# The Balance of <sup>228</sup>Ra in the Upper Atlantic Ocean: Implications for Continental Input of DIC and DOC

Willard S. Moore Department of Geological Sciences University of South Carolina Columbia, SC moore@geol.sc.edu

### Introduction

The half life of <sup>228</sup>Ra is 5.7 years. Each year the Atlantic Ocean loses 12% of its inventory of <sup>228</sup>Ra by radioactive decay. This inventory must be constantly replaced by inputs from rivers, sediments, and submarine ground water discharge (SGD). By evaluating the inputs from rivers and sediments, the input from SGD may be determined by difference.

In this poster I use data from the Transient Tracers in the Ocean (TTO) project to determine the inventory of  $^{228}$ Ra in the upper Atlantic. I then use published estimates of  $^{228}$ Ra input by rivers and sediments to determine the amount derived from SGD. Dividing the SGD flux of  $^{228}$ Ra by the concentration of  $^{228}$ Ra in coastal groundwater yields the flux of SGD.

## What is Submarine Groundwater Discharge?

Submarine groundwater discharge is the advective flux of water through permeable sediments on the continental margin regardless of fluid composition or driving force. You must recognize that SGD consists of a mixture of meteoric water and sea water that has reacted chemically with coastal aquifer solids. Salinity can vary from 0 to 36 and is usually closer to sea water salinity than to fresh water. SGD is usually elevated in concentrations of carbon, nutrients, and metals relative to the endmembers.

General model for quantifying SGD using radium isotopes

# Inputs of <sup>228</sup>Ra

### Inputs from Sediments

 $^{228}$ Ra is continually generated by decay of  $^{232}$ Th in sediments. Some of this <sup>228</sup>Ra dissolves in pore waters and may enter coastal water by diffusion and bioturbation. Here are measurements of the sedimentary flux of  $^{228}$ Ra.

Study Area	Grain size	<sup>228</sup> Ra flux	Reference
		$(10^9 \text{ at } \text{m}^{-2}\text{y}^{-1})$	
Long Island Sound	fine	57	Cochran, 1984
Narragansett Bay	fine	35	Cochran, 1984
Narragansett Bay	fine	52	Santschi et al., 1979
Amazon shelf	fine	110	Moore et al., 1995
North Inlet marsh	fine	4	Rama & Moore, 1996
Port Royal marsh	fine	4	Crotwell & Moore, 2003
Zecks Lagoon	fine	80	Hancock et al., 2000
Great Barrier Reef	fine	26	Hancock et al, 2006
Adopted for shelf	fine	50±25	This paper
San Pedro Bay	coarse	0.13	Colbert, 2004
Newport Bay	coarse	0.92	Colbert, 2004
Great Barrier Reef	coarse	4	Hancock et al., 2006
Adopted for shelf	coarse	1±0.5	This paper
San Pedro Basin slope	fine	5	Hammond et al., 1990

# Why is SGD Important to Carbon Fluxes?

Coastal groundwaters often have elevated concentrations of DIC and DOC. In some cases these concentrations correlate with radium concentrations.





Figure 1. At steady state the losses of <sup>228</sup>Ra (primarily decay) must balance the inputs. Riverine, dust, and sedimentary inputs are evaluated using published studies. SGD is determined by difference.



San Nicolas Basin slope	fine	11	Hammond et al., 1990
Adopted for slope	fine	10±5	This paper

These fluxes are converted to total fluxes using the following: Atlantic shelf area =  $6.94 \times 10^{12} \text{ m}^2$ , slope area between 200-1000 m depth =  $2.5 \times 10^{12} \text{ m}^2$ , fraction of mud on the shelf = 30%. Thus, the shelf flux is  $(1.1\pm0.5) \ge 10^{23}$  atoms yr<sup>-1</sup> and the slope flux is  $(0.2\pm0.1) \ge 10^{23}$  atoms yr<sup>-1</sup>. The total sedimentary flux is  $(1.3\pm0.5) \ge 10^{23}$  atoms yr<sup>-1</sup>, or 37% of the total <sup>228</sup>Ra loss.

### Inputs from Rivers

There have been detailed studies of the input of <sup>228</sup>Ra from large Atlantic rivers: the Amazon, Orinoco, Mississippi, and from 7 smaller rivers along the east coast of the U.S. These studies, as well as others in the literature, all concluded that desorption of <sup>228</sup>Ra from particles is the primary factor controlling the riverine input of <sup>228</sup>Ra. The average dissolved  $^{228}$ Ra is 1.3 x 10<sup>5</sup> atoms L<sup>-1</sup> and approximately 8.6 x 10<sup>6</sup> atoms <sup>228</sup>Ra desorb from each gram of sediment entering the ocean. Given a water flux to the Atlantic of 2.4 x  $10^{16}$  L yr<sup>-1</sup> and a riverine particle flux of 2.6 x  $10^{15}$  gram yr<sup>-1</sup>yields a total <sup>228</sup>Ra flux of 2.5 x  $10^{22}$  atoms yr<sup>-1</sup>, **only 7% of the total** <sup>228</sup>**Ra loss.** 

### Input from Dust

Estimates of the dust flux to the Atlantic for 50 S to 80 N are  $3.33 \times 10^{14}$ g yr<sup>-1</sup>. Assuming that <sup>228</sup>Ra desorption from dust is similar to desorption from riverine particles (8.6 x  $10^6$  atoms gram<sup>-1</sup>) yields 2.9 x  $10^{21}$  atoms yr<sup>-1</sup> due to dust deposition, less than 1% of the total <sup>228</sup>Ra loss.

### Total Conventional Input

Summing the sedimentary, riverine, and dust fluxes yields a total conventional input of 1.6 x  $10^{23}$  atoms y<sup>-1</sup>, only 46% of the required input. The remaining flux of  $1.9 \times 10^{23}$  atoms y<sup>-1</sup> must be derived from SGD.

Figure 4. Concentrations of DIC and DOC measured in monitoring wells in the Okatee, SC, salt marsh. The salinity ranges from 11-40. DIC and DOC data from Mandy Joye.



# Converting the <sup>228</sup>Ra flux to a SGD flux

The concentrations of <sup>228</sup>Ra in coastal groundwater samples range over three orders of magnitude.



Figure 3. The concentrations of <sup>228</sup>Ra in 226 Atlantic coastal groundwater samples. The arrow shows the unbiased estimate of the mean

<sup>228</sup>Ra (dpm/L)

Figure 5. Concentrations of DOC and alkalinity measured in monitoring wells 15 km offshore of NC and SC. The salinity ranges from 32-36. DOC data from Mandy Joye and Ron Benner.

These data are similar to other studies that show high concentrations of DOC and DIC in coastal groundwater. Thus, SGD must enrich coastal waters in dissolved carbon.

Conclusions

1. There is probably more water entering the Atlantic Ocean from submarine groundwater discharge than from rivers. 2. SGD is enriched in DOC and DIC relative to river water.

Figure 2. Inventory of <sup>228</sup>Ra (x 10<sup>10</sup> atoms m<sup>-2</sup>) in the upper 1000 m of the Atlantic Ocean based on data from Transient Tracers in the Ocean (TTO). Each dot represents a station with at least 8<sup>228</sup>Ra mesurements in the upper 1000 m. All stations within each 15 x15 box are averaged to produce a bin average. The bin averages are averaged to produce a grand average.

The <sup>228</sup>Ra inventory (atoms m<sup>-2</sup>) for each TTO station was evaluated by linear interpolation between samples 0-1000 m deep. Between 1000-2000 m <sup>228</sup>Ra was below detection with respect to blank. To calculate the total inventory, the stations were grouped into  $15 \times 15$ boxes; all profiles in each box were used to calculate a bin average (Figure 2). These bin averages were used to calculate a grand average. The grand average  $(3.0 \times 10^{10} \text{ atoms m}^{-2})$  was multiplied by the area of the Atlantic to calculate the open Atlantic inventory.

This figure is adjusted slightly to account for higher concentrations of <sup>228</sup>Ra in shelf and slope water. The resulting total upper Atlantic inventory is  $2.9 \times 10^{24}$ atoms; of this  $3.48 \times 10^{23}$  atoms decay each year. The radium residence time with respect to scavenging from the surface ocean is ~500 years; the  $^{228}$ Ra residence time with respect to decay is 8.3 years. Therefore, 1.6% of the <sup>228</sup>Ra inventory is lost by scavenging and 98.4% is lost by decay, for a total loss of  $(3.5\pm0.7) \times 10^{23}$  atoms yr<sup>-1</sup>. This must be balanced by new inputs.

We may use these data to convert the <sup>228</sup>Ra flux into a SGD flux. The data are skewed, so we use the program S-Plus (Insightful Corp.) v3.4r1 to determine an unbiased estimate of the mean of 6.21 x  $10^6$  at L<sup>-1</sup> with lower and upper 1 standard error values of 5.55 and  $6.94 \times 10^6$  at L<sup>-1</sup>. To determine the SGD flux divide the <sup>228</sup>Ra flux by the SGD concentration.

Ra flux:  $1.9 \times 10^{23}$  atoms yr<sup>-1</sup> = SGD flux: 3 x 10<sup>16</sup> L yr<sup>-1</sup> Ra concentration in SGD:  $6.2 \times 10^6$  atoms L<sup>-1</sup>

3. The input of DOC and DIC to the Gulf of Mexico by SGD is likely greater than the input by rivers.

More information is available in Submarine Groundwater Discharge Revealed by <sup>228</sup>Ra Distribution in the Upper Atlantic Ocean Willard S. Moore, Jorge L. Sarmiento and Robert M. Key Nature Geoscience Published online: 20 April 2008; doi:10.1038/ngeo183

Bottom Line

The best estimate of the total SGD flux is  $(2-4) \times 10^{16} \text{ L yr}^{-1}$ or 80-160% of the river water flux to the Atlantic.