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Using radium isotopes to characterize water ages and coastal mixing rates: A sensitivity analysis

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Abstract

Numerous studies have used naturally occurring Ra isotopes (^{223}Ra, ^{224}Ra, ^{226}Ra, and ^{228}Ra, with half-lives of 11.4 d, 3.7 d, 1600 y, and 5.8 y, respectively) to quantify water mass ages, coastal ocean mixing rates, and submarine groundwater discharge (SGD). Using Monte Carlo models, this study investigated how uncertainties in Ra isotope activities and the derived activity ratios (AR) arising from analytical uncertainty and natural variability affect the uncertainty associated with Ra-derived water ages and eddy diffusion coefficients, both of which can be used to calculate SGD. Analytical uncertainties associated with ^{224}Ra, ^{226}Ra, and ^{228}Ra activities were reported in most published studies to be less than 10% of sample activity; those reported for ^{223}Ra ranged from 7% to 40%. Relative uncertainty related to natural variability—estimated from the variability in ^{223}Ra and ^{224}Ra activities of replicate field samples—ranged from 15% to 50% and was similar for ^{223}Ra activity, ^{224}Ra activity, and the ^{224}Ra/^{223}Ra AR. Our analysis revealed that AR-based water ages shorter than 3-5 d often have relative uncertainties greater than 100%, potentially limiting their utility. Uncertainties in eddy diffusion coefficients estimated based on cross-shore gradients in short-lived Ra isotope activity were greater when fewer points were used to determine the linear trend, when the coefficient of determination (R^2) was low, and when ^{224}Ra, rather than ^{223}Ra, was used. By exploring the uncertainties associated with Ra-derived water ages and eddy diffusion coefficients, this study will enable researchers to apply these methods more effectively and to reduce uncertainty.

Radium (Ra) is present at elevated concentrations in brackish to saline coastal groundwater (e.g., Charette et al. 2001; Crotwell and Moore 2003; Kim et al. 2008) and in locations where sediments come into contact with brackish to saline water, such as river estuaries with a high sediment load (e.g., Li and Chan 1979; Hancock and Murray 1996; Moore 1997). Over the past decade, several different Ra-based mass balance methods have been used to quantify submarine groundwater discharge (SGD), in some cases incorporating the calculation of a Ra-based water age (Moore 2000a; Moore et al. 2006) or horizontal eddy diffusion coefficient (Moore 2000b). Ra-based methods of calculating water ages and eddy diffusion coefficients have been used to infer coastal residence times and mixing rates and then derive SGD fluxes in published studies of coastal waters in the continental United States (e.g., Charette et al. 2001; Dulaiova et al. 2006; Boehm et al. 2006), Hawai`i (Paytan et al. 2006; Street et al. 2008; Knee et al. 2008), Europe (Garcia-Solsona 2008a, 2010a,b; Rapaglia et al. 2010), Brazil (Windom et al. 2006; Moore and de Oliveira 2008), South Korea (Kim et al. 2005), Israel (Shellenbarger et al. 2006; Weinstein et al. 2006), and other locations worldwide.

Water mass ages can be calculated based on Ra activity ratios (AR) in two distinct ways, depending on whether Ra inputs from SGD are localized at the shoreline (Eq. 1; Moore 2000a) or occur over the entire study area, such as in a well-

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mixed estuary (Eq. 2; Moore et al. 2006). Water age (T), or the amount of time that has elapsed since Ra became disconnected from its source (aquifer substrate) and entered the coastal ocean, can be calculated as:

$$T = \frac{\ln(AR_{co}) - \ln(AR_{gw})}{\lambda_S - \lambda_L} \quad (1)$$

where AR_{co} and AR_{gw} are the ratio of the shorter-lived Ra isotope activity to the longer-lived Ra isotope activity in the two end-members of the mixing model (coastal ocean water and discharging groundwater, respectively) and λ_S and λ_L are the decay constants (d^{-1}) of the shorter- and longer-lived isotopes, respectively (Moore 2000a). For a well-mixed estuary, ARs can be used to estimate T as follows (Moore et al. 2006):

$$T = \frac{AR_{gw} - AR_{co}}{AR_{co} \times \lambda_S} \quad (2)$$

Both Eqs. 1 and 2 assume that Ra activities and the ARs of shorter- to longer-lived isotopes are highest in the Ra source (groundwater or Ra-bearing sediments), and that these activities and ARs are elevated in coastal receiving waters relative to offshore waters as a result of submarine groundwater discharge (SGD) or desorption of Ra from sediments. Both equations assume that Ra entering the water has a uniform AR and that the receiving water parcel also has a uniform AR. The difference between these two methods is that Eq. 1 assumes that Ra is only added to coastal water at the shoreline, whereas Eq. 2 assumes that Ra additions occur continuously over a wider area, such as would occur in a marsh, estuary, or bay with multiple springs (Moore et al. 2006). Previous work (Hougham and Moran 2007) has shown that Eq. 1 can underestimate the average age of a water mass composed of a mixture of waters with different ages. Additionally, it is important to note that water age and water residence time are different ways of quantifying mixing within a water body, and when both are calculated for a water body, they may not yield the same results (Moore et al. 2006). Water age is the amount of time that has passed since a parcel of water entered the water body, whereas residence time is the time that it takes for a parcel of water to leave the water body through its outlet to the sea (Monsen et al. 2002; Moore et al. 2006).

Cross-shore gradients in short-lived Ra isotope activity can also be used to estimate the horizontal eddy diffusion coefficient (K_h; km^2d^{-1}), a measure of coastal mixing (Moore 2000*b*) that can be used to derive SGD. The 'eddy diffusion method' (Moore 2000*b*) is based upon the observation that, mathematically, the shoreline can behave like a diffusive source of Ra to the coastal ocean. The combined effects of dispersion and radioactive decay along a shore-perpendicular transect result in a log-linear decrease in the activity of short-lived Ra isotopes (^{223}Ra or ^{224}Ra) with distance from shore, and the change in activity with distance from shore can be used to determine K_h. Similarly, the gradient in the natural log of the ^{224}Ra/^{223}Ra AR with distance from shore can also be used to calculate K_h (Burnett et al. 2008). Although the uncertainty associated with an AR is generally higher than that associated with the activity of a single isotope (Taylor 1997), this method is advantageous when only the AR, but not the individual activities, are measured—for example, when a large but unknown volume of water is sampled for Ra by towing a bag of Ra-collecting fibers behind a boat (W.C. Burnett pers. comm.).

Determining K_h values from Ra isotope activity gradients assumes a point or shore-parallel line source of Ra located near the shoreline and negligible advection (e.g., from sea or tide currents). This set of assumptions is distinct from those associated with AR-based methods of calculating water mass ages (Eqs. 1 and 2). For example, water age could be calculated using Eq. 2 in a bay where groundwater discharges from a large submarine area and not just from the shoreline, whereas the eddy diffusion method could not be used.

Uncertainties in the determination of water ages and eddy diffusion coefficients are important because they affect the uncertainties associated with SGD fluxes calculated based on them, as well as those associated with inputs of nutrients or other pollutants based on those SGD fluxes. For example, assuming that discharging groundwater is the only source of Ra to a bay, SGD into the bay can be estimated as:

$$SGD = \frac{(Ra_{bay} - Ra_{os})}{Ra_{gw}} \times \frac{V_{bay}}{T_{bay}} \quad (3)$$

where Ra_{bay}, Ra_{os}, and Ra_{gw} are the Ra activities in bay water, offshore seawater, and discharging groundwater, respectively; V_{bay} is the volume of the bay; and T_{bay} is the average time that water has spent within the bay (i.e., the water age). Simple mass balance approaches of this type have been incorporated in a number of studies (e.g., Swarzenski et al. 2007; Knee et al. 2008; Lee et al. 2009). If T_{bay} was 3 ± 1 d and all other terms were assumed to have negligible uncertainties, the SGD for T_{bay} = 2 d would be 50% greater than that for T_{bay} = 3 d, and the SGD for T_{bay} = 4 d would be 25% less. Various studies (e.g., Moore et al. 2006; Hougham and Moran 2007) have reported water age uncertainties of this magnitude. While uncertainties of 50% or greater would not invalidate estimated SGD fluxes, they would certainly affect the interpretation of results based on such calculations.

Uncertainties associated with Ra-based water mass ages and eddy diffusion coefficients stem from 1) analytical uncertainty, 2) natural variability, by which we mean the variability in Ra activity that a researcher would encounter when collecting replicate samples at the same location under similar conditions, and 3) uncertainty about how well the assumptions of the Ra-based method are being met. To explore the first source of uncertainty, Garcia-Solsona et al. (2008b) presented a series of calculations enabling the determination of uncertainties associated with the analysis of short-lived Ra isotope activity on a Radium Delayed Coincidence Counter (RaDeCC), accounting for the effects of sample activity, sample volume, and the time elapsed between sampling and analysis.

In contrast to ^{223}Ra and ^{224}Ra, ^{226}Ra and ^{228}Ra activities are typically measured by γ-ray spectroscopy following leaching of the manganese-coated Ra sampling fibers with HCl in a Soxhlet extraction apparatus and co-precipitation with $BaSO_4$ (e.g., Moore 1984; 2000b), or after ashing or compressing the fiber (e.g., Beck et al. 2007; Garcia-Solsona et al. 2010a). Analytical uncertainties associated with these methods have been estimated based on replicate measurements of the same sample or standard (Moore 2000b, Rapaglia et al. 2010) and on counting statistics and uncertainty propagation (Dulaiova and Burnett 2008; Loveless et al. 2008; Peterson et al. 2008). Reported analytical uncertainties in ^{226}Ra and ^{228}Ra activities generally range from 7% to 10% of sample activity (e.g., Moore 2000*b*; Charette et al. 2001; Peterson et al. 2008), but can be over 40% in some cases (e.g., Swarzenski et al. 2006).

Assuming that the analytical uncertainties in short- and long-lived Ra isotope activity are normally distributed and independent of each other, the analytical uncertainty in AR can be calculated as the quadratic sum of the relative analytical uncertainties for each isotope (i.e., Taylor 1997; Garcia-Solsona et al. 2008b):

$$\frac{dAR}{AR} = \sqrt{\left(\frac{dRa_L}{Ra_L}\right)^2 + \left(\frac{dRa_S}{Ra_S}\right)^2} \quad (4)$$

where Ra_L, Ra_S, and AR are long-lived Ra isotope activity, short-lived Ra isotope activity and the ratio of short- to long-lived Ra isotope activity, respectively, and dRa_L, dRa_S, and dAR are the absolute uncertainties associated with these respective quantities. The minimum possible analytical uncertainties using the RaDeCC system for determining the Ra activities are 7% and 4% for ^{223}Ra and ^{224}Ra, respectively (Garcia-Solsona et al. 2008b), which would result in an 8% analytical uncertainty in AR.

In practice, relative analytical uncertainties in the Ra isotope activities of field samples are usually higher than this minimum, on the order of 5% to 40% (Hwang et al. 2005; Garcia-Solsona et al. 2008b; Peterson et al. 2008). The higher ranges of analytical uncertainty (30% to 40%; e.g., Hougham and Moran 2007; Knee et al. 2008; Peterson et al. 2008) are usually associated with ^{223}Ra and attributed to its low activity. When one term in an equation has a much higher uncertainty than the others, the uncertainty in the equation's result is most influenced by the high-uncertainty term (Taylor 1997). Thus, the analytical uncertainty in AR for samples with low activity of one Ra isotope (usually ^{223}Ra) can be 40% or higher.

The second source of uncertainty is natural variability, by which we mean the random variability within a group of replicate samples collected at the same sampling point under similar field conditions. This definition of natural variability refers to the uncertainty that arises from small-scale spatial and temporal heterogeneity or minor differences in sampling procedure that are impossible to control for with current methods. In most studies, including those described in the following paragraph, such samples are regarded as replicates, and the variability among them is regarded as stochastic variability. This definition does not include variables that can, in principle, be measured in the field and controlled for, such as location within the coastal volume, distance from shore (e.g., Moore 2000b; Charette et al. 2001; Street et al. 2008), depth within the water column (Rasmussen 2003; Peterson et al. 2009), weather conditions, tides (Abraham et al. 2003; Charette 2007; Garcia-Orellana et al. 2010), or the strength and direction of waves and currents (Colbert and Hammond 2007).

To characterize natural variability within replicate groups of samples collected at the same station under similar conditions, we re-analyzed data collected by our research groups (Boehm et al. 2004; Knee et al. 2008, 2010), using data from replicate samples to assess the variability in their Ra activity. Replicate samples were collected during the same week- to month-long sampling period but not necessarily on the same date. In data from Huntington Beach, CA collected in summer 2003 (Boehm et al. 2004), 4 groups ($12 \le n \le 16$) of coastal ocean samples, each collected from a single station during the same part of the tidal cycle (neap-high, neap-low, spring-high, and spring-low) over a one-month period, had standard deviations of 31% to 50% of the mean ^{223}Ra activity, 17% to 47% of the mean ^{224}Ra activity, and 33% to 49% of the mean ^{224}Ra/^{223}Ra AR. Data from Hawai`i (Knee et al. 2008, 2010) collected during six sampling trips over the course of 5 years contained 19 duplicate pairs of groundwater samples and 40 duplicate pairs of coastal ocean samples, with each pair collected during the same one- to three-week sampling trip at the same station, water depth, and point in the tidal cycle. Pairs that differed in salinity by more than 1 were removed from analysis. The relative difference between duplicates in each pair was calculated as the absolute value of the difference between duplicates divided by their mean value. For groundwater pairs, the median relative difference was 25% for ^{223}Ra, 27% for ^{224}Ra, and 23% for the ^{224}Ra/^{223}Ra AR. For coastal ocean pairs, the median relative differences in ^{223}Ra, ^{224}Ra, and AR were 37%, 20%, and 32%, respectively. For a given group of replicates, the variability of AR was sometimes less than that of ^{223}Ra and/or ^{224}Ra activity, probably as a result of the dilution of high-Ra groundwater with different amounts of low-Ra seawater, which would cause variability in isotope activity but not in AR. While data from these two areas (Southern California and Hawai`i) may not be representative of all locations, they suggest that uncertainties associated with natural variability are generally on the order of 15% to 50% for ^{223}Ra activity, ^{224}Ra activity, and ^{224}Ra/^{223}Ra AR.

High spatial resolution sampling of coastal brackish groundwater near a Rhode Island salt pond (Swearman et al. 2006) revealed that activities of ^{223}Ra, ^{224}Ra, ^{226}Ra, and ^{228}Ra can vary by more than an order of magnitude over less than half a meter change in depth. Salinity varied much less over the same depth transect, from 24 to 29. Other variables such as redox conditions, temperature, and the abundance of Mn or Fe oxides in the aquifer substrate, which might explain variability in Ra, were not reported. The variability in AR was also high; for example, at one site the ^{224}Ra/^{223}Ra AR changed from

4.0 to 1.1 with a 40 cm increase in depth and a salinity increase of 0.4. It is generally not possible to determine the exact relative contributions of groundwater originating from slightly different depths within an aquifer to the total SGD at a given location. Thus, these results indicate that the uncertainty associated with natural variability in the Ra isotope activities and ARs of the discharging groundwater end-member could, at times, be 100% or even higher—considerably greater than the uncertainty due to counting error. The small-scale variability in groundwater Ra activity and AR likely depends on the hydrogeologic setting. Further study is needed to characterize the natural variability of groundwater Ra isotope activities in the various types of aquifers where SGD occurs and assess whether they are similar to that in Rhode Island salt ponds (Swearman et al. 2006).

The third source of uncertainty is related to how well field sampling and conditions satisfy the assumptions and data requirements of the Ra model. For example, if multiple groundwater sources with different ARs were discharging into the same water body, the Ra age calculated based on one of the groundwater ARs—or even the average of the multiple ARs (Hougham and Moran 2007)—would be incorrect because the model requires a single Ra source with a uniform AR. The resulting uncertainties would not be random, and we do not deal with them in the analysis presented here. Ra fluxes and the uncertainties associated with them could still be calculated in a system with multiple Ra sources if sources and flushing rates were quantified independently (Moore et al. 2006).

A number of studies (e.g., Moore et al. 2006; Swearman et al. 2006; Hougham and Moran 2007) have noted that uncertainty related to natural variability in AR, especially the AR in the groundwater source, can introduce significant uncertainty into the calculated Ra age. Moore et al. (2006) estimated that a 10% uncertainty in groundwater AR was associated with a 1-d uncertainty in Ra age. Hougham and Moran (2007) reported Ra age uncertainties of 1-3 days, or 10% to 50% of the age estimates, for Rhode Island salt ponds.

In the present study, we investigate how uncertainties in Ra activities and activity ratios arising from analytical uncertainty and natural variability relate to and are impacted by other variables associated with Ra sampling and Ra-based mixing calculations. Specifically, we (1) explore how uncertainties in AR affect the uncertainty in calculated water mass age; (2) investigate how uncertainty in Ra isotope activity and the number of samples collected affect the uncertainty in the eddy diffusion constant, K_h, estimated using the eddy diffusion method; and (3) provide guidelines and practical suggestions for the use of the AR and eddy diffusion methods, focusing on how to reduce uncertainty.

Procedures

Using AR to estimate water mass age (Eq. 1; Moore 2000a)

To assess the sensitivity of the AR-based method of estimating water mass age described by Moore (2000a; Eq. 1), we considered a coastal ocean volume (such as a bay or a surf zone) with a single groundwater source discharging into it at the shoreline. Three different ARs were considered: $^{224}Ra/^{223}Ra$, $^{224}Ra/^{228}Ra$, and $^{223}Ra/^{228}Ra$. We did not include any ARs involving ^{226}Ra because the activity of this isotope can be significant in offshore waters (Moore 2000*b*; Godoy et al. 2006; Street et al. 2008) and would thus affect the AR gradient. Additionally, ARs including ^{226}Ra are not often used in water age calculations. Offshore ^{228}Ra activity at some sites can also be high enough to affect the $^{224}Ra/^{228}Ra$ AR in coastal waters (Garcia-Solsona et al. 2010*b*), but since many published studies (e.g., Moore et al. 2006; Beck et al. 2007; Rapaglia et al. 2010) use ARs involving ^{228}Ra, we chose to include these ARs in our analysis. Significant offshore ^{228}Ra activity would fall under the third category of uncertainty—that associated with a violation of model assumptions—and is thus not considered in the present sensitivity analysis.

We assumed that groundwater ARs ($^{224}Ra/^{223}Ra$, $^{224}Ra/^{228}Ra$, and $^{223}Ra/^{228}Ra$) were normally distributed with mean μ_{gw} and standard deviation σ_{gw}. The value of μ_{gw} was assumed to be 19.3 for the $^{224}Ra/^{223}Ra$ AR, 1.37 for the $^{224}Ra/^{228}Ra$ AR, and 0.07 for the $^{223}Ra/^{228}Ra$ AR. These were the values reported for groundwater discharging into the Okatee Estuary, South Carolina (Moore et al. 2006); actual groundwater ARs vary with geographic location depending on bedrock, recharge rates, and other considerations. The assumed μ_{gw} values listed above were selected arbitrarily because the results of the analysis do not depend on the groundwater AR value.

We assumed that the AR of water at a given coastal ocean sampling point was normally distributed with mean μ_{co} and standard deviation σ_{co}. The value for μ_{co} was derived from μ_{gw} using Eq. 5 (Moore 2000*a*):

$$\mu_{co} = \mu_{gw} \times \frac{e^{-\lambda_S T}}{e^{-\lambda_L T}} \quad (5)$$

where λ_S (d^{-1}) is the decay constant of the shorter-lived isotope, λ_L (d^{-1}) is the decay constant of the longer-lived isotope, and T (d) is the length of time since Ra entered the coastal ocean via SGD. Ranges of discrete values of T, from minima of 1 h for the $^{224}Ra/^{223}Ra$ and $^{224}Ra/^{228}Ra$ ARs and of 1 d for the $^{223}Ra/^{228}Ra$ AR to maxima of approximately six half-lives of the shorter-lived isotope (21 d for the $^{224}Ra/^{223}Ra$ and $^{224}Ra/^{228}Ra$ ARs; 60 d for the $^{223}Ra/^{228}Ra$ AR) were considered. These value ranges were chosen because they are representative of coastal water ages reported in the literature (e.g., Moore 2000a; Hougham and Moran 2007; Peterson et al. 2008).

An issue not explicitly addressed by this analysis is that as water age increases, the activities of short-lived isotopes decrease due to radioactive decay, and the relative uncertainties resulting from counting error begin to increase. After a certain point, which depends on the initial groundwater Ra activity, the sample volume collected, the amount of dilution and the time elapsed between sampling and counting, the Ra activities become too low to measure accurately because they

are similar to the background. Thus, water ages longer than 21 d (for the $^{224}Ra/^{223}Ra$ and $^{224}Ra/^{228}Ra$ ARs) and 60 d (for the $^{223}Ra/^{228}Ra$ AR) were not considered because after 6 half lives over 98% of the original short-lived Ra isotope would have decayed and the activity would likely have fallen below the analytical detection limit. Apart from limiting the water ages we considered to <6 half-lives of the shorter-lived isotope, we did not address the issue of increasing uncertainty due to radioactive decay in this study.

σ_{gw} and σ_{co} represent the combined uncertainty (analytical uncertainty and natural variability) in the groundwater and coastal ocean ARs, respectively. The relative analytical uncertainty in AR alone (*dAR/AR* in Eq. 4) represents the lower limit on σ_{gw} and σ_{co}. The upper limits on σ_{gw} and σ_{co} were based on the variability of replicate field samples (Boehm et al. 2004; Knee et al. 2008, 2010) and the small-scale heterogeneity of Ra activities and ARs observed in groundwater (Swearman et al. 2006). We modeled σ_{gw} as having a uniform distribution ranging from 5% to 100% of μ_{gw} and σ_{co} as having a uniform distribution ranging from 5% to 40% of μ_{co}. σ_{gw} and σ_{co} were assumed to be independent of each other based on the observation that groundwater and coastal ocean samples collected from the same location can have different degrees of natural variability (e.g., Dulaiova et al. 2006; Moore 2006; Swarzenski et al. 2006) because the factors controlling groundwater and surface water Ra activity are different. We chose a uniform distribution to enable us to compare different levels of relative uncertainty within a certain range. This modeling choice does not imply an assumption that AR uncertainties in field samples are uniformly distributed.

A Monte Carlo Model (MCM) implemented in MATLAB (The MathWorks; Student Version Release 2010a) was used to assess how different values of μ_{co}, σ_{gw} and σ_{co} affected the apparent age of coastal ocean water (T_{co}). T_{co} was calculated using Eq. 1, where AR_{co} and AR_{gw} are individual coastal ocean and groundwater AR values chosen randomly from the normal distributions defined by μ_{gw}, μ_{co}, σ_{gw}, and σ_{co}.

Ten thousand random trials of the MCM were run for 12 discrete values of T (time elapsed since Ra entered the coastal ocean control volume via SGD) for each AR ($^{224}Ra/^{223}Ra$, $^{224}Ra/^{228}Ra$, and $^{223}Ra/^{228}Ra$). Considering three ARs and 12 discrete values of T for each (6 h, 12 h, 1 d, 2 d, 3 d, 4 d, 5 d, 6 d, 7 d, 10 d, 14 d, and 21 d for ARs involving ^{224}Ra; 1 d, 2 d, 3 d, 5 d, 7 d, 10 d, 14 d, 21 d, 30 d, 40 d, 50 d, and 60 d for the $^{223}Ra/^{228}Ra$ AR), this amounted to a total of 360,000 individual random trials. Choosing randomly from a normal distribution occasionally yielded negative AR values, especially for low ARs. These negative AR values, which can be interpreted as having Ra activities so low that they are not significantly different from zero, were removed and the model continued running until 10,000 acceptable runs for each unique pair of AR and T had been completed. Equation 6 calculates the relative uncertainty in apparent water age $\left(\frac{dT_{co}}{T_{co}}\right)$:

$$\frac{dT_{co}}{T_{co}} = \frac{\left[T - T_{co}\right]}{T} \quad (6)$$

The relative uncertainty in the apparent water age was then related to the true water age (T), the relative uncertainties in groundwater and coastal ocean AR (σ_{gw} and σ_{co}, respectively), and the particular activity ratio used ($^{224}Ra/^{223}Ra$, $^{224}Ra/^{228}Ra$, and $^{223}Ra/^{228}Ra$) to compile a set of recommendations for uncertainty reduction.

Using AR to estimate water mass age (Eq. 2; Moore et al. 2006)

The sensitivity of AR-based estimates of water mass ages in settings with diffuse Ra inputs, such as estuaries (Moore et al. 2006; Eq. 2), was analyzed similarly to that of Eq. 1 (Moore 2000a), with the following modifications. First, the $^{224}Ra/^{223}Ra$ AR was not included in the analysis. Because this method accounts for the decay of only one isotope, it is not appropriate to use an AR in which both isotopes could decay to an appreciable extent. Second, μ_{co} was calculated based on Eq. 2 rather than Eq. 1.

Eddy diffusion method (Moore 2000b)

For the purpose of this study, we considered a straight coastline constituting a line source of Ra to the coastal ocean where all cross-shore transport is attributable to eddy diffusion and there is no alongshore variation. In the model, Ra activities were determined in samples collected at n equally spaced sampling points along a shore-perpendicular transect with length L. We selected six discrete n values corresponding to 3, 5, 10, 15, 20, and 30 sampling points along the transect. Lower n values (3, 5, and 10) were typical of previous published studies (Table 1), while higher n values (15, 20, and 30) were included to investigate the potential benefits of additional sampling effort. We assumed that advection was negligible and that eddy diffusion and radioactive decay were the only processes controlling ^{223}Ra and ^{224}Ra activity along the transect. Because long-lived Ra isotopes (^{226}Ra and ^{228}Ra) are not used to calculate K_h itself, we did not consider these isotopes in our analysis of the eddy diffusion method.

^{223}Ra or ^{224}Ra activity at a given distance from shore (x) along the transect was assumed to be normally distributed with mean μ_x conforming exactly to a log-linear trend with x. μ_x could represent either the Ra activity of a single sample or the mean Ra activity of a group of replicate samples collected at the same transect point under similar conditions (e.g., Moore 2000*b*). The value of μ_x at the shoreline (μ_0) was chosen randomly from a uniform distribution from 0.17 to 1.7 Bq m^{-3} for ^{223}Ra and from 1.7 to 42 Bq m^{-3} for ^{224}Ra based on ranges reported in previous studies (Moore 2000b; Boehm et al. 2006; Dulaiova et al. 2006). The slope (m; km^{-1}) of the natural log-linear relationship between Ra activity and distance from shore was chosen randomly from a uniform distribution ranging from –0.05 to –5, which is representative of the ranges of slopes and K_h values reported in the literature (e.g., Moore

Table 1. Summary of published studies using the cross-shore gradient in short-lived Ra isotope activity to estimate the eddy diffusion coefficient (K_h). ln *Ra0* is the natural log of Ra activity at the shoreline (Bq m^{-3}). *m* and R^2 are the slope and coefficient of determination, respectively, of the line of best fit between the natural log of Ra activity (Bq m^{-3}) and distance offshore (km) for a given transect.

				ln *Ra0*		*m*		R^2	
Study	**Location**	**Transect length (km)**	***n***	**^{223}Ra**	**^{224}Ra**	**^{223}Ra**	**^{224}Ra**	**^{223}Ra**	**^{224}Ra**
Moore 2000b	South Atlantic Bight, USA	50	10*	0.45	3.3	0.17	0.18	0.97	0.99
Boehm et al. 2006	Huntington Beach, CA, USA	0.6	4	0.27	20	1.8	3.0	0.98	0.92
Dulaiova et al. 2006	West Neck Bay, NY, USA	4	9	1.0	5.5	0.22	0.22	0.93	0.67
Charette et al. 2007	Crozet Plateau, Southern Ocean	15	6	0.75	9.1	0.23	0.21	0.81	0.74
Gomes et al. 2009	Ilha Grande Bay, Brazil	26	10	—	—	0.17	0.17	0.90	0.92
Swarzenski and Izbicki 2009	Santa Barbara, CA, USA	3	4	0.45	6.7	0.35	0.40	0.89	0.95

*Each transect point represents the average of 4-8 individual measurements.

2000b; Boehm et al. 2006; Colbert and Hammond 2007; Tables 1, 2). The range of reported slopes for ^{223}Ra and ^{224}Ra is quite similar, so the same range was used in the model for both isotopes. The transect length was assumed to correspond exactly to the zone of coastal Ra enrichment; the offshore end of the transect was thus defined as the distance at which ^{223}Ra activity equaled 0.0017 Bq m^{-3} or ^{224}Ra activity equaled 0.017 Bq m^{-3}. These activities represent ^{223}Ra and ^{224}Ra activities that have been observed in different parts of the open ocean, after the cross-shore gradients in Ra activity leveled off (Moore 2000b; Dulaiova et al. 2006; Knee et al. 2010).

μ_x values at points in the middle of the transect were calculated based on the log-linear relationship between short-lived Ra isotope activity and distance from shore:

$$\ln(\mu_x) = mx + \ln(\mu_0) \quad (7)$$

The standard deviation of short-lived Ra isotope activity at each point, σ_x, was assumed to have a uniform distribution ranging from 0% to 40% of μ_x, and the same relative value was used for all μ_x in the same transect.

The MCM was run 10,000 times in MATLAB for each value of *n* and for each isotope (^{223}Ra and ^{224}Ra), for a total of 120,000 individual random runs. In each run, short-lived Ra isotope activities at *n* transect points were chosen randomly from normal distributions defined by μ_x and σ_x at each value of *x*. The line of best fit for the relation between the natural log of short-lived Ra isotope activity and *x* was calculated. The slope (m_a), *y*-intercept, coefficient of determination (R^2), and statistical significance (*p*-value) of each regression were recorded.

For each run, the apparent eddy diffusion coefficient (K_h; km^2 d^{-1}) was calculated using the equation presented by Moore (2000b):

$$K_h = \frac{\lambda}{(m_a)^2} \quad (8)$$

in which λ is the decay constant of ^{223}Ra (0.061 d^{-1}) or ^{224}Ra (0.19 d^{-1}). The analytically determined mean K_h ($\overline{K_h}$) when the Ra activity at all *x* for a given transect is μ_x, was calculated from the randomly chosen slope *m*. ($\overline{K_h}$) represents the slope that would be calculated if there were no random uncertainty ($\sigma_x = 0$). The relative error in apparent K_h was calculated as

$$\frac{(K_h - \overline{K_h})}{\overline{K_h}}.$$

Our analysis of the eddy diffusion method is also applicable if the gradient in ^{224}Ra/^{223}Ra AR, rather than the activity of either isotope, is used to calculate K_h (Burnett et al. 2008). The only modifications are that the uncertainty in AR would need to be calculated from the analytical uncertainties of the two isotopes and a combined value of λ (0.128 d^{-1}) representing the difference between the decay rates of the two isotopes (Moore 2006) would be used.

Assessment

Using AR to estimate water mass age (Eq. 1; Moore 2000a)

The uncertainty in estimated water age depended not only on the input uncertainties in groundwater and coastal ocean water ARs, but also on the specific Ra isotopes used for determining the AR used in the age calculation (Fig. 1). The ^{224}Ra/^{228}Ra AR yielded a slightly lower relative uncertainty associated with water age estimates than did the ^{224}Ra/^{223}Ra AR. This effect, which was more pronounced for younger water, arises because the difference in the decay constants of ^{224}Ra and ^{228}Ra is greater than the difference in the decay constants of ^{224}Ra and ^{223}Ra. Thus, the ^{224}Ra/^{228}Ra AR decreases more, relative to its original value, than does the ^{224}Ra/^{223}Ra AR for the same time elapsed, and the difference between the original AR and the AR at time *T* is less likely to be obscured by random errors. Similarly, using the ^{223}Ra/^{228}Ra AR to calculate water ages yielded higher uncertainties because ^{223}Ra activity decreases less than does ^{224}Ra activity during the same period; thus, the decrease is more likely to be masked by analytical uncertainty and/or natural variability.

The actual age of the coastal ocean water sample to which the calculation is applied affected the relative uncertainty associated with its estimate (Fig. 1). Relative uncertainties were

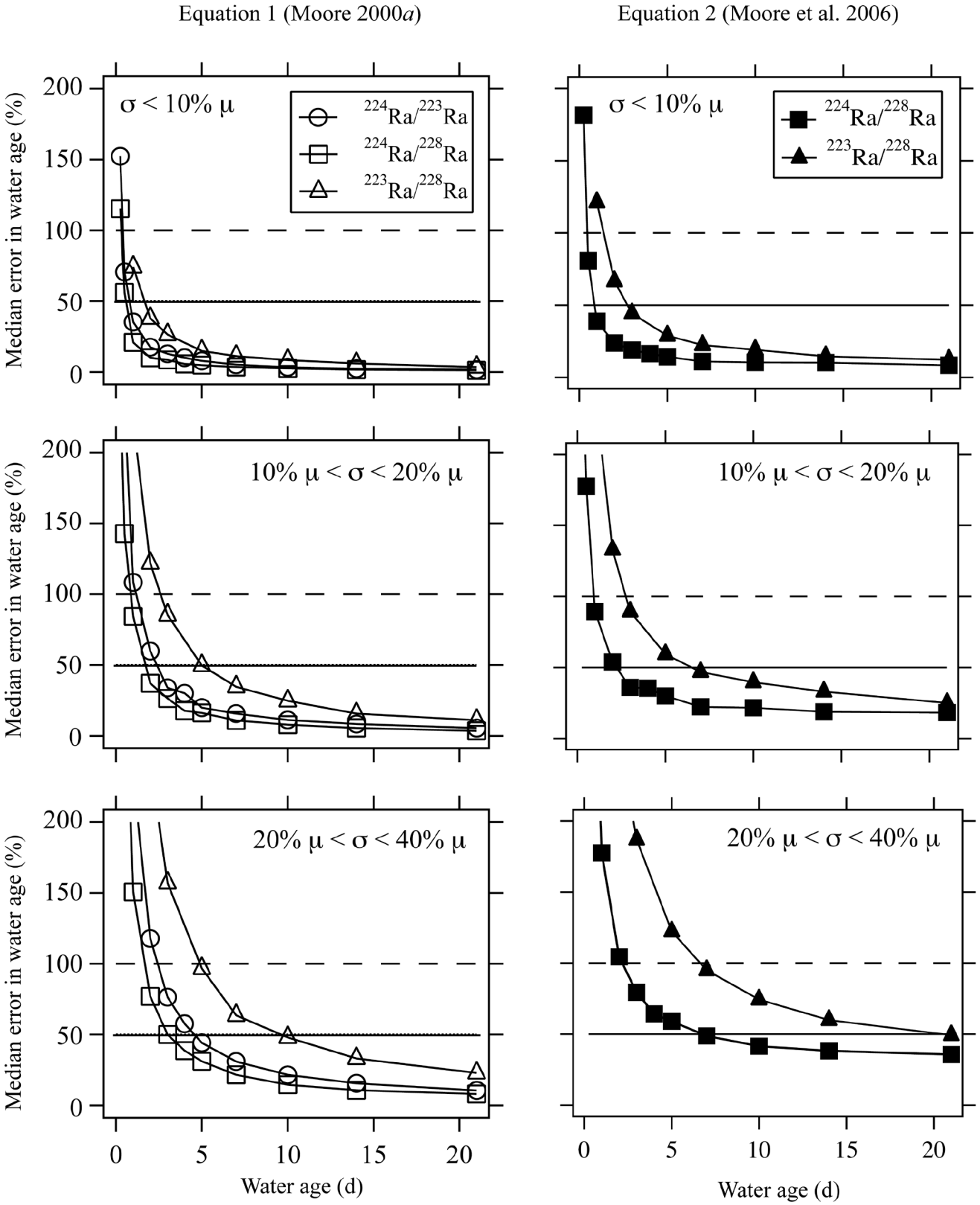

Fig. 1. Relative errors in water age estimated using Eq. 1 (Moore 2000a) and Eq. 2 (Moore et al. 2006) for water ages up to 21 d. Solid and dashed horizontal lines represent 50% and 100% relative errors, respectively, in calculated water age. The relative uncertainty in AR (σ) is assumed to be the same for groundwater and coastal water. Each point represents the median relative error of 10,000 random runs of the Monte Carlo model.

higher for sites with faster water exchange (lower water ages), especially those where water age was less than 3-5 d (Fig. 1). This age-dependent effect was more pronounced when the uncertainty in the AR of groundwater and/or coastal ocean water was greater. For example, for the $^{224}Ra/^{223}Ra$ AR with uncertainties (σ) of less than 10% for both groundwater and coastal ocean, there was a 7% chance that the relative uncertainty associated with a water age estimate of 1 d would be 100%. For a water age of 4 d, that probability was less than 1% (Fig. 2). When σ for both groundwater and coastal ocean was 10% to 20%, there was a 53% probability that the relative uncertainty associated with a water age estimate of 1 day would be 100%, but the probability was still less than 1% when the water age was 4 d. When σ was 20% to 40%, there was a 76% chance that the relative uncertainty associated with a water age estimate of 1 d would be 100% and a 15% chance for a water age of 4 d. The probability of an uncertainty 100% did not decrease to less than 1% until the water age reached 14 d.

Using AR to estimate water mass age (Eq. 2; Moore et al. 2006)

The effects of input uncertainties in AR and actual water age on water ages calculated using Eq. 2 were similar to those observed for Eq. 1, with two main differences. First, for a given level of input uncertainty and actual water age, the uncertainty in calculated water age (Fig. 1) and the chance of a relative uncertainty ≥100% (Fig. 2) were always greater for Eq. 2. Second, the uncertainty in calculated water age and chance of a relative uncertainty ≥100% decreased more sharply for the same increase in water age when Eq. 1 was used, and the difference in uncertainty between the two methods was greater for longer water ages (Figs. 1, 2).

For both $^{224}Ra/^{228}Ra$ and $^{223}Ra/^{228}Ra$, the difference between Eqs. 1 and 2 was more pronounced when input uncertainties in AR were greater. For example, considering the $^{224}Ra/^{228}Ra$ AR and σ of less than 10% for both groundwater and coastal ocean water, the 95th percentile of uncertainty in calculated water age fell below 100% at a water age of 1 d for Eq. 1 and a water age of 2 d for Eq. 2. When σ was between 20% and 40%, the cutoff for a 95th percentile uncertainty of less than 100% for Eq. 1 was 5 d, whereas it was never reached for Eq. 2, which had a greater than 10% chance of an uncertainty greater than 100% even for a water age of 21 d. We note that these two methods are suitable for different field conditions, so it would not be appropriate to choose between them based on the anticipated uncertainty.

Eddy diffusion method (Moore 2000b)

The transect length, L, which was calculated for each run based on the shoreline Ra activity and the slope of the cross-shore Ra gradient, varied from a minimum of 0.5 km for a ^{224}Ra activity of 0.17 Bq m^{-3} or a ^{223}Ra activity of 0.017 Bq m^{-3} at the shoreline and a K_h value of 0.0076 $km^2\ d^{-1}$ to a maximum of 110 km for a ^{224}Ra activity of 42 Bq m^{-3} at the shoreline and a K_h value of 76 $km^2\ d^{-1}$. In the model, L corresponded exactly to the cross-shore extent of Ra enrichment, or the entire area

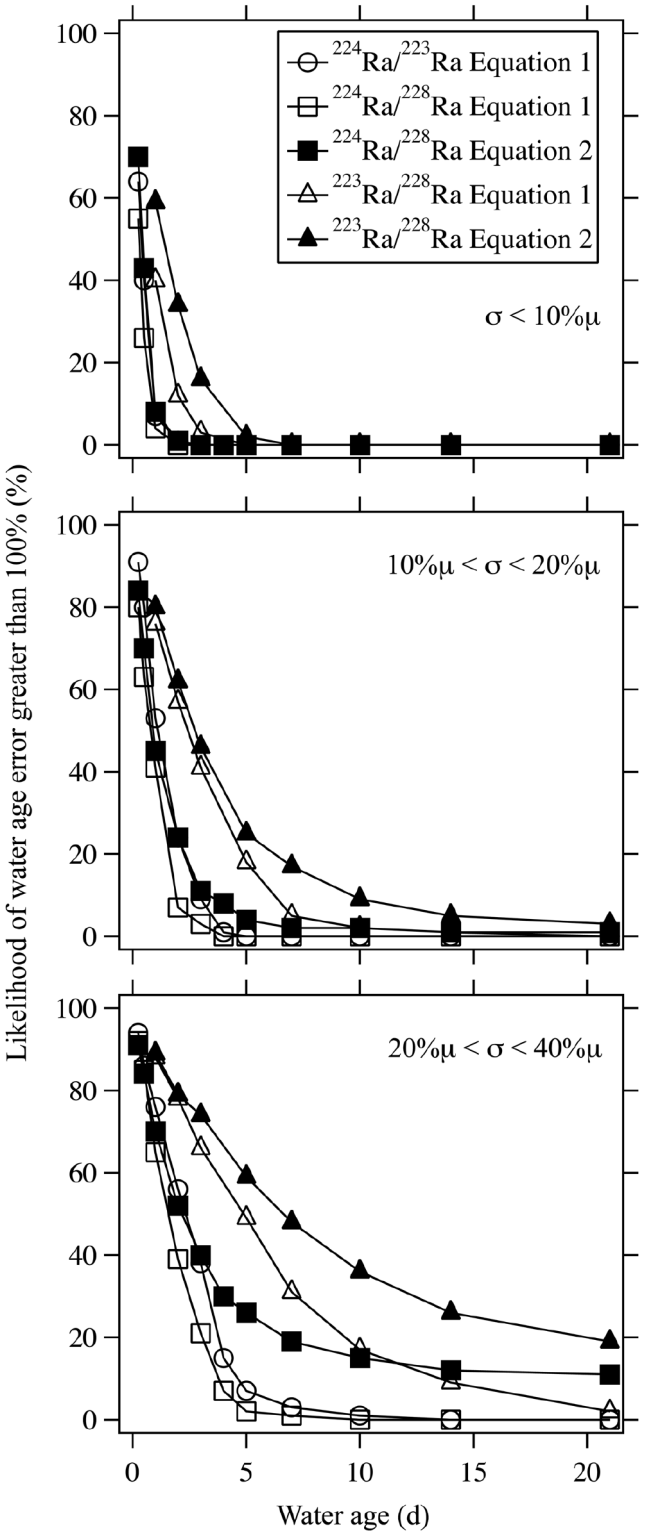

Fig. 2. Probability that a water age estimated using Eq. 1 (Moore 2000a; open symbols) or Eq. 2 (Moore et al. 2006; filled symbols) will have a relative error of greater than 100%. The relative uncertainty in AR (σ is assumed to be the same for groundwater and coastal water. Each point represents the median relative error of 10,000 random runs of the Monte Carlo model.

Table 2. Ranges of ideal transect length (L; km) for the eddy diffusion method, based on reported ranges of Ra isotope activity at the shoreline (Ra_0; [Bq m^{-3}]) and slope (m; km^{-1}) of the line of best fit for the relation between the natural log of Ra isotope activity and distance from shore. Ra_L (Bq m^{-3}) is the Ra activity at the end of the transect, where it is equal to average offshore activity. K_h is the eddy diffusion coefficient (km^2 d^{-1}) calculated from m according to Eq. 8.

Ra isotope	ln Ra_0	ln Ra_L	m	K_h	L
^{224}Ra	3.7	–1.8	–0.05	76	110
	3.7	–1.8	–5	0.0076	1.1
	0.5	–1.8	–0.05	76	46
	0.5	–1.8	–5	0.0076	0.5
^{223}Ra	0.5	–4.1	–0.05	24	92
	0.5	–4.1	–5	0.0024	0.9
	–1.8	–4.1	–0.05	24	46
	–1.8	–4.1	–5	0.0024	0.5

where ^{223}Ra activity was above 0.0017 Bq m^{-3} or ^{224}Ra activity was above 0.017 Bq m^{-3}. The considerable variability of L underscores the value of trying to estimate the cross-shore extent of the zone of Ra enrichment before beginning a labor-intensive sampling program. Within the ranges of shoreline Ra activity and K_h considered, K_h was the most important determinant of L, whereas the Ra isotope used and the Ra activity at the shoreline had a relatively small effect (Table 2). The K_h ranges considered here were based on literature values, which had a span of 0.02 km^2 d^{-1} (Boehm et al. 2006; Colbert and Hammond 2007) to 36 km^2 d^{-1} (Moore 2000b).

Relative uncertainties in calculated K_h values were low compared with 1) the uncertainty associated with the Ra activity at transect points and 2) the uncertainties associated with water ages calculated using Eqs. 1 and 2. The median, rather than the mean, was used as a measure of central tendency for relative uncertainties in K_h because, especially for lower n, the relative errors were not normally distributed and included some extremely high values. For $n \geq 10$, the median error in K_h was lower than the uncertainty associated with the Ra activity at transect points (Fig. 3). Assuming that the transect length exactly coincides with the cross-shore extent of Ra enrichment, neither the Ra activity at the shoreline nor the true value of K_h affected the error associated with K_h estimates. However, we note that when there are few transect points, a given level of relative uncertainty in Ra activity would have a greater effect on uncertainty in K_h when it is associated with Ra activity at the shoreline (rather than at offshore points) because the magnitude of shoreline Ra activity is higher.

High σ_x and low n were associated with greater relative uncertainty in K_h for both ^{223}Ra and ^{224}Ra (Fig. 3), and the benefit of additional transect points was greater when σ_x was higher. For example, increasing n from 5 to 15 decreased the uncertainty in K_h estimated using ^{224}Ra from 6% to 3% when σ_x was less than 10% and from 39% to 23% when σ_x was between 20% to 40%. Adding more sampling points also led to a greater decrease in uncertainty when the initial n was lower (Fig. 3). For both high and low σ_x, the relative error decreased by about half when n increased from 5 to 15; however in our opinion this difference is more relevant to data interpretation when the relative uncertainty is high, as in the case where σ_x was between 20% to 40%.

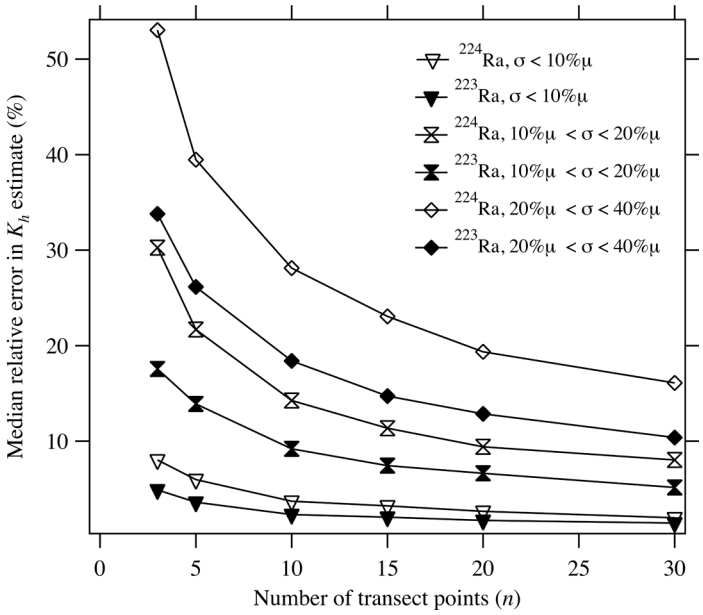

Fig. 3. Relative error in estimated eddy diffusion coefficient (K_h) as a function of the level of relative uncertainty in short-lived Ra isotope activity (σ). Different numbers of transect points (n) are shown to illustrate how the effect of σ is modulated by n. Each point represents the median relative error of 10,000 random runs of the Monte Carlo model for each n and Ra isotope.

When σ_x and n were held constant, relative uncertainties in estimated K_h were systematically higher when ^{224}Ra, rather than ^{223}Ra, was used (Fig. 3). This effect was greatest for transects with high σ_x and/or low n. For example, for 20% < σ_x < 40% and n = 3, K_h estimates made using ^{224}Ra had a median relative error of 53%, compared with 34% for K_h estimates based on ^{223}Ra. This is because, for the same K_h, the slope of the cross-shore gradient in ^{224}Ra is steeper than that of ^{223}Ra,

so the same magnitude of uncertainty in the ^{224}Ra slope leads to a greater error in the estimated value of K_h. However, the benefit of using ^{223}Ra to estimate K_h from real data may be reduced because the uncertainty associated with measuring ^{223}Ra activity is often significantly higher than that associated with measuring ^{224}Ra activity (Garcia-Solsona et al. 2008b; Knee et al. 2008). Both of these effects should be taken into account when choosing which isotope to use for eddy diffusion calculations (Table 3) especially if the calculated K_h values for the two isotopes differ.

Not surprisingly, for a given n and σ_x, the relative error in K_h was lower when R^2 was higher. The importance of R^2 in pre-

Table 3. Relative error in estimated K_h for linear regressions with R^2 values ranging from 0.5 to 1.0. Numbers in the table are the median relative error in estimated K_h for a group of regressions defined by Ra isotope, number of transect points (n), relative uncertainty in Ra activity at transect points (σ_x), and R^2.

			R^2				
Ra isotope	***n***	σ_x	**0.5-0.6**	**0.6-0.7**	**0.7-0.8**	**0.8-0.9**	**0.9-1.0**
^{223}Ra	3	<10%	—	—	—	—	5%
		10-20%	—	—	204%	104%	17%
		20-40%	250%	202%	140%	62%	30%
	5	<10%	—	—	—	—	4%
		10-20%	—	—	43%	42%	14%
		20-40%	111%	86%	55%	35%	23%
	10	<10%	—	—	—	—	2%
		10-20%	—	—	—	27%	9%
		20-40%	116%	50%	30%	22%	16%
	15	<10%	—	—	—	-	2%
		10-20%	—	—	25%	10%	7%
		20-40%	96%	39%	26%	17%	13%
	20	<10%	—	—	—	—	2%
		10-20%	—	—	—	12%	7%
		20-40%	63%	44%	22%	15%	11%
	30	<10%	—	—	—	-	1%
		10-20%	—	—	—	14%	5%
		20-40%	50%	45%	18%	12%	9%
^{224}Ra	3	<10%	—	—	197%	53%	8%
		10-20%	242%	141%	95%	47%	27%
		20-40%	160%	66%	52%	49%	44%
	5	<10%	—	—	—	40%	6%
		10-20%	172%	99%	53%	29%	20%
		20-40%	68%	48%	37%	34%	32%
	10	<10%	—	—	—	20%	4%
		10-20%	127%	62%	30%	17%	13%
		20-40%	46%	33%	26%	24%	21%
	15	<10%	—	—	—	39%	3%
		10-20%	—	61%	25%	14%	10%
		20-40%	33%	24%	22%	21%	19%
	20	<10%	—	—	—	—	3%
		10-20%	—	54%	28%	12%	9%
		20-40%	32%	22%	18%	17%	16%
	30	<10%	—	—	—	30%	2%
		10-20%	—	41%	27%	10%	7%
		20-40%	25%	18%	15%	13%	12%

dicting the relative error in K_h was greater for ^{223}Ra than for ^{224}Ra and also greater when n was low than when n was high. In general, transects with $R^2 > 0.9$ had low relative K_h errors (0% to 30%), and transects with $0.8 < R^2 < 0.9$ almost always had relative errors in K_h lower than 30% when n was 10. The results presented in Table 3 can be used to predict the uncertainty associated with a K_h estimate from R^2 and n if σ_x is known or can be approximated.

The p value also provided a useful indicator of the uncertainty associated with K_h estimates, especially for low values of n. For example, in regressions between ln ^{224}Ra and distance from shore where $n = 3$, those with $P < 0.05$ had a median relative K_h error of 17%, with a 95th percentile K_h error of 94%. In contrast, regressions with $P > 0.05$ had a median relative K_h error of 43%, with a 95th percentile K_h error of over 1000%. Regressions with higher n and high p (low significance) had even higher K_h errors. However, these regressions were rare. When $n = 10$, less than 2% of regressions had $P > 0.05$.

Discussion and recommendations

Using AR to estimate water mass ages (Moore 2000a and Moore et al. 2006)

Our results indicate that both Eq. 1 and Eq. 2 are likely to yield a calculated water age with an uncertainty of 100% or greater if the water age is shorter than 3-5 d, unless the uncertainties associated with both isotopes used for defining the AR are very low (<10%). This is an important finding because many coastal areas where submarine groundwater discharge occurs—including many beaches (Boehm et al. 2004; Scopel et al. 2006; Shellenbarger et al. 2006), coastal bays (Brooks et al. 1999; Garcia-Solsona et al. 2008a; Peterson et al. 2009), estuaries (Arega et al. 2008; Breier et al. 2009), and man-made harbors (Gallagher 1980) —have short residence times, with water ages shorter than 3-5 d.

Estimates of water ages, mixing rates, and/or SGD fluxes with uncertainties of 100% or greater are not unusual and may still represent valuable information. However, if the coastal water age is expected to be lower than 3-5 d, all reasonable measures (such as collecting a larger volume sample, running the sample soon after collection, and/or making sure the background is very low) should be taken to reduce the analytical error. It would be useful to conduct preliminary sampling to assess the variability in AR of the coastal ocean and especially groundwater end-members and estimate what the uncertainty in Ra-derived water ages is likely to be, considering the observed variability in AR. The uncertainty associated with the groundwater end-member AR may also be reduced by collecting multiple (n 3) samples of the groundwater end-member and calculating the AR as the slope of the linear regression between short- and long-lived Ra isotope activities (Garcia-Solsona et al. 2010*b*). However, we note that in some situations Ra isotope activities in groundwater are highly variable on a small spatial scale (e.g., Swearman et al. 2006; Gonneea et al. 2008) due to the multiple processes that affect groundwater chemistry in the subterranean estuary, making it difficult or impossible to identify which groundwater should be considered the discharging end-member or to define what the characteristics of this end-member are.

If a precise water age is required and the water age is expected to be short, researchers may also consider calculating coastal mixing rates based on observations of waves and rip cells (Longuet-Higgins 1983; Boehm et al. 2006), tidal prism calculations (Charette et al. 2003; Crotwell and Moore 2003; Garcia-Solsona et al. 2008a), or measurements of current speeds combined with hydrodynamic modeling (Brooks et al. 1999; Shellenbarger et al. 2006; Rapaglia et al. 2010). However, there is uncertainty associated with each of these methods, and it may not be lower than that of Ra-based methods. When possible, it can be advantageous to use multiple methods of calculating water age and/or mixing rates in the same study (e.g., Moore et al. 2006; Garcia-Solsona et al. 2008*a*; Rapaglia et al. 2010), since obtaining similar results via multiple methods would support the validity of the results, even if the uncertainty associated with each method remains high.

If the ultimate goal of calculating water ages or mixing rates is to calculate SGD fluxes (e.g., Rama and Moore 1996; Charette et al. 2001), and the uncertainties associated with these water ages or mixing rates are expected to be high, another option would be to use methods of estimating SGD fluxes that do not depend on knowing the residence time. Such methods include solving a system of equations using multiple natural tracers (Hwang et al. 2005), using seepage meters to measure SGD directly (Lee 1977; Shaw and Prepas 1989; Taniguchi et al. 2003), or modeling (Turner et al. 1997; Robinson et al. 2007; Garcia-Orellana et al. 2010). However, as mentioned previously, the uncertainties associated with alternate methods are not necessarily lower than those associated with Ra-based ones. A combination of different methods may also be used to provide a result with more confidence (e.g., Burnett et al. 2006, 2008; Santos et al. 2008).

For Eq. 1 (Moore 2000*a*), this analysis indicates that using the ^{224}Ra/^{228}Ra AR is generally preferable to using the ^{224}Ra/^{223}Ra AR because the uncertainty associated with the water age estimate is lower. Two other factors—the fact that ^{224}Ra and ^{228}Ra originate from the same decay series, and the typically lower analytical uncertainty associated with ^{228}Ra compared with ^{223}Ra—were not considered in this model, but would tend to increase the advantage of the ^{224}Ra/^{228}Ra AR over the ^{224}Ra/^{223}Ra AR for estimating water ages. If ^{228}Ra activity offshore is not low, however, ARs incorporating this isotope will be less reliable. For example, relatively high ^{228}Ra levels in seawater may be found in carbonate regions due to a continuous source in the sediments, which consist of ^{232}Th concentrated in relatively insoluble residues derived from dissolution of carbonate rocks. The uncertainties associated with water ages estimated using the ^{223}Ra/^{228}Ra AR were significantly higher than those estimated using the ^{224}Ra/^{223}Ra or ^{224}Ra/^{228}Ra AR when the water age was less than about 10 d

(Fig. 1); at higher water ages the uncertainties associated with all three ARs were about the same.

Our analysis indicates that both Eq. 1 and Eq. 2 yield the most accurate results for water ages of approximately 5-14 d if the $^{224}Ra/^{223}Ra$ AR or the $^{224}Ra/^{228}Ra$ AR is used and approximately 14-40 d if the $^{223}Ra/^{228}Ra$ AR is used. Water ages and water residence times within this range are typical for many coastal bays (Hougham and Moran 2007; Peterson et al. 2008) and wide continental shelf settings (Moore and de Oliveira 2008). Because AR uncertainty affects the water age calculation, it is important to design a sampling strategy that minimizes the uncertainties associated with the ARs of the groundwater and coastal ocean end-members. Input AR uncertainties can be kept low by optimizing sampling and counting techniques to minimize analytical uncertainty (Garcia-Solsona et al. 2008b) and/or by defining sample groups to reduce intragroup variability in AR while still ensuring that the samples are representative of conditions at the field site. Using the $^{224}Ra/^{228}Ra$ AR rather than the $^{224}Ra/^{223}Ra$ AR would also tend to decrease the uncertainty in estimated water age.

Eddy diffusion method (Moore 2000b)

In general, uncertainties in Ra isotope activities had less of an effect on the uncertainty in K_h than they did on the uncertainty in Ra-derived water age. This is because random uncertainties in the points comprising a linear regression tend to balance each other out, rather than skew the results in one direction or another, as long as the number of transect points is not very low. Our analysis underscored the importance of sampling a sufficient number of transect points, especially if uncertainty in Ra activity is moderate to high. When model runs were grouped by n, σ_x, and isotope used (^{223}Ra or ^{224}Ra), the 95th percentile of relative error in K_h was less than 100% for all groups with $n \geq 15$. It was also less than 100% for all groups with $n \geq 10$ except for the highest-uncertainty ^{224}Ra group ($20\% < \sigma_x < 40\%$). These results indicate that it is very unlikely for the uncertainty in K_h to be greater than the magnitude of K_h if at least 10 transect points are sampled.

When deciding how many transect points to sample, it is important to note that most studies using the eddy diffusion method (Table 1) were not able to use all the transect points they sampled for their final calculations because the required linear trends did not apply to the entire transect length. For example, Moore (2000b) was only able to use about half of the points sampled because the cross-shore gradients in Ra isotope activities changed abruptly at about 50 km from shore. The length of the cross-shore gradient in Ra activity can vary widely, from less than 1 km to over 50 km. Thus, estimating the length of the cross-short Ra gradient through preliminary sampling and/or inferences from previous studies would increase the likelihood of sampling an appropriate number of points within the actual gradient.

Having at least 10 transect points also makes any natural log-linear trends that are present almost certain to be statistically significant at the $\alpha = 0.05$ significance level, given the assumptions of the model. For example, with three transect points only 33% of linear regressions between ln ^{224}Ra activity and distance from shore were statistically significant ($P < 0.05$). However, with 10 transect points over 98% of the regressions were statistically significant.

This analysis indicates that if the assumptions of the eddy diffusion method are met and the uncertainty in short-lived Ra isotope activity is random and on the order of analytical uncertainty alone, K_h can often be calculated with a high level of accuracy and statistical significance with only 5-10 transect points. However, although the method is accurate for a single transect, K_h could also vary at different points within a study area. Thus, it may be beneficial to sample multiple transects to assess the central tendency and degree of spatial variability in K_h in the alongshore direction.

Additionally, there are many situations where the simple eddy diffusion method (Moore 2000*b*) should not be used. These include coastal areas where significant advection occurs or where the coastline has significant curvature with respect to the transect being considered. In some of these cases, it may be possible to develop a more complicated Ra-based eddy diffusion model that accounts for other factors such as variation in K_h over short time scales (Colbert and Hammond 2007), spatial scale dependence of K_h (Colbert and Hammond 2007), or advection (Li and Cai 2011).

As is apparent from Table 1, the majority of studies incorporating the eddy diffusion method have been conducted in bays or other sites with curved shorelines. Curved shorelines, especially bays, could violate the assumption of a shore-perpendicular transect because some of the shoreline Ra source is located to the side of the transect. Future work should assess how different degrees of curvature affect the results of the eddy diffusion method and how to determine whether a coastline is straight enough to satisfy the assumptions of the method. In addition, it is important to keep in mind that this method of calculating K_h assumes that Ra entering the ocean at the coastline has time to undergo significant radioactive decay along the length of the transect. If this is not the case (e.g., if there is rapid coastal mixing and a short residence time), the short-lived isotope is in effect behaving like a long-lived isotope, and the method is not valid.

Study limitations

The analyses presented here offer practical guidelines that can help researchers decide whether Ra-based methods of estimating water ages and coastal mixing rates are appropriate for a given field situation and suggestions of how to reduce the uncertainties associated with these methods. However, it is important to recognize some limitations of this analysis. One important limitation is that we treated uncertainties in Ra isotope activities and activity ratios as random and normally distributed. This is a reasonable and testable assumption in terms of analytical uncertainty, but it may not always apply to natural variability in the field.

Another issue is that uncertainties associated with the measurement of Ra activities on a delayed coincidence counter (RaDeCC) are proportionally greater at lower activities (Garcia-Solsona et al. 2008b). High uncertainties associated with low activities are generally a bigger problem for ^{223}Ra than for ^{224}Ra because ^{223}Ra tends to have lower activity in most discharging groundwater (Garcia-Solsona et al. 2008b). Low Ra activities may also reduce the applicability of the eddy diffusion method if the activities are low enough to increase the uncertainty before the short-lived isotope exhibits measurable decay.

Finally, it has long been recognized that the eddy diffusion coefficient is spatially scale-dependent, with higher eddy diffusion values obtained when a greater length scale (i.e., a longer cross-shore transect) is considered (Stommel 1949; Okubo 1971, 1976). This scale-dependence occurs because both large and small eddies can disperse solutes in the water, and a greater length scale not only contains a proportionally greater number of small eddies, but also larger eddies that are not captured when a smaller scale is considered. Okubo (1976) proposed the following relationship:

$$K_h = 0.0680 \times l^{1.15} \quad (9)$$

where L (km) is the length scale. Thus an order of magnitude increase in length scale—for example, going from a 1-km transect to a 10-km transect—would result in a fourteen-fold increase in K_h. A recent study conducted in Southern California (Colbert and Hammond 2007) found that scale dependence was only important at distances greater than 455 m from shore. Most work incorporating the eddy diffusion method (e.g., Moore 2000b; Dulaiova et al. 2006; Gomes et al. 2009; Table 1) has used transects kilometers or tens of kilometers long, although in some cases the zone of Ra enrichment is limited to less than 1 km offshore (Boehm et al. 2006; Knee et al. 2008). Thus, it is important to assess whether scale-dependent mixing is likely to affect offshore Ra gradients along transects and, if so, to use a more complex mixing model that takes this scale dependence into account. More research on how scale-dependent mixing and spatial variability in K_h affect the application of the Ra-based eddy diffusion method is needed.

The results presented here will help researchers understand and reduce the uncertainties associated with Ra-based water ages and eddy diffusion coefficients, as well as the SGD estimates based upon them. This information is essential to put SGD-related fluxes of nutrients (e.g., Portnoy et al. 1998; Krest et al. 2000; Slomp and Van Capellen 2004), dissolved metals (e.g., Basu et al. 2001; Montluçon and Sañudo-Wilhelmy 2001; Windom et al. 2006), and other pollutants (e.g., de Sieyes et al. 2008; Standley et al. 2008) in context and use them to inform nutrient budgets, assessments of risk to humans and coastal ecosystems, monitoring programs and management decisions.

References

Abraham, D. M., M. A. Charette, M. C. Allen, A. Rago, and K. D. Kroeger. 2003. Radiochemical estimates of submarine groundwater discharge to Waquoit Bay, Massachusetts. Biol. Bull. 205:246-247 [doi:10.2307/1543277].

Arega, F., S. Armstrong, and A. W. Badr. 2008. Modeling of residence time in the East Scott Creek Estuary, South Carolina, USA. J. Hydro-environ. Res. 2:99-108 [doi:10.1016/j.jher.2008.07.003].

Basu, A. R., S. B. Jacobsen, R. J. Poreda, C. B. Dowling, and P. K. Aggarwal. 2001. Large groundwater strontium flux to the oceans from the Bengal basin and the marine strontium isotope record. Science 293:1470-1473 [doi:10.1126/science.1060524].

Beck, A. J., J. P. Rapaglia, J. K. Cochran, and H. J. Bokuniewicz. 2007. Radium mass-balance in Jamaica Bay, NY: Evidence for a substantial flux of submarine groundwater. Mar. Chem. 106:419-441 [doi:10.1016/j.marchem.2007.03.008].

Boehm, A. B., G. G. Shellenbarger, and A. Paytan. 2004. Groundwater discharge: Potential association with fecal indicator bacteria in the surf zone. Environ. Sci. Technol. 38:3558-3566 [doi:10.1021/es035385a].

———, A. Paytan, G. G. Shellenbarger, and K. A. Davis. 2006. Composition and flux of groundwater from a California beach aquifer: Implications for nutrient supply to the surf zone. Cont. Shelf Res. 26:269-282 [doi:10.1016/j.csr.2005.11.008].

Breier, J. A., N. Nidzieko, S. Monismith, W. Moore, and A. Paytan. 2009. Tidally regulated chemical fluxes across the sediment-water interface in Elkhorn Slough, California: Evidence from a coupled geochemical and hydrodynamic approach. Limnol. Oceanogr. 54:1964-1980 [doi:10.4319/lo.2009.54.6.1964].

Brooks, D. A., M. W. Baca, and Y.-T. Lo. 1999. Tidal circulation and residence time in a macrotidal estuary: Cobscook Bay, Maine. Estuar. Coast. Shelf S. 49:647-665 [doi:10.1006/ecss.1999.0544].

Burnett, W. C., and others. 2006. Quantifying submarine groundwater discharge in the coastal zone via multiple methods. Sci. Total Environ. 367:498-543 [doi:10.1016/j.scitotenv.2006.05.009].

———, R. Peterson, W. S. Moore, and J. de Oliveira. 2008. Radon and radium isotopes as tracers of submarine groundwater discharge? Results from the Ubatuba, Brazil SGD assessment intercomparison. Estuar. Coast. Shelf S. 76:501-511 [doi:10.1016/j.ecss.2007.07.027].

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. Limnol. Oceanogr. 52:230-239 [doi:10.4319/lo.2007.52.1.0230].

———, K. O. Buesseler, and J. E. Andrews. 2001. Utility of radium isotopes for evaluating the input and transport of

groundwater-derived nitrogen to a Cape Cod estuary. Limnol. Oceanogr. 46:465-470 [doi:10.4319/lo.2001.46.2.0465].

———, R. Splivallo, C. Herbold, M. S. Bollinger, and W. S. Moore. 2003. Salt marsh submarine groundwater discharge as traced by radium isotopes. Mar. Chem. 84:113-121 [doi:10.1016/j.marchem.2003.07.001].

———,M. E. Gonneea, P. J. Morris, P. Statham, G. Fones, H. Planquette, I. Salter, and A. N. Garabato. 2007. Radium isotopes as tracers of iron sources fueling a Southern Ocean phytoplankton bloom. Deep-Sea Res. II 54:1989-1998 [doi:10.1016/j.dsr2.2007.06.003].

Colbert, S. L., and D. E. Hammond. 2007. Temporal and spatial variability of radium in the coastal ocean and its impact on computation of nearshore cross-shelf mixing rates. Cont. Shelf Res. 27:1477-1500 [doi:10.1016/j.csr.2007.01.003].

Crotwell, A. M., and W. S. Moore. 2003. Nutrient and radium fluxes from submarine groundwater discharge to Port Royal Sound, South Carolina. Aquat. Geochem. 9:191-208 [doi:10.1023/B:AQUA.0000022954.89019.c9].

de Sieyes, N. R., K. M. Yamahara, B. A. Layton, E. H. Joyce, and A. B. Boehm. 2008. Submarine discharge of nutrient-enriched fresh groundwater at Stinson Beach, California is enhanced during neap tides. Limnol. Oceanogr. 53:1434-1445 [doi:10.4319/lo.2008.53.4.1434].

Dulaiova, H., W. C. Burnett, J. P. Chanton, W. S. Moore, H. J. Bokuniewicz, M. A. Charette, and E. Sholkovitz. 2006. Assessment of groundwater discharges into West Neck Bay, New York, via natural tracers. Cont. Shelf Res. 26:1971-1983 [doi:10.1016/j.csr.2006.07.011].

———, and W. C. Burnett. 2008. Evaluation of the flushing rates of Apalachicola Bay, Florida via natural geochemical tracers. Mar. Chem. 109:395-408 [doi:10.1016/j.marchem.2007.09.001].

Gallagher, B. 1980. Physical structure and circulation in Honokohau, a small Hawaiian harbor affected by groundwater. Pac. Sci. 34:301-311.

Garcia-Orellana, J., J. K. Cochran, H. Bokuniewicz, S. Yang, and A. J. Beck. 2010. Time-series sampling of ^{223}Ra and ^{224}Ra at the inlet to Great South Bay (New York): a strategy for characterizing the dominant terms in the Ra budget of the bay. J. Environ. Rad. 101:582-588 [doi:10.1016/j.jenvrad.2009.12.005].

Garcia-Solsona, E., and others. 2008a. Estimating submarine groundwater discharge around Isola La Cura, northern Venice Lagoon (Italy), by using the radium quartet. Mar. Chem. 109:292-306 [doi:10.1016/j.marchem.2008.02.007].

———, J. Garcia-Orellana, P. Masqué, and H. Dulaiova. 2008b. Uncertainties associated with ^{223}Ra and ^{224}Ra measurements in water via a Delayed Coincidence Counter (RaDeCC). Mar. Chem. 109:198-219 [doi:10.1016/j.marchem.2007.11.006].

———, and others. 2010a. An assessment of karstic submarine groundwater and associated nutrient discharge to a Mediterranean coastal area (Balearic Islands, Spain) using radium isotopes. Biogeochemistry 97:211-229.

———, J. Garcia-Orellana, P. Masqué, V. Rodellas, M. Mejías, B. Ballesteros, and J. A. Domínguez. 2010b. Groundwater and nutrient discharge through karstic coastal springs (Castelló, Spain). Biogeosciences 7:2625-2638.

Godoy, J. M., Z. L. de Carvalho, F. da Costa Fernandes, O. M. Danelon, M. L. D. P. Godoy, A. C. M. Ferreira, and L. A. Roldão. 2006. ^{228}Ra and ^{226}Ra in coastal seawater samples from the Ubatuba region–Brazilian southeastern coastal region. J. Braz. Chem. Soc. 17:730-736.

Gomes, F. C., J. M. Godoy, Z. L. Carvalho, and R. T. Lopes. 2009. Short and long-lived radium isotopes in surface waters from Ilha Grande bay, Angra dos Reis, Brazil. Radioprotection 44:237-241 [doi:10.1051/radiopro/20095047].

Gonneea, M. E., P. J. Morris, H. Dulaiova, and M. A. Charette. 2008. New perspectives on Ra behavior within a subterranean estuary. Mar. Chem. 109:250-267 [doi:10.1016/j.marchem.2007.12.002].

Hancock, G. J., and A. S. Murray. 1996. Source and distribution of dissolved radium in the Bega River estuary, Southeastern Australia. Earth Planet. Sci. Lett. 138:145-155 [doi:10.1016/0012-821X(95)00218-2].

Hougham, A. L., and S. B. Moran. 2007. Water mass ages of coastal ponds estimated using ^{223}Ra and ^{224}Ra as tracers. Mar. Chem. 105:194-207 [doi:10.1016/j.marchem.2007.01.013].

Hwang, D.-W., G. Kim, Y.-W. Lee, and H.-S. Yang. 2005. Estimating submarine inputs of groundwater and nutrients to a coastal bay using radium isotopes. Mar. Chem. 96:61-71 [doi:10.1016/j.marchem.2004.11.002].

Kim, G., J.-W. Ryu, H.-S. Yang, and S.-T. Yun. 2005. Submarine groundwater discharge (SGD) into the Yellow Sea revealed by ^{228}Ra and ^{226}Ra isotopes: Implications for global silicate fluxes. Earth Planet. Sci. Lett. 237:156-166 [doi:10.1016/j.epsl.2005.06.011].

———, J.-W. Ryu, and D.-W. Hwang. 2008. Radium tracing of submarine groundwater discharge (SGD) and associated nutrient fluxes in a highly-permeable bed coastal zone, Korea. Mar. Chem. 109:307-317 [doi:10.1016/j.marchem.2007.07.002].

Knee, K. L., B. A. Layton, J. H. Street, A. B. Boehm, and A. Paytan. 2008. Sources of nutrients and fecal indicator bacteria to nearshore waters on the north shore of Kaua`i. Estuar. Coast. 31:607-622 [doi:10.1007/s12237-008-9055-6].

———, J. H. Street, E. E. Grossman, A. B. Boehm, and A. Paytan. 2010. Nutrient inputs to the coastal ocean from submarine groundwater discharge in a groundwater-dominated system: Relation to land use (Kona coast, Hawai`i, USA). Limnol. Oceanogr. [doi:10.4319/lo.2010.55.3.1105].

Krest, J. M., W. S. Moore, L. R. Gardner, and J. T. Morris. 2000. Marsh nutrient export supplied by groundwater discharge: Evidence from radium measurements. Global Biogeochem.

Cyc. 14:167-176 [doi:10.1029/1999GB001197].

Lee, D. R. 1977. A device for measuring seepage flux in lakes and estuaries. Limnol. Oceanogr. 22:140-147 [doi:10.4319/lo.1977.22.1.0140].

Lee, Y.-W., D.-W. Hwang, G. Kim, W.-C. Lee, H.-T. Oh. 2009. Nutrient inputs from submarine groundwater discharge (SGD) in Masan Bay, an embayment surrounded by heavily industrialized cities, Korea. Sci. Total Environ. 407:3181-3188 [doi:10.1016/j.scitotenv.2008.04.013].

Li, C., and W.-J. Cai. 2011. On the calculation of the eddy diffusivity in the shelf water from radium isotopes: High sensitivity to advection. J. Marine Syst. 86:28-33 [doi:10.1016/j.jmarsys.2011.01.003].

Li, Y.-H., and L.-H. Chan. 1979. Desorption of Ba and ^{226}Ra from river-borne sediments in the Hudson estuary. Earth Planet. Sci. Lett. 43:343-350 [doi:10.1016/0012-821X(79)90089-X].

Longuet-Higgins, M. S. 1983. Wave set-up, percolation and undertow in the surf zone. Proc. Roy. Soc. London. 390:283-291 [doi:10.1098/rspa.1983.0132].

Loveless, A. M., C. E. Oldham, and G. J. Hancock. 2008. Radium isotopes reveal seasonal groundwater inputs to Cockburn Sound, a marine embayment in Western Australia. J. Hydrol. 351:203-217 [doi:10.1016/j.jhydrol.2007.12.010].

Monsen, N. E., J. E. Cloern, and L. V. Lucas. 2002. A comment on the use of flushing time, residence time, and age as transport time scales. Limnol. Oceanogr. 47:1545-1553.

Montluçon, D., and S. A. Sañudo-Wilhelmy. 2001. Influence of groundwater seepage on nutrient and metal concentrations in a coastal environment: Flanders Bay, Long Island, NY. Environ. Sci. Technol. 35:480-486.

Moore, W. S. 1984. Radium isotope measurements using germanium detectors. Nucl. Instrum. Meth. Phys. Res. B. 223:407-411.

———. 1997. High fluxes of radium and barium from the mouth of the Ganges-Brahmaputra River during low river discharge suggest a large groundwater source. Earth Planet. Sci. Lett. 150:141-150 [doi:10.1016/S0012-821X(97)00083-6].

———. 2000a. Ages of continental shelf waters determined from ^{223}Ra and ^{224}Ra. J. Geophys. Res. 105:117-122 [doi:10.1029/1999JC000289].

———. 2000b. Determining coastal mixing rates using radium isotopes. Cont. Shelf Res. 20:1993-2007 [doi:10.1016/S0278-4343(00)00054-6].

———. 2006. Radium isotopes as tracers of submarine groundwater discharge in Sicily. Cont. Shelf Res. 26:852-861 [doi:10.1016/j.csr.2005.12.004].

———, J. O. Blanton, and S. B. Joye. 2006. Estimates of flushing times, submarine groundwater discharge, and nutrient fluxes to Okatee Estuary, South Carolina. J. Geophys. Res. 111:C09006 [doi:10.1029/2005JC003041].

———, and J. de Oliveira. 2008. Determination of residence time and mixing processes of the Ubatuba, Brazil, inner shelf waters using natural Ra isotopes. Estuar. Coast. Shelf S. 76:512-521 [doi:10.1016/j.ecss.2007.07.042].

Okubo, A. 1971. Oceanic diffusion diagrams. Deep-Sea Res. 18:789-802.

———. 1976. Remarks on the use of 'diffusion diagrams' in modeling scale-dependent diffusion. Deep-Sea Res. 23:1213-1214.

Paytan, A., G. G. Shellenbarger, J. H. Street, M. E. Gonneea, K. Davis, M. B. Young, and W. S. Moore. 2006. Submarine groundwater discharge: An important source of new inorganic nitrogen to coral reef ecosystems. Limnol. Oceanogr. 51:343-348 [doi:10.4319/lo.2006.51.1.0343].

Peterson, R. N., W. C. Burnett, M. Taniguchi, J. Chen, I. R. Santos, and S. Misra. 2008. Determination of transport rates in the Yellow River-Bohai Sea mixing zone via natural geochemical tracers. Cont. Shelf Res. 28:2700-2707 [doi:10.1016/j.csr.2008.09.002].

———, W. C. Burnett, C. R. Glenn, and A. G. Johnson. 2009. Quantification of point-source groundwater discharges to the ocean from the shoreline of the Big Island, Hawai`i. Limnol. Oceanogr. 54:890-904 [doi:10.4319/lo.2009.54.3.0890].

Portnoy, J. W., B. L. Nowicki, C. T. Roman, and D. W. Urish. 1998. The discharge of nitrate-contaminated groundwater from developed shoreline to marsh-fringed estuary. Water Resour. Res. 34:3095-3104 [doi:10.1029/98WR02167].

Rama, and W. S. Moore. 1996. Using the radium quartet for evaluating groundwater input and water exchange in salt marshes. Geochim. Cosmochim. Acta 60:4645-4652 [doi:10.1016/S0016-7037(96)00289-X].

Rapaglia, J., C. Ferrain, L. Zaggia, W. S. Moore, G. Umgiesser, E. Garcia-Solsona, J. Garcia-Orellana, and Pere Masqué. 2010. Investigation of residence time and groundwater flux in Venice Lagoon: Comparing radium isotope and hydrodynamical models. J. Environ. Radioact. 101:571-581 [doi:10.1016/j.jenvrad.2009.08.010].

Rasmussen, L. L. 2003. Radium isotopes as tracers of coastal circulation pathways in the Mid-Atlantic Bight, Ph.D. Dissertation, Massachusetts Institute of Technology and Woods Hole Oceanographic Institution, 2003.

Robinson, C., L. Li, and D. A. Barry. 2007. Effect of tidal forcing on a subterranean estuary. Adv. Water Resour. 30:851-865 [doi:10.1016/j.advwatres.2006.07.006].

Santos, I. R., and others. 2008. Tracing anthropogenically driven groundwater discharge into a coastal lagoon from southern Brazil. J. Hydrol. 353:275-293.

Scopel, C. O., J. Harris, and S. L. McLellan. 2006. Influence of nearshore water dynamics and pollution sources on beach monitoring outcomes at two adjacent Lake Michigan beaches. J. Great Lakes Res. 32:543-552 [doi:10.3394/0380-1330(2006)32[543:IONWDA]2.0.CO;2].

Shaw, R. D., and E. E. Prepas. 1989. Anomalous, short-term influx of water into seepage meters. Limnol. Oceanogr. 34:1343-1351 [doi:10.4319/lo.1989.34.7.1343].

Shellenbarger, G. G., S. G. Monismith, A. Genin, and A. Paytan. 2006. The importance of submarine groundwater discharge to the nearshore nutrient supply in the Gulf of Aqaba (Israel). Limnol. Oceanogr. 51:1876-1886 [doi:10.4319/lo.2006.51.4.1876].

Slomp, C. P., and P. Van Cappellen. 2004. Nutrient inputs to the coastal ocean through submarine groundwater discharge: Controls and potential impact. J. Hydrol. 295:64-86 [doi:10.1016/j.jhydrol.2004.02.018].

Standley, L. J., R. A. Rudel, C. H. Swartz, K. R. Attfield, J. Christian, M. Erickson, and J. G. Brody. 2008. Wastewater-contaminated groundwater as a source of endogenous hormones and pharmaceuticals to surface water ecosystems. Environ. Toxicol. Chem. 27:2457-2468 [doi:10.1897/07-604.1].

Stommel, H. 1949. Horizontal diffusion due to oceanic turbulence. J.Mar. Res. 8:199-225.

Street, J. H., K. L. Knee, E. E. Grossman, and A. Paytan. 2008. Submarine groundwater discharge and nutrient addition to the coastal zone and coral reefs of leeward Hawai`i. Mar. Chem. 109:355-376 [doi:10.1016/j.marchem.2007.08.009].

Swarzenski, P. W., W. H. Orem, B. F. McPherson, M. Baskaran, and Y. Wan. 2006. Biogeochemical transport in the Loxahatchee River estuary, Florida: The role of submarine groundwater discharge. Mar. Chem. 101:248-265 [doi:10.1016/j.marchem.2006.03.007].

———, C. Reich, K. D. Kroeger, and M. Baskaran. 2007. Ra and Rn isotopes as natural tracers of submarine groundwater discharge in Tampa Bay, Florida. Mar. Chem. 104:69-84 [doi:10.1016/j.marchem.2006.08.001].

———, and J. A. Izbicki. 2009. Coastal groundwater dynamics off Santa Barbara, California; Combining geochemical tracers, electromagnetic seepage meters, and electrical resistivity. Estuar. Coast. Shelf S. 83:77-89 [doi:10.1016/j.ecss.2009.03.027].

Swearman, J. W., S. B. Moran, and R. P. Kelly. 2006. Variability in coastal groundwater radium activity: Implications for radium-derived residence time and groundwater flux. Papers from the Summer Undergraduate Research Fellowship Program in Oceanography at the University of Rhode Island, Graduate School of Oceanography and Department of Ocean Engineering. June-August 2006. GSO Technical Report No. 2006-02. 51-55.

Taniguchi, M., W. C. Burnett, C. F. Smith, R. J. Paulsen, D. O'Rourke, S. L. Krupa, and J. L. Christoff. 2003. Spatial and temporal distributions of submarine groundwater discharge rates obtained from various types of seepage meters at a site in the Northeastern Gulf of Mexico. Biogeochemistry 66:35-53 [doi:10.1023/B:BIOG.0000006090.25949.8d].

Taylor, J. R. 1997. An introduction to error analysis, pp. 160-168. 2nd ed. University Science Books.

Turner, I. L., B. P. Coates, and R. I. Acworth. 1997. Tides, waves, and the super-elevation of groundwater at the coast. J. Coast. Res. 13:46-60.

Weinstein, Y., G. Less, U. Kafri, and B. Herut. 2006. Submarine groundwater discharge in the southeastern Mediterranean (Israel). Radioact. Environ. 8:360-372 [doi:10.1016/S1569-4860(05)08029-0].

Windom, H. L., W. S. Moore, L. F. H. Niencheski, and R. A. Jahnke. 2006. Submarine groundwater discharge: A large, previously unrecognized source of dissolved iron to the South Atlantic Ocean. Mar. Chem. 102:252-266 [doi:10.1016/j.marchem.2006.06.016].

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