A New Focus on Groundwater–Seawater Interactions
(Proceedings of Symposium HS1001 at IUGG2007, Perugia, July 2007). IAHS Publ. 312, 2007.

Remaining uncertainties in the use of Rn-222 as a quantitative tracer of submarine groundwater discharge

WILLIAM C. BURNETT[1], ISAAC R. SANTOS[1], YISHAI WEINSTEIN[2], PETER W. SWARZENSKI[3] & BARAK HERUT[4]

1 *Department of Oceanography, Florida State University, Tallahassee, Florida 32306, USA*
wburnett@mailer.fsu.edu

2 *Bar-Ilan University, Ramat-Gan, 52900, Israel*

3 *US Geological Survey, St Petersburg, Florida 33701, USA*

4 *Israel Oceanographic and Limnological Research, Haifa, Israel*

Abstract Research performed in many locations over the past decade has shown that radon is an effective tracer for quantifying submarine groundwater discharge (SGD). The technique works because both fresh and saline groundwaters acquire radon from the subterranean environment and display activities that are typically orders of magnitude greater than those found in coastal seawaters. However, some uncertainties and unanswered problems remain. We focus here on three components of the mass balance, each of which has some unresolved issues: (1) End-member radon – what to do if groundwater Rn measurements are highly variable? (2) Atmospheric evasion – do the standard gas exchange equations work under high-energy coastal mixing scenarios? And (3) "mixing" losses – are there other significant radon losses (e.g. recharge of coastal waters into the aquifer) besides those attributed to mixing with lower-activity waters offshore? We address these issues using data sets collected from several different types of coastal environment.

Key words radon; submarine groundwater discharge; mass balance model

INTRODUCTION

The discharge of fresh and saline groundwater into the coastal zone is now recognized as an important pathway between land and sea for nutrients and other dissolved species (Slomp & Van Cappellen, 2004). Quantifying the amount of this flow is difficult as it typically occurs as a low unit flux process but influencing a large area. One of the more successful assessment techniques has been through the use of natural isotopic tracers such as radon and radium isotopes (Moore, 1996; Burnett *et al.*, 2006). The radon approach works because groundwaters often have ^{222}Rn activities orders of magnitude greater than coastal seawaters, radon is conservative, having a half-life on the same order as many coastal processes, and is relatively easy to measure. In addition, improvements in automated monitoring systems (e.g. Dulaiova *et al.*, 2005) have made continuous measurements of radon at environmental activities a reality.

Estimating groundwater discharges via radon is based on a mass balance approach. Inventories are measured, either as a snapshot or continuously over time (usually over at least one tidal cycle), and these inventories are converted to input fluxes after making allowances for losses due to decay, atmospheric evasion, and net coastal

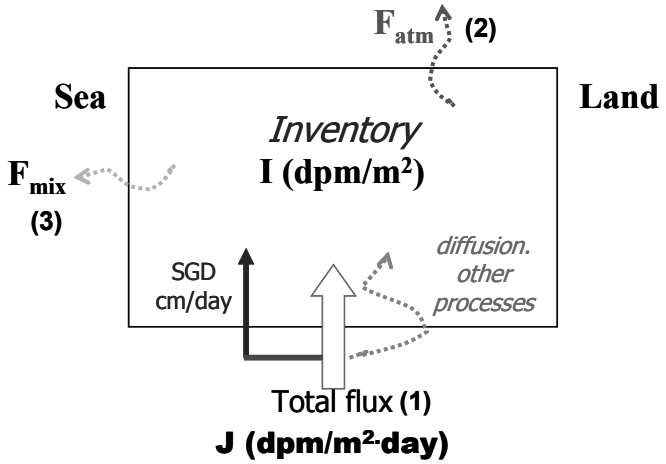

Fig. 1 Diagrammatic view of the radon mass balance with designations of the three fluxes discussed here (arrows). The inventory is measured over time and assessments are made for the atmospheric (F_{atm}) and mixing (F_{mix}) losses, allowing the total flux (J) to be calculated (Burnett & Dulaiova, 2003).

"mixing" terms (Fig. 1). Although changing radon concentrations in coastal waters could be in response to a number of processes (sediment re-suspension, long-shore currents, etc.), advective transport of radon-rich groundwater (pore water) through sediment is often the dominant process. Thus, if one can measure or estimate the radon concentration in these advecting fluids, the ^{222}Rn fluxes may be easily converted to water fluxes.

We examine here the problems and implications of assessing the various portions of the radon mass balance. Namely, we will discuss the issues concerning estimates of: (1) the "groundwater end-member" ^{222}Rn activity; (2) atmospheric evasion losses; and (3) mixing losses of radon – all essential components of the mass balance model.

GROUNDWATER END-MEMBER

Perhaps the most serious issue with the radon mass balance approach is the selection of the appropriate end-member radon activity. The mass balance is constructed in terms of radon fluxes, so in order to convert to a water flux (e.g. $m^3\ m^{-2}\ h^{-1}$), we divide the calculated total radon flux (e.g. dpm $m^{-2}\ h^{-1}$) into the reservoir by the estimated radon-in-water activity (e.g. dpm m^{-3}).

What is the best approach to estimate the average radon in the fluids advecting into the coastal waters? One can rely on measurements made from monitoring wells on shore, piezometers in the coastal zone, fluids sampled from seepage meters offshore, or perform "sediment equilibration experiments" to assess the equilibrium activity of radon in pore solutions (Cable *et al.*, 1996). In areas where seepage through sandy sediments is the main mode of discharge, equilibrating seawater with sediments from the study site should be an excellent manner to estimate the radon activity of advecting fluids. With flow rates typically on the order of a few centimetres per day, there should be ample time for the fluids to equilibrate with the radium in the solid phases of the sediment. We have found that in some cases the ^{222}Rn data from shallow wells

matches the sediment equilibration results very well (e.g. Florida Bay; Corbett *et al.*, 2000). In other cases, there may be large discrepancies between these different approaches. For example, an investigation in a harbour in Sicily suggested that much of the water being discharged was from a mixture of shallow low-radon water with much higher activity water from a deeper aquifer (Burnett & Dulaiova, 2006). A mixing model based on radium isotopes allowed us to discern the relative fraction of each component (Moore, 2006).

During a recent investigation of an embayment on the Mediterranean coast of Israel (Dor Beach), measurements were made in several piezometers and shallow wells established in the thin sandy surficial aquifer and the deeper fossilized sandstone aquifer (called "Kurkar") as well as a few seepage meters offshore (Weinstein *et al.*, 2007). The seepage meter data fits on a good mixing line between the Kurkar data and that of the coastal seawater (Fig. 2(a)). This provides evidence that the majority of the groundwater discharge into the embayment is derived from mixtures of water from this deeper aquifer with seawater, and only limited amounts from the sand aquifer.

On the other hand, data from the Florida State University Marine Laboratory (FSUML) on the Gulf of Mexico show that radon in seepage meter chambers does not fall on a good mixing line with many of the monitoring wells sampled on shore (Fig. 2(b)). There is one good radon-salinity mixing line from well B4 through the seepage meter results to the mean value of the coastal seawater (r^2 = 0.81). Sediment equilibration experiments on samples from this site indicated a radon-in-water end-member of 129 dpm/L (n = 6) that overlaps the seepage meter results shown in Fig. 2 (Lambert & Burnett, 2003). However, if one used either well B1 or B5, the end-member activity would have been overestimated by more than an order of magnitude.

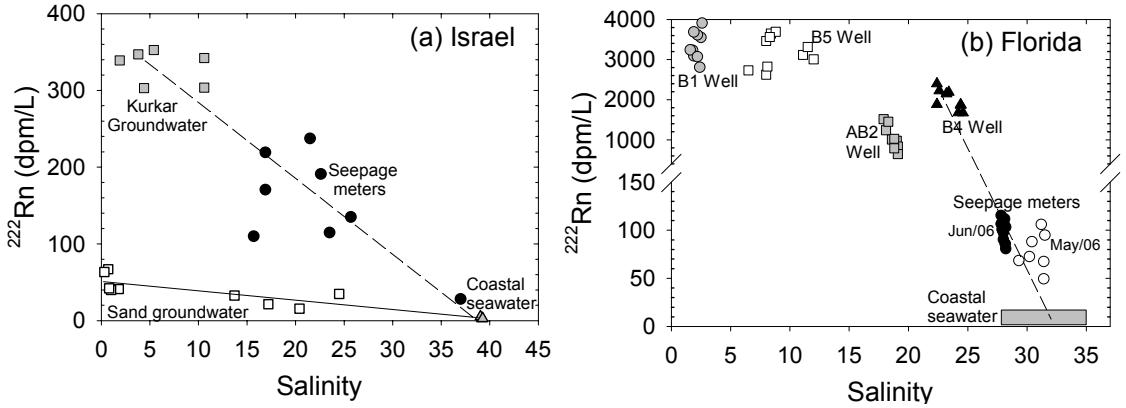

Fig. 2 (a) ^{222}Rn versus salinity from Dor Beach, Israel (Weinstein *et al.*, 2007); and (b) ^{222}Rn *vs* salinity for a site near FSUML, Gulf of Mexico (unpublished). Note that the break in scale in (b) distorts the relationships somewhat – well "B4" fits best on a mixing line with the mean value of coastal seawater and samples collected from seepage meters.

ATMOSPHERIC EVASION

In order to calculate a mass balance, we should account for the loss of radon to the atmosphere. Radon flux (F_{atm}) across the air–sea boundary is governed by molecular

diffusion produced by the concentration gradient across the air–water interface and turbulent transfer, and can be calculated from:

$$F_{atm} = k\left(C_w - \alpha C_{atm}\right) \quad (1)$$

where C_w and C_{atm} are the radon concentrations in water and air, respectively; α is Ostwald's solubility coefficient; and k is the gas transfer coefficient or "piston velocity". This coefficient is a function of kinematic viscosity, molecular diffusion, and turbulence. The evaluation of k is often based on empirical relationships observed in different environments for different gases. The piston velocity depends on the Schmidt number (Sc, the ratio of kinematic viscosity and molecular diffusion) which offers a way to convert the coefficients from one gas to another. The Schmidt number of each gas is a function of temperature and salinity with k being proportional to $Sc^{-2/3}$ for a smooth liquid and proportional to $Sc^{-1/2}$ for a rough surface (Wanninkhof, 1992).

Based on a number of field studies, empirical equations that relate k to wind speed as a source of turbulence have been proposed. We have elected to use an equation presented in MacIntyre *et al.* (1995) where k represents the piston velocity for a given wind speed normalized to the Schmidt number for CO_2:

$$k(600) = 0.45u_{10}^{1.6}(Sc/600)^{-2/3} \quad (2)$$

where u_{10} is the wind speed at 10 m height above the water surface and Sc for the dissolved gas of interest is divided by 600 to normalize k to CO_2 at 20°C in freshwater. Turner *et al.* (1996) showed in calculating the gas transfer coefficient for DMS as a function of wind speed, that the (Sc/600) term in equation (2) should be raised to the power of –2/3 for $u_{10} \leq 3.6$ m/s and –1/2 for $u_{10} > 3.6$ m/s. Happell (1995) suggested that k is independent of wind speed below 1.6 m/s.

We were able to test this theoretical approach experimentally by sampling ^{222}Rn and ^{224}Ra on a transect away from the Chao Phraya River estuary (Gulf of Thailand) that has elevated radon and radium activities due to inputs by groundwater discharge and desorption processes (Dulaiova & Burnett, 2006). Since ^{224}Ra stays dissolved in seawater until it decays or it is transported away by mixing but radon also escapes to the atmosphere, we can assess the difference in the ^{222}Rn/^{224}Ra ratio as a function of radon evasion.

The isotope distributions were plotted against the corresponding "radium ages" (Moore, 2000a) in the estuary, and fitted by exponential regressions (Fig. 3(a)). As expected, in each case radon has a steeper profile with a more negative slope than ^{224}Ra. The slope of each equation at different points along the transect is equivalent to the rate of loss of the isotope from the water column over time (dpm m^{-3} day^{-1}) and may be calculated as the first derivatives of the trend lines. The difference in the slopes of the radon and radium curves at corresponding points will provide the estimates of radon loss by atmospheric evasion (dpm m^{-3} day^{-1}). The difference of the ^{224}Ra–^{222}Rn slopes at each radium sampling point is than multiplied by the water depth (there was no stratification when these samples were collected) to derive an estimated radon flux from the water column (dpm m^{-2} h^{-1}). The result is an exponential function with the apparent radium age as a variable. Because we know the relationship between distance and the radium age we can also plot atmospheric evasion against distance (Fig. 3(b)). The resulting radon fluxes from these estimates were 10 to 200 dpm m^{-2} h^{-1}. The higher

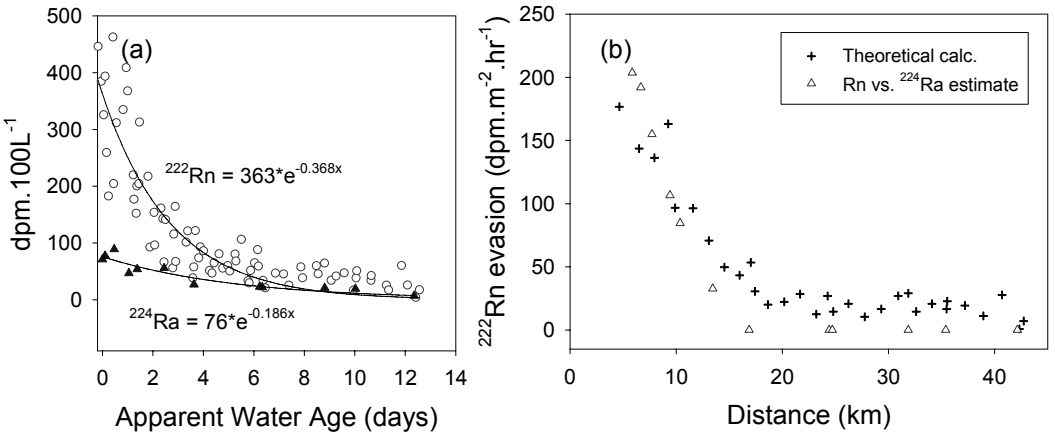

Fig. 3 (a) Radon and ^{224}Ra transects away from the Chao Phraya River mouth (Gulf of Thailand). Activities of ^{222}Rn (circles) and ^{224}Ra (triangles) *vs* apparent water age as calculated from the ^{224}Ra/^{223}Ra ratios (Moore, 2000a). Since the mixing processes and half-lives of ^{222}Rn and ^{224}Ra are nearly the same, the difference in slopes is due to radon evasion. (b) Atmospheric evasion based on the experimental data (triangles) and calculated from the gas exchange equations (crosses).

fluxes were near the river mouth (higher activities) and they decrease as the water radon concentrations drop offshore. While this experimental approach becomes imprecise where radon and radium concentrations get close to their supported values offshore, the agreement between the theoretical and experimental values are generally excellent.

We also had an occasion to experimentally test the gas exchange equations during a period of alternating high winds (~10 m/s) during the afternoons and very calm (~0 m/s) winds in the evening in a protected small boat harbour in Donnalucata, Sicily (Burnett & Dulaiova, 2006). In that case, the calculated fluxes during the high wind periods corresponded very closely to the observed change in inventories. The protected nature of the harbour and its very low tides may have simplified the system sufficiently that these estimates were better than would be expected in more "open" environments.

While the gas exchange equations do appear to work reasonably well in many conditions, it is likely that they do not predict the correct evasion rates under more extreme circumstances. For example, storms in most coastal areas will be associated with considerable turbulence that is not predictable by the standard equations. Breaking waves, bubble formation and bursting, tidal surges, etc., would likely all contribute to gas exchange in complex ways.

We show two examples of recent experiments that captured the change in radon inventories during storm events (Fig. 4). The first example, from Dor Beach (Israel) shows a very large drop in radon inventories during the storm – in some cases leaving no detectable ^{222}Rn in the water column. While the wind speeds during this storm were not extremely high with velocities generally less than 10 m/s, there was an increase in water level (~29 cm rise in the high tide with respect to the pre-storm conditions). The storm surge running up on the beach likely contributed to unaccounted-for radon loss. Perhaps more importantly, the trend in maximum wave height (H_{max}, the maximum height of individual waves relative to mean sea level over 1-hour observations) coincides almost exactly with the depletion in radon inventory. Assuming an average depth in the bay of 1.0–1.5 m, we expect to have breaking waves at 0.6–0.8 times

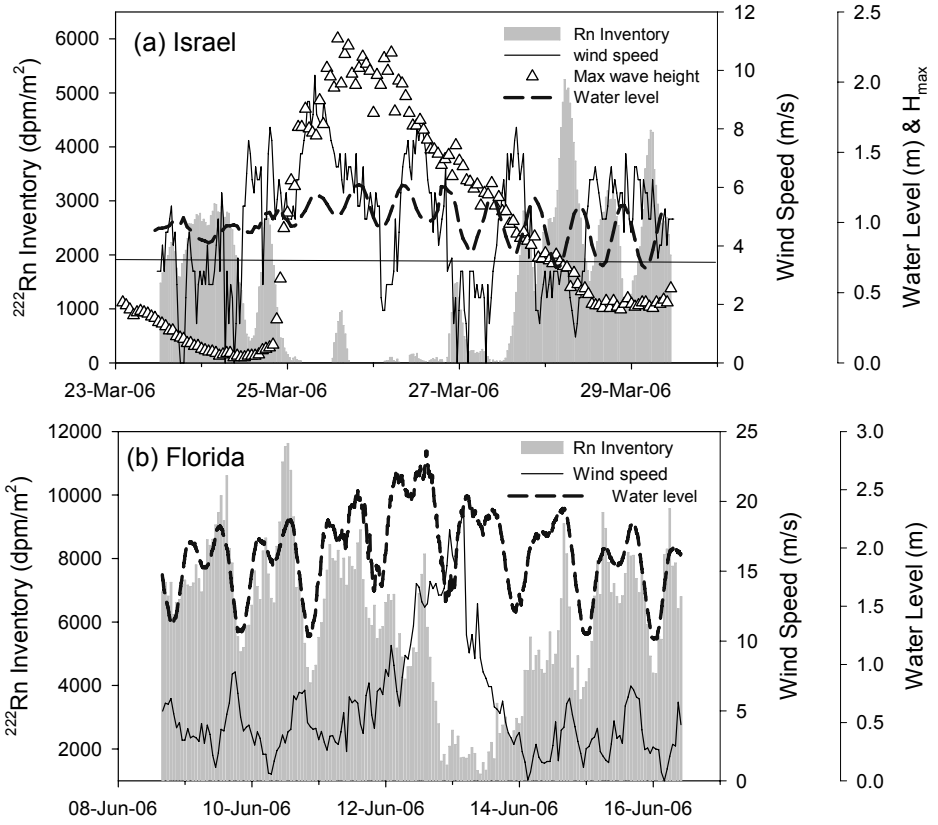

Fig. 4 Radon inventories, wind speeds, and water levels over time from: (a) Dor Beach Israel; and (b) FSUML, Gulf of Mexico. Both examples display dramatic reductions in ^{222}Rn inventories resulting from storm events. Maximum wave heights (H_{max}) are also shown for Dor. Note that the drop in radon inventories corresponds closely to the period when H_{max} exceeds ~0.7 m height (indicated by horizontal line) in (a).

water depth or about when $H_{max} \geq 0.7$ m. Waves would be especially effective in an area surrounded by rocks as Dor, as this would produce sea spray that would enhance gas exchange.

The gas exchange equations would obviously break down during periods of zero radon inventories as the calculation is based on a concentration gradient between the water and air phases. Based on pre-storm conditions, we estimate that it would have been necessary to have prolonged atmospheric evasion rates of approx. 500 dpm m^{-2} h^{-1} to deplete the inventory, yet the gas exchange equations only predicted an average of 24 dpm m^{-2} h^{-1} and a maximum of 270 dpm m^{-2} h^{-1}during the storm period.

In the case of Florida (Fig. 4(b)), the storm (tropical storm "Alberto") had much higher winds (up to ~20 m/s) and a significant storm surge (~0.5 m maximum) compared to the case in Israel. In this case, the gas exchange equations underestimated the observed drop in inventories by ~40–80%. The underestimate in this case may simply be due to the losses via "mixing" with lower activity waters offshore, i.e. we cannot independently test the theoretical approach for atmospheric loss as we do not have an independent estimate for the mixing losses. We do note that the average atmospheric evasion fluxes during the storm (160 dpm m^{-2} h^{-1}) are essentially the same as those estimated during pre-storm conditions (150 dpm m^{-2} h^{-1}). Apparently, the

large drop in ^{222}Rn inventories compensated for the increased flux that would be expected at higher wind speeds.

MIXING LOSSES

We evaluate what we have called "net" radon fluxes by taking the change in inventories over time after correcting for atmospheric evasion and normalizing to a common tidal height. Invariably, we observe both positive and negative fluxes and these are often systematically related to the tidal record. We interpret the positive fluxes as due to input of radon-rich groundwater while the negative fluxes are the result of mixing with lower activity waters offshore. Note in the plot from an experiment on Shelter Island, New York (Fig. 5) that the negative fluxes are mostly associated with the incoming tide while the positive fluxes begin showing up on the outgoing tide and reach a maximum at low tide. If we assume that groundwater flow is low or absent during the rising tides, we can estimate the minimum flux due to mixing based on the most negative values of these fluxes (indicated in Fig. 5 by the dashed line). Of course, it is certainly possible that flow continues even at high tide and so these evaluations would be lower estimates. In the case of Shelter Island, seepage meter measurements support the low to no-flow assumption (Paulsen *et al.*, 2001). While the record is not always so clear, this illustrates a fairly typical example of how the mixing term can be handled.

One can also assess mixing losses of radon by application of the mixing model presented by Moore (2000b) using short-lived radium isotopes as tracers. One can calculate a mixing coefficient, k_h, which would then be multiplied by the mixed layer thickness and the linear radon gradient obtained along the same transect. The final step is to then convert this offshore flux to a seabed flux that is used for the mass balance model. This is done by multiplying the offshore flux by the ratio of the cross-sectional area (layer thickness by width) by the estimated seepage area (seabed area). We have had occasion to use this approach during four experiments and the results have overlapped the radon-based estimates each time (Table 1). We should caution, however, that the calculation may be quite sensitive to some parameters. For example,

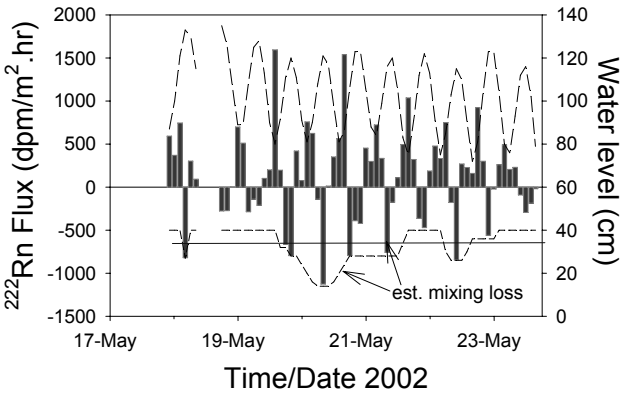

Fig. 5 Calculated "net" radon fluxes (bars), water level (top dashed curve), and mixing losses estimated from inspection of the radon fluxes (dashed line) and via use of short-lived radium isotopes (straight horizontal line; Dulaiova *et al.*, 2006).

the Ra isotope-based value (90 dpm m^{-2} h^{-1}) calculated for the Kona experiment assumed that the mixed layer thickness was only 0.5 m on average. If we had used a 1-m thick layer, the result would have been much higher at 375 dpm m^{-2} h^{-1}. So, while the results are encouraging, the possibility of having higher mixing rates is clearly present.

We have also considered the question of how recharge of coastal waters into the aquifer may represent part of what we have been calling the "mixing" loss. In most cases, we think that this is likely a minor component of the overall balance. Consider the case of Dor Beach (Israel). We use the average measured radon activity in the bay waters during the March 2006 sampling (2200 dpm/m^3) and assume that the recharge rates are comparable to the discharge rates (~10 cm/day). Based on these assumptions, we calculate that the radon loss by this process would only represent ~9 dpm m^{-2} h^{-1} or only about 2% of the estimated mixing loss of 450 dpm m^{-2} h^{-1}. While some other environments or situations would be different, it is likely that recharge does not typically represent an important part of the radon mass balance.

How important are the atmospheric and mixing losses relative to the total mass balance of ^{222}Rn? In most cases, the atmospheric evasion represents a minor loss compared to mixing losses with offshore waters. We compiled data from five different coastal environments showing how the absolute fluxes compare to the measured inventories, mixing losses, and to each other (Table 1). Note that of the examples shown, the evasion rates are highest at FSUML (Florida) and Dor Beach (Israel) while very low in the embayments of Shelter Island (New York) and Ubatuba (Brazil) as well as in Kona (Hawaii) where the setting was also relatively protected. As a percent of the total estimated flux into each system (not shown in Table 1, but the total flux is equal to the sum of the atmospheric plus mixing losses), the atmospheric evasion is highest at ~18–25% of the total at the Florida and Israel sites and ~4–7% of the total flux at the other locations.

Table 1 Radon average inventories, calculated atmospheric fluxes, and mixing estimates based on inspection of the radon fluxes and independent estimates based on short-lived radium isotopes. NA = not available.

Location/Date	Description	^{222}Rn inventories (dpm/m^2)	Atm fluxes (dpm/m^2 h)	Mixing Est from ^{222}Rn (dpm/m^2 h)	Mixing est Ra isotopes (dpm/m^2 h)	Reference
FSUML, Gulf of Mexico/Oct01	Coastal plain; silt/sand overlying limestone	7580	150	690 ± 460	390 ± 140	Burnett & Dulaiova (2003)
Shelter Island, NY/May02	Glacial till aquifer; shallow enclosed embayment	4130	30	670 ± 200	730 ± 260	Dulaiova *et al*. (2006)
Ubatuba, Brazil/Nov03	Fractured rock aquifer; small tropical embayment	7150	40	1060 ± 420	1220 ± 440	Burnett *et al*. (2007)
Kona coast, Hawaii/Feb06	Volcanic aquifer; springs discharging directly to ocean	1510	5	70 ± 70	90 ± 30	Peterson *et al*. (2007)
Dor Beach, Israel/Mar06 before storm	Coastal plain embayment; sandy aquifer overlying consolidated calcaranitic sandstones called "Kurkar"	1820	100	330 ± 120	NA	Weinstein *et al*. (2006)
Dor Beach, Israel/Mar06 after storm		390	100	450 ± 150	NA	Swarzenski *et al*. (2006)

CONCLUSIONS

Radon is a useful tool for studying coastal processes. Because of its very high activity in most groundwaters and the development of improved technologies for measurement, one can now investigate the spatial distribution and temporal dynamics of groundwater discharges as well as make discharge estimates based on a mass balance approach. In most situations, the groundwater end-member concentration represents the largest uncertainty for calculating discharge via a radon mass balance. We recommend that investigations include multiple assessments of this value in order to evaluate the range for any particular situation. End-member estimates may be assessed via sediment equilibration techniques as well as sampling from monitoring wells, piezometers, and seepage meters. Atmospheric losses can be reliably evaluated under "normal" conditions using standard gas exchange equations. While there is some debate concerning the best approach for determining piston velocities (k), our experience has been that the loss via atmospheric evasion is typically less than ~25% of the overall mass balance. Thus, precise determinations, while always desirable, are not critical. Mixing losses are typically more important than atmospheric fluxes but conservative assessments can easily be made by inspection of the radon "net" fluxes. Comparisons of these fluxes to estimates based on short-lived radium isotopes have been favourable.

Acknowledgements We thank the graduate students from FSU (R. Peterson, N. Dimova and B. Mwashote) for their assistance in the field. We thank Eng. Dov Rosen for providing sea state and wind data from Hadera Sea Level Observing Station (IOLR) in Israel. The authors gratefully acknowledge financial support from the Chemical Oceanography Program of the National Science Foundation (OCE04-51379 and OCE05-20723) and the US-Israel Bi-National Science Foundation (BSF2002-381). I.R. Santos acknowledges support from a fellowship from the Brazilian government (CAPES/Fulbright 2150/04-2).

REFERENCES

Burnett, W. C. & Dulaiova, H. (2003) Estimating the dynamics of groundwater input into the coastal zone via continuous radon-222 measurements. *J. Environ. Radioact.* **69**(1-2), 21–35.

Burnett, W. C. & Dulaiova, H. (2006) Radon as a tracer of submarine groundwater discharge into a boat basin in Donnalucata, Sicily. *Cont. Shelf Res.* **26**(7), 862–873.

Burnett, W. C., Aggarwal, P. K., Aureli, A., Bokuniewicz, H., Cable, J. E., Charette, M. A., Kontar, E., Krupa, S., Kulkarni, K. M., Loveless, A., Moore, W. S., Oberdorfer, J. A., Oliveira, J., Ozyurt, I. N., Povinec, P., Privitera, A. M. G., Rajar, R., Ramessur, R. T., Schollten, J., Stieglitz, T., Taniguchi, M. & Turner, J. V. (2006) Quantifying submarine groundwater discharge in the coastal zone via multiple methods. *Sci. Total Environ.* **367**(2-3), 498–543.

Burnett W. C., Peterson R., Moore W. S. & Oliveira J. (2007) Radon and radium isotopes as tracers of submarine groundwater discharge - results from the Ubatuba, Brazil SGD assessment intercomparison. *Estuar. Coast. Shelf Sci.* (submitted).

Cable, J. E., Burnett, W. C., Chanton, J. P. & Weatherly, G. (1996) Modeling groundwater flow into the ocean based on ^{222}Rn. *Earth Planet. Sci. Lett.* **144**, 591–604.

Corbett, D. R., Dillon, K., Burnett, W. C. & Chanton, J. P. (2000) Estimating the groundwater contribution into Florida Bay via natural tracers ^{222}Rn and CH_4. *Limnol. Oceanogr.* **45** 1546–1557.

Dulaiova, H. & Burnett, W. C. (2006) Radon loss across the water-air interface (Gulf of Thailand) estimated experimentally from ^{222}Rn-^{224}Ra. *Geophys. Res. Lett.* **33** L05606, doi:10.1029/2005GL025023.

Dulaiova, H., Burnett, W. C., Chanton, J. P., Moore, W. S., Bokuniewicz, H. J., Charette, M. A. & Sholkovitz, E. (2006) Assessment of groundwater discharges into West Neck Bay, New York, via natural tracers. *Cont. Shelf Res.* **26**(16), 1971–1983.

Dulaiova, H., Peterson, R., Burnett, W. & Lane-Smith, D. (2005) A multi-detector continuous monitor for assessment of ^{222}Rn in the coastal ocean. *J. Radioanal. Nucl. Chem.* **263**(2), 361–365.

Happell, J. D., Chanton, J. P. & Showers, W. J. (1995) Methane transfer across the air-water interface in stagnant wooded swamps of Florida: evaluation of mass-transfer coefficients and isotopic fractionation. *Limnol. Oceanogr.* **40**(2), 290–298.

Lambert, M. & Burnett, W. C. (2003) Submarine groundwater discharge estimates at a Florida coastal site based on continuous radon measurements. *Biogeochem.* **66**, 55–73.

MacIntyre, S. R., Wanninkhof, G. B. & Chanton, J. P. (1995) Trace gas exchange across the air-sea interface in freshwater and coastal marine environments. In: *Biogenic Trace Gases: Measuring Emissions from Soil and Water* (ed. by P. A. Matson & R. C. Harris), 52–97. Blackwell Science, Malden, Massachusetts, USA.

Moore, W. S. (1996) Large groundwater inputs to coastal environments revealed by ^{226}Ra enrichments. *Nature* **380**, 612–614.

Moore, W. S. (2000a) Ages of continental shelf waters determined from ^{223}Ra and ^{224}Ra. *J. Geophys. Res.* **105**(C9), 117–122.

Moore, W. S. (2000b) Determining coastal mixing rates using radium isotopes. *Continental Shelf Res.* **20**, 1995–2007.

Moore, W. S. (2006) Radium isotopes as tracers of submarine groundwater discharge in Sicily. *Cont. Shelf Res.* **26**(7), 852–861.

Paulsen, R., Smith, C. F., O'Rourke, D. & Wong, T. F. (2001) Development and evaluation of an ultrasonic groundwater seepage meter. *Ground Water* **39**(6), 904–911.

Peterson, R. N., Burnett, W. C., Glenn, C. R. & Johnson, A. J. (2007) A box model to quantify groundwater discharge along the Kona coast of Hawaii using natural tracers. In: *A New Focus on Groundwater–Seawater Interactions* (ed. by W. Sandford, C. Langevin, M. Polemio & P. Povinec) (Proc. Symposium HS1001 at IUGG2007, Perugia, July 2007). IAHS Publ. 312. IAHS Press, Wallingford, UK (this volume).

Slomp, C. P. & Van Cappellen, P. (2004) Nutrient inputs to the coastal ocean through submarine groundwater discharge: controls and potential impact. *J. Hydrol.* **295**(1-4), 64–86.

Swarzenski, P. W., Burnett, W. C., Greenwood, W. J., Herut, B., Peterson, R., Dimova, N., Shalem, Y., Yechieli, Y. & Weinstein, Y. (2006) Combined time-series resistivity and geochemical tracer techniques to examine submarine groundwater discharge at Dor Beach, Israel. *Geophys. Res. Lett.* **33**, L24405, doi:10.1029/2006GL028282.

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.

Wanninkhof, G. B. (1992) Relationship between wind speed and gas exchange over the ocean. *J. Geophys. Res.* **97**, 7373–7382.

Weinstein, Y., Less, G., Kafri, U. & Herut, B. (2006) Submarine groundwater discharge in the southeastern Mediterranean (Israel), preliminary results. *Radioactivity in the Environment* **8**, 360–372.

Weinstein, Y., Burnett, W. C., Swarzenski, P. W, Shalem, Y., Yechieli, Y. & Herut, B. (2007) The role of coastal aquifer heterogeneity in determining fresh groundwater discharge and seawater recycling: an example from the Carmel coast, Israel. *J. Geophys. Res*. (submitted).