A multi-detector continuous monitor for assessment of ^{222}Rn in the coastal ocean

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Radon-222 is a good natural tracer of groundwater discharge and other physical processes in the coastal ocean. Unfortunately, its usefulness is limited by the time consuming nature of collecting individual samples and traditional analysis schemes. We demonstrate here an automated multi-detector system that can be used in a continuous survey basis to assess radon activities in coastal ocean waters. The system analyses ^{222}Rn from a constant stream of water delivered by a submersible pump to an air-water exchanger where radon in the water phase equilibrates with radon in a closed air loop. The air stream is fed to 3 commercial radon-in-air monitors connected in parallel to determine the activity of ^{222}Rn. By running the detectors out of phase, we are able to obtain as many as 6 readings per hour with a precision of approximately ±5–15% for typical coastal seawater concentrations.

Introduction

There are many reasons why one might want to make continuous measurements of ^{222}Rn in natural waters. Geophysical applications include groundwater monitoring associated with earthquake and volcanic eruption prediction, air-sea gas exchange processes, horizontal and vertical eddy diffusion in the ocean, and assessment of submarine groundwater discharge. In addition, continuous monitoring of the radon content of municipal water supplies and of water supplied to bottling plants and other industries would be attractive for radiation protection purposes. In such cases continuous monitoring may be preferable to the conventional, standard process of taking a sample and sending it for later analysis because radon activities in natural waters may change on many time scales.

Our interest in radon concerns its use as a tracer of groundwater inputs to the coastal ocean. Groundwater is an important source of nutrients and other dissolved constituents to the coastal ocean in some areas.[1] Estimates of the location and magnitude of groundwater flow are scarce because measurements cannot be performed easily and sites of discharge are not always obvious – groundwater is an "invisible pathway" between land and sea.[2–4]

Groundwater discharge estimates via radon tracing is an indirect method of assessment. Due to the huge radon concentration difference between groundwater and surface water (often 1000-fold or higher ^{222}Rn levels in groundwater), dilution is not as important as other potential tracers. In addition, radon is completely inert so biogeochemical reactions do not need to be considered. By using a modeling approach in conjunction with radon analyses in the receiving waters, one can estimate the total flux of groundwater into a region.[5,6] A practical application of such an approach would be the identification of seepage sites and assessment of fluxes of a contaminant that has a groundwater pathway into a coastal zone.

In spite of the fact that we have made significant progress in our ability to assess groundwater fluxes in one area using a radon tracing approach, we are hampered in making regional-scale assessments by the time-consuming logistical requirements of collecting and analyzing samples in the conventional manner.[7] We recently developed a "continuous" radon monitor that provides high-resolution measurements of the radon concentration at one location over time.[8] While this has been a significant improvement, we still do not have the ability to map radon concentrations very effectively because the method relies on counting the radioactive daughters of ^{222}Rn and this typically requires thirty minutes to two hours per analysis at the activities encountered in most coastal waters. We describe here a new version of this system that we specifically designed for surveying that uses a high-flow air–water exchanger and multiple detectors in order to increase analysis throughput.

Experimental

Single-detector system

Our single-detector system (Fig. 1) analyses ^{222}Rn from a constant stream of water passing through an air-water exchanger that distributes radon from the running water to a closed air loop. The air stream is fed to a commercial radon-in-air monitor (RAD-7, Durridge Co.) that determines the activity of ^{222}Rn by collection and

measurement of the α-emitting daughters, [214]Po and [218]Po. Since the distribution of radon at equilibrium between the air and water phases is governed by a well-known temperature dependence, the radon activity in the water is easily calculated if one also measures the water temperature.

The RAD-7 uses a high electric field with a silicon semiconductor detector at ground potential to attract the positively-charged polonium daughters, ^{218}Po$^+$ ($T_{1/2} = 3.10$ min; $E_\alpha = 6.00$ MeV) and ^{214}Po$^+$ ($T_{1/2} = 164$ μs; $E_\alpha = 7.67$ MeV) which are then counted as a measure of the radon activity in air. For faster analyses, the [218]Po is preferred, as it will reach radioactive equilibrium with [222]Rn in only about 15 minutes ([214]Po requires about 3 hours for equilibrium because of the intermediate [214]Pb and [214]Bi daughters).

The air–water exchanger is simply a plastic cylinder that has water entering continuously via a nozzle that aspirates the water into fine droplets so that radon is emanated into a stream of air that is circulated through the exchanger, a drying system, then to the RAD-7 for measurement, and then returned to the exchanger to begin another loop. After some time, the radon activity in the air reaches equilibrium with the radon in the water, the ratio at equilibrium being determined by the water temperature.[9]

In order to make quicker measurements, it is important to achieve the air–water equilibrium as quickly as possible. Faster flow rates of the water phase should aid the equilibrium process. We tested a high-flow exchanger system by running tap water from our laboratory using a nozzle (WL-4) that has a large enough opening to allow flow rates of up to about 9 l/min. The tap water in our building is always moderately high in [222]Rn (~6,000–14,000 Bq/m^3, not unusual for a groundwater source) although the levels are not constant over long periods because the city utility mixes different water sources. The results of our tests showed that there is a substantial decrease in the time required for equilibration between the lowest flow (2.5 l/min) tested and the intermediate rate (5.5 l/min) while the improvement is only marginal when the flow rate is raised to the maximum level possible (9 l/min) on our experimental setup. It appears that under conditions of flow exceeding about 5 l/min, equilibrium is obtained in 20–25 minutes, just slightly longer than the theoretical value for radioactive equilibrium.

In order to determine the time lag that we can expect when waters of variable radon activity are encountered, we designed an experiment that would evaluate the response when the equilibrium system is subjected to drastic changes in the activity of radon in the water flowing through the exchanger. We set up a reservoir of radium-free deionized water that had a radon activity of ~350 Bq/m^3 during the period of the test and alternated the inflow to the exchanger between this relatively low

radon water and the much higher radon tap water. When the system was switched from the low to high radon source the response is fast, reaching equilibrium in approximately 20 minutes (Fig. 2), close to the results from the earlier tests. When switched back to the low radon water, the response is initially rapid with a drop of about 85% from the high equilibrium activity in 30 minutes, but then the rate slows with a tail extending out to about 85 minutes. We think that the system is more sluggish on the change to lower activity because the excess radon in the air from the high-radon water must first re-dissolve in the water phase in order to be eliminated from the system. This is apparently a slower process than releasing radon from the water to the air phase that is assisted by spraying the water through a nozzle.

Multi-detector system

We have now developed a 3-stage approach that uses one high-flow exchanger with a drying system connected in parallel to 3 radon detection systems (Fig. 3). The advantage of this approach is that we can triple the time resolution with little additional effort. Since the air–water equilibrium is based on concentration, there should be no reduction in the activity of radon in the air being circulated, in spite of the much larger volume of air circulating through the system. Thus, there would be no reduction in the sensitivity of each of the 3 radon monitors compared to a single detector system. Since approximately three times the air is being run through the system, it would be desirable to increase the flow rate of the water in order to minimize the time required to reach equilibrium. Another relevant factor is that the flow rate of the air coming back to the exchanger will be effectively tripled as three air flows (each driven by the internal pump in the RAD-7 at about 1 l/min) are joined together at a four-way valve and then sent back to the single exchanger. This increased flow should assist in stripping radon from the water phase in the exchanger. Thus, there are two effects in expanding the equilibrium system from one detector to three: (1) an increase in the air volume by approximately a factor of three, and (2) an increase in the air flow rate through the exchanger, again by roughly a factor of about three. These processes affect the timing of the approach to equilibrium in opposite directions and thus may nearly counterbalance each other.

Results and discussion

Laboratory tests

The response time of the system depends upon the half-life of [218]Po, the volume of the air loop, the speed of transfer of radon from the water to the air (which

likely depends on the size of the water droplets and the efficiency of the aeration), the flow rate of the re-circulating air, the volume of water in the exchanger, and the flow rate of water through the exchanger.[8,10] The half-life of ^{218}Po, 3.1 minutes, dictates an ultimate theoretical limit, for the 95% response time, of about 15 minutes, assuming everything else was instantaneous. The solubility coefficient of ^{222}Rn at 20 °C is about 0.25, meaning that there is about four times more radon in the air phase than the aqueous phase at equilibrium. Thus, 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.

We first tested this 3-stage setup in the laboratory by connecting it to our building tap water. A completely independent single detection system was also deployed in a neighboring laboratory (same water supply) to ensure that the results were compatible. All three detectors reached equilibrium quickly (~20 minutes) and gave statistically identical results to each other, as did

the control system in the other laboratory. In addition, the system displayed no significant difference in activity when the flow rate was lowered from 4.5 to 2.0 l/min.
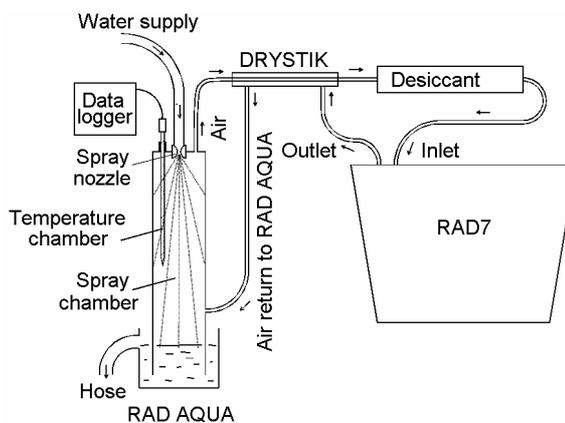

Fig. 1. Diagrammatic view of the experimental setup for a single RAD-7 exchanger continuous radon-in-water monitor. The "Drystik" is a Nafion drying tube that helps preserve the Drierite desiccant
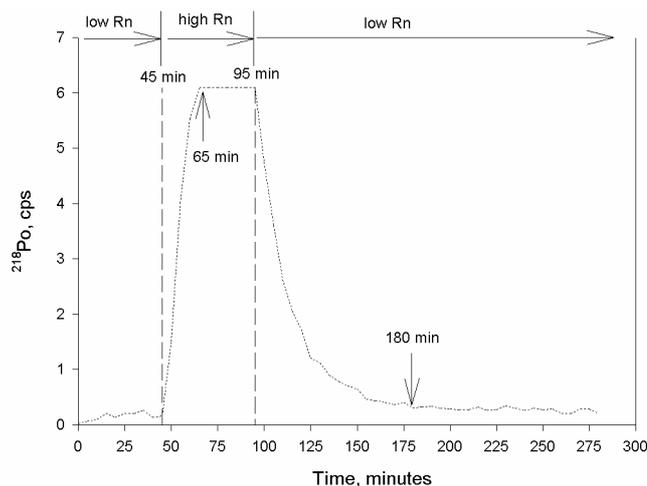

Fig. 2. Count rate in the ^{218}Po channel of the RAD-7 when the water entering the exchanger is switched from low-radon to high-radon water and then back again. This experiment was performed with an exchanger using a 60° nozzle and with water flow rate of 5.0 l/min
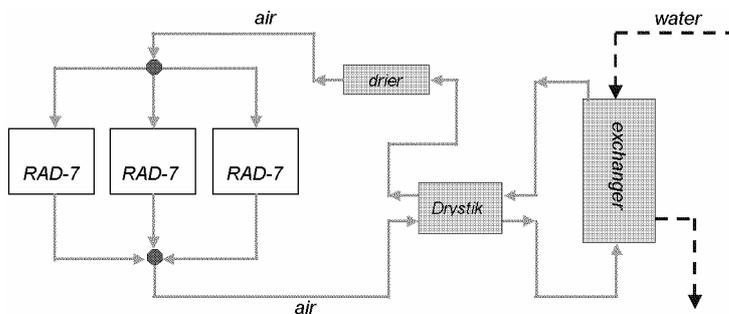

Fig. 3. A simplified sketch of an equilibrium three-stage radon measurement system. Lines shown represent the water pumped through the exchanger by a submersible pump (dashed) and a closed air loop (solid) that flows through three RAD-7 radon analyzers in parallel

All detectors also showed a similar and rapid (~20 min) return to baseline when switched from tap water to air.

In order to maximize the data while in a survey mode, we would run the three systems out of phase, i.e., the timing between each unit would be set so data outputs would be equally spaced. To test an out-of-phase operation, we programmed each RAD-7 to run a 21-minute cycle and started each counting interval seven minutes apart. This results in a new reading every 7 minutes. The system was started in tap water (~13,300 Bq/m^3 on the day this experiment was performed), switched to radium-free deionized water (~350 Bq/m^3), and then the cycle was repeated. The results show a very good coherence between the results from the three detectors (Fig. 4). The approach to equilibrium was slower and the apparent activity in the low-radon deionized water appears somewhat too high because the low-flow (1.5 l/min) pump used that day resulted in more sluggish response times.

Field tests

We performed a field test of the system on March 28, 2003 off the Florida State University Marine Laboratory (FSUML) on the northeast Gulf of Mexico. We positioned a submersible bilge pump with a capacity of 230 l/min (3700 gph) over the side of a 10-meter pontoon boat that provided the exchanger approximately 5 l/min flow of seawater from about 1.5 meters below the surface. We programmed the three RAD-7 monitors for 30-minute cycles, 10 minutes out of phase, so a new reading would be obtained every 10 minutes. Before beginning the survey, we stayed at the dock with the system running long enough to obtain air-water and radioactive equilibriums. We then left the dock, driving at a slow speed (approximately 2–3 knots) to increase the spatial resolution of our data and continued straight out to sea for a distance of about 5 km and then returned with the system running continuously. We also collected occasional grab samples using a peristaltic pump with a tube whose opening was positioned adjacent to the pump sending water to the exchanger. These grab samples were analyzed using conventional radon emanation techniques[11] over the next several days for both ^{222}Rn and ^{226}Ra and total ^{222}Rn was calculated after making appropriate decay corrections.

While it is not possible to make actual side-by-side comparisons because of the nature of how we are operating this system, we will show that the trends in the data from both the automated system and grab samples are essentially the same. Grab samples represent an "instantaneous" look at a limited volume of water (5 liters in this case) while the automated analyses are based on an integration of the radon concentrations over a discrete distance (up to several hundred meters in this case). More direct comparisons of our automated system deployed in a stationary mode to traditional grab sampling and analysis have been presented before and showed very good agreement.[8,12]

The results of this field test (Fig. 5) look very encouraging. The location "uncertainties" arise because the boat is moving during data collection – the reading thus represents an integrated view of the activity over a finite distance (depending upon speed), rather than discrete sampling points. In addition to the observed spatial variation, there is typically a change in radon activity over time depending upon the tidal stage at this location.[7]
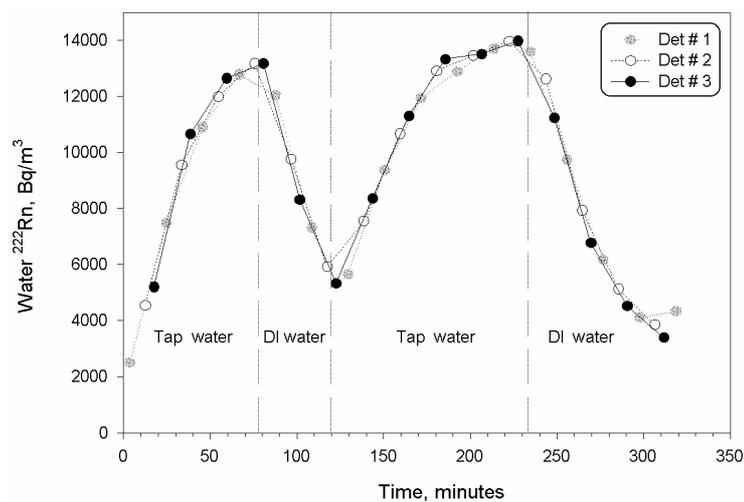

Fig. 4. Results from a 3-stage system starting in tap water (~13,300 Bq/m^3) and cycling to radium-free (~350 Bq/m^3) deionized water as indicated by the dashed lines. The 3 detection systems were 7 minutes out of phase and each had a counting interval of 21 minutes. The experiment was performed with a 60° nozzle and a water flow rate of 1.5 l/min
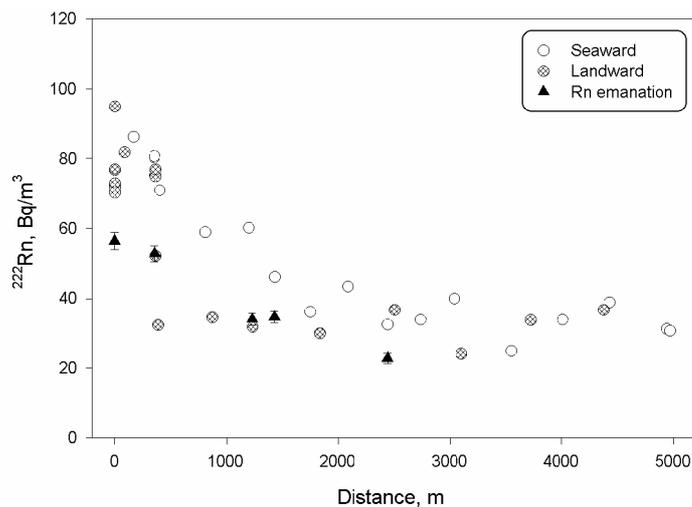
Fig. 5. Distribution of ^{222}Rn as a function of distance offshore the FSU Marine Laboratory on March 28, 2003. The measurements were collected within a few hour period using the automated radon system described in this paper. The open circles represent the earlier measurements made at a lower tide and the closed circles were taken near the end of the survey when the tide was higher

The results collected earlier in the day going in a seaward direction (open circles) were from a lower tide period when the ^{222}Rn is generally higher while the later results obtained going back towards land (closed circles) were collected during a rising tide when ^{222}Rn tends to be lower.[7] The grab samples (closed triangles) have virtually no uncertainty in the sample location (except for navigation) and somewhat less measurement uncertainty but it is clear that the automated system produces much more data with basically the same pattern and with much less effort. Based on our experience with the system thus far, we are able to measure radon concentrations with precisions varying from ±5–15%, depending upon the radon concentrations. A precision of ±20% is usually sufficient for the use of radon as geochemical tracer.

Conclusions

We find these results very encouraging in terms of having a system that can analyze radon on the fly with results essentially complete when data are downloaded from the RAD-7 monitors after arriving back at the dock.

Future enhancements under consideration include integrating the continuous monitors into a navigational GIS-based system so results can be more effectively displayed and tied to more exact locations. We also are considering expanding the system with a larger pump and exchanger and up to six detectors for work further offshore where radon concentrations are generally lower and longer integration times would be necessary.

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