresh groundwater and recirculated seawater in conveying nutrients to the coastal ocean? *Environmental Science and Technology*, *45*(12), 5195–5200. https://doi.org/10.1021/es104394r

Welch, C., Cook, P. G., Harrington, G. A., & Robinson, N. I. (2013). Propagation of solutes and pressure into aquifers following river stage rise. *Water Resources Research*, *49*, 5246–5259. https://doi.org/10.1002/wrcr.20408

Wilson, A. M., Woodward, G. L., & Savidge, W. B. (2016). Using heat as a tracer to estimate the depth of rapid porewater advection below the sediment-water interface. *Journal of Hydrology*, *538*, 743–753. https://doi.org/10.1016/j.jhydrol.2016.04.047

Wu, Y., Wen, X., & Zhang, Y. (2004). Analysis of the exchange of groundwater and river water by using Radon-222 in the middle Heihe Basin of northwestern China. *Environmental Geology*, *45*(5), 647–653. https://doi.org/10.1007/s00254-003-0914-y

Yu, M. C. L., Cartwright, I., Braden, J. L., & de Bree, S. T. (2013). Examining the spatial and temporal variation of groundwater inflows to a valley-to-floodplain river using 222Rn, geochemistry and river discharge: The Ovens River, southeast Australia. *Hydrology and Earth System Sciences*, *17*(12), 4907–4924. https://doi.org/10.5194/hess-17-4907-2013