

# Investigating Contaminant Inputs via Submarine Groundwater Discharge to Coastal Waters Using Radium Isotopes

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Grant Number: N00014-99-1-0038  
<http://cafethorium.whoi.edu>

## LONG-TERM GOALS

Our long-term goal is to determine if submarine groundwater discharge (SGWD) is an important mechanism for delivering contaminants (i.e. heavy metals, organics) to harbors. We plan to accomplish this goal using a suite of naturally occurring radium isotopes as tracers of SGWD and the dispersion of contaminants from the embayment (Buesseler/WHOI). In addition, we plan to develop a comprehensive hydrological model (Harvey/MIT) to determine the importance of SGWD in the transport of pollutants to coastal harbors.

## OBJECTIVES

We will apply recently developed analytical techniques for measuring radium ( $^{223}\text{Ra}$ ,  $^{224}\text{Ra}$  delayed coincidence counting;  $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$  low-background gamma counting) in the study of contaminant fluxes via SGWD. Recent studies suggest that groundwater may be important in the mass balance of many elements in nearshore environments and cannot be ignored in the accurate prediction of the fate of contaminants originating in marine sediments and pore waters. Even if SGWD flows are modest, pollutant concentrations in groundwater may be sufficiently high for SGWD to have an important impact on the source and fate of pollutants in coastal harbors and estuaries.

## APPROACH

Our scientific approach involves the use of radium isotopes and hydrodynamic models to study the contaminant flux via SGWD in coastal harbors. The short-lived radium isotopes are then used to predict contaminant residence times within the harbors. We spent much of the past year revisiting field sites occupied during Year 1 of the proposal. Specifically, we performed additional seepage meter deployments in our local study estuary (Waquoit Bay, MA) which has been well studied and is known to contain zones of high SGWD. Also, two additional weeklong surveys of our main study area Boston Harbor were completed to assess general circulation patterns in the harbor as well as the baseline

## Report Documentation Page

*Form Approved*  
*OMB No. 0704-0188*

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1. REPORT DATE <b>30 SEP 2001</b>		2. REPORT TYPE		3. DATES COVERED <b>00-00-2001 to 00-00-2001</b>	
4. TITLE AND SUBTITLE <b>Investigating Contaminant Inputs via Submarine Groundwater Discharge to Coastal Waters Using Radium Isotopes</b>				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) <b>Department of Marine Chemistry and Geochemistry,, Woods Hole Oceanographic Institution,, Woods Hole,, MA, 02543</b>				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT <b>Approved for public release; distribution unlimited</b>					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT <b>Our long-term goal is to determine if submarine groundwater discharge (SGWD) is an important mechanism for delivering contaminants (i.e. heavy metals, organics) to harbors. We plan to accomplish this goal using a suite of naturally occurring radium isotopes as tracers of SGWD and the dispersion of contaminants from the embayment (Buesseler/WHOI). In addition, we plan to develop a comprehensive hydrological model (Harvey/MIT) to determine the importance of SGWD in the transport of pollutants to coastal harbors.</b>					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a REPORT <b>unclassified</b>	b ABSTRACT <b>unclassified</b>	c THIS PAGE <b>unclassified</b>			

distribution of radium isotopes. We performed a weeklong study of Norfolk Harbor, VA using a sampling approach similar to our Boston Harbor study site.

## **WORK COMPLETED**

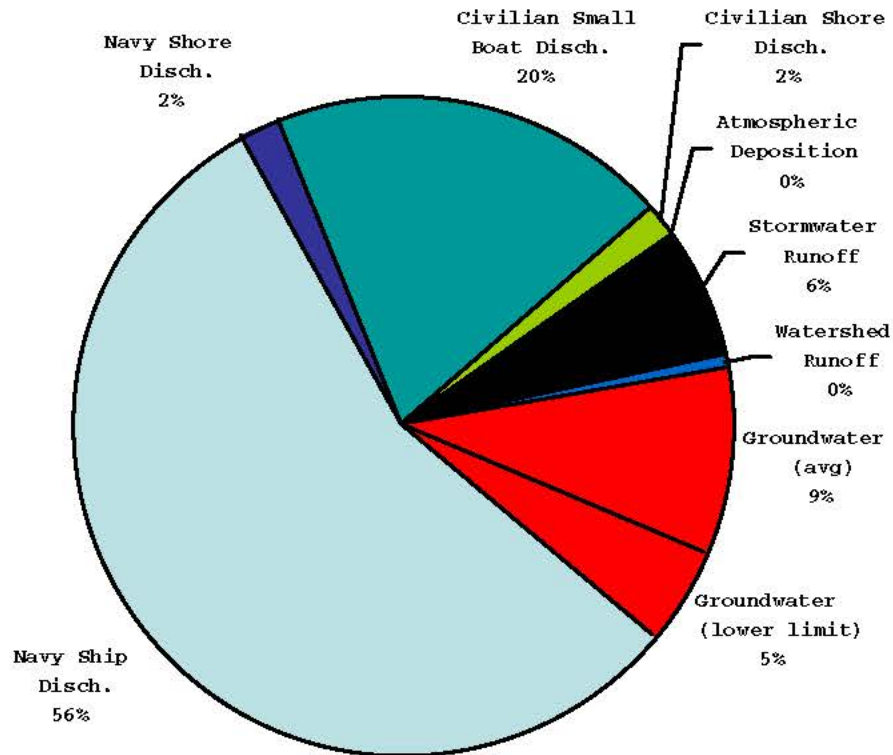
During May 2000, we conducted an intensive weeklong sampling effort in Norfolk Harbor (Elizabeth River Estuary), VA. We collected samples for water column radium isotopes, salinity/temperature, nutrients, trace metals, and trace organics. The same parameters were also measured in shallow groundwater located along the land-water interface of the estuary. We coordinated sampling efforts with other ONR-Harbor Processes PIs (J. Donat, B. Sunda, A. Gordon).

This past summer (June and September), we surveyed water column radium activities in Boston Harbor during two weeklong cruises. The data is currently being processed and will be combined with data obtained during a cruise in Year 1 of the proposal. We performed measurements of four radium isotopes and salinity/temperature profiles at over 50 stations including two transects extending over 15 km from shore. New to this year's Boston Harbor program was the collection of trace metal samples, which were analyzed during the Fall/Winter 2000.

A total of five seepage meter experiments were conducted at Waquoit Bay in order to determine the spatial and temporal patterns and variability in submarine groundwater discharge. The meters provide direct measurement of the groundwater flux, as well as water samples that are analyzed for radium concentrations and salinity. Three experiments were conducted using a 67 x 150m grid of 40 seepage meters sampled at 2-hour intervals over a tidal cycle. One experiment utilized clusters of meters to determine discharge variability over several weeks. The final experiment involved two clusters of meters spaced along a transect of seepage meters extending into the bay. These meters were sampled every two hours over a period of more than three tidal cycles in order to determine the extent to which SGWD is affected by tidal fluctuation.

## **RESULTS**

In Norfolk Harbor, VA, we used radium isotopes to estimate the SGWD input of Cu and associated trace metals. First we calculated the regional  $^{226}\text{Ra}$  excess due to groundwater discharge via a simple activity balance eliminating all sources other than SGWD (i.e. rivers, sediments, tidal exchange). We then used the measured groundwater  $^{226}\text{Ra}$  "endmember" to estimate SGWD flux to the Harbor. In order to calculate a SGWD range, we assumed two endmembers in the calculation: (1) the average local GW  $^{226}\text{Ra}$  activity from the surficial aquifer ( $n = 9$ ), and (2) the maximum observed groundwater  $^{226}\text{Ra}$  activity. The former value provides an average SGWD while the latter produces a more conservative, lower-limit estimate. These calculations predicted a SGWD for Norfolk Harbor of between 1,900 and 5,700  $\text{m}^3 \text{y}^{-1}$ . The magnitude of these fluid fluxes is equivalent to 1.2-3.5% of the total annual discharge of all Chesapeake Bay rivers. Using the average measured groundwater Cu concentration of 32  $\text{nmol kg}^{-1}$ , we estimate the SGWD-derived Cu flux to be 1,400 and 4,300  $\text{kg y}^{-1}$ . These fluxes represent a significant fraction (5-14%) of the estimated Cu budget for Norfolk Harbor (Fig. 1).



**Figure 1. Dissolved Cu budget for Norfolk Harbor, VA including the contribution from SGWD. The total revised Cu input is  $30,572 \text{ kg y}^{-1}$  (adapted from Johnson et al., 1998 to include SGWD estimate from this study).**

In Waquoit Bay, a distinct spatial seepage pattern was observed indicating that most of the groundwater discharge occurs in a narrow band which is between 25 and 45 meters from the shoreline. This band is not predicted by traditional coastal hydrologic models, according to which we would expect most of the discharge to occur at the shoreline. We have come up with two hypotheses to explain this banded pattern. The first is that there is subsurface heterogeneity in which a region of high hydraulic conductivity acts as a preferential flowpath into the bay. We were able to test this hypothesis by performing slug tests along a transect into the bay. The resulting estimated hydraulic conductivity is greatest near the shoreline and decreases with distance from shore, indicating that the band is not caused by heterogeneity. The second hypothesis is that the interaction between density-dependent flow and tides leads to a complicated system that produces this banded effect. This hypothesis is supported by recent numerical simulations (Ataie-Ashtiani 1999; Robinson 1999), which have shown that incorporating tidal dynamics into a model significantly affects the configuration of salt-concentration and equipotential contours in the subsurface as well as groundwater flow patterns. We were able to investigate this theory via a seepage meter test on a narrow peninsula jutting off of an island in Waquoit Bay. In this test, the freshwater component of flow is expected to be negligible compared to that at the head of the bay, resulting in an experiment which does not, for the most part, incorporate density-dependent effects. We found that the discharge pattern at this site was essentially

uniform with distance from shore, indicating that density-dependent interaction with tides may in fact be the cause of the banded pattern.

Tests using seepage meter clusters indicate significant variability in discharge at the meter scale. However, statistical analysis indicates that 20 seepage meters or more are sufficient to obtain a reliable estimate of both the amount of seepage and the spatial discharge pattern at the 50 meter scale.

Measurements over multiple tidal cycles indicate that discharge nearer to shore is most affected by tidal fluctuation. The discharge between 0 and 20 meters from shore is greatest during low tide and lowest during high tide; while the discharge farther from shore is relatively unaffected by tides.

Salinity analysis of the seepage meter samples indicates that most of the discharge is between 0 and 5 percent freshwater, with the exception of fresher discharge very near the shoreline. The behavior of the saltwater-freshwater interface during a tidal cycle, as well as radium concentrations near the interface, were characterized with samples drawn from a transect of piezometers perpendicular to the shoreline, driven to depths of up to 5 m.

A temperature probe was designed and constructed to measure vertical temperature gradients continuously over long periods of time. Because the thermal conductivity and capacity of submarine sediments are well known, this probe has the potential to provide an accurate measurement of localized groundwater flux. The probe was driven in to Waquoit Bay sediments and data collected for long periods of time (more than one month) in both the winter and summer. During the final groundwater experiment the probe was buried underneath a seepage meter so that the flux measurements can be compared. This data is in the process of being analyzed.

These localized submarine groundwater discharge measurements were obtained in order to understand coastal groundwater flow in Waquoit Bay so that a comparison may be made between direct discharge estimates and those obtained using Radium measurements. This comparison can be further investigated through Radium measurements in the seepage meter bag samples. We were able to measure Radium isotope activities in the seepage meters as they vary both with distance from shore and with time during a tidal cycle. Both fresh and saline groundwater samples were also taken and the Radium activity measured. These data show that Radium activity is very highly variable in both groundwater and seepage samples over a range of salinity. This variability indicates that it is extremely difficult to accurately estimate a groundwater endmember value from well sampling alone, and that an inaccurate estimate may result in a SGWD estimate that may be off by an order of magnitude.

In addition, the sharp decline in radium activity with distance from shore (Fig. 2) indicates that discharging groundwater does not have uniform radium activity. This trend is exhibited in all four radium isotopes. Our results show that 15% of the radium flux into the bay can be attributed to 2% of the discharging water nearest the shore, and that the bulk of the SGWD further from shore has radium activities near that of the bay water. Thus, the radium activity in the bay water is elevated by near shore discharge, and is largely unaffected by the bulk of saline discharge farther from shore. So, if the activity in the near-shore slightly-fresh water is used as a single endmember in the radium budget for the Bay, the near-shore SGWD may be calculated. But, if the average radium value is used, a larger flux may be calculated representing groundwater discharge over a larger area, which would include saline groundwater discharge.

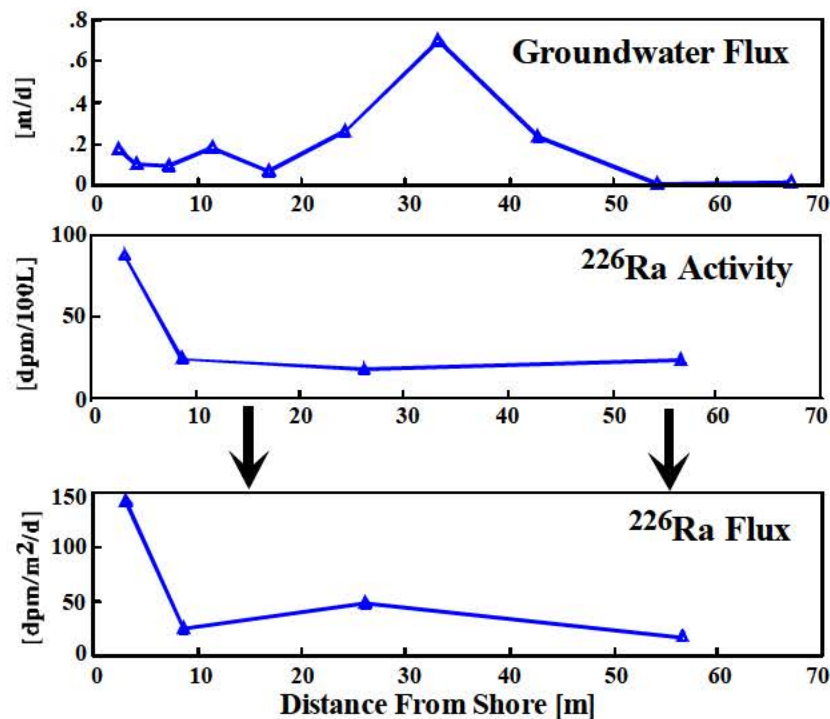


Figure 2. Groundwater flux, <sup>226</sup>Ra activity, and <sup>226</sup>Ra flux vs. distance from shore for Waquoit Bay seepage meter samples.

## IMPACT/APPLICATIONS

The investigation of SGWD-derived Cu input to Norfolk Harbor revealed that this source term is a non-negligible component of the overall dissolved Cu budget. The Waquoit Bay seepage meter data, combined with information from radium measurements, will aid in the future development of both a conceptual and numerical model of submarine groundwater flow patterns and discharge into nearshore marine environments.

## TRANSITIONS

The nuclear detection equipment (well-type gamma detector and delayed coincidence counters) partially funded by ONR have received much use in studies other than this project. These include sedimentation studies in Lake Sisskiwit, MI and Santa Barbara Basin, CA, estimates of shelf water exchange in the Mid-Atlantic Bight, and nutrient and SGWD studies in West Falmouth Harbor, MA and Great Sippiwisset Marsh, MA.

## **PUBLICATIONS**

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