Isotopic Techniques For Assessment of Groundwater Discharge to the Coastal Ocean

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LONG-TERM GOALS

One of the persistent uncertainties in establishing marine geochemical mass balances is evaluating the influence of submarine groundwater discharge (SGD) into the ocean. Our long-term goal is to develop geochemical tools (e.g., radon and radium isotopes) to quantify the magnitude of SGD on a local to regional scale. Improvements in field-based analytical devises is also sought in order to allow evaluations on a more time efficient basis. Since there is no standard methodology for measurement of groundwater flow into the ocean, we are actively involved in coordinating and participating in assessment intercomparisons.

OBJECTIVES

We are setting out to test the following hypotheses: (i) the apparent discrepancy between groundwater flux results based on geochemical tracing and hydrological modeling (Burnett et al., 2002) arises because the tracers are measuring total flow while the models are only accounting for the fresh water component of that flow; (ii) the radon tracing model can be much better constrained by the combining use of radon and short-lived Ra-isotopes (^{223}Ra and ^{224}Ra) to independently derive a near-shore mixing rate; and (iii) the most efficient manner to evaluate the quality of SGD assessment methodologies is by direct intercomparisons of independent approaches.

APPROACH

Radon is a good natural tracer of SGD because its concentration is very high in groundwater but low in seawater, it behaves conservatively, and it is relatively easy to measure. Assessment of possible temporal trends of radon is important because groundwater flow is known to be extremely variable — in some cases even reversing direction in response to external forcing (tides, change in water table height, etc.). Radium isotopes are also very useful as natural tracers and can complement the radon investigations. Our approach during this project is: (1) to develop further our continuous Rn monitor and implement the use of Ra isotopes; and (2) to test these systems in the field in different environments and over different time scales to evaluate short (tidal) to long-term (seasonal) patterns.

The main principle of using continuous radon measurements to decipher rates of SGD is to convert temporal changes observed in Rn inventories to fluxes by monitoring the inventory of 222Rn over time, making allowances for losses due to atmospheric evasion and mixing with low concentration

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14. ABSTRACT

One of the persistent uncertainties in establishing marine geochemical mass balances is evaluating the influence of submarine groundwater discharge (SGD) into the ocean. Our long-term goal is to develop geochemical tools (e.g., radon and radium isotopes) to quantify the magnitude of SGD on a local to regional scale. Improvements in field-based analytical devises is also sought in order to allow evaluations on a more time efficient basis. Since there is no standard methodology for measurement of groundwater flow into the ocean, we are actively involved in coordinating and participating in assessment intercomparisons.

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waters offshore. We illustrate below this approach by an example from an intercomparison experiment conducted on Shelter Island, New York in May 2003 (Fig. 1).

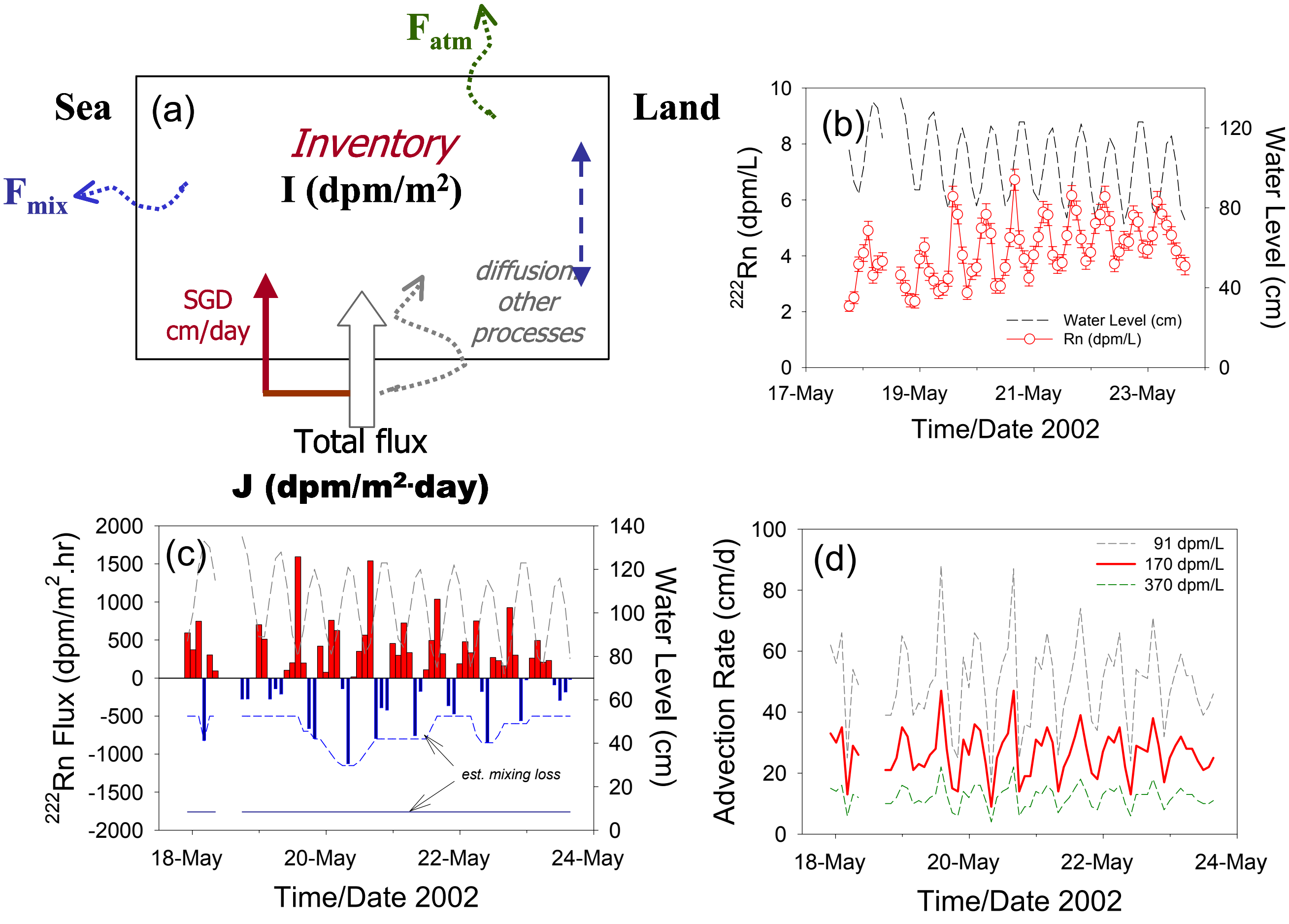

Figure 1. Conceptual model and example (Shelter Island, New York) of use of continuous Rn measurements for estimating groundwater discharge into the coastal zone. [(a) conceptual model; (b) Rn data and water level; (c) calculated fluxes; and (d) estimated discharge rates]

Our conceptual model is basically a radon mass balance with the measured inventories of ^{222}Rn a balance between benthic inputs (assumed to be dominated by fluid advection) and outputs via atmospheric evasion and mixing with lower concentration waters offshore (Fig. 1a). A continuous Rn record from the coastal zone off Shelter Island (Fig. 1b) is converted to fluxes (Fig. 1c) based on the change in inventory per unit time after correcting for tidal variations and atmospheric loss. The amount of mixing was estimated by (i) inspection of Rn fluxes (dashed blue line); and (ii) application of short-lived Ra isotopes (solid dark line) following the methodology of Moore (2000). The fluid advection rates (Fig. 1d) were calculated using the Ra-derived mixing rate and dividing the radon fluxes by various estimates of the pore water Rn activity. The red line (based on an average groundwater concentration of 170 dpm/L) is considered our best estimate and the derived advection rates agree closely with those measured by a dye-dilution seepage flux chamber deployed at the same site and time by a team from Woods Hole (Sholkovitz et al., 2003). The 12-hr periodicity in the radon results (as well as from the seepage meter data) shows that tidal modulation strongly influences fluid fluxes in this area. Detailed descriptions of the radon measurement techniques and modeling have been reported in Burnett et al. (2001) and Burnett and Dulaiova (2003).

WORK COMPLETED

The principal milestones completed during the current funding cycle included (i) organization and participation in an SGD assessment intercomparison on eastern Long Island (highlights from our portion of the experiment reviewed above); (ii) participation in a coastal experiment in Sicily; and (iii) development of a multi-detector radon system for more efficient measurements of radon in the coastal zone. We review below one of the main outcomes of the Sicily experiment involving confirmation of the air-sea radon exchange calculations and development of a multi-detector radon system.

RESULTS

An important loss term in the radon model as applied to coastal waters is atmospheric evasion. Radon losses to the atmosphere are governed by the molecular diffusion produced by the concentration gradient across the air-water interface and turbulent transfer, which is dependent on physical processes, primarily governed by wind speed. The flux of radon across the air-water interface can be calculated from a formula presented by MacIntyre et al. (1995):

$$F = k\left(C_w - \alpha C_{atm}\right) \qquad [1]$$

where C_w and C_{atm} are the radon concentrations in surface water and air, respectively; α is Ostwald's solubility coefficient; and *k* is the gas transfer coefficient. The gas transfer coefficient is a function of the physical processes at the air-sea boundary, especially the turbulence and kinematic viscosity of the water (ν), and the molecular diffusion coefficient of the gas ($D_m = 1.16 \times 10^{-5}\ \mathrm{cm^2.s^{-1}}$ at 20^{o}C for radon). The Schmidt number (Sc) is the ratio of the kinematic viscosity to the molecular diffusion coefficient, i.e., $Sc = \nu/D_m$. Based on a number of field studies, empirical equations that relate *k* to wind speed have been proposed. Macintyre et al. (1995) present an equation where *k* represents the piston velocity for a given wind speed normalized to the Schmidt number for CO_2:

$$k(600) = 0.45 u_{10}^{1.6} (Sc/600)^{-0.5} \qquad [2]$$

where u_{10} is the wind speed at 10 m height above the water surface and Sc is divided by 600 to normalize *k* to CO_2 at 20^{o}C in freshwater. Turner et al. (1996) showed in calculating the gas transfer coefficient for DMS as a function of wind speed, that the (Sc/600) term in Eq 2 should be raised to the power of –0.667 for $u_{10} \leq 3.6\ \mathrm{m.s^{-1}}$ and –0.5 for $u_{10} > 3.6\ \mathrm{m.s^{-1}}$.

An opportunity arose last year to test this approach. Our group was invited by the International Atomic Energy Agency (IAEA) to participate in an experiment in Donnalucata, Sicily from March 18-24, 2002. Our main goal was to assess SGD by radon measurements in a boat basin known to be influenced by several fresh water springs. Following the procedure we have adopted at other locations, we deployed a continuous radon monitor at several locations in the basin for various lengths of time.

There was a very constant pattern in the change of wind velocities each day during the experimental period. Winds were calm in the very early morning hours and increased to >10 m/s by mid-day before decreasing again. This pattern from calm to very windy conditions provided a good opportunity to make an independent evaluation of radon losses. We monitored wind speed, temperature, water depth, and concentrations of ^{222}Rn in both the atmosphere and surface waters at one station over a 24-hour period (Fig. 2). The variations in radon inventories at this station appeared to be influenced mainly by fluctuations in wind-induced turbulence. Using the equations presented above for calculating radon fluxes across the air-water interface, we see an average flux of 8.9 mBq/m^2.s during the windy period (shown on the figure with the dashed line). Using an average high radon inventory of 800±80 Bq/m^2 and an average low inventory of 530±40 Bq/m^2 for the two periods shown by the solid horizontal lines in the diagram, we calculate an observed average loss of 8.3±2.8 mBq/m^2.s. Although this calculation doesn't account for possible changes in radon input during this period, it is encouraging that the observed loss of radon appears to be close to what we would predict based on the kinematic model.

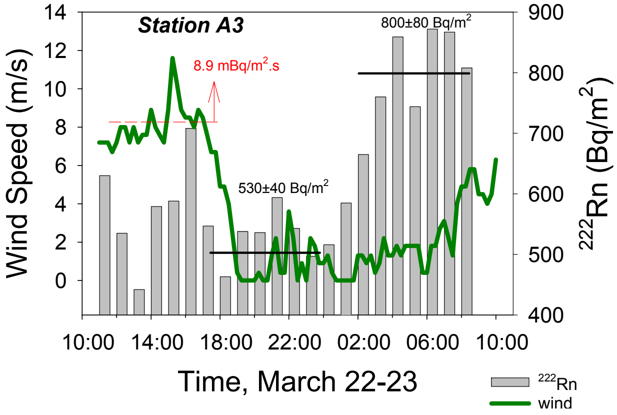

Figure 2 Temporal variations of ^{222}Rn inventories (bars) and wind speed (solid green line) for one 24-hour period at a coastal station in southeastern Sicily during March 2002. [Lower inventories during the late afternoon hours are thought to be a direct consequence of enhanced winds during the preceding several hours.]

While the continuous monitor developed early in our ONR research has been a significant improvement over the traditional grab sample-laboratory approach, measurements still require integration times up to over two hours. This is because the radon concentration delivered from the air-water exchanger can never exceed the equilibrium concentration, which is determined by the ^{222}Rn concentration in the water and the temperature. In order to improve the time (and thus spatial if mapping) resolution of our continuous equilibrium radon measurement system, we have begun experimenting with a three-stage approach that uses one high-flow exchanger and drying system connected in parallel to three radon detectors (Fig. 3). The advantage of this approach is that we can triple the data flow with no additional sampling effort. Since the air phase reaches an equilibrium concentration with the water phase, there will be no reduction in the overall sensitivity.

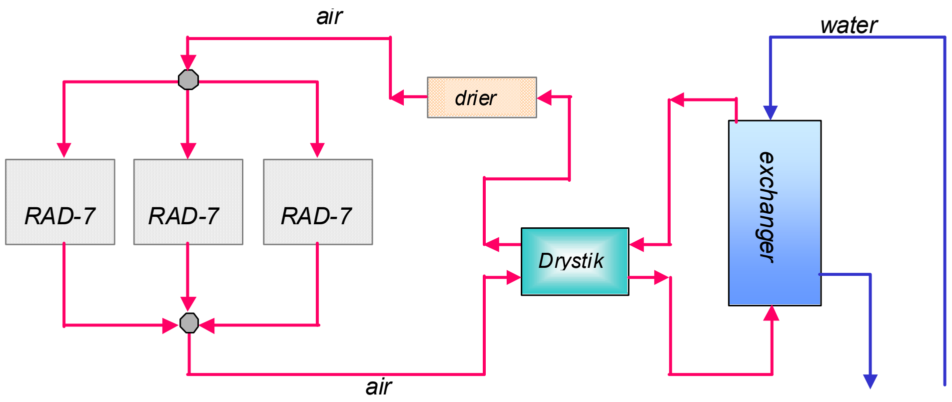

Figure 3 A simplified sketch of an equilibrium three-stage radon measurement system. [Lines shown represent the water pumped through the exchanger by a submersible pump (blue) and a closed air loop (red) that flows through three RAD-7 radon analyzers in parallel.]

We field tested this system in Sarasota Bay, Florida in May 2003 using a 3-detector arrangement, running 30-minute cycles 10 minutes out of phase. After the initial water-air equilibrium is achieved (about 20 minutes), new results are generated every 10 minutes. This allowed us to map most of the coastal area of the bay in only 2 days. Fortunately, the ^{222}Rn concentrations are quite high (up to 50 dpm/L) in Sarasota Bay, so the short integration times were fine. With additional funding we would scale up to 6 detectors so that the longer integration times needed for more typical concentrations (coastal waters typically ≤10 dpm/L) may be used without loss of resolution. We could also integrate continuous GPS navigation and depth sounding into the system. Since some commercially available GPS and depth sounding units are equipped with data loggers and report data with time marks, this information could easily be linked to the outputs of our multi-detector radon system. In principle, one could tie all the radon detectors, GPS unit, depth recorder, and other sensors (e.g., temperature, conductivity) to a PC via a wireless link (using radio modems). Such remote downloading would be particularly useful for extended deployments of the system on an offshore platform.

IMPACT/APPLICATION

The radon monitor and associated mass balance model has proven to be successful for evaluating the magnitude and dynamics of SGD in the coastal zone. The addition of several detectors, integrated with GPS navigational units, continuous depth recorders, and other sensors could provide a powerful and efficient system for assessment of groundwater discharges into the coastal zone. In an era with increasing contamination of coastal aquifers from septic systems, fertilizer use, etc., assessment of diffuse pollution into the coastal zone could benefit greatly from such a system.

TRANSITIONS

Many of the field experiments we participated in were organized by a SCOR/LOICZ Working Group (http://www.jhu.edu/~scor/wg112.htm) on SGD and through collaborations with the IAEA. The primary goal of the working group has been to define more accurately and completely how SGD influences chemical and biological processes in the coastal ocean. This working group is now in its final stages with a planned product consisting of a special issue of Biogeochemistry (eds., W. Burnett and J. Chanton) on submarine groundwater discharge due out in late 2003. An overview of the working group's organization, objectives, and plans may be found in Burnett (1999) and a synopsis of their 1st assessment intercomparison experiment was reported in Burnett et al. (2002). Similar activities with the IAEA and IOC are planned to continue for the next several years (see next section).

RELATED PROJECTS

We are active participants in the IOC program "Assessment and Management Implications of Submarine Groundwater Discharge Into the Coastal Zone" (SGD link on http://ioc.unesco.org/icam/) and the IAEA's Cooperative Research Project (CRP) entitled "Nuclear and Isotopic Techniques for the Characterization of Submarine Groundwater Discharge (SGD) in Coastal Zones." The IOC program intends to: (1) develop, test, and standardize methodologies for assessment of SGD into the coastal zone; and (2) evaluate the management implications of SGD and provide appropriate training for coastal zone managers via ICAM (Integrated Coastal Area Management). The IAEA program is similar but geared more towards improvement and development of isotopic techniques.

HONORS/AWARDS/PRIZES

During the past fiscal year, W.C. Burnett, P.I. on this grant, was named the Carl Henry Oppenheimer Professor of Oceanography by Florida State University. Ms. Henrieta Dulaiova, a grtaduate student who has been closely associated with this project, was awarded a NOAA Fellowship to pursue research in the Apalachicola National Estuarine Research Reserve.

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