Radon loss across the water-air interface (Gulf of Thailand) estimated experimentally from ^{222}Rn-^{224}Ra

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[1] We used ^{222}Rn and ^{224}Ra measured in the Upper Gulf of Thailand to estimate ^{222}Rn atmospheric evasion across the water-air interface. The Chao Phraya estuary represents a steady-state source of these tracers and we looked at their horizontal distribution on a transect leading away from the estuary into the Gulf. The isotopes ^{222}Rn and ^{224}Ra have very similar half-lives and are affected in the same manner by mixing processes but only radon will emanate to the atmosphere. We thus are able to estimate the radon air-water exchange rate from the difference in the slopes of the ^{222}Rn and ^{224}Ra horizontal distributions. Estimated gas exchange velocities (k) based on our results were 1.1 cm hr^{-1} in the dry season (January 2004) and 2.1 cm hr^{-1} during the wet season (July 2004). These rates agreed reasonably well with some theoretical models developed for lakes, estuaries and coastal systems. **Citation:** Dulaiova, H., and W. C. Burnett (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.

1. Introduction

[2] Radon may be used to study air-water gas exchange [*Peng et al.*,1979; *Elsinger and Moore*, 1983]. It is a naturally occurring, radioactive noble gas typically present in much higher concentrations in water than air and relatively easy to measure – thus a good opportunistic tracer for interpretation of atmospheric evasion processes.

[3] Here we take advantage of a specific radon source, submarine groundwater discharge (SGD), which results in coastal waters having ^{222}Rn concentrations well above levels supported by ^{226}Ra in the water and diffusion from sediments [*Burnett et al.*, 2003; *Kim and Hwang*, 2002]. SGD also enriches the coastal zone in the four naturally occurring radium isotopes: ^{223}Ra, ^{224}Ra, ^{226}Ra, ^{228}Ra [*Moore*, 1996]. Radium isotopes are also released in estuaries via ion exchange from particles carried by rivers when they encounter saline waters [*Li et al.*, 1977].

[4] Should radon and radium be introduced to coastal waters in a constant activity ratio by these processes, one could use that steady-state source to study atmospheric evasion of ^{222}Rn. Ra-224 would be particularly helpful as it has a very similar half-life (3.6 days) as ^{222}Rn (3.8 days). After release into the water ^{224}Ra stays dissolved in seawater until it decays or it is transported away by mixing. The same is true for radon except that as a gas some of it escapes to the atmosphere. We would thus expect that the ^{222}Rn/^{224}Ra ratio would vary as a function of wind speed, changes in water temperature, currents or other factors that may enhance gas exchange.

[5] We were able to test this hypothesis by sampling ^{222}Rn and ^{224}Ra in the Gulf of Thailand on a transect away from the Chao Phraya Estuary (Figure 1) which has elevated radon and radium activities in its estuary due to inputs by groundwater discharge and desorption (H. Dulaiova et al., Are groundwater inputs into river-dominated areas important? The Chao Phraya River–Gulf of Thailand, submitted to *Limnology and Oceanography*, 2006, hereinafter referred to as Dulaiova et al., submitted manuscript, 2006). We also compare these experimentally-determined radon losses to those based on some current models of air-water gas transfer [*MacIntyre et al.*, 1995; *Raymond and Cole*, 2001].

2. Sampling Methods

[6] Results presented here are based on two surveys (wet/dry seasons) of the Chao Phraya Estuary-Gulf of Thailand in 2004. We measured radon in a continuous survey mode and radium by discrete sampling on two cruises aboard the R/V *Chula Vijai* (Chulalongkorn University). During the dry season sampling in January 2004, the river discharge was 47 m^3 s^{-1}, and during our fieldwork in July 2004 it was 430 m^3 s^{-1} (detailed characteristics provided in the Table S1)[1]. In both seasons we sampled along transects leading from a distance of about 48 km upstream to 42 km offshore from the river mouth. The analysis provided here will focus on just the offshore section from ~5 to 20 km offshore. Radon measurements were made with an automated radon mapping system that was continuously measuring radon at ~1 meter below the surface [*Dulaiova et al.*, 2005]. Surface water samples (~100 L) were collected at several stations (n ≈ 30 for each survey) along the transect for radium analysis. At each radium station we also deployed a CTD profiler. In addition, we continuously monitored radon in air from the boat and obtained wind speed data from meteorological stations at Hua Hin and Ko Sichang (Figure 1).

3. Results and Discussion

[7] The measured radon concentrations peaked during both seasons at a distance of about 5 km seaward of the river mouth (Figure 2). There is no additional radon input into the water after this point so the radon concentration drops due to decay, mixing and evasion to ^{226}Ra supported levels at a distance of about 25–30 km offshore.

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[1]Auxiliary material is available at ftp://ftp.agu.org/apend/gl/2005GL025023.

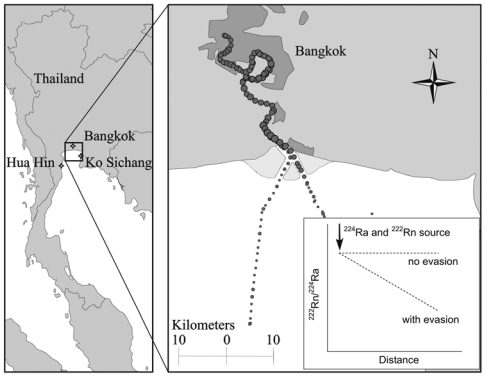

Figure 1. Map of the upper Gulf of Thailand and the Chao Phraya River. The radon survey trajectory is presented by the circles, proportional to the measured radon activities in the water. A theoretical plot of ^{222}Rn and ^{224}Ra concentration ratios over distance from their common source (indicated by arrow) shows that the ratio of ^{222}Rn/^{224}Ra would only change due to atmospheric losses of radon.

[8] The peak ^{224}Ra concentrations also had the highest levels at ~5 km off the river mouth (Figure 2). The sources of ^{224}Ra to the estuary include river water, groundwater, and radium desorption from particles as they encounter seawater. Although the sources of the two tracers are somewhat different, our hypothesis only requires that the radon and radium input ratios be in steady state over a period of several days, no matter what the source. Under the conditions present during our cruises (no significant rain events or changes in river discharge), the inputs of these tracers were likely in approximate steady-state over periods of days to weeks.

3.1. Apparent Water Ages

[9] For the atmospheric evasion calculations we used the data measured on the offshore portion of the transect from about 5 to 20 km (Figure 2; analytical data and calculated ages provided in Table S2). Using the measured ^{224}Ra/^{223}Ra activity ratios we were able to estimate apparent water "ages" over distance, i.e., the amount of time elapsed since these tracers entered the system. Assuming that unsupported radium enters these waters 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) one can estimate "radium ages" [*Moore*, 2000]. These estimated ages were plotted against distance and the following relationships determined: (January) Ra age (days) = 0.28x distance (km), R^2 = 0.80; (July) Ra age (days) = 0.35x distance (km), R^2 = 0.88 (Dulaiova et al., submitted manuscript, 2006).

3.2. Water-to-Air Rn Transfer Estimates Via ^{222}Rn and ^{224}Ra

[10] Since ^{222}Rn and ^{224}Ra do not decay exactly at the same rate and we know the time that elapsed since the isotopes entered the estuary, we have corrected the ^{224}Ra values by multiplying them by the ratio $\exp(\lambda_{224}*t)/\exp(\lambda_{222}*t)$, where t is the radium age of the water. The isotope distributions were then plotted against the corresponding ages, and fitted by exponential regressions (Figure 3). As expected, in each case radon has a more negative slope than ^{224}Ra. We normalized the two equations to the same y intercept by multiplying both sides of the radium equations by the ratio of the two intercepts (4580/860 for January and 3630/760 for July). 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 trendlines. 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 data along the transect represents a tracer distribution that evolved over a period of 6–7 days so these losses should vary as a function of radon concentration, wind speed, changes in water temperature or any other factor effecting radon evasion. The difference of the ^{224}Ra-^{222}Rn slopes at each radium sampling point is than multiplied by the water depth in January (a period of no stratification) or the depth of the surface mixed layer (Table S2) in July to derive an estimated radon flux from the water column (dpm m^{-2} day^{-1}). The result is an exponential function with the radium age as a variable. Because we know the relationship between the distance and age we can also plot atmospheric evasion against distance (Figure 4). The resulting radon fluxes from these estimates were 100 to 760 dpm m^{-2} day^{-1} and 100 to 2000 dpm m^{-2} day^{-1} in January and July, respectively. The corresponding gas transfer velocity (k) values for these radon fluxes are 1.1 cm hr^{-1} in January and 2.1 cm hr^{-1} in July.

[11] The highest radon fluxes are at stations toward the river mouth and decrease systematically offshore as the Rn activities drop. An error analysis of these calculations showed that water age and the determination of the differ-

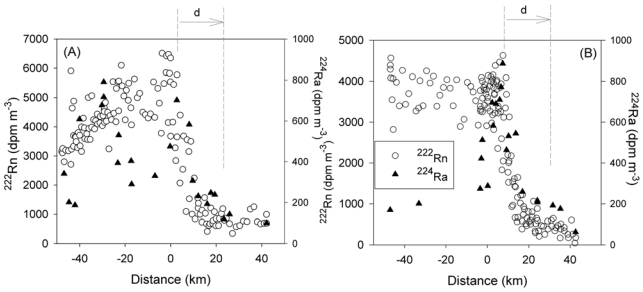

Figure 2. Radon and ^{224}Ra plotted together on different scales to compare their trends against distance (a) in January and (b) in July 2004. The river mouth is at 0 km. The "d" designation refers to the distance offshore over which we investigated the trends in ^{222}Rn and ^{224}Ra.

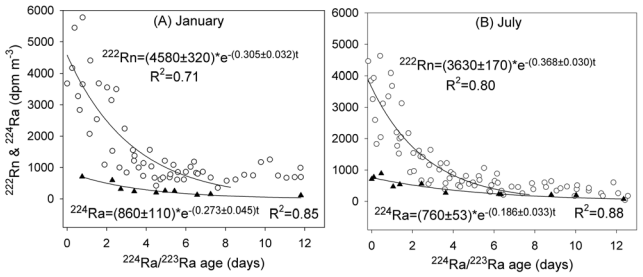

Figure 3. Radon and ^{224}Ra plotted on the same activity scale against the apparent radium ages along the offshore transect (a) in January and (b) in July 2004.

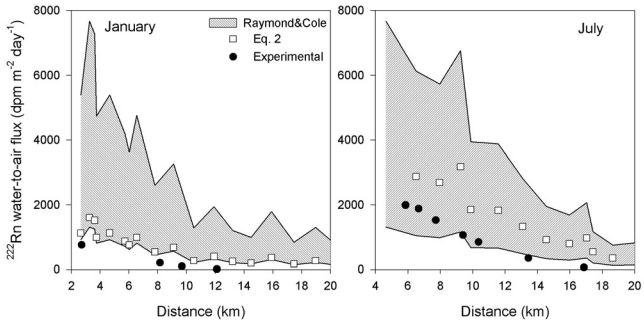

Figure 4. Radon evasion from water to air calculated from the ^{222}Rn-^{224}Ra slopes (solid symbols), via the *MacIntyre et al.* [1995] approach (equation (2), open squares) and based on k_{600} ranges listed for estuaries by *Raymond and Cole* [2001] (shaded area).

ence of slopes, which include the radionuclide measurement errors, have relative uncertainties of 10–18%. We assume a 10% uncertainty in the water depth that exchanges radon with air, which is reasonable since we had a CTD cast at every station. Thus the overall error of the radon flux estimates is about 16 to 21%.

3.3. Radon Flux Based on Models

[12] Radon flux (F_{atm}) to the atmosphere is governed by molecular diffusion produced by the concentration gradient across the air-water interface and turbulent transfer, and can be calculated as

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

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 velocity, a function of kinematic viscosity, molecular diffusion, and turbulence. The evaluation of k is based on empirical relationships observed in different environments for different gases. Based on a number of field studies, empirical equations that relate k to wind speed as a source of turbulence have been proposed. For example, two review papers presented the equations:

$$k_{600} = 0.45u_{10}^{1.6}, \quad (2)$$

MacIntyre et al. [1995]

$$k_{600} = 1.91e^{(0.35u_{10})}, \quad (3)$$

Raymond and Cole [2001]

where k_{600} represents the piston velocity (cm hr^{-1}) for wind speed u_{10} (m s^{-1}) at 10 m height above the water surface. The subscript "600" refers to the ratio of kinematic viscosity to molecular diffusivity called the Schmidt number, S_c, which for CO_2 in freshwater at 20°C equals 600. *Hahm et al.* [2006] showed that in the coastal zone not only winds but also the tidal currents influence k values.

[13] Based on estuarine studies it has been suggested that k depends on water currents, wind speed, and fetch limitation [*Borges et al.*, 2004a]. *Borges et al.* [2004b] constructed an empirical relationship for the Scheldt Estuary to compute k that accounts for contributions from wind, water currents and water depth:

$$k_{600} = 1 + 1.719w^{0.5}h^{-0.5} + 2.58u_{10} \quad (4)$$

where w is the water current (cm s^{-1}), and h is the effective depth of water exchanging with the atmosphere (m).

[14] *Raymond and Cole* [2001] suggested that unless an estuary has above average winds, is exceptionally shallow, or has rapid tidal velocities, the expected k values should be in the range of 3–7 cm hr^{-1}, and according to *Zappa et al.* [2003] this value could be in a range of 1.2–12 cm hr^{-1}.

[15] We calculated the gas transfer velocities and radon fluxes based on these models with the exception of those requiring water current measurements that were unavailable. For all approaches we calculated k via an integration of the 5-day wind speeds measured prior to and during our samplings (detailed records of wind speeds provided in Table S3). The measured radon in air concentrations ranged from 460 to 780 dpm m^{-3} in January and from 130 to 600 dpm m^{-3} in July. We used the same Rn in water values as applied to the calculations presented earlier (Table S2). For each radon measurement we computed the Schmidt number based on the corresponding temperature and salinity values assuming a linear relationship of *Sc* and salinity [*Wanninkhof*, 1992].

[16] Based on the wind speeds equation (2) resulted in average values of gas transfer velocities k = 1.2 and 3.7 cm hr^{-1}, and equation (3) resulted in k = 3.9 and 7.4 cm hr^{-1}. We did not have water current measurements in the area of our study so we could not apply the model of *Borges et al.* [2004b]. But even using a conservative estimate of currents of 4 cm s^{-1} for the upper Gulf of Thailand determined by *Wattayakorn et al.* [1998], the model resulted in k values of 5 and 10 cm hr^{-1} for January and July, respectively. These values are the highest from all the models compared here and may confirm *Borges et al.*'s [2004a] idea that k-wind parameterizations are site specific.

3.4. Comparison of Radon Flux Estimates

[17] All approaches agree that there are much higher radon fluxes near the river mouth, a reflection of the higher ^{222}Rn concentrations in the water. The results show that the ^{224}Ra-^{222}Rn-slope experimental procedure and the *MacIntyre et al.* [1995] model of atmospheric evasion provide estimates that are within 50–100 % of each other both in January and July (Figure 4). Generally, the ^{224}Ra-^{222}Rn-slope method resulted in lower radon fluxes. Equation (3) [*Raymond and Cole*, 2001] resulted in about four times higher radon fluxes than the ^{224}Ra-^{222}Rn-slope method.

[18] The ratio of the radon atmospheric flux to the radon inventory represents the fraction of radon lost from the water column per time. In the near-shore region, this fraction is approximately 18 and 60% of the radon inventory per day in January and July, respectively.

4. Conclusions

[19] As expected, our radon evasion estimates for the Upper Gulf of Thailand were much lower in January when the water temperatures were cooler and the wind speed was

lower than in July. The water-air radon fluxes estimated experimentally via ^{222}Rn-^{224}Ra horizontal distributions resulted in values reasonable close to those calculated by some theoretical approaches. The experimental approach using the natural tracers ^{222}Rn and ^{224}Ra offers an independent method for examining water-to-air gas exchange.

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