

## A simple laboratory system for diffusive radon flux measurements

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**Abstract.** This study designed a simple, custom-made system to estimate the diffusive radon flux from solid materials (e.g., sediments, soils, building materials). Determination of the radon flux is based on the measurement of the radon activity in the air over time inside a closed loop system. For sediments, the system consists of wet sediment and water inside a gas-tight flask connected in a closed loop to a drying system and a radon analyzer (Durridge RAD7). The flux is determined based on an initial slope method in which the slope of radon activities vs. time plot during the first 12 h is evaluated. The slope is then multiplied by the total air volume and divided by the exposed sediment area to obtain the radon flux. The minimal thickness or mass of wet sediment should be about 4 cm. or (equivalent to approximately 150 g of wet sediment) to obtain a reliable radon diffusive flux in this study.

### 1. Introduction

The magnitude of terrestrial groundwater discharge to coastal water bodies has been reported in recent literature, with global fluxes estimated to range from 0.01 to 10% of total riverine discharge [1]. Therefore, groundwater discharge may also be an important pathway for the diffuse pollution to the coastal zone where coastal aquifers have become contaminated by septic systems [2]. These include nutrient elements, nitrogen, phosphorus and silicon [3-6] and dissolved gases such as methane (CH<sub>4</sub>) and radon [7-9]. <sup>222</sup>Rn has seen an increasing use as a tracer for studying the exchange rate across both air-sea and sediment-water interfaces. In addition, <sup>222</sup>Rn has also been used in a wide range of environments for tracing submarine groundwater discharged (SGD) into the coastal zone and rivers. <sup>222</sup>Rn, which has a half-life of 3.82 days, is a naturally occurring radionuclide that originates from the <sup>238</sup>U decay series through the alpha decay of <sup>226</sup>Ra. Because it is a noble gas, it behaves conservatively in most chemical and biological reactions in nature. Its distribution will be controlled by balancing between the production from its parent (<sup>226</sup>Ra), radioactive decay, and the physical transport process, including the biological mixing of sediment [10].

In the mass balance models that have been used for the estimation of sediment-water transport processes or SGD, information is needed regarding the flux of <sup>222</sup>Rn via the diffusion from sediments and the <sup>222</sup>Rn activity of the discharging water. The diffusive term can be assessed in a number of

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ways including *in situ* benthic flux chambers and laboratory incubations of sediment cores [11, 12]. All of these approaches are time consuming and may present numerous logistical difficulties. In some cases there is a considerable amount of spatial variability and an alternative approach is needed. One useful method is to conduct sediment equilibration in the laboratory where representative sediment sampled from the field site are reacted with water over sufficient period (e.g. 20 days) to ensure equilibrium between the  $^{222}\text{Rn}$  in the water and the  $^{222}\text{Rn}$  produced by the sediment-bound  $^{226}\text{Ra}$ . Since typical SGD flow rates are on the order of centimetres per day,  $^{222}\text{Rn}$  in the groundwater should have obtained the same level of equilibrium as measured in the laboratory.

In this paper, we present a simple, custom-made setup using an automated radon-in-air analyzer that is capable of generating data necessary for the evaluation of radon flux from sediments in a matter of hours to a day. Our results have demonstrated the feasibility and reliability of the setup and its potential use to estimate radon flux from all types of solid materials.

## 2. Experimental

### 2.1 Sediment samples

The sediments used in this study were collected on July 2013 from sampling station No.32 in the northern part of Tonle Sap Lake, Cambodia. Tonle Sap, the largest freshwater lake in Southeast Asia, is a classic flood-pulse system and hosts one of the most productive inland fisheries in the world, accounting for more than 75% of Cambodia's inland fish caught and about 60% of the country's protein needs [13].

### 2.2 Laboratory Setup

A 700-mL wide-mouth glass bottle with tight lid connected to plastic tubes was used as a reaction flask. The minimal mass/thickness of the sediment was evaluated by running the experiment with the same sediment under different mass/thickness conditions. We tested 25, 50, 100, 150, 200, 250 and 300g of wet sediment. All wet sediment-weight samples were added to a separate flask and then the sediment was covered with 300 ml of radon free water. After the sample had settled, the height of wet sediment in the flasks was measured. The wet sediment was added to the reaction flask without any modification since the sampling. The sediment was kept in a closed container the entire time from the sampling until the start of experiment. The flask was connected in a closed loop with a Tygon tube to a laboratory drying tube filled with Drierite desiccant and then to a DurrIDGE RAD7 radon-in-air analyzer (figure 1).

The RAD7 radon detector is a high performance instrument that can determine the activity of  $^{222}\text{Rn}$  continuously by means of electrostatic collection and measurement of the alpha-emitting daughters,  $^{218}\text{Po}$  and  $^{214}\text{Po}$ . The internal air pump of the RAD7 was set to the "auto" mode, which allowed the pump to operate continuously until the relative humidity reached 10% or less. Once that level is obtained, the pump operates for 1 min in very 5-min interval. The air is directed to the inlet tube of the reaction flask, which is submerged in the water with a gas diffusion stone on the end. The air is then channelled through the plastic outlet to the dryer and the radon analyzer. For most of the experiments the program on the RAD7 was set to run on a 2-hour cycles up to 48 h, although the results reported here represent just the first 12 hours. For prolonged experiments, two drying tubes were set in series to ensure the low level of humidity. The temperature in the room was monitored and held steady at  $24.5 \pm 0.5$  °C.

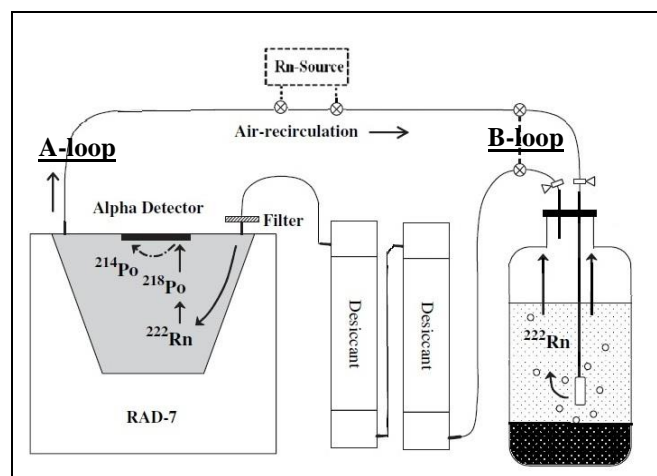
### 2.3 Leak tests

It is known that the internal air pump of the RAD7 radon analyzer has a slow steady air leak [14,15]. This occurs because there is a pressure drop across the inlet filter and a pressure rise across the internal air pump and the pump itself is not 100% airtight. The extent of this leakage is very low and can be ignored for most radon analysis routines for up to several hours. However, as shown here, the leakage must be accounted for to get accurate results for a closed loop application with runs up to a few days.

Since the experimental system is a closed air loop, decay and leakage would lead to lower activities over time once radon has entered the system. If there was no leakage at all, observed drops in  $^{222}\text{Rn}$  activities would be equal to the expected losses by decay. However, after an elevated activity of  $^{222}\text{Rn}$  was introduced into the system, we observed slow drops in the activity above the decay losses virtually every time when the system operated longer than about 12 h. The extent of these losses could be evaluated by plotting the observed activities over time compared to those based on theoretical decay. This experiment was done by introducing a relatively high activity ( $\sim 20,000$ – $30,000$  Bq/m<sup>3</sup>) of radon into the system from a Pylon  $^{226}\text{Ra}$  standard source (Model RN-1025) that contains 98.138 kBq  $^{226}\text{Ra}$  and monitored the activities for over about 40 h. The difference between the observed and the theoretical activity at each time step (1 h) could be evaluated by assessing a leak factor (LF) in the following manner:

$$LF(\% / hr) = 100 \bullet \left( \frac{A_{decay} - A_{obs}}{A_{decay}} \right) / t \quad (1)$$

where  $A_{decay}$  represents the theoretical activity (Bq/m<sup>3</sup>) at each time step;  $A_{obs}$  is the observed activity (Bq/m<sup>3</sup>) at the same time; and  $t$  is the cumulative time (h) from the start of the experiment. Our final leak factor term is based on the mean of the last five experimental results.



**Figure 1.** Schematic sketch of the experimental setup for evaluating  $^{222}\text{Rn}$  released from sediment over time. The dashed lines with 3-way ( $\oplus$ ) are bypasses for the  $^{222}\text{Rn}$  source to separate two parts of the system: the A-loop and the B-loop. See details in text.

### 3. Results and discussion

#### 3.1 Leakage rates

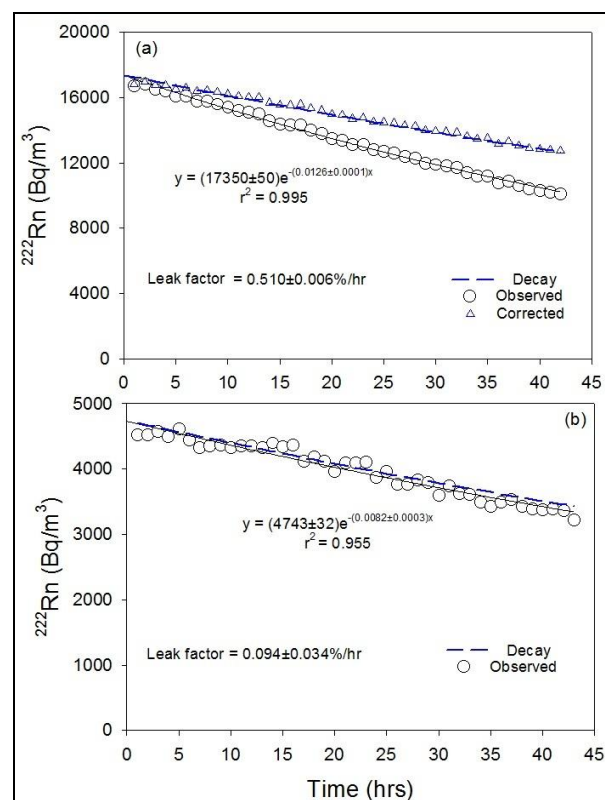
We repeated leak tests 3 times on the same RAD7 (serial #1444) that was used for all the sediment equilibration experiments. Two of the tests were run with the pump in “auto” mode (result of one test is shown in figure 2a) and the third test was performed without the pump running (figure 2b). The results show the activities of  $^{222}\text{Rn}$  steadily differ from the theoretical decay line as a function of time when the pump is run longer than about 12 h. To evaluate the extent of leakage, a graph of observed activities time was plotted in comparison to the theoretical decay. After 40 h, the observed trend is about 20% lower than the decay line. When the test ran with the pump turned off, there was very little difference between the observed and theoretical decay.

The loss rate of RAD7 was calculated to be  $0.510 \pm 0.006$  % per h based on the data in figure 2a. Since the estimated total air volume in our system was  $1850 \text{ cm}^3$ , the average rate of exchange between ambient air and the air inside the system was  $9.3 \text{ cm}^3$  per hour. Xu [15] reported a RAD7 air loss of 5% in 20 h, which was equivalent to 0.25% per hour. This reported rate level was only half of the rate presented in this study. However, their experimental setup had four RAD7s in line together with a 12-liter reservoir for a total estimated air volume of  $15,350 \text{ cm}^3$ . This equates to an average air exchange rate of about  $9.6 \text{ cm}^3$  per hour for each RAD7 pump, which was close to the value presented here. Therefore, it should be evaluated for each RAD7 used when running a closed loop for more than a few h.

Determination of the leakage rate, it has to correct the observed values by applying the following equation:

$$A_{cor} = A_{obs} + \left( \frac{LF}{100} \cdot A_{obs} \cdot t \right) \quad (2)$$

where  $A_{cor}$  is the activity of  $^{222}\text{Rn}$  corrected for leakage. These are the activities that will be used to evaluate the radon diffusive flux.



**Figure 2.** (a) Radon activity observed over time compared to theoretical decay. (b) A leakage test performed in exactly the same manner as in “a” but without the RAD7 air pump. In this case, the observed radon activities are in good agreement with the decay curve.

### 3.2 Radon diffusion from sediments

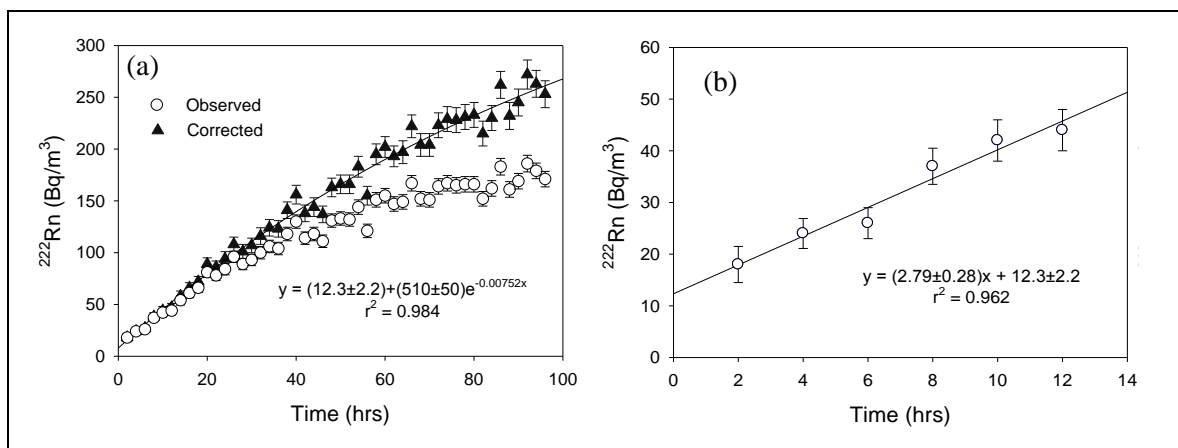
Radon activity in the air observed from the closed loop experiments are plotted as a function of time. Figure 3a shows the results of a 96 h run and the first 12 h are shown separately (Figure 3b). The  $^{222}\text{Rn}$  activity was shown to steadily increase. As more time passes, it can observe that the activity trend

started to bend as a consequence of the leakage and decay. Therefore, we correct for the leakage as described above (equation 2) and then base on our analysis the leakage-corrected results.

In order to determine the radon diffusion rate from the sediment in this study, one could rely on the nearly linear gradient during the first several hours in the closed system. The diffusive flux of radon ( $J_D$ ) can be derived from the initial slope approach and is calculated as follows [14]:

$$J_D (\text{Bq} / \text{m}^2 \text{ day}) = \frac{\text{slope} (\text{Bq} / \text{m}^3 \text{ hr}) \bullet V_{\text{air}} (\text{m}^3)}{\text{Area} (\text{m}^2)} \bullet \frac{24 \text{ hr}}{\text{day}} \quad (3)$$

where  $V_{\text{air}}$  is the total air volume ( $1.850 \times 10^{-3} \text{ m}^3$ ) and the area is the exposed area of the sediment in the reaction flask ( $0.0067 \text{ m}^2$ ). Therefore, based on the data shown in figure 3b, the linear slope of  $2.79 \pm 0.28 \text{ Bq/m}^3 \text{ hour}$  was evaluated after the first 12 hours and the flux was calculated using equation 3 at  $18.5 \pm 1.9 \text{ Bq/m}^2 \text{ day}$ .



**Figure 3.** (a) A full 96-hour run on the 150 g sediment showing the best fit to an exponentially increasing function rising to a maximum. (b) First 12 h of the same run showing the linear gradient of  $2.79 \pm 0.28 \text{ Bq/m}^3 \cdot \text{h}$  and y-intercept regression of  $12.3 \pm 2.2 \text{ Bq/m}^3$  [14].

In the case of evaluating the radon diffusion from sediment by running the experiment for a few days to estimate the equilibrium  $^{222}\text{Rn}$  activity, longer-term results can be used for curve fitting to evaluate the equilibrium level for the estimation of the radon flux. In our study, the same samples were run for 96 h to perform a best-fit analysis of the leakage-corrected results (figure 3a) using an exponentially increasing function rising to a maximum in the form [14]:

$$y = y_o + A_{eq} (1 - e^{-\lambda_{222} t}) \quad (4)$$

where the y-intercept ( $\text{Bq/m}^3$ ),  $y_o$ , is taken from the linear regression based on results from the first several hours (Figure 3b);  $A_{eq}$  is the calculated equilibrium activity ( $\text{Bq/m}^3$ ); and  $\lambda_{222}$  is the decay constant of  $^{222}\text{Rn}$  ( $0.00752/\text{hr}$ ). The equilibrium value can be determined by varying the  $A_{eq}$  coefficient until the best match is obtained for the trend of the leakage-corrected  $^{222}\text{Rn}$  results over time. Therefore, the solid line through the leak-corrected points (figure 3a) represents the best-fit with an equilibrium value of  $510 \pm 50 \text{ Bq/m}^3$ . The radon flux can be calculated from the following equation [14]:

$$J_D (\text{Bq/m}^2 \text{ day}) = \left( \frac{A_{eq} (\text{Bq/m}^3) \bullet V_{\text{air}} (\text{m}^3) + A_{\text{water}} (\text{Bq/m}^3) \bullet V_{\text{water}} (\text{m}^3)}{\text{Area} (\text{m}^2)} \right) \bullet \lambda_{222} (1/\text{day}) \quad (5)$$

where  $A_{water}$  is the  $^{222}\text{Rn}$  activity ( $\text{Bq/m}^3$ ) in the water;  $V_{air}$  and  $V_{water}$  represent the volumes of the air and water respectively; and  $\lambda_{222}$  is the decay constant of  $^{222}\text{Rn}$  (0.181/day). Figure 3b shows the y-intercept of  $12.3 \text{ Bq/m}^3$ , which is close to the average radon activity in the room air (5 - 20  $\text{Bq/m}^3$ ) used to circulate through the closed system.  $A_{eq}$  is calculated based on the curve fitting equation (equation 4) and with a water volume of  $3.0 \times 10^{-4} \text{ m}^3$ . The total air volume for our system was estimated to be  $1.85 \times 10^{-3} \text{ m}^3$ .  $A_{water}$  is calculated based on the derived equilibrium  $^{222}\text{Rn}$  activity in the air multiplied by the temperature dependent solubility coefficient,  $k$  [16]:

$$k = 0.105 + 0.405e^{-0.0502T} \quad (6)$$

where  $T$  is the temperature in  $^{\circ}\text{C}$  (varied from 24.5 to 25.5  $^{\circ}\text{C}$  during all the experiments).

A comparison of the two approaches used in estimating the radon diffusive flux from sediments shows that the equilibrium approach generally provides better precision with lower uncertainties (table 1). The initial slope method had propagated uncertainties estimated to be between 10 to 30% while the equilibrium approach displayed about 10% of uncertainty for all the runs reported here. The initial slope method depends on assessing the radon-in-air activities that are quite low (e.g., < 40  $\text{Bq/m}^3$  for measurement 2: table 1) while the equilibrium approach is based on activities that 4-5 times higher. Thus, there is less uncertainty in individual measurements and less scattering of data in the curve fitting.

**Table 1.** Calculated radon diffusion from Tonle Sap sediment sample ran in triplicate based on: (1) a linear gradient over the first 12 hours of the experiment; and (2) an equilibrium model.

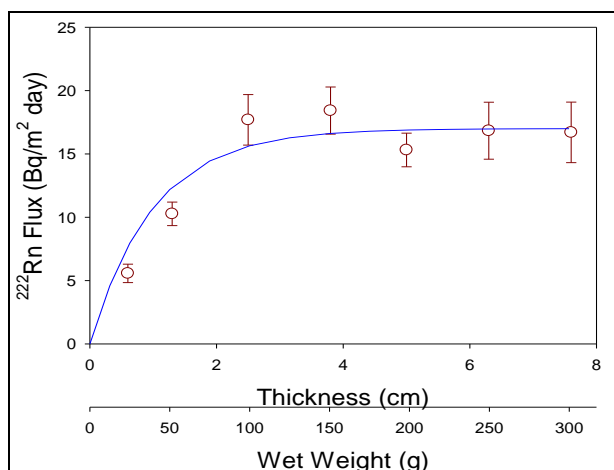
Measurement Number	(1) Initial Slope ( $\text{Bq/m}^3\text{hour}$ )	(1)Flux $\text{Bq/m}^2 \text{ day}$	(2) Equilibrium $\text{Bq/m}^3$	(2) Flux $\text{Bq/m}^2 \text{ day}$
1	$3.8 \pm 1.1$	$25.4 \pm 7.3$	$580 \pm 20$	$30.2 \pm 2.4$
2	$2.8 \pm 0.3$	$18.5 \pm 1.9$	$510 \pm 30$	$26.5 \pm 2.4$
3	$2.7 \pm 0.3$	$17.6 \pm 2.0$	$480 \pm 30$	$25.0 \pm 2.6$

**Table 2.** Calculated radon diffusion flux from 7 different mass/thickness conditions of wet sediment.

ID	Sediment Weight (g)	Sediment Thickness (cm)	Initial Slope ( $\text{Bq/m}^3\text{hour}$ )	Flux $\text{Bq/m}^2 \text{ day}$
1	25	1.3	$0.5 \pm 0.1$	$3.4 \pm 0.9$
2	50	1.8	$1.6 \pm 0.1$	$10.3 \pm 0.9$
3	100	2.5	$2.7 \pm 0.3$	$17.7 \pm 2.0$
4	150	3.8	$2.8 \pm 0.3$	$18.4 \pm 1.9$
5	200	5.3	$2.9 \pm 0.6$	$19.0 \pm 4.2$
6	250	6.0	$2.5 \pm 0.3$	$16.8 \pm 2.3$
7	300	6.8	$2.6 \pm 0.8$	$17.5 \pm 5.4$

To evaluate the minimal thickness/mass of the wet sediment for a reliable radon diffusive flux in this study, the linear gradient was used during the first 12 h for each different mass/thickness condition. Table 2 shows the calculated radon diffusion flux from 7 different mass/thickness conditions. These results (figure 4) show that radon flux increases with the sediment weight from 25 g (0.5 cm) to 100 g (2.5 cm) whereas the radon flux values at sediment weight of 100g (2.5 cm) to 300 g (7.6 cm) seem to be constant within the experiment uncertainty. Corbett [17] reported that most radon diffusion in muddy lake sediments does occur in the upper 4-5 cm, which is consistent with our

results. At some point, the sample weight of wet sediments should reach “infinite thickness”, i.e., additional mass in same area has no effect. Based on our results, one reaches an infinite thickness at about 4 cm. (wet sediment weight of 150g in this case).



**Figure 4.** Radon diffusion flux from different mass/thickness conditions.

#### 4. Conclusions

To calculate the reliable and accurate flux, an initial slope approach could be used during the first 12 h. During this period, the small leakage of RAD7 could be ignored. In addition, the thickness of wet sediment of about 4 cm. (wet weight of 150g) was required for a reliable estimation of radon diffusive flux from muddy sediments.

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