Submarine groundwater discharge revealed by ^{228}Ra distribution in the upper Atlantic Ocean

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Submarine groundwater discharge is defined as any flow of water at continental margins from the seabed to the coastal ocean, regardless of fluid composition or driving force[1]. The flux of submarine groundwater discharge has been hypothesized to be a pathway for enriching coastal waters in nutrients, carbon and metals[2]. Here, we estimate the submarine groundwater flux from the inventory of ^{228}Ra in the upper Atlantic Ocean, obtained by interpolating measurements at over 150 stations. Only 46% of the loss in ^{228}Ra from radioactive decay is replenished by input from dust, rivers and coastal sediments. We infer that the remainder must come from submarine groundwater discharge. Using estimates of ^{228}Ra concentrations in submarine groundwater discharge, we arrive at a total flux from submarine groundwater discharge of 2–4 × 10^{13} $m^3\,yr^{-1}$, between 80 and 160% of the amount of freshwater entering the Atlantic Ocean from rivers. Submarine groundwater discharge is not a freshwater flux, but a flux of terrestrial and sea water that has penetrated permeable coastal sediments. Our assessment of the volume of submarine groundwater discharge confirms that this flux represents an important vehicle for the delivery of nutrients, carbon and metal to the ocean.

Our strategy for determining the submarine groundwater discharge (SGD) flux to the Atlantic derives from the fact that radioactive decay is the primary sink for ^{228}Ra in the upper Atlantic. Exactly 12% of the ^{228}Ra inventory disappears each year by this process, that is, $\lambda = 0.12\,yr^{-1}$. To maintain steady-state, there must be an equivalent flux from continental margins, as ^{228}Ra released from deep-sea sediments does not penetrate into the upper 1,000 m (ref. 3). No other isotope, element or compound shares these attributes of widespread distribution throughout the upper ocean, a removal term that is highly constrained and a supply term that is due almost entirely to input from continental margins.

The Transient Tracers in the Ocean (TTO) project mapped ^{228}Ra and ^{226}Ra distributions in the Atlantic Ocean during the: North Atlantic Study (1981); Tropical Atlantic Study (1982–1983); South Atlantic Ventilation Experiment (1987–1989). These data[4–6] are used here to determine the inventory of ^{228}Ra in the upper Atlantic. Over 150 TTO stations have at least 8 samples collected in depth profiles in the upper 1,000 m.

The ^{228}Ra inventory (atoms m^{-2}) for each TTO station was evaluated by linear interpolation between samples 0 to 1,000 m deep. Between 1,000 and 2,000 m, ^{228}Ra was below detection with respect to the 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 (Fig. 1). These bin averages were used to calculate a grand average. The grand average (3.0×10^{10} atoms m^{-2}) was multiplied by the area of the Atlantic to calculate the open Atlantic inventory. We adjusted this figure slightly to account for higher concentrations of ^{228}Ra in shelf and slope water (see the Supplementary Information). The resulting total upper Atlantic inventory is 2.9×10^{24} atoms; of this, 3.48×10^{23} atoms decay each year. We estimate the error on the inventory to be ±20% (see the Supplementary Information). The radium residence time with respect to scavenging from the surface ocean is ~500 yr (ref. 7); the ^{228}Ra residence time with respect to decay is 8.3 yr. Therefore, 1.6% of the ^{228}Ra inventory is lost by scavenging and 98.4% is lost by decay, for a total loss of $(3.5 \pm 0.7) \times 10^{23}$ atoms yr^{-1}.

The distribution of ^{228}Ra in the upper Atlantic Ocean yields two important observations. There must be a continual flux of ^{228}Ra from the continents to maintain its inventory in the upper Atlantic; this inventory increases from the South Atlantic to the North Atlantic as the surface limb of the ocean conveyor moves water northward. The vertical distribution of ^{228}Ra added from the margins implies that the vertical mixing time of the upper 500–1,000 m must be similar to the 30 yr lifetime of ^{228}Ra.

There are four possible vectors of ^{228}Ra from continental margins to the ocean: (1) riverine, (2) atmospheric dust, (3) regeneration and release from continental shelf and slope sediments and (4) SGD. The first three, which we call conventional sources, are evaluated using existing data; ^{228}Ra supply by SGD is evaluated as the difference between the loss of ^{228}Ra and its supply by conventional sources.

There have been detailed studies of the input of ^{228}Ra from large Atlantic rivers: the Amazon[8,9], Orinoco[10], Mississippi[11], and from 7 smaller rivers along the east coast of the USA (ref. 12). These studies, as well as others in the literature (see ref. 12), all concluded that desorption of ^{228}Ra from particles is the primary factor controlling the riverine input of ^{228}Ra. The average dissolved ^{228}Ra is 1.3×10^5 atoms L^{-1} and approximately 8.6×10^6 atoms ^{228}Ra desorb from each gram of sediment entering the ocean[12]. A water flux to the Atlantic of 2.4×10^{16} L yr^{-1} and a riverine particle flux of 2.6×10^{15} g yr^{-1} (ref. 13) yield a total ^{228}Ra flux of 2.5×10^{22} atoms yr^{-1}, only 7% of the total ^{228}Ra loss.

Estimates of the dust flux to the Atlantic for 50° S–80° N are 333 Tg yr^{-1} (ref. 14). Assuming that ^{228}Ra desorption from dust is similar to desorption from riverine particles (8.6×10^6 atoms g^{-1})

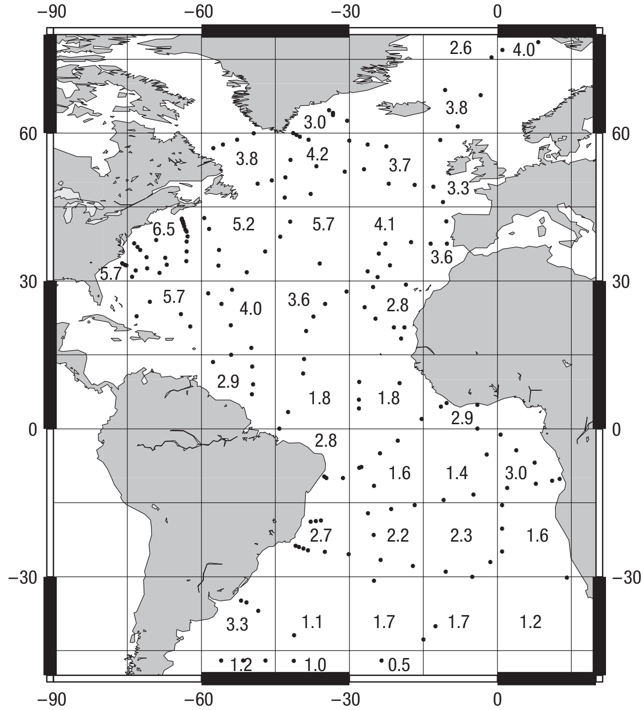

Figure 1 Inventory of ^{228}Ra ($\times 10^{10}$ atoms m^{-2}) in the upper 1,000 m of the Atlantic Ocean. The points show the distribution of stations that were used to calculate ^{228}Ra inventories. All stations within each 15° × 15° box were averaged to yield a bin average, shown as a number in each box.

yields 2.9×10^{21} atoms yr^{-1} due to dust deposition, less than 1% of the loss.

Decay of ^{232}Th within continental margin sediments continuously generates ^{228}Ra. Some of this ^{228}Ra enters the water column by desorption into pore water and exchange of pore water into the ocean. This flux is a function of the ^{232}Th content of the sediment, the ease with which ^{228}Ra can escape and the rate of pore water exchange. Fine-grained, non-carbonate sediments generally contain higher concentrations of ^{232}Th. Stirring the sediment by physical and biological means facilitates the escape of pore water containing ^{228}Ra. Here, we attempt to separate advective pore water exchange (SGD) from pore water exchange due to diffusion and bioturbation.

Numerous studies have estimated the flux of ^{228}Ra due to diffusion and bioturbation from salt marsh, near-shore and shelf sediments to the water column (see Supplementary Information, Table S1). Estimates of fluxes from fine-grained (mud) sediments range from 4×10^9 atoms m^{-2} yr^{-1} for cohesive, but bioturbated, salt marsh sediments to 110×10^9 atoms m^{-2} yr^{-1} for fluid muds on the Amazon shelf that are frequently mixed to depths of 1–2 m. Values intermediate to these extremes have been reported at other locations. A flux of $(50 \pm 25) \times 10^9$ atoms m^{-2} yr^{-1} captures all of the reported fluxes except for the extremely high and low values. See Supplementary Information for details.

Colbert[15] estimated fluxes of ^{228}Ra from coarse-grained sediments in San Pedro Bay and Newport Beach, California, of $(0.15–0.92) \times 10^9$ atoms m^{-2} yr^{-1}. These low values are consistent with the low ^{232}Th content of most relict sand. This study is consistent with that of Hancock *et al.*[16] who found benthic fluxes on the northwest Australia margin decreased offshore as grain size increased. We will use $(1 \pm 0.5) \times 10^9$ atoms m^{-2} yr^{-1} for fluxes from sandy shelf sediments.

Table 1 Summary of ^{228}Ra inputs (10^{23} atoms yr^{-1}) to the near-surface Atlantic Ocean.

Input sources	Flux
Sedimentary	
Shelf mud	1.0 ± 0.5
Shelf sand	0.05 ± 0.02
Slope	0.25 ± 0.12
River	
Dissolved	0.03 ± 0.015
Desorbed	0.22 ± 0.11
Dust	0.03 ± 0.015
Total conventional	1.6 ± 0.5
Inferred SGD	1.9 ± 0.8

The only study of ^{228}Ra fluxes from the slope is that of Hammond *et al.*[17] who studied two basins off the California coast. These were in the range 5.2×10^9 atoms m^{-2} yr^{-1} for anoxic and varved San Pedro Basin sediments to 11×10^9 atoms m^{-2} yr^{-1} for bioturbated San Nicolas Basin sediments. We will use an estimate similar to that of the San Nicolas sediments of $(10 \pm 5) \times 10^9$ atoms m^{-2} yr^{-1} for slope fluxes.

Sediments on continental shelves are typically relict sands; only about 30% of this sediment is mud[18]. The mud fraction increases on the continental slope; however, the carbonate (low ^{232}Th) fraction also increases. To estimate total sediment fluxes to the Atlantic, we use the following factors from Emery and Uchupi[19]: Atlantic shelf area $= 6.94 \times 10^{12}$ m^2, slope area between 200 and 1,000 m depth $= 2.5 \times 10^{12}$ m^2. Taking the fraction of mud on the shelf to be 30%, the shelf flux is $(1.1 \pm 0.5) \times 10^{23}$ atoms yr^{-1} and the slope flux (assuming 100% mud) is $(0.2 \pm 0.1) \times 10^{23}$ atoms yr^{-1}. The total sedimentary flux is $(1.3 \pm 0.5) \times 10^{23}$ atoms yr^{-1}, or 37 ± 16% of the required flux.

From this analysis, summarized in Table 1, it is clear that the ^{228}Ra flux from muddy near-shore and shelf sediments is the primary conventional source to the ocean, accounting for 63% of the conventional input. The uncertainties associated with river and dust fluxes do not significantly affect this result. We think we have made a fair estimate of the muddy shelf flux by choosing a value near the mean of the measurements. The highest fluxes result from rapid turnover of fluid muds in high-energy river mouths such as the Amazon. These extreme environments comprise only a small fraction of the shelf.

Summing fluxes from conventional sources gives a total ^{228}Ra flux of $(1.6 \pm 0.5) \times 10^{23}$ atoms yr^{-1}, less than half the annual loss of ^{228}Ra from the upper Atlantic. The remaining $(1.9 \pm 0.8) \times 10^{23}$ atoms yr^{-1} must be derived from SGD. See Supplementary Information for details of uncertainty estimates.

We have fewer data for ^{228}Ra in SGD compared with the data for the ocean (see Supplementary Information, Table S2). Thus, converting the ^{228}Ra flux to a flux of SGD introduces further uncertainty. The concentrations (see Supplementary Information, Table S3) range from $(0.004$ to $125) \times 10^6$ atoms L^{-1}. Figure 2 shows a histogram of the $\log_{10}$ transform of the ^{228}Ra concentration for 226 coastal groundwater samples collected throughout the Atlantic coast. Here, we are interested in the accuracy of the mean rather than the scatter of the data. The data are skewed, so we used S-Plus (Insightful Corp.) v3.4r1 for SUN SPARC to establish an unbiased estimate of the mean of 6.21×10^6 atoms L^{-1} with lower and upper 1 standard error values of 5.55 and 6.94×10^6 atoms L^{-1}. We used this as a representative ^{228}Ra SGD concentration assuming our samples were collected without bias. This value is about 100-fold enriched compared with that of North Atlantic

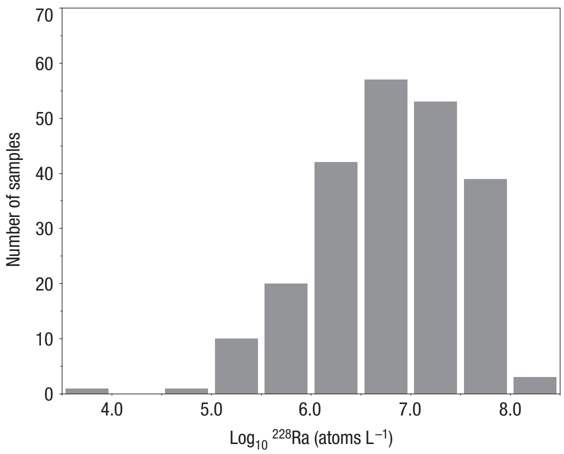

Figure 2 Distribution of ^{228}Ra in groundwater samples from throughout the Atlantic coastline. The full 226 point data set from wells and temporary samplers is in Supplementary Information, Table S3.

surface water[4]. To balance the ^{228}Ra loss from the upper Atlantic requires a SGD flux of $(2–4) \times 10^{16}$ L yr^{-1}. Thus, the SGD flux is probably between 0.8 and 1.6 times the river flux to the Atlantic.

We can compare the total Atlantic SGD flux with intermediate-scale SGD studies. Moore[2] estimated a flux of 3.4×10^{10} L km^{-1} yr^{-1} for a 320 km coastline along North and South Carolina, USA, on the basis of an assumed groundwater ^{226}Ra (half life = 1,600 yr) activity of 7 dpm L^{-1}, a figure that now seems a factor of 3–4 high[20]. Using 2 dpm L^{-1} increases this flux to 1.2×10^{11} L km^{-1} yr^{-1}. Windom *et al.*[21] estimated a similar SGD flux of 1.3×10^{11} L km^{-1} yr^{-1} for a 240 km coastline adjacent to Patos Lagoon, Brazil. Both studies emphasized that the estimate only included near-shore and shallow (0–20 m) SGD fluxes. To compare these studies with ours, we divide the Atlantic SGD flux by the 85,000 km Atlantic shoreline (minus that of the Mediterranean and Black seas)[19] to yield a flux of 3.5×10^{11} L km^{-1} yr^{-1}, significantly greater than those of intermediate studies. As our study also captures SGD leaking from the mid and outer shelf (20–150 m), the flux should be greater than that of studies that only estimate near-shore flux.

We must emphasize that SGD is not a freshwater flux, but a flux of terrestrial water that has mixed with sea water in the subterranean estuary[22], where ^{228}Ra concentrations increase 100-fold. This is not simply recycled sea water because chemical alteration modifies the composition of water in the subterranean estuary before it enters the ocean as SGD. In addition to ^{228}Ra, SGD is enriched in nutrients, carbon and trace metals[22]. Because SGD concentrations of nutrients may exceed river concentrations, the SGD flux of nutrients may be more important than the river flux[23–25]. The SGD nutrient flux may sustain coastal productivity or possibly lead to eutrophication and harmful algae blooms[26–28]. SGD carbon fluxes are an important component of the carbon cycle in coastal waters[29]. SGD iron fluxes may rival atmospheric fluxes to the southern Atlantic[21]. With this new understanding of the magnitude of the total SGD flux, we may better appreciate the role it plays in the coastal ecosystem and the open ocean.

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