Continuous Radon-222 Measurements in the Coastal Zone

Better Time Resolution and Higher Sensitivity from New Technologies Applied to Solving Old Problems

By Derek R. Lane-Smith
President
Durridge Co. Inc.
Bedford, Massachusetts

William C. Burnett
Director of the Environmental Radioactivity Measurement Facility

Henrieta Dulaiova
Department of Oceanography
Florida State University
Tallahassee, Florida

There are many reasons why one might want to take continuous measurements of ²²²Rn in natural waters. What we present here is a measurement approach for low-level ²²²Rn in coastal ocean waters. We also describe the geophysical application of estimating groundwater flow into the ocean from these measurements.

A multi-disciplinary group of investigators made estimates of submarine groundwater discharge based on manual and automated seepage meter measurements, natural isotopic tracers and hydrogeological modeling approaches. A continuous radon monitor measured radon concentrations in the shallow coastal zones during all experiments. A mass balance approach was used to calculate groundwater inputs into all systems based on these radon measurements. Results suggest good correspondence between geochemical tracers and seepage meters, while hydrogeological modeling results appear lower, perhaps because of re-circulated seawater, detected via tracers and seepage meters but not accounted for by modeling.

Introduction

Although not as obvious as river discharge, continental groundwaters also discharge directly into the sea. Like surface water, groundwater flows down-gradient. Therefore, groundwater flows directly into the ocean wherever a coastal aquifer is connected to the sea. Furthermore, artesian aquifers can extend for considerable distances from shore, discharging groundwaters to the ocean at their points of outcrop. In some cases, these deeper aquifers may have fractures or other breaches in the overlying confining layers, allowing groundwater to flow into the sea. Although such submarine springs...
Since there is about four times more radon in the air phase than the aqueous phase at equilibrium, at least four times more water than the volume of the air loop must flow through the system to deliver all the radon that is required to the RAD-7.

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. This perception is changing. Within the last decade or two, recognition has emerged that, at least in some cases, submarine groundwater discharge (SGD) may be both volumetrically and chemically important. Estimates of global SGD fluxes vary widely; some estimates are as high as 10 percent of the river flow, while most are considerably lower. 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. 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.

How can we measure this flow? 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.

Continuous Measurement of Rn-222

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. One potential means of evaluating groundwater pathways and fluxes into the coastal zone more accurately is through the use of natural tracers.

The research group at Florida State University (FSU) has been investigating this approach for several years and has demonstrated that $^{222}$Rn is an excellent tracer. The very large enrichment of $^{222}$Rn concentration in ground waters over surface waters (usually 1,000-fold or greater), its unreactive nature and short half-life ($t_{1/2} = 3.83$ d) make $^{222}$Rn an excellent tracer to identify areas of significant groundwater discharge.

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 have been hampered in making regional-scale and long-term temporal assessments by the time-consuming logistical requirements of collecting and analyzing samples in the conventional manner. Measurement of the radon concentrations in the water column may be accomplished by standard oceanographic sampling and analysis techniques for measurement of $^{222}$Rn, taking the special care required for trace gas sampling. Alternatively, more automated systems may be applied in order to increase the sampling resolution and efficiency of the process. We recently developed a continuous radon monitoring system that provides reasonably high-resolution data on the radon concentration at one location over time.

That system analyzes $^{222}$Rn from a constant stream of water 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 $^{222}$Rn by collection and measurement of the α-emitting daughters, $^{210}$Po and $^{210}$Po. 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, from the Durridge Co., for the radon-in-air monitor because it is portable, durable,
sensitive and operates in a continuous mode. The RAD-7 uses a high electric field with a silicon ion-implanted semiconductor detector at ground potential to attract the positively charged polonium daughters, $^{210}$Po ($t_{1/2} = 3.10 \text{ min}; \alpha$-energy $= 6.00 \text{ MeV}$) and $^{212}$Po ($t_{1/2} = 164 \mu\text{s}; 7.67 \text{ MeV}$), which are then counted as a measure of the radon concentration in air. Importantly, the RAD-7 has energy window settings that allow one to discriminate between all alpha-emitting polonium isotopes, including the longer-lived $^{210}$Po ($t_{1/2} = 138.4 \text{ d}; 5.30 \text{ MeV}$), and the $^{220}$Rn (thoron) daughter, $^{216}$Po ($t_{1/2} = 0.145 \text{ s}; 6.78 \text{ MeV}$).

This feature creates a significant advantage in terms of detection limits, as the background for the specific energy windows of interest remains very low, close to zero. If one did monitor the entire spectrum, as is done in many monitors, the inevitable build-up of the long-lived beta-emitter $^{210}$Pb ($t_{1/2} = 22.3 \text{ y}$) would result in increased $^{210}$Po levels with time, which could have a serious effect on background levels. Furthermore, energy discrimination allows one to select either, or both, the $^{210}$Po or $^{212}$Po windows for $^{222}$Rn assessment. For faster analyses, the $^{212}$Po is preferred, as it will reach radioactive equilibrium with $^{222}$Rn in only about 15 minutes. The $^{216}$Po lags behind because of the intermediate beta-emitting daughters $^{210}$Pb ($t_{1/2} = 27 \text{ m}$) and $^{214}$Bi ($t_{1/2} = 19.9 \text{ m}$), resulting in an equilibration time of approximately three hours.

The water-air exchanger is a cylinder that has water entering continuously as a fine spray, with a stream of air which is re-circulated through a bed of desiccant and then to the RAD-7 for measurement. After some time, the radon concentration in the air reaches equilibrium with the radon in the water, the ratio of equilibrium being determined by the water temperature:

$$a' = 0.105 + 0.405e^{-0.0027T}$$

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 Celsius.

The RAD Aqua has alternative spray nozzles, to accommodate different water flow rates, and a temperature probe, with data logger, that is inserted into the spray chamber.

The response time of the system depends on the half life of the $^{210}$Po, 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 atomization and the mixing of the air and spray), the flow rate of the re-circulating air and the flow rate of water to the exchanger.

The half-life of $^{210}$Po, 3.05 m indicates an ultimate theoretical limit for the 95 percent response time of about 15 minutes, 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 than the volume of the air loop must flow through the system to deliver all the radon that is required to the RAD-7. In practice, we find that the shortest time necessary for complete equilibration is close to 30 minutes.

Once the equilibrium radon concentration is obtained, the length of time necessary to collect sufficient information for a measurement depends upon the precision required and the radon content in the water. In several tests with our system, we found that integration times of one to two hours were appropriate for coastal waters.

This system has proven very valuable for studies of temporal variation within a limited area. For example, we deployed the system during a groundwater discharge assessment intercomparison experiment August 14-18, 2000, at a site near the FSU Marine Laboratory (FSSML), located along an open shoreline within Apalachicola Bay, about 60 kilometers south of Tal-
lahassee, Florida. Several grab samples of seawater were also collected from the same location at various times and analyzed by conventional radon emanation techniques with results equal within the analytical uncertainty to those provided by the continuous monitor. The water depth was continuously monitored at the same location, so we were able to produce a continuous record of $^{222}$Rn inventory over time at this site.

**Groundwater Flow Using $^{222}$Rn**

In order to provide estimates of SGD from the radon data, we divided the inventory record into three levels, which accounts for most of the variation. A calculated inventory of $^{222}$Rn within these waters based solely on diffusion from bottom sediments is estimated to be only about 720 dpm/m$^2$, indicating that there must be an additional source of radon. In order to balance the $^{222}$Rn inventories via SGD, one must first calculate a flux required to support the observed inventory and also have knowledge of, or assume a concentration of, $^{222}$Rn in the advecting fluids. Since we were able to monitor the $^{222}$Rn inventory through time, we were able to estimate the fluxes for the baseline levels shown, as well as the shape increases that tended to occur during falling tides. Once the flux information is established, we can estimate the upwelling rate of groundwater through the sediments by dividing the radon flux by the concentrations in the pore fluids. We estimated the relevant $^{222}$Rn concentration within the interstitial fluids by performing sediment equilibration experiments.

The discharge estimates into the study domain (~20,000 m$^2$), based on seepage meters (1.6–2.5 m$^3$/min), radon (1.2–1.8 m$^3$/min) and radium isotope (2.0 m$^3$/min) measurements, compare very well, offering encouragement for these approaches. This seems especially true for the geochemical approaches in view of the relative effort involved.

The seepage meter results are based on transect integrations of a total of 12 manual (Lee-type) seepage meters. These meters were attended to by approximately six people for eight hours each day over a four-day period, a total of 192 man-hours. The radon results were collected at one station by an automatic continuous radon monitor. This required minimal maintenance of about two hours per day, or approximately eight man-hours over the four-day measurement period. Obviously, for larger-scale studies natural tracers have a great advantage in efficiency of effort.

**Future Technological Developments**

Further advances are necessary to increase the efficiency of the radon-tracing tool. We have worked together on a preconcentrator system which will speed up the analysis process and provide a system more amenable to mapping over large areas. A prototype system was recently delivered by Durridge to FSU.

The preconcentrator consists of an auto-regenerating desiccator and two active charcoal traps. The system is managed by a micro-controller that also controls the RAD-7 and talks to a PC when one is connected to the system. Air from the water-air exchanger is dried and passed through one of the charcoal traps at room temperature for 30 minutes. The trap is then switched out of the air path and put into a closed loop with the RAD-7. The charcoal is heated to 450°C and the RAD-7 pump operated for five minutes to circulate air around the loop.

During this time, the charcoal trap is continuously purged by the circulating air and the output from the trap mixed with the air in the RAD-7 measurement chamber. In the end, there is a nearly uniform distribution of radon around the loop, most of which is in the RAD-7 measurement chamber, whose volume, nearly one liter, is much greater than the rest of the loop. After the pumping, while the RAD-7 is measuring the radon in its chamber, the charcoal is cooled back to room temperature.

The two charcoal traps swap functions every cycle so that while one is trapping radon, the other is desorbing its radon into the RAD-7 and then cooling back to room temperature. Thus, a new reading is generated every 30 minutes.

There is enough charcoal in each trap to absorb the radon from over 300 liters of air before breakthrough occurs. With a flow rate of two liters per minute for 30 minutes, only 60 liters of air pass through the trap each cycle. We can be confident, therefore, that almost all the radon in the air is trapped in the charcoal. At 450°C, the retention of radon by the charcoal is minimal, and we can also be confident that most of the radon trapped at room temperature is released into the air loop.
The maximum theoretical gain of the system is, therefore, equal to the volume of sample air passing through the charcoal, divided by the volume of the closed air loop or, for 30 minute cycles at two liters per minute desorbing into one liter, a gain of about 60.

In practice, there are several factors that influence the gain of the system. A major consideration is that the radon is stripped from the air and returned to the exchanger. With radon-free air entering the spray chamber, the exchanger is never in equilibrium. For the radon in the air leaving the exchanger to be close to equilibrium with radon in the water, the water flow rate must be more than four times the air flow rate and there must be a fine spray inside the exchanger. Ongoing development with the prototype preconcentrator includes the use of a variety of spray nozzles in the exchanger, with different water flow rates.

Other factors influencing the gain include: the air sample flow rate is not necessarily exactly two liters per minute, and may be less; some of the air flow (about 20 percent) is used to purge the regenerating desiccant and is never passed through the charcoal trap, so its radon is not collected; there is never 100 percent retention of the radon by the charcoal trap, nor 100 percent release of the radon at 450°C; and the closed loop volume with the RAD-7, a small drying tube and the charcoal trap is actually a little more than one liter.

In practice, the gain of this system, for 30 minute cycles, is about 30, so that what previously took two hours counting can now be achieved in less than five minutes. A 30-minute cycle with the preconcentrator gives more than six times better precision than a reading of the same radon concentration previously taken over two hours. The preconcentrator can provide two independent readings per hour at even the lowest water radon concentrations.

Other Applications

The same techniques described above may, of course, be used in fresh water lakes and inland seas. The background radon level in the lake may be higher than in the ocean, which would raise the lower limit of detection of groundwater radon in the lake, but otherwise the methodology would be the same.

The RAD Aqua continuous air-water exchange technology also has applications in endeavors such as the continuous monitoring of the radon content of municipal water supplies and of water supplied to bottling plants and other industry. Not only does the method provide continuous monitoring of the radon, which may change on a daily or even hourly basis, but also it is far more sensitive, even without the preconcentrator, with an LLD of less than 0.1 pCi/L, and probably more accurate than the conventional standard process of taking a sample and sending it for later analysis.

The preconcentrator, besides enabling rapid and precise measurements of radon in coastal waters, is useful in applications requiring the monitoring of extremely low radon concentrations, measured in nanoCi/L. Clean rooms, where the air is passed through charcoal filters to remove most of the radon, and underground particle detectors are examples in point.

Acknowledgments

The SGD working group is supported by the Scientific Committee on Oceanic Research (SCOR) and the Land-Ocean Interactions in the Coastal Zone (LOICZ) project of IGBP. Scientific support for this research was provided by various grants to WCB from the Office of Naval Research (N00014-00-0175) and NOAA's Cooperative Institute for Coastal and Estuarine Environmental Technology, CICEET (02-606).

References

Derek R. Lane-Smith is president of Durridge Co., Inc., manufacturer of the RAD-7 Professional Electronic Radon Detector. He earned a Ph.D. in atmospheric physics from Durham University, England, in 1969, and has spent much of his life as an academic. He has been a member of the International Commission on Atmospheric Electricity and chairman of its Subcommittee on Instrumentation. In 1980 he founded the Shad Valley Program for gifted high school students, in Canada. With Durridge Co., he is currently involved in the development of several new products.

William C. Burnett is a professor of oceanography and director of the Environmental Radioactivity Measurement Facility at Florida State University. He earned a Ph.D. from the University of Hawaii in 1974 and joined FSU after a postdoctoral appointment at SUNY Stony Brook and a visiting scientist position in Brazil. He currently directs a research program that emphasizes application of natural U/Th series nuclides to problems in the earth, marine and environmental sciences. This research also includes development of improved methods for measurement of radioactive species in the environment.

Henrieta Dulaiova is currently pursuing her Ph.D. degree in chemical oceanography at Florida State University. She received her M.S. degree in nuclear chemistry in 1997 at the Czech Technical University in Prague. After receiving her degree, she worked at the National Radiation Protection Institute in the Czech Republic for three years.