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Radon and radium isotopes as tracers of submarine groundwater discharge – Results from the Ubatuba, Brazil SGD assessment intercomparison

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Abstract

We determined groundwater flow rates shortly after the wet season into an embayment near Ubatuba, Brazil as part of an international intercomparison experiment for submarine groundwater discharge (SGD) assessment techniques. Our estimated rates were determined by the combined use of continuous radon measurements and assessment of radium isotope patterns. The spatial distribution of the short-lived radium isotopes (^{223}Ra and ^{224}Ra) provided the means for independent evaluations of radon losses by mixing and atmospheric evasion. We were thus able to construct a well-constrained mass balance for radon that included a groundwater flux term. Our results showed that the groundwater discharge into this embayment from the fractured crystalline rock aquifer is not steady-state but varies with tidal modulation and rain-induced forcing. Tidally modulated and rain-induced flow rates were comparable during this period. The SGD rates estimated from radon ranged from 1 cm/day to 29 cm/day (cm^3/cm^2 day) with a mean and standard deviation of 13 ± 6 cm/day. These estimates were mostly similar to a dye-dilution automatic seepage meter (15 ± 19 cm/day) and were within the broad ranges estimated by manual and continuous heat seepage meters but lower than indicated by an artificial tracer test performed nearshore.

Keywords: groundwater; discharge; radon; radium isotopes; Brazil

1. Introduction

One of the persistent uncertainties in establishing marine geochemical mass balances is evaluating the effect of submarine groundwater discharge (SGD) on the ocean. We have been developing geochemical tools (e.g., radon and radium isotopes) to quantify the magnitude of SGD on a local to regional scale. Since there is no standard methodology for measurement of groundwater flow into the ocean, we are also actively involved in coordinating and participating in SGD assessment intercomparisons.

Several investigators have shown that one can estimate the magnitude of groundwater discharge into the coastal zone using radium isotopes (e.g., Moore, 1996; Krest et al., 2000; Charette et al., 2001; Kelly and Moran, 2002; Krest and Harvey, 2003). Moore (1996) first showed that ^{226}Ra onshore-to-offshore gradients develop because of inputs via SGD and subsequent mixing (either via advection or eddy diffusion) with lower concentration waters offshore. One may determine water exchange rates from independent observations (such as tidal wedge calculations) or use the distribution of the short-lived isotopes of radium (^{223}Ra, $t_{1/2} = 11$ d; ^{224}Ra, $t_{1/2} = 3.66$ d) to estimate the mixing

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coefficients (Moore, 2000a). These mixing rates can then be used to calculate the offshore flux of ^{226}Ra. Assuming that the radium gradients are steady-state, at least over the time scale of the mixing processes, and that the excess radium is supplied by SGD near the coast, one can estimate the groundwater discharge by dividing the radium flux by the concentration of radium in the groundwater.

Radon is also a good natural tracer of SGD because: (1) its concentration is very high in groundwater but low in seawater; (2) it behaves conservatively; and (3) it is relatively easy to measure (Cable et al., 1996). Assessment of possible temporal trends of radon is important because groundwater flow is known to be extremely variable – in some cases even reversing direction in response to external forcing (tides, change in water table height, etc.). The short-lived radium isotopes can be used in conjunction with radon to constrain the mixing losses (Burnett and Dulaiova, 2003).

The principle reason that groundwater estimates have not attained the precision base that is typically achieved of other oceanic inputs is that the direct discharge of groundwater into the coastal zone is inherently very difficult to measure. In order to develop the scientific and technical knowledge that will enable these measurements to be addressed with a higher degree of confidence, a group of scientists ran a series of intercomparison experiments to evaluate SGD assessment techniques. The project was initiated originally by a joint team sponsored by the Scientific Committee on Oceanic Research and the Land–Ocean Interactions in the Coastal Zone project (SCOR-LOICZ Working Group 112; Burnett, 1999). Shortly afterwards, the project was expanded with the involvement of the International Atomic Energy Agency (IAEA) and UNESCO's Intergovernmental Oceanographic Commission (IOC) and International Hydrologic Program (IHP). Our approach was to design side-by-side experiments in different types of coastal environments (karst, coastal plain, glacial, deltaic, etc.) in order to provide testing grounds for different assessment methodologies. The concept was that several techniques would all be employed at the same time and place in order to make comparisons (and eventual improvements) on a level playing field. This paper reports our isotopic results from an SGD assessment intercomparison held off a marine laboratory of the Oceanographic Institute of the University of São Paulo during the period Nov. 16–22, 2003 in Ubatuba, Brazil – an area of fractured crystalline rocks. Other reports in this issue present further results and a summary of the entire project's results and recommendations may be found in Burnett et al. (2006).

2. Study site and methods

2.1. Ubatuba, Brazil study site

There are a series of small embayments near Ubatuba, São Paulo State, Brazil, covering latitudes between 23°26′S and 23°46′S and longitudes between 45°02′W and 45°11′W (Fig. 1). The study area comprises the northernmost part of São Paulo Bight, southeastern Brazil, and is considered a tropical coastal area. The field site is located approximately 270 km north of São Paulo city. The embayments investigated here include Flamengo Bay (Ubatuba Marine Laboratory site) and Fortaleza Bay, just to the west. The SGD rates were shown to be significant in this area by Oliveira et al. (2003). Even if SGD fluxes at the Ubatuba coastal area were modest, pollutant concentrations in groundwater may be sufficiently high (mostly in the summer season, when anthropogenic nitrogen fluxes rise) to have an important impact on the fate of contaminants delivered to the local embayments.

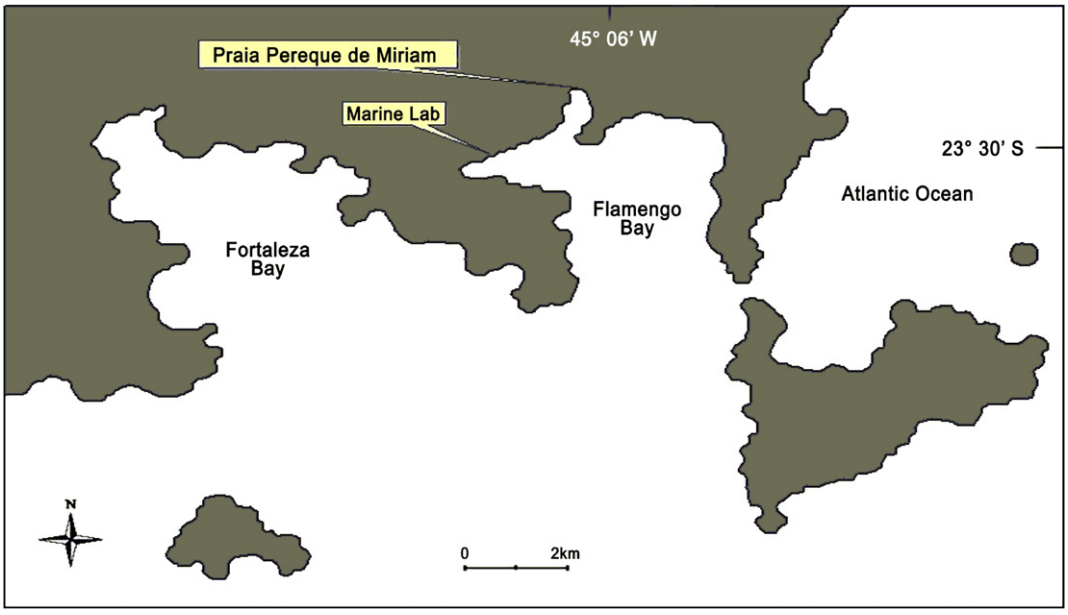

Fig. 1. Index map showing the locations of the two embayments and the marine laboratory. The continuous radon measurements were made from a float ~200 m off the lab.

The geologic/geomorphologic characteristics of the area are strongly controlled by the presence of granites and migmatites of a mountain chain locally called Serra do Mar (altitudes up to 1000 m). This chain reaches the shore in almost all of the study area, and limits the extension of the drainage systems and of the Quaternary coastal plains (Mahiques, 1995). The mean annual rainfall in the area is roughly 1800 mm, with the maximum rainfall rates being observed in February. Sea level varies from 0.5 m to 1.5 m, the highest values occurring in the months of August and September due to a greater volume of warm waters of the Brazil Current (Mesquita, 1997).

2.2. Radon measurements

We deployed a continuous radon monitor on a float located about 200 m off the marine station (northwest Flamengo Bay) to make a time-series record during the entire period of the experiment (Nov. 15–20, 2003). The instrument made repeated integrated measurements of radon concentration in the seawater every 1-h period. The automated radon system analyses ^{222}Rn from a constant stream of water (driven by a submersible pump from near the water surface) passing through an air–water exchanger that distributes radon from a running flow of water to a closed air loop. The air stream is fed to a commercial radon-in-air monitor (Durridge Co., Inc. RAD-7) that determines the concentration of ^{222}Rn by collection and measurement of the α-emitting daughters, ^{214}Po and ^{218}Po. Since the distribution of radon at equilibrium between the air and water phases is governed by well-known temperature dependence, the radon concentration in the water may be easily calculated (Burnett et al., 2001).

We also used a multi-detector system for radon mapping of surface waters in both Flamengo Bay and neighboring Fortaleza Bay and out to about 10 km offshore. This system is based on the same technology as the one described above but uses three detectors in parallel instead of one and also incorporates integrated GPS navigation, depth sounding, and salinity (conductivity)–temperature measurements (Dulaiova et al., 2005).

Total ^{222}Rn and ^{226}Ra were also determined in grab samples from three vertical profiles (FB-1, FB-2 and FB-3) inside Flamengo Bay by standard radon emanation methods. We also collected and analyzed water from two streams that drain into Flamengo Bay at Perequê Mirim Beach. The depth profile samples were collected at 1–2 m intervals using a peristaltic pump and 4-L evacuated glass bottles. Radon was extracted by sparging with helium, collected in cold traps at liquid nitrogen temperature, transferred to alpha scintillation cells, and counted using portable Scintrex radon monitors (RDA-200). The samples were then sealed and stored for at least 5 days for ^{222}Rn in-growth and then extracted again in order to determine the ^{226}Ra activity. Excess ^{222}Rn values were decay-corrected back to the time of sampling in order to assess the in situ excess radon concentrations. Radon inventories were calculated by integrating the excess radon activities over water depth.

Pore water radon activities and diffusive fluxes were estimated by sediment equilibration experiments (Martens et al., 1980). Six sediment samples collected in Flamengo Bay were equilibrated with bay water for periods of over 3 weeks, long enough for radioactive equilibration between ^{226}Ra and ^{222}Rn. A porosity (ϕ) of 0.51 ± 0.07 was determined for sediment samples ($n = 2$) collected in Flamengo Bay. The corresponding activity of ^{222}Rn in equilibrium with wet sediment determined experimentally (C_{eq}) was 1.8×10^5 dpm m^{-3} of wet sediment. This is equivalent to a pore water ^{222}Rn activity of 243 dpm/L.

2.3. Radium isotopes

We used "Mn fibers" (Moore, 1976) to preconcentrate Ra isotopes from samples of coastal seawater. Such fibers are prepared by impregnating acrylic fiber with MnO_2 by cooking in a solution of potassium permanganate. The fibers are then loaded into a cartridge and water samples are passed through at rates less than 2 L per min to ensure quantitative adsorption of radium onto the MnO_2. For some samples, we passed measured volumes of water (up to $\sim$100 L) for quantitative determinations of all four natural Ra isotopes. In other cases, we towed fibers for various lengths of time in a mesh bag behind the boat to determine the activity ratios. In both cases the Mn fibers were measured initially on delayed coincidence counters at the marine base for the short-lived ^{224}Ra and ^{223}Ra determinations and then sent back to our laboratory for additional measurements by the same technique 5–20 days later (Moore and Arnold, 1996). The long-lived ^{226}Ra and ^{228}Ra were determined at a later date by gamma spectrometry using custom-made stainless steel crucibles to ash the fibers for volume and mass reduction followed by crushing the crucible with a hydraulic press into a flat counting disc (Dulaiova and Burnett, 2004).

2.4. Other measurements

The water depth was monitored continuously at the dock of the marine laboratory using an Infinities Inc. electronic water level data logger. In addition, we made continuous measurements of wind speed, barometric pressure, and air temperature using a Davis Instruments Vantage PRO Model 6150C weather station with data logger. Water temperatures were recorded continuously in the radon exchanger using a temperature probe with data logger (Cole Palmer 23500 series). We used a Consort K911 conductivity meter (Topac Inc.) to monitor the salinity distributions in the bays during the surveys. Atmospheric radon was measured at 2-h intervals during the experimental period with another RAD-7 radon monitor set up in one of the laboratories with an outside air intake. Many geophysical and hydrogeological measurements were also made during this period and are reported in companion papers in this issue (e.g., Oberdorfer et al., 2008).

2.5. SGD calculations based on ^{222}Rn mass balance

Variations in the time-series radon record made off the marine laboratory were used to calculate the rates of groundwater seepage by a non-steady-state mass balance with the unknown term being radon supplied by fluid advection through

sediments (Burnett and Dulaiova, 2003). The Rn mass balance may be expressed as:

$$J_{\text{benthic}} + \lambda I_{\text{Ra}} - J_{\text{atm}} - \lambda I_{\text{Rn}} \pm J_{\text{hor}} = 0 \quad (1)$$

The term J_{benthic} represents the combined advective (pore water) and diffusive flux of Rn to the overlying water column, λ is the decay constant of ^{222}Rn, and I_{Ra} and I_{Rn} are the inventories of Ra and Rn, respectively. The terms λI_{Ra} and λI_{Rn} account for the production and decay of radon in the water column. J_{atm} is the flux of Rn to the atmosphere, and J_{hor} is the horizontal "mixing" of Rn into or out of the study area, i.e., dilution of radon via mixing with low-radon waters offshore.

Our procedure for estimating groundwater fluxes from continuous radon measurements at one location may be summarized by the following steps:

(1) ^{222}Rn inventories were calculated for each hourly measurement by multiplying the excess ^{222}Rn activity (dpm/m^3) by the water depth (m) = (dpm/m^2). This assumes that the water column is well-mixed, reasonable for the 2–3 m deep location where the time-series was performed. Excess ^{222}Rn (total ^{222}Rn minus ^{226}Ra) activities in the water column were estimated from spot measurements of ^{226}Ra using the Rn in-growth method (0.46 dpm/L, $n = 6$; Oliveira et al., 2003). We considered loss of ^{222}Rn by radioactive decay negligible because of the short duration between the time steps in our measurements, i.e., 1 h.

(2) Inventories were corrected for atmospheric evasion losses during each measurement interval. The total flux across the air–water interface depends on the molecular diffusion produced by the concentration gradient across this interface and turbulent transfer, which is dependent on physical processes, primarily governed by wind speed. We used equations presented by Macintyre et al. (1995) and Turner et al. (1996) that relate gas exchange across the sea–air interface to the gradient in radon concentration, temperature, and wind speed. All relevant parameters to assess the atmospheric exchange were measured including continuous measurements of the atmospheric radon concentration (Burnett et al., 2003).

(3) The advective flux of radon from the sediment was assumed to dominate the total flux so diffusive flux was ignored. We estimate that less than 5% of the measured inventories could be due solely to diffusion.

(4) Horizontal mixing losses were estimated based on inspection of the change in the measured inventories (corrected for atmospheric loss) over time. These "net" ^{222}Rn fluxes were determined by evaluating the change in inventories (dpm/m^2) over each 1-h time interval. When examined in this manner, one observes both positive (sources > losses) and negative (losses > sources) fluxes. The only losses to the radon mass balance should be by radioactive decay, atmospheric evasion, and mixing. Since decay is unimportant on this time scale (1-h interval) and atmospheric losses are corrected for before the net fluxes are calculated, the negative fluxes must be due to mixing. We estimated mixing losses for different periods based on the maximum absolute values of the negative fluxes. These estimates should represent conservative (lower) estimates of the mixing losses as they are based on measurements of the remaining radon inventories present at any one time. Higher losses could be compensated for by higher input fluxes occurring at the same time. These estimated losses are then added to the measured net fluxes to derive total Rn input fluxes to the study domain (Burnett and Dulaiova, 2003).

(5) To convert radon flux estimates to water flux, we simply divide by the radon pore water concentration. This concentration was determined by the use of sediment equilibration measurements (Corbett et al., 1998). A more complete description (including a list of equations) of the calculations and corrections for estimating SGD rates based on continuous radon measurements may be found in Lambert and Burnett (2003) and Burnett and Dulaiova (2003).

2.6. Mixing rates and ages based on radium isotopes

Trends in the ^{224}Ra/^{223}Ra activity ratios (AR) may be used to calculate mixing coefficients and "radium ages." In order to make an independent assessment of the radon loss via mixing for our mass balance model, we will use short-lived radium isotopes to calculate a mixing coefficient. Then that mixing term will be multiplied by the observed gradient of ^{222}Rn offshore and by the average water depth or thickness of the mixed layer. This provides a flux of radon offshore along the measured transect. Since the decay term is known precisely (the AR will decay with a combined half-life of 5.4 days), a mixing coefficient (K_h) can be calculated from the slope of the ln AR versus distance regression line based on the following equation derived by Moore (2000a):

$$\text{Slope} = \sqrt{\frac{\lambda_{224} - \lambda_{223}}{K_h}} \quad (2)$$

where λ is the decay constant of either ^{224}Ra or ^{223}Ra. We will show in this paper that the short-lived Ra isotopes can constrain the mixing rate in the radon model and can also be used to make independent estimates of the radon atmospheric evasion rate.

The radium isotopic results may also be used to estimate "radium ages" of the water, assuming that the radium enters into the coastal waters at the shoreline with a constant isotopic composition at least over a period comparable to the effective mean life of the ^{224}Ra/^{223}Ra activity ratio (7.8 days). Based on the ^{224}Ra/^{223}Ra activity ratio, one may use the following equation as presented by Moore (2000b):

$$\left[\frac{^{224}\text{Ra}}{^{223}\text{Ra}}\right]_{\text{obs}} = \left[\frac{^{224}\text{Ra}}{^{223}\text{Ra}}\right]_{i} \frac{e^{-\lambda_{224} t}}{e^{-\lambda_{223} t}} \quad (3)$$

or, rearranging in terms of the radium age (t):

$$t = \ln\left(\frac{(\text{AR})_{\text{i}}}{(\text{AR})_{\text{obs}}}\right) \frac{1}{\lambda_{224} - \lambda_{223}} \quad (4)$$

where $(\text{AR})_{\text{i}}$ and $(\text{AR})_{\text{obs}}$ represent the initial and observed ^{224}Ra/^{223}Ra activity ratios, respectively.

3. Results

3.1. Atmospheric Rn patterns

Winds were generally moderate during the intercomparison experiment with only one brief period towards the end when winds exceeded 10 m/s. Atmospheric radon concentrations ranged from below detection (< 2 Bq/m^3; 0.1 dpm/L) to over 30 Bq/m^3 (1.8 dpm/L). The highest radon concentrations occurred during easterly or northerly winds that brought continental air masses over the station. The very highest-level atmospheric radon concentration was reached on Nov. 19th during a period of low E–ENE winds a few hours after a low-pressure episode.

3.2. Radon and salinity mapping

We measured the spatial distribution of radon in the surface waters along the shorelines of the two embayments using a newly developed multi-detector radon system (Dulaiova et al., 2005). This was done to make a qualitative assessment of surface water radon activities to get a feel for where groundwater points of seepage may be highest. One air–water exchanger was fed surface seawater from a submersible pump while being towed from a boat at an average speed of about 7 km/h. The air from this exchanger was in turn delivered to three radon detector systems arranged in parallel. Each detector was set to integrate counts over a 30-min period and the detectors were phase shifted by 10 min. Thus, a new data point was recorded every 10 min. The results (Fig. 2) show that there are definite areas of radon variations within the two embayments investigated. The highest area was along a rocky shoreline in the north central area of Flamengo Bay, a few hundred meters off Perequê Mirim Beach. We observed small springs in this area that consistently showed up as positive radon anomalies with somewhat lower salinities. In general, salinities did not show much variation and were almost always in the narrow range of 28–30 with no apparent relationship to the radon activities.

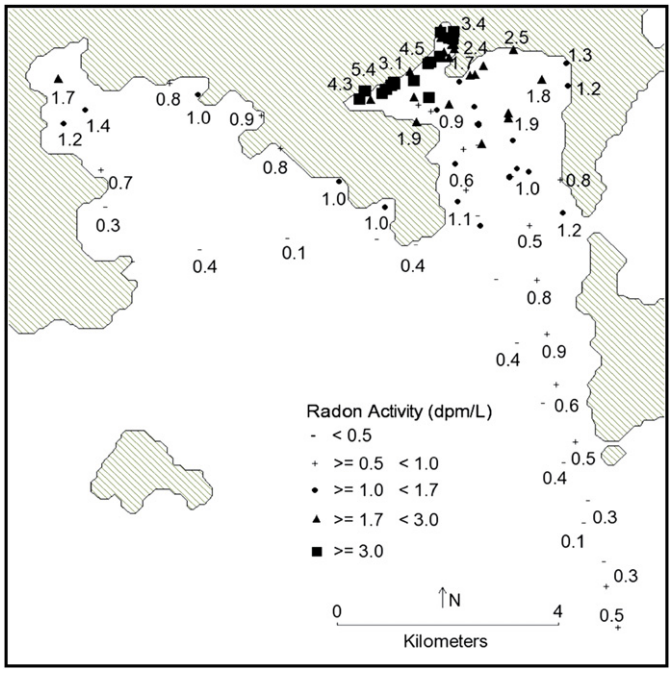

Fig. 2. Distribution of ^{222}Rn in surface waters of the study area measured by a multi-detector radon mapping system. All concentrations are reported in units of dpm/L.

3.3. Radium isotope mapping

At the same time we were conducting the radon survey, we towed "Mn fibers" in a mesh bag behind the boat for periods of 30–40 min for the determination of radium isotope ratios. The towed fibers cannot be used to quantify the abundance of individual isotopes because there is no volume measurement. However, the isotopic ratios (e.g., ^{224}Ra/^{223}Ra) can still be determined and these are useful for determining water exchange rates as described earlier. While both the radon and radium isotopic approaches are valuable, they can be most powerful if applied together to the same system.

Results for the ^{224}Ra/^{223}Ra activity ratios (Fig. 3) show that there is a systematic trend from high ratios nearshore and steadily decreasing ratios as one moves offshore. The highest ^{224}Ra/^{223}Ra activity ratios measured were in the nearshore waters of Flamengo Bay. We consistently measured high ratios (~25) in the same area of north central Flamengo Bay where the high ^{222}Rn activities were observed. We see systematically decreasing trends (Fig. 4) if we plot the natural logarithm of

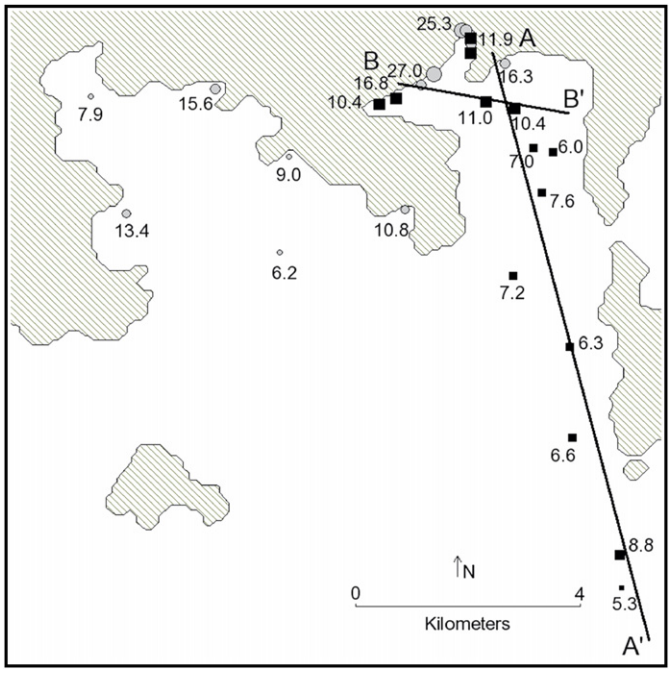

Fig. 3. Map showing the distribution of the ^{224}Ra/^{223}Ra activity ratios in the coastal waters off the Ubatuba marine base. High activity ratios were measured along the same rocky shoreline where high ^{222}Rn activities were found. Transit A–A′ corresponds to points measured on the same day (Nov. 19) that were used to estimate atmospheric evasion of radon. Transect line B–B′ was used to calculate mixing away from the point where the continuous Rn measurements were made.

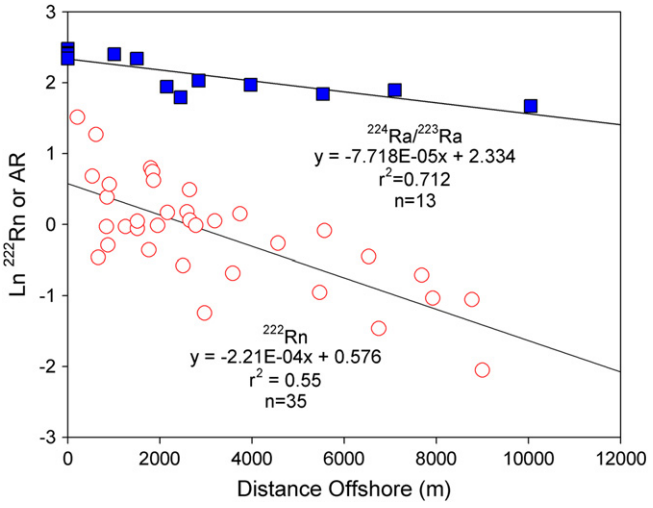

Fig. 4. Distribution of the natural logarithm of the $^{224}Ra/^{223}Ra$ activity ratio and ^{222}Rn versus distance offshore along transect line A–A′ (Fig. 3) from the interior of Flamengo Bay to about 10 km offshore.

the $^{224}Ra/^{223}Ra$ activity ratios (AR) and the ^{222}Rn activities versus distance offshore along a shore-normal transect (line A–A′ in Fig. 3) made on Nov. 19th. This shows that both radium isotopes and radon decrease in a log-normal pattern in the offshore direction although their slopes are different. We also show trend lines for $^{224}Ra/^{223}Ra$ AR and ^{222}Rn versus distance along line B–B′ that will be used later for mixing rate estimates (Fig. 5).

3.4. Radon time-series experiment

We made continuous radon measurements of coastal waters (~2–3 m water depth) at a fixed location off a float near the marine lab from the afternoon of Nov. 15 to about noon of Nov. 20, 2003. There was a short period on Nov. 16th when the system was down for maintenance. The record of radon concentrations shows that they ranged generally from about 2 dpm/L to 6 dpm/L and showed the highest activities at the lowest tidal stages (Fig. 6). Furthermore, the radon maxima tend to have a period of 24-h corresponding to the lowest low tide each day in this semi-diurnal mixed tidal environment. There is one exception to this observation during Nov. 17th when there is an "extra" peak, thought to be related to a rain event, occurring at about the highest tide that day. A dye-dilution automatic seepage meter (Sholkovitz et al., 2003) was deployed during part of the same interval and produced a similar pattern showing high seepage at the lowest tides. The spikes in the seepage meter record are sharper as the chamber was deployed very close to the shore directly on the seabed while the radon is being measured in the water column further offshore.

Recent investigations have reported longer-term (weeks to months) tidally modulated cycles in seepage based on continuous measurements of the groundwater tracers radon and methane (Kim and Hwang, 2002) and automated seepage meter observations. Taniguchi (2002) recorded seepage flux rates in Osaka Bay, Japan, from May to August 2001 and analyzed these data via the Fast Fourier Transfer (FFT) method to discern the dominant periods of variation. Both these tracers and seepage meter studies showed that there is not only a semi-diurnal to diurnal tidal relationship to SGD but also a semi-monthly variation in flow reflecting the neap–spring lunar tidal cycle. Superimposed on this predictable behavior in tidally driven response are variations in terrestrial hydrologic parameters (water table height, etc.). While our time-series experiment was not long enough to evaluate the possible influence of a lunar cycle, we note that our experiment began just about as the neap tide was reached.

4. Discussion

4.1. SGD estimates

We estimated SGD rates from the continuous ^{222}Rn measurements as described earlier. Measurements off the marine base were recorded hourly from Nov. 16 to 20, 2003. The

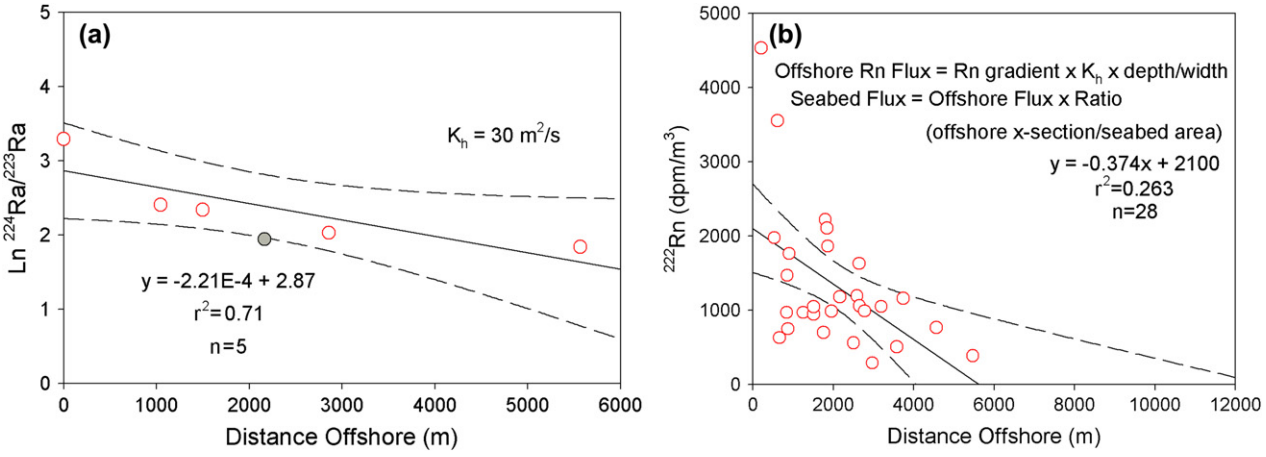

Fig. 5. (a) Distribution of the natural logarithm of the $^{224}Ra/^{223}Ra$ activity ratios along transit line B–B′ (Fig. 3) as a function of distance away from the float where the radon monitor was located. The single point shown in grey was not used in the regression because of its low abundance. (b) Radon activity versus distance along the same line.

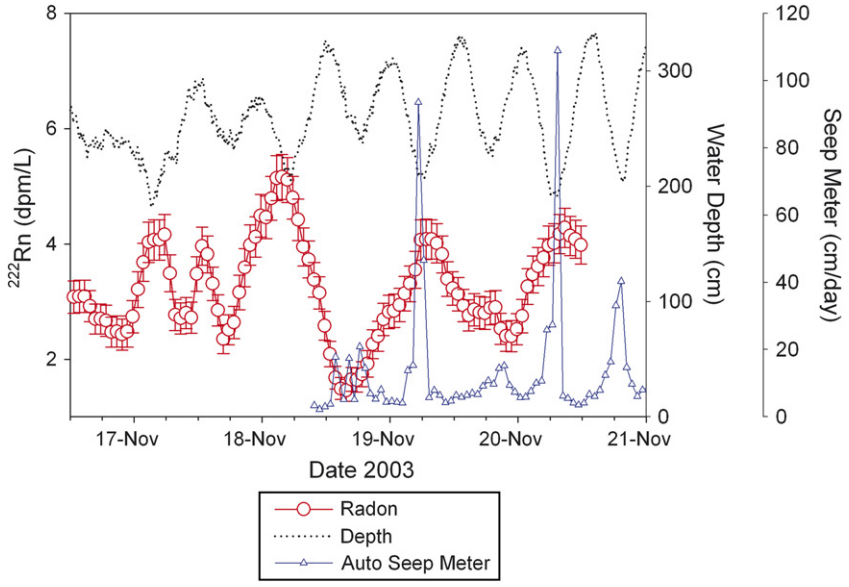

Fig. 6. Time-series radon measurements at a fixed location from a float approximately 200 m from the shoreline. The water level record is also shown for comparison. The submersible pump delivered water from ~1.5 m water depth at this station. Results from an automated seepage meter deployed nearshore during the second half of the experiment shows a similar pattern.

calculated net fluxes are converted to water fluxes by dividing by the estimated pore water ^{222}Rn activity. Although there are a few small streams that enter Flamengo Bay, their contribution to the radon budget is considered unimportant as they have extremely low flows and often do not flow at all. Our pore water ^{222}Rn value, 243 dpm/L ($n = 6$; Oliveira et al., 2003), is within the range of measured pore water ^{222}Rn values determined for nearshore sediments of Flamengo Bay by Cable and Martin (2008) during the same period as our measurements. Their results, based on 27 pore water ^{222}Rn measurements, showed a mean activity of 260 ± 360 dpm/L.

The estimated SGD rates (Fig. 7a) show a similar pattern as the ^{222}Rn concentrations (Fig. 6) and a somewhat similar pattern as seen by some of the manual and automated seepage meters deployed by other groups (Bokuniewicz et al., 2008; Taniguchi et al., 2008). Over a 109-h period, the estimated SGD based on our radon measurements ranged from 1 cm/day to 29 cm/day with an average of 13 ± 6 cm/day. That rate is very close to the 15 ± 19 cm/day average for the dye-dilution seepage meter although that device indicated a much broader range in flow – from about 2 cm/day up to over 100 cm/day for short periods during the lowest tides. Our results are also similar to the 8–22 cm/day range estimated from pore water inventories although lower than the 29–185 cm/day rates indicated by an artificial tracer test (Cable and Martin, 2008). Overall, these results suggest that the advection of pore water fluids across the seabed is not steady-state over time scales of hours but episodic with a period that suggests tidal forcing or modulation. This is very similar to observations elsewhere

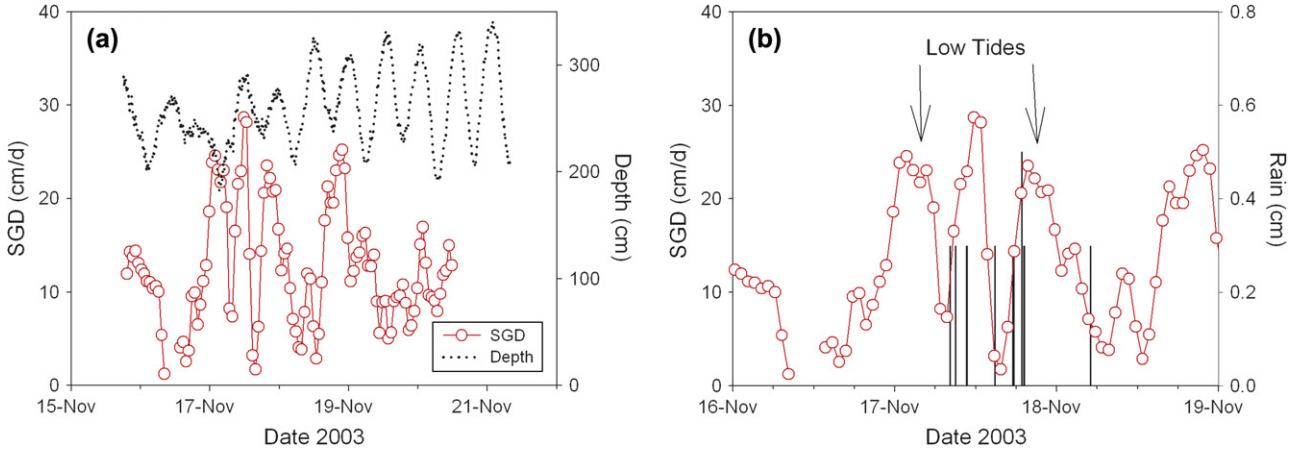

Fig. 7. (a) Calculated SGD rates (open circles, left-hand scale) based on the continuous radon measurements (Fig. 6) 200 m off the marine laboratory together with water level fluctuations (dotted line, right-hand scale). (b) A portion of the same record showing that the SGD peak that did not correspond to a low tide may have been related to a rain event at that time. Rain amounts (cm) are shown by vertical bars.

(e.g., Burnett et al., 2002; Taniguchi et al., 2002; Sholkovitz et al., 2003).

Most of the radon-derived seepage spikes that were observed by this analysis occurred during the lowest tides with the exception of the one peak around noon of Nov. 17th. Inspection of the rainfall record shows that this was also a period when there was a significant amount of rain (Fig. 7b). Thus, the ''extra peak'' seen in the radon record on Nov. 17th may be due to a rapid response of a shallow aquifer to this rainfall event. While this supposition is clearly uncertain, the fractured crystalline rock terrain of this area should be conducive to rapid flow from storm events via conduit flow. A rapid SGD response to climatic conditions was also seen on the volcanic island of Jeju (Korea) reported by Kim et al. (2003) and Hwang et al. (2005).

We can also estimate SGD rates based on the inventories from the three vertical profiles collected inside Flamengo Bay if we assume that these profiles are reasonably steady-state and supported by a combination of advection and diffusion. The radon-depth profiles do not show much vertical structure but indicate that the water column is relatively well-mixed in this shallow embayment. The excess ^{222}Rn inventories for stations FB-1, FB-2, and FB-3 are 6100 ± 1600 dpm/m^2, $12{,}800 \pm 3600$ dpm/m^2, and $12{,}200 \pm 3900$ dpm/m^2, respectively (Table 1). Applying a one-dimensional advection–diffusion model (Cable et al., 1996) with the porosity and pore water values mentioned earlier results in estimated groundwater advective rates necessary to balance these inventories equal to 0.48 cm/day, 1.3 cm/day and 1.2 cm/day. These rates are at the low end of what was estimated based on the continuous radon measurements but are reasonable as these profiles were located in the deeper areas of the bay further from the shoreline.

Table 1
Total ^{222}Rn, ^{226}Ra and excess ^{222}Rn activities observed for vertical profiles in Flamengo Bay stations FB-1 (23°29.597′S, 45°06.324′W; 4.8 m), FB-2 (23°30.422′S, 45°06.202′W; 8 m), and FB-3 (23°30.422′S, 45°06.202′W; 11 m) and in samples from two streams entering the bay from Perequê Mirim Beach

Date	Sample (*n*)	Depth (m)	Total ^{222}Rn (dpm/L)	^{226}Ra (dpm/L)	Excess ^{222}Rn (dpm/L)
18-Nov-2003	FB1-1 (1)	1	1.8 ± 0.3	0.25 ± 0.06	1.6 ± 0.4
18-Nov-2003	FB1-2 (1)	2	1.2 ± 0.2	0.28 ± 0.07	0.98 ± 0.25
18-Nov-2003	FB1-3 (1)	3	1.5 ± 0.3	1.2 ± 0.2	0.32 ± 0.06
18-Nov-2003	FB1-4 (2)	4	2.5 ± 0.5	0.90 ± 0.18	1.7 ± 0.5
18-Nov-2003	FB1-4.5 (1)	4.5	3.4 ± 0.6	0.59 ± 0.12	3.0 ± 0.7
18-Nov-2003	FB2-1 (1)	1	1.1 ± 0.2	0.59 ± 0.12	0.61 ± 0.28
18-Nov-2003	FB2-3 (2)	3	1.8 ± 0.32	0.22 ± 0.06	1.8 ± 0.4
18-Nov-2003	FB2-5 (2)	5	1.9 ± 0.4	0.67 ± 0.13	1.5 ± 0.5
18-Nov-2003	FB2-7 (7)	7	2.8 ± 0.5	0.69 ± 0.14	2.5 ± 0.6
20-Nov-2003	FB3-1 (2)	1	1.0 ± 0.2	0.59 ± 0.12	0.42 ± 0.23
20-Nov-2003	FB3-3 (1)	3	1.4 ± 0.3	0.84 ± 0.17	0.57 ± 0.32
20-Nov-2003	FB3-5 (1)	5	1.6 ± 0.3	0.59 ± 0.12	1.1 ± 0.3
20-Nov-2003	FB3-7 (1)	7	2.3 ± 0.4	0.57 ± 0.11	1.8 ± 0.4
20-Nov-2003	FB3-9 (1)	9	2.5 ± 0.5	0.82 ± 0.16	1.8 ± 0.5
20-Nov-2003	FB3-10 (2)	10	1.8 ± 0.3	0.97 ± 0.17	0.81 ± 0.40
20-Nov-2003	West stream (1)	Surface	136 ± 24	0.67 ± 0.13	138 ± 24
20-Nov-2003	East stream (1)	Surface	207 ± 36	0.62 ± 0.12	209 ± 37

4.2. Mixing loss assessment

We used the radium isotope trend along the transect line B–B′ (Fig. 3) that started at the float where the continuous radon monitor was deployed and extended out to the mouth of Flamengo Bay, about 5.6 km. This line was used rather than A–A′ because it includes the more enclosed section of the bay (where the time-series Rn measurements were made) and the mixing could be different than the more open shoreline along the other transect. We had 6 radium activity ratios (towed Mn fibers) and 28 radon measurements (multi-detector Rn monitor) along this line (Fig. 5). If one assumes that: (1) the system is steady-state on about a 2-week time scale; (2) all radium enters at the shoreline; and (3) there is no significant horizontal advective transport, then this trend is due to a combination of diffusive mixing and radioactive decay (Moore, 2000a). We think that these assumptions are reasonable as we were at the field site for a sufficiently long period to observe that the environmental conditions were reasonably constant (assumption #1). While it is likely that some radium does enter the system at other points than at the shoreline (Moore and Oliveira, 2008), our data consistently show higher activities as we approach the shore (assumption #2). Finally, the log-linear plots of short-lived radioisotopes versus distance along both lines A–A′ (Fig. 4) and B–B′ (Fig. 5) indicate that the advection is likely not important (assumption #3). Analysis of long-lived radium isotopes (^{226}Ra and ^{228}Ra) along the shore-normal transects showed linear trends, also indicating that advection is not important (Moore and Oliveira, 2008).

Analysis of the radium activity ratio trends along B–B′ resulted in a mixing coefficient of 30 m^2/s, which when multiplied by the linear radon gradient (0.374 dpm/m^3 m) and the average depth of the mixed layer (13 m; as determined by CTD profiles offshore) gives a flux away from the radon monitor of 5.25×10^5 dpm/m^2 h per m width of shoreline. In order to convert this to a flux per unit area of seabed, we simply multiply this flux by the ratio of the cross-sectional area of the offshore flux (13 m^2) to that of the area of the seabed along the transect (5600 m long $\times$ 1 m width or 5600 m^2). This calculation results in an estimated mixing loss of ^{222}Rn of 1220 dpm/m^2 h – a value that is consistent with the mixing loss estimated by inspection of the radon net fluxes that averaged 1100 ± 420 dpm/m^2 h.

4.3. Independent assessment of radon atmospheric evasion

In order to make an independent assessment of the radon evasion rate, we can examine the distribution of the short-lived radium isotopes compared to radon. In principle, their distributions should be similar except for atmospheric evasion if they have a common source once the differences in decay are taken into account. We used an initial ^{224}Ra/^{223}Ra AR of 11.9 that

was measured at a station in the north central area of Flamengo Bay in an area where the radon was typically at the highest levels. The water at this station is thus defined as "zero age." We then calculated Ra ages based on Eq. (4) for the same 13 stations where we had the towed Mn fibers (Fig. 4). These ages were then plotted against distance offshore along the transect (Fig. 8) to develop a relationship between position offshore and Ra age. While a few stations had an activity ratio higher than 11.9 (water collected in some seepage meters had an AR between 20 and 40), these stations were within interior sections of the bay where groundwater may enter with different isotopic signatures than found along the shoreline fronting the area of our transect. If one had used an initial AR closer to samples collected from inside the seepage chambers (Moore and Oliveira, 2008), the calculated ages would be 3–5 days older. However, use of a higher or lower value for the initial activity ratio would not change the slope of the age versus distance relationship that is central to our approach.

We then plotted the ^{222}Rn values along the same transect measured by the multi-detector system versus the derived Ra ages to establish an observed gradient of the change in radon concentration per unit time offshore. The *y*-intercept on this plot would thus represent an initial value of ^{222}Rn present in the nearshore waters assuming that these inputs are steady-state when averaged over several days. While it has already been shown that SGD inputs are not steady-state over time scales of a tidal cycle (Fig. 6), the inputs averaged over a time period corresponding to the mean life of the radium activity ratio (7.8 days) is likely to be more constant. We then draw a theoretical distribution of radon based on its initial value and corrected for decay (Fig. 9). The difference in the slopes of the observed and theoretical distributions of radon multiplied by the average thickness of the mixed layer

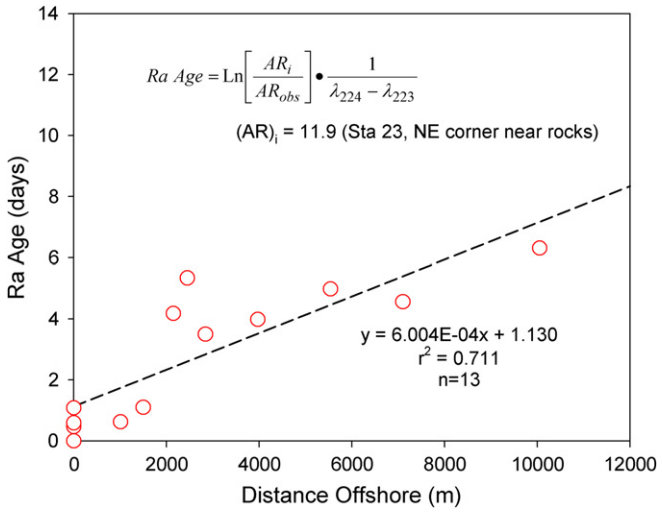

Fig. 8. Radium ages (based on ^{224}Ra/^{223}Ra activity ratios) versus distance offshore for 13 towed Mn-fiber samples collected along transect line A–A′ (Fig. 3) on Nov. 19, 2003 from the interior of Flamengo Bay to about 10 km offshore. While a linear regression provides a reasonably good fit of the data, we recognize that the actual age distribution is not necessarily linear.

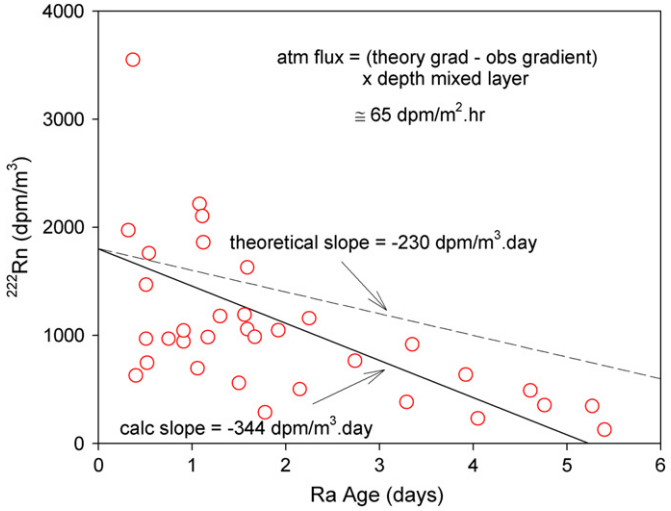

Fig. 9. Observed distribution of ^{222}Rn as a function of Ra age along a transect A–A′ (Fig. 3) off Flamengo Bay compared to its theoretical distribution (loss only by decay). The difference in the two slopes should be a measure of the radon loss by atmospheric evasion.

(13 m) will then be a direct estimation of the loss of radon by atmospheric evasion. Since the measurements were made along the same transect at the same time, the influence by mixing will be the same and the decay differences are already accounted for in the analysis. This approach provided an estimate of 65 dpm/m^2 h as the flux of radon across the air–sea interface during the few hour period on Nov. 19th when the survey was performed. This estimate is well within the range estimated theoretically for the same period based on wind speed, temperature, and concentration gradients (range = 30–100 dpm/m^2 h; average = 51 ± 27 dpm/m^2 h) and thus provides additional confidence in the calculation approach. Another recent study (Upper Gulf of Thailand) applied the ^{224}Ra–^{222}Rn experimental approach to assess air–sea gas flux and showed that the results were similar to those based on the same gas exchange equations applied here (Dulaiova and Burnett, 2006).

5. Conclusions

We have reached the following conclusions based on the isotopic measurements during the SGD assessment intercomparison in Brazil:

(1) The results from the radon time-series experiment in the coastal waters of Flamengo Bay show that ^{222}Rn and the calculated groundwater discharges are not steady-state on short time scales but generally highest during the lowest low tide each day. The average calculated rate of discharge according to the radon model is 13 ± 6 cm/day, closest to the average of 15 ± 19 cm/day measured by a dye-dilution automatic seepage meter, and within the same range (8–22 cm/day) as estimated by an analysis of pore water Rn inventories.
(2) Analysis of the distributions of ^{222}Rn and the activity ratio of short-lived radium isotopes can be used to constrain the

estimated rate of radon loss via mixing in the radon mass balance model.

(3) A mean atmospheric evasion rate of radon can also be estimated by combined use of ^{222}Rn distributions and the ^{224}Ra/^{223}Ra activity ratio in a transect away from a common source.

(4) Estimations of both mixing and atmospheric losses in the radon mass balance using the combined isotopic approach are consistent with assessments made by independent approaches.

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