Improved Automated Analysis of Radon (Rn-222) and Thoron (Rn-220) in Natural Waters

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Improved Automated Analysis of Radon (^{222}Rn) and Thoron (^{220}Rn) in Natural Waters

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Natural radon (^{222}Rn) and thoron (^{220}Rn) can be used as tracers of various chemical and physical processes in the environment. We present here results from an extended series of laboratory experiments intended to improve the automated analysis of ^{222}Rn and ^{220}Rn in water using a modified RAD AQUA (Durridge Inc.) system. Previous experience with similar equipment showed that it takes about 30−40 min for the system to equilibrate to radon-in-water concentration increases and even longer for the response to return to baseline after a sharp spike. While the original water/gas exchanger setup was built only for radon-in-water measurement, our goal here is to provide an automated system capable of high resolution and good sensitivity for both radon- and thoron-in-water detections. We found that faster water flow rates substantially improved the response for both isotopes while thoron is detected most efficiently at airflow rates of 3 L/min. Our results show that the optimum conditions for fastest response and sensitivity for both isotopes are at water flow rates up to 17 L/min and an airflow rate of 3 L/min through the detector. Applications for such measurements include prospecting for naturally occurring radioactive material (NORM) in pipelines and locating points of groundwater/surface water interaction.

1. Introduction

A recently developed automated radon-in-water measurement system (*1*) based on the commercially available RAD7 radon-in-air monitor, product of Durridge Inc., has triggered extensive coastal oceanography studies using radon as a tracer. This variation has been used by oceanographers in two different modes. In one configuration we record changes in the radon-in-water concentration over time at a fixed point. We then estimate groundwater discharge using a simple radon mass balance box model to account for all sources and sinks in the seepage area (*2*−*5*). The same instrumentation may also be combined with GPS navigation, depth sounding, and sensors for salinity, conductivity, and temperature and set up on a small boat for "mapping" the shoreline for groundwater sources (*6, 7*). Our mapping experience shows that the conventional RAD AQUA system does not respond quickly to sudden changes in the radon-in-water concentration in areas with multiple distinct sources such as submarine springs.

Natural waters may be enriched in both radon isotopes if there is a source but their distributions are influenced by their respective half-lives and mixing of water masses. While the half-life of ^{222}Rn ($t_{1/2}$ = 3.82 days) is long enough so that its concentration could be maintained during transport over relatively long distances, ^{220}Rn ($t_{1/2}$ = 55 s) dissipates very quickly. This provides an opportunity to prospect for ^{220}Rn-enriched sources such as groundwater discharges using ^{220}Rn as a tracer. Just the presence of ^{220}Rn in coastal waters would indicate that one must be close to a source.

Thoron may be used as prospecting tool for locating ^{228}Ra-bearing scale deposits in old drinking water systems. Such an approach includes ^{220}Rn measurements at points along a pipeline, or at a single site while varying the water flow rate (*8*). Radium-bearing scale deposits have been widely reported over the past decade in both drinking water distribution systems (*9*−*11*) and in the oil- and gas-production industry (*12*). Determination of the precise location of radioactive scale could avoid expensive and unnecessary remediation.

In this paper we present results from extensive laboratory experiments in an effort to optimize the parameters for simultaneous detection of both ^{222}Rn and ^{220}Rn while varying water and air flow rates through two different variations of the conventional RAD AQUA system.

2. Experimental Section

The designs for our experiments were driven by two main goals: (1) to shorten the response time for ^{222}Rn-in-water measurement, and (2) to increase the sensitivity of ^{220}Rn detection while maintaining high ^{222}Rn efficiency. The response of the system will be a function of the water-to-air and air-to-water exchange that occurs in the mixing chamber of our device (Figure 1). Higher water flows will presumably deliver the radon gas faster to the system while higher airflows will promote mixing and delivery to the detector. This will be especially important for thoron detection because of its very short half-life.

To evaluate the influence of the water and gas flow rates we performed a series of experiments with a modified version of the commercially available RAD AQUA setup. This setup includes a radon-in-air monitor which uses a solid state passivated ion-implanted silicon (PIPS) detector, and thus has the ability to electronically determine the energy of each α particle. The RAD7 groups the spectrum's 200 channels into 8 separate "windows". Window "A" covers the energy interval of the ^{218}Po (E = 6.00 MeV), the first ^{222}Rn daughter, while the direct daughter of ^{220}Rn, ^{216}Po (E = 6.78 MeV) appears in the range of window "B". This makes a concurrent detection of ^{220}Rn and ^{222}Rn with the same instrumentation possible.

Previous experiments (*6*) to evaluate these factors used water flow rates up to 5 L/min. To be able to process water flow rates larger than this through the system we employed a larger nozzle (BETE MP187W, BETE Fog Nozzle, Inc.) mounted directly to the head of a regular RAD AQUA exchanger and used a high-capacity Redi-Flo Variable Frequency Drive (VFD) submersible pump (Redi-Flo2, GRUNDFOS Pumps Corporation) to deliver the water. Because much larger water volumes were processed, the regular gas-mixing chamber base was replaced by a larger volume receiver. In addition, we also used an external air pump (UNMP850 KNDC-B, KNF Neuberger Inc.) to circulate the radon-enriched air between the mixing chamber and the RAD7.

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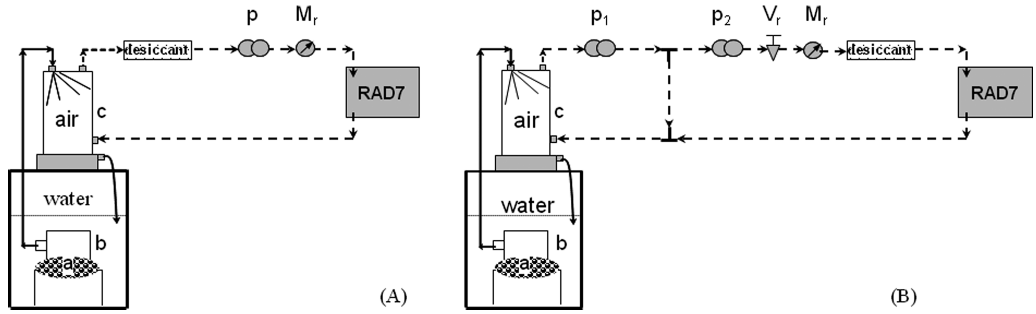

FIGURE 1. "Single loop" (A) and "dual loop" (B) experimental setups for measuring thoron (^{220}Rn) in water. The thoron source (a) (^{232}Th impregnated MnO_2-fiber) is coiled around a submersible pump (b) placed into a 50-L tank with pure water. Thoron-enriched water (solid line) circulates through the source and the RAD AQUA exchanger (c) at different flow rates in both variations. Single loop (A): air path (dashed line) connects the exchanger to the chamber of the detector (RAD7). An external air pump (p) circulates the thoron-enriched air at various flow rates. A drying tube filled with desiccant precedes the RAD7 detector to maintain dry air. An air flow meter (M_r) indicates the air flow rate through the loop. Dual loop (B): the first loop (water/air) is analogous to the single loop system (A). A second (adjacent) air loop is attached via two T-junctions to the first air loop and the air is delivered via a second external air pump (p_2) upstream to the detector. A needle valve (Vt) and an air flow meter (M_r) is placed before the desiccant. The same setups can be modified for evaluating radon (^{222}Rn) in water measurement parameters. In this case the exchanger is simply connected to a tap water high in ^{222}Rn (groundwater) faucet and water is subsequently discharged.

For the purpose of our thoron laboratory experiments we produced a high activity source (~1500 dpm total activity) based on ^{232}Th that was known to be at least 40 years old, i.e., has all daughters in secular equilibrium. We adsorbed thorium and daughters onto a MnO_2- impregnated fiber following a procedure described in *13*. The fiber was then submerged into a 50-L tank coiled around the submersible pump that delivers water to the exchanger (Figure 1).

For the radon optimization experiments we used tap water as a ^{222}Rn source. The tap water in our laboratory is groundwater-derived and thus relatively enriched in radon (~300−500 dpm/L). We also ran an additional RAD AQUA system as a control so we were able to monitor any changes in the radon in tap water concentrations that are not due to the experimental settings.

For all our experiments we used 2-min integration time, which is the shortest possible on the RAD7 detection unit. This allowed us to detect any short-time changes in the count rate. The two radon sources were chosen to be relatively high in order to obtain low uncertainty within this short integration time. We assumed that the system was in equilibrium when we had at least three consecutive readings that matched within the analytical uncertainty (1σ).

To optimize both radon and thoron detection we explored two different variations of the modified RAD AQUA setup: a "single loop" and a "double loop" system (Figure 1).

2.1. Single Loop Experimental Setup. The first variation of the RAD AQUA system is very similar to the original setup as described by *1*. For thoron experiments (Figure 1A) ^{220}Rn enriched water is pumped via a high capacity pump to the large nozzle on the exchanger. The thoron-enriched air is then routed to the RAD7 detector chamber via an external air pump. With this setup we can examine different combinations of water and airflow rates to obtain the maximum thoron response. The ^{222}Rn setup is basically the same except that the exchanger is connected to a regular tap water faucet. The selected flow rates were measured by using air (VFB-67-SSV, Cole-Parmer) and water flow (polycarbonate LFME-13-F2, Dwyer Instruments) meters with precisions of ±4% and ±5% respectively.

2.2. Dual Loop Experimental Setup. The dual loop variation was designed as two adjacent air loops (Figure 1B). The first air loop circulates the air volume of the RAD AQUA exchanger via an external air pump (p_1) similar to the single loop mode. This loop is connected via two T-connectors to a second loop that includes the RAD7 detector. A second external air pump (p_2) circulates the air of this loop independently from the first loop. A needle valve (V_r) is placed in the second loop to regulate the airflow rate. Using the dual loop setup much higher air flow rates can be achieved through the exchanger while keeping the air flow through the RAD7 detection unit at a constant and optimum rate.

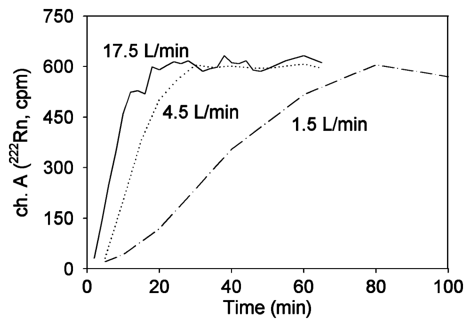

FIGURE 2. Radon response time (counts per minute, cpm) as a function of water flow rate using the single loop variation of the system at constant air flow rate (0.7 L/min). The count rate levels off as the radon-in-air equilibrates with the radon-in-water.

In all scenarios the air pumps have to be placed upstream (Figure 1). Air flow meters (M_r) are used to monitor the airflow rates through the loops.

To mimic sharp concentration gradients in radon/thoron-in-water we used an extra 50-L water tank filled with Ra-free and low-Rn (equilibrium with the atmosphere) water and used a two-way valve so we could direct the water flow through either the high ^{222}Rn (or ^{220}Rn) or low activity containers and simulate a low−high−low concentration transition similar to that described in *6*.

3. Results and Discussion

3.1. Single Loop System: Radon and Thoron. We first examined the time for radon water/gas equilibration as a function of different water flow rates at a constant air flow rate (0.7 L/min) driven by the internal pump of the RAD7. We found that it takes only about 15 min for the radon to achieve gas equilibrium at a water flow rate of 17.5 L/min. (Figure 2). This is equivalent to the time required for the $^{222}Rn-^{218}Po$ pair to approach radioactive equilibrium and therefore no further improvement is possible. On the other hand it requires only ~25−30 min at a water flow rate of 4.5 L/min to achieve stable readings and one may prefer to use such conditions since there is no need for a high-capacity pump.

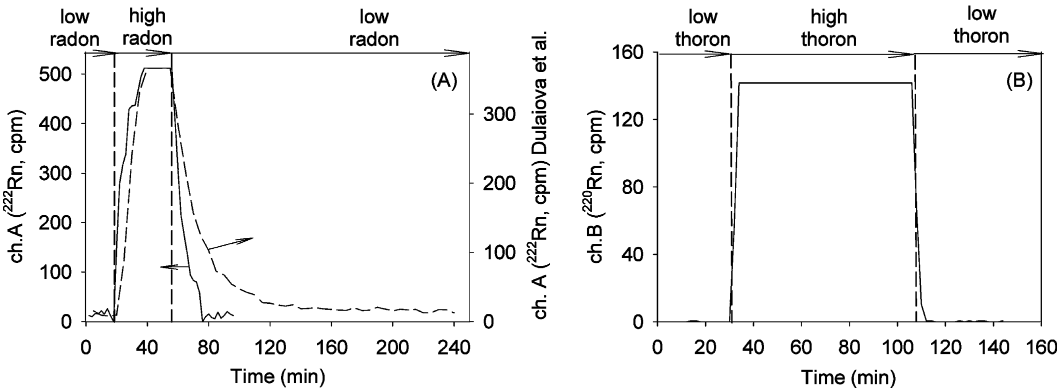

FIGURE 3. Radon (A) and thoron (B) response over time during sharp concentration changes using the single loop variation of the system. The dashed line in (A) (right-hand scale) represents results from the standard system with a water flow rate of 5 L/min (*6*). The solid line (left-hand scale) is our result with much higher (12.5 L/min) water flow rate.

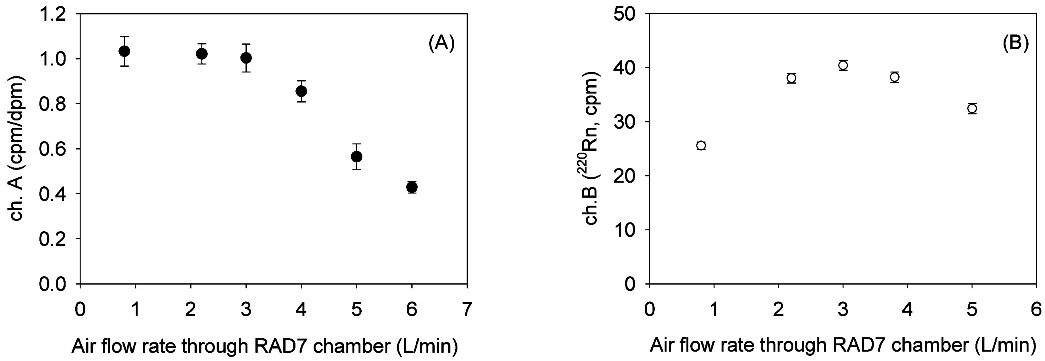

FIGURE 4. Radon and thoron sensitivities to air flow rates. Results show optimum response at 3 L/min for ^{220}Rn and lowered response for ^{222}Rn when air flow rates are >3 L/min. This experiment was performed on two different days when the ^{222}Rn tap water concentrations were slightly different. To eliminate this effect we used the control system to monitor the concentration over time and account for this variation. We thus present the results here as a ratio of the count rate of the experimental setup to the known activity in disintegrations per minute (cpm/dpm).

To study the response of the single loop system to radon concentration changes we used the 50-L low-Rn water tank and switched between high-radon tap water to the low-level radon reservoir via a two-way valve. We then compared the result from our experiment using a 17.5 L/min water flow and ~0.7 L/min air flow rate to an earlier experiment that used a much lower water flow rate (*6*). The results (Figure 3A) show that at high water flow the response time benefits not only when switching from low to high concentration but also from high to low radon in water, i.e., the radon escapes from the system much faster. To understand the mechanism of these phase transitions, one needs to consider both the kinetics and the thermodynamics of the system. While in both gas transitions, from water to gas phase and from gas to water phase, there is a concentration gradient promoting the molecule exchange from high to low concentration across the phase interface, the thermodynamic conditions are not always favorable for both processes. The dissolution of gas into liquid/water phase is not spontaneous and therefore thermodynamically not a favorable process. In our case this is the only pathway by which the radon enclosed within the air loop can leave the system. To speed up the kinetics one needs to keep a high concentration gradient between the two phases by introducing "fresh", i.e., low-radon water. Similar large transition times were also reported by *14* and observed by other users of the system. The transition time for the previous experimental design was >90 min compared to ~20 min with the high-flow modification. Such long equilibration times with the old variation of the system could result in overlapping ^{222}Rn spikes such as sometimes encountered when surveying for groundwater-derived signals. Thus using the high-flow modification of the RAD AQUA system will significantly improve the spatial resolution of ^{222}Rn based mapping surveys.

Similar experiments with the thoron variation of the single loop at water flow rate 17.5 L/min shows that it only takes a few minutes to fully respond for both concentration transition times (Figure 3B). Such behavior is not surprising in view of the very short half-life of ^{220}Rn. The ^{222}Rn equilibration experiments showed that at higher water flow rates (>5 L/min) the equilibrium time between water and air is very quick and the only delay in the system response is due to the time (approximately 3 times the polonium half-life) for the radioactive ^{222}Rn$-$^{218}Po equilibrium. In case of ^{220}Rn, the subsequent polonium daughter ^{216}Po has a very short half-life ($t_{1/2} = 0.15$ s) and therefore the pair is almost in immediate radioactive equilibrium. This could be a significant advantage when prospecting for ^{228}Ra sources such as areas of NORM contaminations (*8*).

We also investigated the influence of the air flow rates through the exchanger using the same single loop set up while keeping the water flow constant at 5 L/min. We found that the optimum response for thoron registration is obtained at an air flow rate of 3 L/min while higher air flows decrease the response for both ^{220}Rn and ^{222}Rn (Figure 4). We attribute these results to the aerodynamic forces exerted on the charged polonium daughters (^{218}Po$^+$ and ^{216}Po$^+$) en route to the detector surface under an electrostatic field force. We suggest that under certain air flow conditions some polonium ions may deviate from their original flight path down electrostatic field lines. Instead some polonium ions may terminate somewhere other than on the active surface of the detector. Presumably, aerodynamic forces on polonium ions under low air flow conditions would be small compared to the

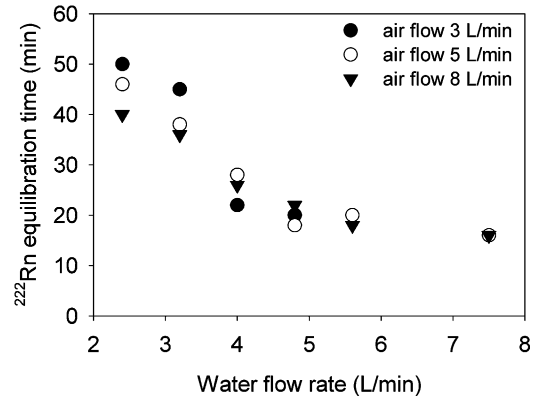

FIGURE 5. Change in equilibration time for ^{222}Rn based on different air/water flow rates using the dual loop variation. Our observations suggest that the water flow rate is the governing factor for the equilibration time. The system benefits from higher air flow rate only at low water flow rates (<4 L/min).

electrostatic forces, but may become significant at higher air flow rates, likely greater than 3 L/min based on our experiments.

3.2. Dual Loop System: Radon and Thoron. The results from our single loop gas flow experiments showed that while the gas equilibration times shorten as we increase the water flow rate through the exchanger, the radon and thoron detection sensitivities decrease at air flow rates >3 L/min (Figure 4). To ensure optimum air flow rates we separated the exchanger and the detector chamber into two semi-independent air loops (Figure 1B). Using the dual loop setup much higher air flow rates can be achieved through the exchanger while keeping the air flow through the RAD7 detection unit at a constant and optimum 3 L/min. We performed ^{222}Rn experiments at 3, 5, and 8 L/min air flow rates through the exchanger at six individual water flow rates between 2.3 and 7.5 L/min (Figure 5). The results show that while the system benefits, i.e., generally reaches faster water−gas equilibrium with higher air flow rates, there is no significant difference at water flow rates greater than 4.0 L/min. Thus, at water flow rates greater than 4.0 L/min the time to reach equilibrium is independent of the air flow rate at least within the range tested here. This again confirms that the water flow rate is the main variable for these kinds of measurements and one needs to maintain high air flow rates through the exchanger only in the case where high water flow rates are not achievable.

The sensitivity of the thoron response (count rate of ^{216}Po in channel B) using the dual loop variation plateaued at about 3 L/min air flow through the exchanger with a water flow rate of 5.3 L/min (Figure 6). This is an important result because it indicates that one can use the single loop variation of the system at an air flow of 3 L/min though the exchanger and detector chamber (Figure 4) to obtain maximum thoron response, when the water flow rate is limited to ∼5 L/min. This would be an important benefit when the system is used in field conditions where it is inconvenient to use a large pump.

We also compare the radon response to concentration gradients using the dual loop variation to the earlier single loop results (*6*). We found that the response of the system from low to high radon is ∼24 min while it takes about 76 min on the transition from high to low radon (Figure 7) at a water flow rate of 5 L/min and an airflow rate through the exchanger of 7.5 L/min and a rate of 0.7 L/min through the detector chamber. This result showed an improvement in the transition times at relatively low water flow rate (5 L/min) and using two air pumps. Therefore, one would prefer to use a dual loop variation with high airflow through the exchanger to decrease the transition times when water flow rates >5 L/min are not achievable.

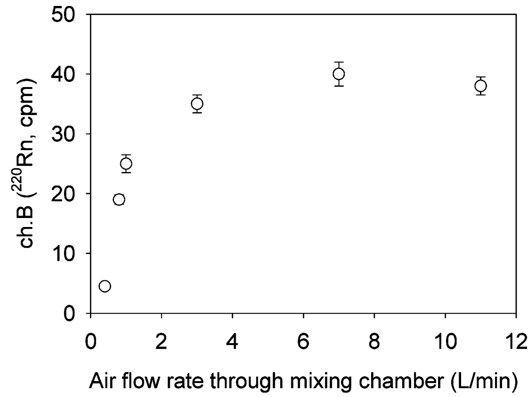

FIGURE 6. Sensitivity of thoron response to different air flow rates in the primary air loop using the dual loop variation. The flow rate through the detector air loop was held constant at 3 L/min.

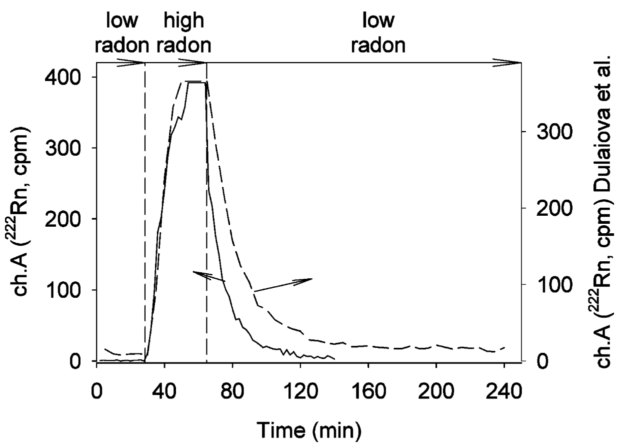

FIGURE 7. Radon response versus time during sharp concentration changes using the dual loop variation of the system compared to single loop variation presented earlier (*6*). Both experiments used the same water flow rate of 5 L/min. The dashed line (right-hand scale) is from *6* and the solid line (left-hand scale) is our result with a 7.5 L/min air flow rate through the exchanger and 3 L/min air flow rate through the detector chamber.

Based on these results, we suggest that one could use either of the variations of RAD AQUA examined here depending on the available logistics. We recommend use of high-capacity water pumps (up to 17 L/min) when the main goal is to measure ^{220}Rn in natural waters. Our experiments showed that these conditions would benefit the ^{222}Rn response times as well and significantly increase the resolution of ^{222}Rn mapping. In field conditions where such high water flow rates are often not achievable, often because of power demands, we recommend using an external air pump to shorten the response times. Our experience indicates that obtaining an approximate 5 L/min water flow rate is easily achievable. In this case the dual loop variation with two external pumps at 3 L/min through the detector chamber and 7.5 L/min through the exchanger would give the best results. We recommend always placing the air pump upstream of the RAD7 and connecting the RAD7 outlet directly to the return air path to maintain the same pressure as in the exchanger.

However, with the much simpler single loop tubing set up one can obtain response times of 20−30 min at a water flow rate of 5−6 L/min and an air flow through the detector chamber of 3 L/min.

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