ELSEVIER

Available online at www.sciencedirect.com



JOURNAL OF ENVIRONMENTAL RADIOACTIVITY

Journal of Environmental Radioactivity 69 (2003) 21-35

www.elsevier.com/locate/jenvrad

Estimating the dynamics of groundwater input into the coastal zone via continuous radon-222 measurements

William C. Burnett *, Henrieta Dulaiova

Department of Oceanography, Florida State University, Tallahassee, FL 32306, USA

Accepted 17 March 2003

Abstract

Submarine groundwater discharge (SGD) into the coastal zone has received increased attention in the last few years as it is now recognized that this process represents an important pathway for material transport. Assessing these material fluxes is difficult, as there is no simple means to gauge the water flux. To meet this challenge, we have explored the use of a continuous radon monitor to measure radon concentrations in coastal zone waters over time periods from hours to days. Changes in the radon inventories over time can be converted to fluxes after one makes allowances for tidal effects, losses to the atmosphere, and mixing with offshore waters. If one assumes that advective flow of radon-enriched groundwater (pore waters) represent the main input of ²²²Rn in the coastal zone, the calculated radon fluxes may be converted to water fluxes by dividing by the estimated or measured ²²²Rn pore water activity.

We have also used short-lived radium isotopes (²²³Ra and ²²⁴Ra) to assess mixing between near-shore and offshore waters in the manner pioneered by Moore (2000). During an experiment in the coastal Gulf of Mexico, we showed that the mixing loss derived from the ²²³Ra gradient agreed very favorably to the estimated range based on the calculated radon fluxes. This allowed an independent constraint on the mixing loss of radon—an important parameter in the mass balance approach. Groundwater discharge was also estimated independently by the radium isotopic approach and was within a factor of two of that determined by the continuous radon measurements and an automated seepage meter deployed at the same site. © 2003 Elsevier Science Ltd. All rights reserved.

Keywords: Groundwater; Coastal zone; Radon; Radium; Tracers; Mixing

^{*} Corresponding author. Tel.: +850-644-6703; fax: +850-644-2581. *E-mail address:* wburnett@mailer.fsu.edu (W.C. Burnett).

1. Introduction

Although not as obvious as river discharge, continental groundwaters also discharge directly into the sea. In spite of the fact that submarine springs and seeps have been known for many years (e.g., written accounts exist from at least the Roman period), these features have traditionally been perceived as hydrologic "curiosities" rather than objects for serious scientific investigation (Kohout, 1966). However, this perception is changing. Within the last two decades recognition has emerged that, at least in some cases, submarine groundwater discharge (SGD) may be both volumetrically and chemically important (Johannes, 1980). Although SGD may not play a significant role in the global water balance, there are reasons to believe that the geochemical cycles of some major and minor elements may be strongly influenced either by the direct discharge of fresh groundwater into the sea or by chemical reactions that occur during the recirculation of seawater through a coastal aquifer system (Zektzer et al., 1973; Moore, 1999). In addition, it is now recognized that groundwater discharge may be an important pathway for diffuse pollution to the coastal zone where coastal aquifers have become contaminated by septic systems or other pollution sources (Buddemeier, 1996).

SGD is not simple to evaluate, as it tends to be patchy, both spatially and temporally. Water balance approaches can be used but these tend to give only average long-term results and are not very precise as the magnitude of SGD is often about the same as the uncertainty in the water balance parameters. Perhaps one of the most promising approaches for regional-scale assessments of SGD is the use of geochemical tracers. The coastal water column tends to integrate natural tracers coming into the system via groundwater pathways. Thus, smaller-scale variations, which would not be of interest for regional studies, are smoothed out. The small-scale variability found in many coastal systems has been one of the serious drawbacks concerning the use of seepage meters, a device that provides direct measurements of SGD (Lee, 1977; Burnett et al., 2001a).

We present here our approach for evaluating near-shore SGD via continuous ²²²Rn measurements. We also compare these results using a completely independent assessment via short- and long-lived radium isotopes as described by Moore (2000). An automatic seepage meter, similar to the type described by Taniguchi and Fukuo (1993) was also deployed in the field area for a further comparison.

2. Tracing groundwater using ²²²Rn

2.1. Radon as an SGD tracer

Although interest in groundwater-surface water interaction has increased dramatically in the last few years, there is actually very little documentation available. One of the principal reasons that information is so limited is because groundwater discharge is so difficult to measure. Traditional hydrogeological or water balance estimates may be off by several orders of magnitude, largely because of difficulties in constraining hydrologic conductivities. One potential means of evaluating groundwater pathways and fluxes into the coastal zone more accurately is through the use of natural tracers. We have been investigating this approach for several years and demonstrated that ²²²Rn is an excellent tracer (Burnett et al., 1996; Cable et al., 1996; Corbett et al., 1997). The very large enrichment of ²²²Rn concentration in groundwaters over surface waters (typically 1000-fold or greater), its unreactive nature, and short half-life (t_{1/2} = 3.83 d) make ²²²Rn an excellent tracer to identify areas of significant groundwater discharge.

2.2. Measurement approach

In spite of the fact that we have made significant progress in our ability to find and measure groundwater seepage areas using a radon monitoring approach, we are hampered in making regional-scale and long-term temporal assessments by the timeconsuming logistical requirements of collecting and analyzing samples in the conventional manner. Historically, measurements of radon concentrations in the water column have been accomplished by standard oceanographic sampling and analysis techniques (radon emanation) for measurement of ²²²Rn taking the special care required for trace gas sampling (Broecker, 1965; Mathieu et al., 1988). Alternatively, more automated systems may be applied in order to increase the sampling resolution and efficiency of the process. We demonstrated recently that a "continuous" radon monitor could provide reasonably high-resolution data on the radon concentration of coastal seawater at one location over time (Burnett et al., 2001b).

The automated radon system (Fig. 1) analyses ²²²Rn from a constant stream of



Fig. 1. Photo of the water exchanger-RAD-7 continuous monitoring system.

water (driven by a submersible pump) 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 that determines the concentration of ²²²Rn by collection and measurement of the α -emitting daughters, ²¹⁴Po and ²¹⁸Po. Since the distribution of radon at equilibrium between the air and water phases is governed by a well-known temperature dependence, the radon concentration in the water is easily calculated.

We are using a RAD-7 (Durridge Co., Inc.) for the radon-in-air monitor because it is portable, durable, very sensitive, and operates in a continuous mode. The RAD-7 uses a high electric field with a silicon semiconductor detector at ground potential to attract the positively charged polonium daughters, ²¹⁸Po⁺ ($t_{1/2} = 3.10$ min; alpha energy = 6.00 MeV) and ²¹⁴Po⁺ ($t_{1/2} = 164 \,\mu s$; 7.67 MeV) that are then counted as a measure of the radon concentration in air. Energy discrimination allows one to select either or both the ²¹⁸Po or ²¹⁴Po windows for ²²²Rn assessment. For faster analyses, the ²¹⁸Po is preferred, as it will reach radioactive equilibrium with ²²²Rn in only about 15 minutes. The ²¹⁴Po lags behind because of the intermediate betaemitting daughters, ²¹⁴Pb ($t_{1/2} = 27$ m) and ²¹⁴Bi ($t_{1/2} = 19.9$ m) resulting in an equilibration time of approximately 3 h.

The water-air exchanger is simply a plastic cylinder that has water pumped from the desired water depth entering continuously via an aspirator and a stream of air that is re-circulated through a bed of desiccant and then to the RAD-7 for ²²²Rn measurements. After some time, the radon concentration in the air reaches equilibrium with the radon in the water, the ratio at equilibrium being determined by the water temperature:

$$\alpha' = 0.105 + 0.405e^{-0.0502T} \tag{1}$$

where a' is the concentration ratio of water to air (about 1:4 at room temperature), and T is the temperature of the water in degrees C.

The response time of the system depends on the half life of the ²¹⁸Po, the volume of the air loop, the speed of transfer of radon from the water to the air (which depends on the efficiency of the aeration, and the speed of the pump), the flow rate of the re-circulating air, the volume of water in the exchanger, and the flow rate of water to the exchanger (Lane-Smith and Shefsky, 1999). The half-life of ²¹⁸Po, 3.1 m, dictates an ultimate theoretical limit, for the 95% response time, of about 15 min, assuming everything else was instantaneous. Since there is about four times more radon in the air phase than the aqueous phase at equilibrium, at least four times more water must flow through the system to deliver all the radon that is required. Again, that is assuming everything is working at maximum efficiency, which is unlikely. In practice, we find that the shortest time necessary for complete equilibration is about 30–40 min. Once the equilibrium concentration has been obtained, the length of time necessary to collect sufficient information (counts) for a precise measurement depends upon the radon content in the water. In several tests with our system, we find that integration times of about 1-2 h are necessary to achieve uncertainties of 5-10%.

2.3. Conceptual model and approach for radon tracing

The main principle of using continuous radon measurements to decipher rates of groundwater seepage is that if we can monitor the inventory of ²²²Rn over time, making allowances for losses due to atmospheric evasion and mixing with lower concentration waters offshore, any changes observed can be converted to fluxes (Fig. 2). Although changing radon concentrations in coastal waters could be in response to a number of processes (sediment resuspension, long-shore currents, etc.), we feel that advective transport of groundwater (pore water) through sediment of Rn-rich solutions is usually the dominate process. Thus, if one can measure or estimate the radon concentration in the advecting fluids, we can easily convert ²²²Rn fluxes to water fluxes. Our complete procedure for estimating groundwater fluxes from continuous radon measurements in the coastal zone may be summarized by the following steps:

- 1. We first perform continuous measurements of ²²²Rn activities (Bq/m³) in the coastal water column, water depth, water and air temperatures, wind speed, and atmospheric ²²²Rn concentrations. All of these measurements may be performed using automated sensors with data logging capabilities.
- 2. We then calculate excess (unsupported by ²²⁶Ra) ²²²Rn inventories for each measurement interval, i.e.,



Fig. 2. Conceptual model of use of continuous radon measurements for estimating submarine groundwater discharge in a coastal zone. The inventory refers to the total amount of excess 222 Rn per unit area. Decay is not considered because the fluxes are evaluated on a very short (1–2 hours) time scale relative to the half-life of 222 Rn.

$$I (Bq/m^2) = Excess \ ^{222}Rn(Bq/m^3) \times \text{water depth (m)}$$
(2)

Excess ²²²Rn activities in the water column are estimated from spot measurements of ²²⁶Ra. While fewer measurements of ²²⁶Ra are made, the water column variations tend to be less than those of radon and the activities are typically much less.

- 3. The calculated inventories are next normalized to mean tidal height to remove the effect of changing inventory due simply to tidal height variations. This normalization is done for each measurement interval by multiplying the unit change in water depth (m) over the measurement interval times the ²²²Rn activity offshore (Bq/m³) during the flood tide and by concentrations in nearshore waters for the ebb tide. The flood tide corrections are negative (since the inventory would be increasing due simply to an increase in water depth) and the ebb tide correction is positive.
- 4. We next correct the tide normalized inventories 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 have used the 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 the trace gas concentration, temperature, and wind speed. After these calculations, the radon water column inventories have now been corrected for supported ²²²Rn (²²⁶Ra), changes in water level, and atmospheric loss. We call these corrected inventories I* (Bq/m²).
- 5. "Net" ²²²Rn fluxes (F_{net}) are then estimated by evaluating the change in these corrected inventories (Bq/m²) over each time interval (Δt , generally 1–2 h.), i.e.,

$$F_{net}(Bq/m^2 \bullet s) = \Delta I^*(Bq/m^2)/\Delta t(s)$$
(4)

These fluxes represent the observed fluxes of ²²²Rn into the coastal water column with all necessary corrections *except* loss via mixing with lower concentration waters offshore. We thus feel that these net fluxes are *minimum* values, as we base the estimate on what remains in the system (what we can measure) and higher mixing rates could be compensated for by higher fluxes.

6. We then estimate minimum mixing losses from inspection of the "net" fluxes over time. We base these values on the maximum negative fluxes that are invariably present. Since greater mixing losses could be compensated by higher benthic radon fluxes, our estimates must be conservative. The estimated mixing losses are added to the net fluxes in order to derive "total" Rn fluxes (F_{total}), i.e.,

$$F_{total}(Bq/m^2 \bullet s) = F_{net} + F_{mix}(Bq/m^2 \bullet s)$$
(5)

We have not considered diffusion in these flux estimates because the advection term in every coastal system we have investigated has been dominant (factors of about 20–100 times greater than estimated diffusion). If one were working in an environment where diffusion may be more important, an advective-diffusion equation as presented in Cable et al. (1996) could be applied.

- 7. In order to convert radon flux estimates to water flux, we must measure or estimate the ²²²Rn concentration of the advecting fluids. In areas where slow seepage through sediment is the dominant process, it is a relatively simple matter to extract pore waters and measure ²²²Rn and/or perform sediment equilibration measurements (Corbett et al., 1998). If an area is characterized by inputs of fresh groundwater (from submarine springs, for example), one could measure the groundwater ²²²Rn activities via collection from monitor wells on shore. Because of processes like tidal pumping, possible non-homogeneous sediment compositions, and the possible influence of different source terms (multiple aquifers, etc.) within a study region, there could be significant variation in the radon concentration term.
- 8. Finally, we convert to water fluxes (ω , m/s) by dividing the estimated total ²²²Rn fluxes (Bq/m².s) by the concentration of excess ²²²Rn (Ex ²²²Rn_{pw}, Bq/m³) in the fluids entering the system, i.e.,

$$\omega(m/s) = \frac{F_{total}}{Ex^{222}Rn_{pw}} \tag{6}$$

We often apply unit conversions to express the groundwater fluxes in cm/day, as these units are convenient—typically in the range of 10–100 cm/day (1.16 \times 10⁻⁶-1.16 \times 10⁻⁵ m/s).

3. Application—Coastal Gulf of Mexico

3.1. Radon results

We installed the continuous radon monitor into the seawater recirculation system at the Florida State University Marine Laboratory (FSUML) from September 28 to October 3, 2001. This is a site located along an open shoreline within Apalachee Bay, about 60 km south of Tallahassee, Florida. The exchanger, set up inside the laboratory, received a continuous stream of water from the seawater system that has an intake about 300 meters offshore in about 1.5 meters of water. The residence time of the seawater in this pumping system is approximately 2 h. This was taken into account when comparing automated radon data to parameters measured offshore. Previous studies at this site included collection and conventional radon analysis of grab samples of seawater from the same place and time as the continuous monitor with results within the analytical uncertainty of those provided by the continuous monitor (Burnett et al., 2001b). The water depth was continuously monitored at the same location using an ultrasonic depth recorder, so we were able to produce a continuous record of ²²²Rn inventory as well as concentration over time (Fig. 3). We also continuously monitored wind speed, air and sea temperatures, and atmospheric radon concentrations over the experimental period. A Taniguchi-style automated seepage meter was deployed within a few meters of the seawater intake. In addition, on one day (Oct. 2) we collected a series of seawater samples (n = 12 at



Fig. 3. (A) Variation of total ²²²Rn activities; and (B) excess ²²²Rn inventories in coastal waters off the FSU Marine Laboratory (FSUML) from September 28 to October 3, 2001.

nine stations) along a transect normal to the shoreline just off FSUML out to a distance of 5 km offshore. These samples were analyzed for ²²²Rn (radon emanation) and radium isotopes (delayed coincidence counting for ²²³Ra and ²²⁴Ra; Moore and Arnold, 1996; and gamma spectrometry for ²²⁶Ra and ²²⁸Ra). This 5-day multi-tracer experiment is part of a seasonal sampling of this environment that will be reported in more detail elsewhere (Dulaiova, in prep.).

After normalizing to a mean tidal height and correcting for supported radon and estimated atmospheric loss, we calculated the net ²²²Rn fluxes (Fig. 4). These fluxes are clearly not in steady state but fluctuate with an apparent period of approximately 12 h, most likely a reflection of the mixed, semi-diurnal tides in this region. Apparent negative fluxes also occur with a fairly systematic period, either 24 or 12 h apart. The dashed line shown in Fig. 4 is our estimate (thought to be conservative) of the mixing loss of radon caused by mixing of nearshore (high radon) waters with offshore (low radon) seawater. These estimated mixing losses are added to the "net"



Fig. 4. Net radon flux vs time based on continuous radon measurements at FSUML from September 28 to October 3, 2001.

fluxes in order to determine the approximate "total" radon flux into the coastal zone at the point of sampling.

We have observed this tidal period cyclicity before, both in this region (e.g., Burnett et al., 2002) and elsewhere (south of Perth, Australia, for example, we observed a 24-h cycle that corresponded to the diurnal tides in that area). Most likely, groundwater, and associated radon, is responding to: (1) lower hydrostatic pressure at low tides causing increased seepage and thus higher radon fluxes; (2) recirculated seawater is moving through the shallow aquifer and sediments in response to tidal pumping; and/or (3) a combination of both processes. Assuming that the hydraulic gradient is more or less constant during the time scale of our experiment, a decrease in hydrostatic pressure with a lower tide could result in increased seepage (and thus higher radon). Although there are some exceptions in this experiment, most of the peaks in radon concentration occur at the lowest tides (Fig. 3a). Tidal pumping and wave set up are known to result in the infiltration of seawater on the high tide with draining on the low tide (Nielsen, 1990; Li et al., 1999). Since draining typically is slower than filling a coastal aquifer, the waters emerging may well have had a residence time quite a bit longer than the tidal cycle. This would also explain how the recirculated seawater, initially low in radon and short-lived radium isotopes, builds up higher concentrations that are detected by our measurements.

We estimated the relevant ²²²Rn concentration within the interstitial fluids $(2170 \pm 830 \text{ Bq/m}^3)$ by performing sediment equilibration experiments from sediments collected in the area (n = 6) in the manner described by Corbett et al. (1998). These measurements are performed in the laboratory by reacting water and sediment for a period long enough that the ²²²Rn in the fluid reaches a steady-state concen-

tration. Dividing the total estimated radon fluxes (Bq/m².s) by the presumed ²²²Rn activity of the advecting fluids (2170 Bq/m³) for each time interval (1 h in this experiment) results in estimated water fluxes over this 5-day period (Fig. 5). Our estimated specific discharges ranged from $0-5.0 \times 10^{-6}$ m/s (0–43 cm/day; average = 13 ± 9 cm/day; n = 111). The data again displays the 12-h periodicity reflecting the radon flux pattern. The zero fluxes are a consequence of our choice of using the maximum negative fluxes as our estimate of mixing losses. Adding these values to the net fluxes produces an apparent interval with essentially zero radon flux and thus no water flux. More realistically, these mixing losses are underestimated and there are probably some, perhaps low, seepage rates all the time.

Using daily (24-h) integrated estimated seepage rates from these calculations and assuming this rate is characteristic of the groundwater fluxes for a 200-m band, we estimate the discharge per unit length of shoreline at $2.3-3.4 \times 10^{-4}$ m³/m.s (20–29 m³/m.day). The width of the dominant seepage in this area has been determined in previous studies (Cable et al., 1997; Burnett et al., 2002). Although the specific seepage rates are not uniform but tend to decrease more-or-less exponentially as one goes further from shore, our assumption of constant rates is reasonable in this case as the rates are based on radon measurements in the water column that should integrate these small-scale variations.

3.2. Radium isotope results

We collected a line of samples at nine stations (three duplicate samples, so n = 12) extending from just offshore out to approximately 5 km offshore and then meas-



Fig. 5. Estimated seepage rates over the experimental period based on the radon model and using a pore water radon concentration of 2170 Bq/m^3 . The dashed gray lines above and below the SGD estimates (open triangles) represent $\pm 25\%$ uncertainties.

ured the activities of both the short-lived (²²³Ra and ²²⁴Ra) and long-lived (²²⁶Ra and ²²⁸Ra) isotopes of radium. Because radium is found at very low concentrations in most natural waters, large volume samples (0.02–0.20 m³) were processed through "Mn-fiber" cartridges to concentrate the radium (Moore, 1976). The isotopic measurements of ²²³Ra and ²²⁴Ra were made within 24 h after collection using delayed coincidence counters and the ²²⁸Ra and ²²⁶Ra measurements were made at a later date via gamma-ray spectrometry.

The distribution of the short-lived radium species will depend on two processes, decay and mixing. Since the decay rates are known precisely (²²³Ra and ²²⁴Ra have half-lives of 11 and 3.5 days, respectively), the mixing rates can be estimated based on the slope of the Ln activity versus distance plot (Fig. 6a). We observed a maximum in ²²³Ra at one of our stations, about 800 m offshore, that may be related to a submarine spring known to occur in that vicinity. Using the methodology of Moore (2000), a regression of all data points from the maximum in ²²³Ra seaward (n = 9) provides an estimated mixing coefficient of 18 ± 6 m²/sec. Multiplying the gradient in the measured ²²⁶Ra concentration over the same distance (-3 Bq/m³.km; Fig. 6b) by this mixing term provides the offshore flux of the groundwater tracer ²²⁶Ra (0.12 Bq/m.s) for a cross section 1 m wide and 2.2 m deep (the average depth of the stations along the transect). Since ²²⁶Ra is long-lived (half life = 1600 years), mixing is the only process that effects its distribution. Assuming that this flux is steady state and balanced by the inflow of groundwater with a known ²²⁶Ra concentration, one can easily convert the radium flux to a SGD flux.

While we appear to have fairly good estimates of the offshore mixing and radium flux, the concentration of ²²⁶Ra in the groundwater coming into the system is less clear. The data suggest the presence of a submarine spring that is adding radium, and perhaps radon, to the system. The distribution of ²²²Rn offshore does not show a clear maximum at the point where all the radium isotopes do but is highest inshore (where seepage is likely the highest). Thus while the spring would be expected to be adding radon to the system as well as radium, it may not have a substantially different concentration of ²²²Rn than waters seeping through the sediments near the shore. Thus, we appear to have a mixed source of radium at this site, seepage through permeable sediments and from the small submarine spring in the area.

Similar measurements were performed about 1 km east of this study in August 2000 (Burnett et al., 2002). In that study, we observed no indications of spring inputs but there was clearly substantial seepage. W. Moore estimated SGD in that case using a ²²⁶Ra concentration of 15 Bq/m³ that was based on a measurement of water collected from a fast-flowing seepage meter at that study site. While that was a completely reasonable assumption in that case, the incoming water in the October 2001 experiment (at a nearby but different location) must have a higher concentration, as some of the water column measurements exceed 17 Bq/m³. We examined samples collected and analyzed for ²²⁶Ra in shallow piezometers at this site in order to estimate a reasonable concentration for the groundwater. Unfortunately, the range in ²²⁶Ra varies tremendously. Using data from Christoff (2001), we see a range from 10 to 1453 Bq/m³ (*n* = 19 samples in 14 different piezometers) with an average of 387 Bq/m³. Since this average is skewed by a few very high values, we have elected



Fig. 6. (A) Variation of Ln ²²³Ra versus distance offshore from the FSU Marine Laboratory, October 2, 2001. The mixing coefficient (K_h) is calculated from the slope of the regression line (filled circles). It is assumed that most of the radium enters near the maximum in the ²²³Ra (station T-3; ~800 m offshore), perhaps from a submarine spring (approximate location shown by arrow), and mixes with lower concentration waters offshore. (B) ²²⁶Ra vs. distance along the same transect as "A". The gradient is calculated from the maximum concentration extending offshore (closed data points). The arrow indicates the approximate position of a submarine spring.

to use the median concentration, 235 Bq/m³ as an estimated ²²⁶Ra activity in shallow groundwater at this site. Using this value, we calculate that the water flux into this area was about 5.0×10^{-4} m³/m.s, i.e., a flow of approximately 43 m³ of groundwater into the sea per unit meter of shoreline per day.

3.3. Comparison of SGD estimates

One of the benefits in applying both the continuous radon and radium isotope approaches to the same system is that we can use the mixing coefficient derived from the short-lived radium to make an independent estimate of the radon loss due to mixing. We have considered that term to be a weak link in the radon SGD assessment. We estimated the total radon flux offshore by multiplying the gradient in the 222 Rn concentration along the inshore-to-offshore transect (-9.4 Bq/m³.km) by the mixing coefficient derived from the ²²³Ra gradient (18 m²/s) and the average depth along the transect (2.2 m). This total ²²²Rn flux per unit width of shore (0.36 Bq/m.s) is also the flux coming from a cross-section 1 m wide and 2.2 m deep. Converting this value to a per unit seabed flux for an assumed 200-m wide seepage area results in a unit flux of 1.8×10^{-3} Bq/m².s. This compares very favorably to our variable mixing fluxes, assigned by inspection of the "net" benthic ²²²Rn fluxes (Fig. 4) that ranged from $8.3 \times 10^{-4} - 2.3 \times 10^{-3}$ Bq/m².s with an average of 1.1×10^{-3} Bq/m².s. If we had instead used a fixed mixing loss of 1.8×10^{-3} Bq/m².s for the entire period of our observations, the average calculated seepage flux would only increase by about 20%.

A comparison of these estimates, both for the August 2000 study as well as the one presented here for October 2001 is given in Table 1. All three approaches, continuous radon, radium isotopes, and automated seepage meters, produced comparable results in the August 2000 study. In October 2001, the radon measurements indicated similar, but slightly higher rates of flow ([2.3–3.4] × 10⁻⁴ m³/m.s or 20–29 m³/m.day) than those calculated from the automated seepage meter ([1.4–2.3] × 10⁻⁴ m³/m.s or 12–20 m³/m.day). Both the radon and seepage meter measurements

Table 1

Estimates of water flux per unit width of shoreline near FSUML during August, 2000 and October, 2001. The August experiment was performed about 1 km east of the one in October. The mixing coefficients based on ²²³Ra are also shown.

Approach	August 2000×10^{-4} m ³ /m.s	October 2001 \times 10 ⁻⁴ m ³ /m.s
Continuous radon	2.9–4.2	2.3–3.4
Radium isotopes	2.6 ^a	5.0
(Mixing coefficient)	(2.6 m ² /s)	(18 m ² /s)
Automatic seepage meter	3.0 ^b	1.4–2.3

^a August 2000 measurements by W. Moore, reported in Burnett et al. (2002).

^b Measurements in August 2000 by M. Taniguchi, reported in Burnett et al. (2002).

indicated that the flow was not actually steady state but displayed systematic variations related to the semi-diurnal tides in the area. The estimate based on radium isotopes (5.0×10^{-4} m³/m.s or 43 m³/m.day) indicates a flow about a factor of two greater. Because of the apparently mixed sources of radium isotopes into this area, and the wide range in possible ²²⁶Ra values in the discharging fluids, there is clearly a fairly high degree of uncertainty concerning this estimate. The August 2000 study, located nearby but at a site apparently not influenced by springs, showed better agreement.

It should be pointed out that all the approaches used in this study measure total flow, i.e., seepage meters and the geochemical tracers applied here do not distinguish between flow driven by terrestrial processes (hydraulic gradient) and recirculated seawater driven by oceanic forcing (tidal pumping, wave set up, etc.). Since there could be many management scenarios where it would be useful to differentiate the source of flow, efforts should be made to quantify the terrestrial versus marine based flows. Coupling isotopic techniques for assessing groundwater flow through the seabed with high precision conductivity measurements should allow one to differentiate between fresh groundwater and recirculated seawater. Other approaches and perhaps tracers will be necessary if the terrestrial groundwater is not fresh.

Acknowledgements

The authors wish to acknowledge the excellent support from the staff of the Florida State University Marine Laboratory (FSUML) who helped ensure that this experiment was a success. Deok-Soo Moon and Svetlana Nour assisted with the fieldwork and subsequent measurements. We thank Makoto Taniguchi for the use of the automated seepage meter. Financial support for this research was provided by grants from the Office of Naval Research (N00014-00-0175) and Florida Sea Grant (R/C-E-42).

References

- Buddemeier, R.W., 1996. Groundwater flux to the ocean: definitions, data, applications, uncertainties. In Buddemeier, R.W. (Ed.), Groundwater Discharge in the Coastal Zone: Proceedings of an International Symposium. LOICZ IGBP. LOICZ/R&S/96-8, iv+179pp. LOICZ, Texel, The Netherlands, pp.16–21.
- Broecker, W.S., 1965. An application of natural radon to problems in oceanic circulation. In: Proc. Symp. On Diffusion in the Oceans and Freshwaters. Lamont Geological Observatory, New York, pp.116–145.
- Burnett, W.C., Cable, J.E., Corbett, D.R., Chanton, J.P., 1996. Tracing groundwater flow into surface waters using natural ²²²Rn. In Buddemeier, R.W. (Ed.), Groundwater Discharge in the Coastal Zone: Proceedings of an International Symposium. LOICZ IGBP. LOICZ/R&S/96-8, iv+179pp. LOICZ, Texel, The Netherlands, 22-28.
- Burnett, W.C., Taniguchi, M., Oberdorfer, J., 2001a. Measurement and significance of the direct discharge of groundwater into the coastal zone. J. Sea Research 46 (2), 109–116.
- Burnett, W.C., Kim, G., Lane-Smith, D., 2001b. A continuous radon monitor for assessment of radon in coastal ocean waters. J. Radioanal. Nucl. Chem. 249, 167–172.
- Burnett, W.C., Chanton, J., Christoff, J., Kontar, E., Krupa, S., Lambert, M., Moore, W., O'Rourke,

D., Paulsen, R., Smith, C., Smith, L., Taniguchi, M., 2002. Assessing methodologies for measuring groundwater discharge to the ocean. EOS 83, 117–123.

- Cable, J.E., Burnett, W.C., Chanton, J.P., Weatherly, G., 1996. Modeling groundwater flow into the ocean based on ²²²Rn. Earth Planet. Sci. Lett 144, 591–604.
- Cable, J.E., Burnett, W.C., Chanton, J.P., 1997. Magnitudes and variations of groundwater seepage into shallow waters of the Gulf of Mexico. Biogeochemistry 38, 189–205.
- Christoff, J.L., 2001. Quantifying groundwater seepage into a shallow near-shore coastal zone by two techniques. M.S. Thesis, Florida State University, p.120
- Corbett, D.R., Burnett, W.C., Cable, P.H., 1997. Tracing of groundwater input into Par Pond, Savannah River Site by Rn-222. J. Hydrology 203, 209–227.
- Corbett, D.R., Burnett, W.C., Cable, P.H., Clark, S.B., 1998. A multiple approach to the determination of radon fluxes from sediments. J. Radioanal. Nucl. Chem. 236, 247–252.
- Johannes, R.E., 1980. The ecological significance of the submarine discharge of groundwater. Marine Ecology—Progress Series 3, 365–373.
- Kohout, F.A., 1966. Submarine springs: A neglected phenomenon of coastal hydrology. Hydrology 26, 391–413.
- Lane-Smith, D., Shefsky, S., 1999. Proceedings of the American Association of Radon Scientists and Technologists, Las Vegas, NV, November 7–10, 1999.
- Lee, D.R., 1977. A device for measuring seepage flux in lake and estuaries. Limnol. Oceanogr 22, 140-147.
- Li, L., Barry, D.A., Stagnitti, F., Parlange, J.-Y., 1999. Submarine groundwater discharge and associate chemical input to a coastal sea. Water Resources Research 35, 3253–3259.
- Macintyre, S., Wanninkhof, R., Chanton, J.P., 1995. Trace gas exchange across the air-sea interface in freshwater and coastal marine environments. In: Matson, P.A., Harris, R.C. (Eds.), Biogenic Trace Gases: Measuring Emissions from Soil and Water. Blackwell Science Ltd, pp. 52–97.
- Mathieu, G., Biscayne, P., Lupton, R., Hammond, D., 1988. System for measurements of ²²²Rn at low levels in natural waters. Health Physics 55, 989–992.
- Moore, W.S., 1976. Sampling Ra-228 in the deep ocean. Deep-Sea Res 23, 647-651.
- Moore, W.S., 1999. The subterranean estuary: A reaction zone of groundwater and sea water. Marine Chemistry, 1–24.
- Moore, W.S., 2000. Determining coastal mixing rates using radium isotopes. Continental Shelf Res 20, 1995–2007.
- Moore, W., Arnold, R., 1996. Measurement of ²²³Ra and ²²⁴Ra in coastal waters using a delayed coincidence counter. J. Geophys. Res. 101, 1321–1329.
- Nielsen, P., 1990. Tidal dynamics in the water table in a beach. Water Resources Research 26, 2127-2134.
- Taniguchi, M., Fukuo, Y., 1993. Continuous measurements of ground-water seepage using an automatic seepage meter. Ground Water 31, 675–679.
- Turner, S.M., Malin, G., Nightingale, P.D., Liss, P.S., 1996. Seasonal variation of dimethyl sulphide in the North Sea and an assessment of fluxes to the atmosphere. Marine Chemistry 54, 245–262.
- Zektzer, I.S., Ivanov, V.A., Meskheteli, A.V., 1973. The problem of direct groundwater discharge to the seas. J. Hydrology 20, 1–36.