

Submarine groundwater discharge of nutrients and copper to an urban subestuary of Chesapeake Bay (Elizabeth River)

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Abstract

We investigated the role submarine groundwater discharge (SGD) plays in the delivery of nutrients and copper to the Elizabeth River (Virginia) estuary, a major subestuary of lower Chesapeake Bay. Using an approach based on radium isotopes, we concluded that two distinct sources of groundwater were equally impacting the estuary: a surface (marsh) aquifer and deep aquifer source each with a unique $^{228}\text{Ra}/^{226}\text{Ra}$ activity ratio. Considering each of these sources, we calculated an SGD flux of $1 \times 10^6 \text{ m}^3 \text{ d}^{-1}$ ($\pm 10\%$), which represented $\sim 6\%$ of the SGD flux for the entire Chesapeake Bay and $\sim 5\%$ of the James River, a major source of freshwater to lower Chesapeake Bay. SGD-derived dissolved inorganic nitrogen (DIN) and dissolved inorganic phosphorus (DIP) fluxes averaged 4.5 (± 4.6) and 0.16 (± 0.17) $\text{mmol m}^{-2} \text{ d}^{-1}$, respectively, and compared well with area-normalized fluxes to Chesapeake Bay. In contrast, SGD-derived Cu input of 730 (± 390) kg yr^{-1} was a relatively small source of Cu ($\sim 3\%$) to the Elizabeth estuary given that surface water inputs, such as antifouling paints associated with naval operations, are a major component of the Cu budget for this system. These findings were in general agreement with prior studies of SGD for this region.

Submarine groundwater discharge (SGD) is often ignored when constructing geochemical budgets for elements in near-shore environments, mainly because the volume flux is difficult to estimate. However, many studies indicate that SGD may carry significant quantities of nutrients and trace metals to the ocean (Simmons 1992; Moore 1996; Krest et al. 2000; Montlucon and Sanudo-Wilhelmy 2001). In the case of nutrients, SGD has been the principal mechanism for eutrophication in many coastal embayments throughout the world (e.g., Valiela et al. 1990).

Various approaches for quantifying SGD include water budgets, seepage meters, and natural tracers (*see* review by Burnett et al. 2001). The water budget approach, which attempts to balance aquifer inputs (precipitation) with losses (evapotranspiration), often results in a large uncertainty, since SGD is the difference between two very large numbers (e.g., Cambareri and Eichner 1998). Seepage meters, though useful for understanding local-scale patterns of SGD, are labor intensive and therefore require significant effort for quantifying SGD on large spatial scales (e.g., Michael et al.

2003). Natural tracers, the most valuable of which are orders of magnitude more enriched in groundwater relative to the receiving water body, are useful because their excess concentration in the study area of interest represents an integrated measure of SGD (e.g., Cable et al. 1996; Moore 1996).

There are two general approaches to defining submarine groundwater discharge (SGD): (1) the amount of freshwater that enters the coastal ocean from a hydraulically connected aquifer or (2) the advective flow of mixtures of fresh and brackish waters into the coastal zone (Burnett et al. 2001). Most SGD derives from inland precipitation that recharges aquifers, which then flows into the sea. Freshwater flowing down gradient from the water table may either discharge from a seepage face at the shore or flow directly into the sea. The hydraulic gradient that drives freshwater toward the sea along the interface also drives saltwater back to sea, creating a saltwater circulation cell (Li et al. 1999). Hence, SGD often consists of a substantial amount of cycled seawater, which can significantly alter the chemical composition of the discharging fluid (Moore 1999; Charette and Sholkovitz 2002; Testa et al. 2002). Therefore, studies aimed at understanding chemical fluxes to the coastal zone derived from SGD must consider both fresh and saline groundwater.

Radium isotopes have proved to be useful tracers of total SGD in many environments on both small and large scales from salt marshes (e.g., Rama and Moore 1996) to the continental shelf (Moore 1996). In addition to being orders of magnitude more enriched in groundwater relative to seawater, there are four isotopes of Ra (^{224}Ra , $t_{1/2} = 3.66 \text{ d}$; ^{223}Ra , $t_{1/2} = 11.4 \text{ d}$; ^{228}Ra , $t_{1/2} = 5.75 \text{ yr}$; ^{226}Ra , $t_{1/2} = 1,600 \text{ yr}$) with a wide range of half-lives that make Ra useful for evaluating sources and rates of SGD, as well as nutrients and trace metals carried by this process.

The goal of this work was to investigate the role of SGD in the delivery of nutrients and copper to an urban estuary using radium isotopes. We chose the Elizabeth River, Vir-

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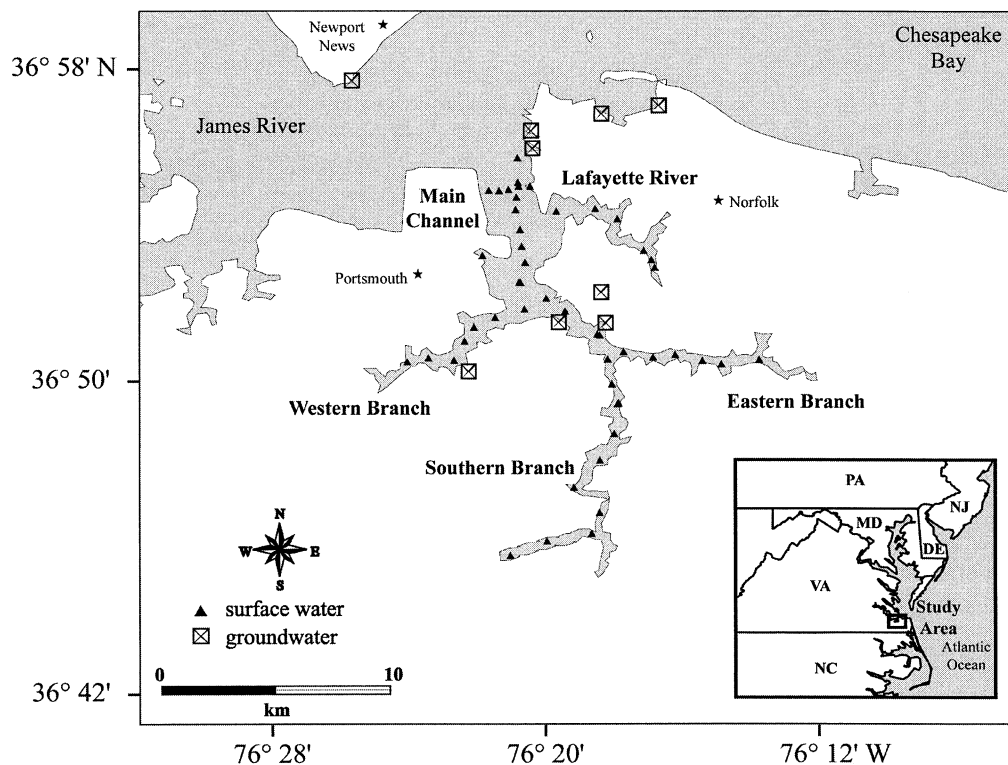


Fig. 1. Location of sampling stations in the Elizabeth estuary and its four main branches.

ginia, which is characterized by a heavily urbanized and industrialized watershed that includes the largest naval port in the world. As a tributary of lower Chesapeake Bay, the river itself consists of a main stem and four major branches (Fig. 1). The shorelines of the main stem, Southern Branch, and Eastern Branch consist of a single deep (dredged) channel with heavily developed shorelines (e.g., industry, shipyards). In contrast, the Western Branch and the Lafayette River are significantly less industrialized, as evidenced by their abundance of natural salt marshes. The Southern Branch continues south into the Great Dismal Swamp, which connects the Intracoastal Waterway of Virginia and North Carolina. Tidal flushing controls water residence times in the Elizabeth River and freshwater influx, which is restricted by canal locks in the upper river. In combination with the industrial activity, slow flushing of the estuary has led to severe contamination of sediments and water column from a variety of trace metals and organic compounds (Rule 1986; Bender et al. 1988; Mitra et al. 1999; Diaz et al. 2003).

Eastern Virginia is characterized by a coastal plain-type geology, with abundant sources of groundwater typical of other coastal plain regions. For the Elizabeth estuary, sources of groundwater include the Columbia and Yorktown aquifers. The Columbia aquifer is shallow and unconfined, consisting of thin, discontinuous layers of sand and shell lenses. The hydraulic conductivity ranges from 28 to 1,200 cm d^{-1} (Meng and Harsh 1988). The underlying Yorktown aquifer, confined by beds of silt and clay, consists of fine shelly sand, silty sand, and shell beds. It is breached in certain areas due to stream erosion and possibly dredging, which is common practice to maintain navigation channels for naval opera-

tions. Hydraulic conductivities are 2–5 orders of magnitude lower than in the Columbia aquifer, ranging from 0.01 to 0.63 cm d^{-1} (Meng and Harsh 1988).

Methods

Field sampling in the Elizabeth estuary was conducted during 1 to 5 May 2000 aboard the R/V *Mytilus*. Filtered ($1\text{-}\mu\text{m}$ Hytrec II cartridge) seawater samples (~ 100 liters) were collected at a depth of 1 m in polypropylene barrels using a deck-board pump. The water was then repumped slowly (flow rate ~ 1 liter min^{-1}) through a column of Mn-impregnated acrylic fibers, which quantitatively extract radium isotopes (Moore and Reid 1973). Subsamples for salinity and nutrient analyses were collected from the same deck-board pumping system; glass bottles were used for salinity samples, and acid-cleaned polyethylene bottles were used for nutrient samples. Nutrient samples were stored frozen until analysis. Trace metal samples (~ 1 liter) were collected in acid-cleaned polyethylene bottles using a peristaltic pump and acid-cleaned polypropylene tubing. The tubing was attached to a ~ 3 m long clear PVC pipe, which was extended away from the ship to reduce the risk of sample contamination. Samples were then vacuum filtered through a $<1\text{-}\mu\text{m}$ acid-cleaned Nuclepore in a laminar flow clean bench and acidified (pH ~ 2) with SeaStar nitric acid.

Groundwater samples were collected from monitoring wells ($n = 8$) or a drive point piezometer ($n = 1$) using acid-cleaned polypropylene tubing and a peristaltic pump. The wells were all screened at relatively shallow depths

Table 1. Nutrient concentrations and radium activities from the Elizabeth estuary and its four branches.

Station ID	Salinity	NO ³⁻ /NO ²⁻	PO ₄ ³⁻	NH ₄ ⁺	²²⁴ Ra	²²³ Ra	²²⁶ Ra	²²⁸ Ra	²²⁸ Ra/ ²²⁶ Ra	²²³ Ra/ ²²⁸ Ra _{ex}
		(μmol L ⁻¹)			(dpm 100 L ⁻¹)				AR	AR
Main Channel										
1	12.83	7.1	0.38	3.5	17.4	1.2	12.9	34.1	2.6	0.036
2	13.42	7.8	0.43	3.6	20.2	1.3	14.3	36.0	2.5	0.038
3	13.30	7.8	0.43	3.8	19.3	2.3	15.0	40.4	2.7	0.060
4	13.65	11.9	0.41	3.9	20.1	2.2	16.9	46.6	2.8	0.050
5	14.23	10.6	0.41	5.3	21.1	1.5	15.6	41.7	2.7	0.037
6	14.39	10.3	0.43	5.4	18.4	1.8	15.4	43.9	2.9	0.043
7	14.79	11.2	0.41	6.1	20.4	2.3	17.2	45.8	2.7	0.053
8	14.56	11.9	0.40	5.0	20.1	2.8	17.0	46.6	2.7	0.062
9	14.62	11.1	0.42	4.9	20.8	1.6	23.0	61.4	2.7	0.027
10	15.31	14.4	0.61	14.3	19.1	2.1	17.1	46.8	2.7	0.047
11	15.26	15.8	0.66	16.9	19.7	1.7	18.5	48.1	2.6	0.036
12	15.21	16.2	0.69	18.0	18.8	2.4	18.2	46.7	2.6	0.054
16	15.29	10.5	0.58	6.3	26.0	3.6	18.0	52.7	2.9	0.071
17	16.39	9.7	0.36	8.4	30.3	2.8	19.8	61.0	3.1	0.047
58	15.96	5.6	0.47	6.0	27.2	1.6	14.0	37.8	2.7	0.045
59	15.95	5.4	0.42	3.0	22.2	2.1	16.9	59.4	3.5	0.036
60	16.03	5.3	0.41	2.6	13.3	0.5	16.0	51.1	3.2	0.011
61	16.79	5.1	0.43	3.4	20.1	2.1	12.6	34.5	2.7	0.064
62	16.67	6.8	0.50	3.7	19.5	1.5	13.8	37.6	2.7	0.041
Average	15.0	9.7	0.47	6.5	20.7	2.0	16.4	45.9	2.8	0.045
±	1.2	3.4	0.10	4.7	3.7	0.7	2.5	8.4	0.2	0.014
Southern Branch										
13	14.87	18.2	0.81	24.5	17.5	2.4	20.0	52.2	2.6	0.048
14	14.63	18.7	0.81	25.7	17.6	1.8	23.2	54.1	2.3	0.035
15	14.49	19.2	0.83	26.1	19.1	2.3	20.2	51.6	2.5	0.046
30	16.13	19.4	0.87	22.6	57.6	5.2	32.6	85.0	2.6	0.063
31	15.67	20.4	0.80	53.8	22.9	2.1	19.4	48.2	2.5	0.044
32	14.95	21.4	0.75	27.2	27.4	3.9	21.5	52.8	2.5	0.076
33	12.59	21.6	0.57	20.1	24.5	3.3	33.2	116	3.5	0.029
34	7.59	19.5	0.38	18.9	19.1	1.2	16.3	29.7	1.8	0.044
35	4.16	17.3	0.33	19.7	17.3	1.3	15.2	26.5	1.7	0.052
36	2.41	15.1	0.31	18.2	16.8	1.7	12.2	20.1	1.6	0.092
37	3.15	15.5	0.33	17.9	18.5	1.6	17.4	24.9	1.4	0.070
Average	11.0	18.7	0.62	25.0	23.5	2.5	21.0	51.0	2.3	0.054
±	5.5	2.1	0.24	10.1	11.8	1.2	6.6	28.4	0.6	0.019
Western Branch										
18	15.94	9.6	0.55	7.6	38.0	5.7	19.8	52.0	2.6	0.114
19	15.28	7.2	0.59	5.6	54.6	5.2	21.7	60.3	2.8	0.089
20	15.16	6.9	0.65	4.8	56.9	4.8	21.2	62.4	3.0	0.079
21	14.50	5.1	0.82	3.0	74.3	9.9	21.8	66.9	3.1	0.152
22	13.68	3.3	0.91	2.7	82.2	5.4	22.9	72.1	3.1	0.076
23	12.98	2.4	0.96	2.0	100	8.6	24.6	77.4	3.2	0.114
Average	14.6	5.7	0.75	4.3	67.7	6.6	22.0	65.2	3.0	0.104
±	1.1	2.7	0.17	2.1	22.3	2.1	1.6	9.0	0.2	0.029
Eastern Branch										
24	15.58	15.0	1.02	13.8	34.5	5.7	23.6	64.9	2.7	0.090
25	15.00	14.5	0.71	10.0	34.3	3.4	19.0	48.9	2.6	0.071
26	14.51	13.9	0.70	8.7	43.9	3.8	19.6	55.3	2.8	0.071
27	13.89	12.2	0.60	3.8	50.6	4.7	20.3	54.9	2.7	0.089
28*	13.44	9.3	0.60	1.2	66.8	5.2	8.3	24.1	2.9	0.232
29	12.27	2.9	0.68	0.9	87.0	6.5	19.5	56.3	2.9	0.119
Average	14.1	11.3	0.72	6.4	50.1	4.8	20.4	56.0	2.7	0.088
±	1.2	4.6	0.16	5.2	21.8	1.3	1.9	5.7	0.1	0.020

Table 1. Continued.

Station ID	Salinity	NO ₃ ⁻ /NO ₂ ⁻	PO ₄ ³⁻	NH ₄ ⁺	²²⁴ Ra	²²³ Ra	²²⁶ Ra	²²⁸ Ra	²²⁸ Ra/ ²²⁶ Ra	²²³ Ra/ ²²⁸ Ra _{ex}
		(μmol L ⁻¹)			(dpm 100 L ⁻¹)			AR	AR	
Lafayette River										
46	16.66	4.5	0.23	2.4	36.9	3.3	24.1	69.2	2.9	0.048
47	15.87	6.5	0.23	1.9	59.8	6.5	20.4	63.3	3.1	0.106
48	15.65	6.3	0.22	2.6	64.3	9.7	20.8	70.5	3.4	0.140
49	15.13	4.4	0.22	2.5	116	8.5	39.9	140	3.5	0.062
50	14.95	3.5	0.22	2.9	151	8.3	49.5	166	3.3	0.050
51	14.91	3.5	0.22	2.4	162	16.7	25.2	90.2	3.6	0.189
Average	15.5	4.8	0.22	2.4	98.5	8.8	30.0	99.8	3.3	0.099
±	0.7	1.3	0.01	0.3	52.2	4.5	12.0	42.8	0.3	0.057

* Possible poor Ra extraction efficiency on Mn fiber; data not used in calculating Ra averages.

ranging from 3 to 10 m. Radium isotopes were processed in the same manner as the surface water samples, though lesser volumes were needed (~20 liters). The same pump and tubing were used to collect salinity, nutrient, and trace metal samples. The same bottles and storage techniques employed in the surface water samples were used for the groundwater samples.

Upon returning to the laboratory, the Mn fibers were partially dried and placed in a delayed coincidence counter for measuring ²²³Ra and ²²⁴Ra (Moore and Arnold 1996). Samples were recounted after 3 weeks to correct for supported ²²⁴Ra (via ²²⁸Th). Then, the Mn fibers were ashed at 820°C for 16 h, homogenized, and placed in counting vials (Charrette et al. 2001). The ash was placed in a well-type gamma spectrometer to measure ²²⁶Ra and ²²⁸Ra activities. Each detector was standardized using NIST (National Institute of Standards and Technology)-certified SRMs (Standard Reference Materials) sorbed to Mn fibers and prepared in the same geometry as the samples. The short-lived radium isotopes (²²³Ra, ²²⁴Ra) were decay-corrected to the time of sampling; propagated errors on these measurements were less than 10%. A suite of nutrients (NO₃⁻/NO₂⁻, NH₄⁺, PO₄³⁻, and SiO₄⁻) was quantified using a Lachat QuickChem 8000 FIA (Flow Injection Analyzer). Salinity samples were analyzed using a Guideline AutoSal salinometer.

The trace metal samples were analyzed for Cu using the isotope dilution technique developed by Wu and Boyle (1997). Briefly, samples were diluted 20-fold in 2% SeaStar nitric acid, followed by the addition of a ⁶⁵Cu-enriched isotope spike. Measurements were made using a magnetic sector inductively coupled mass spectrometer (Element1, Thermo Finnigan MAT GmbH) at low resolution (LR: $R = 300$ where $R = M/\Delta M$ at 10% peak height). To ensure that there was no blank carryover, the method included a 5-min washing with 10% HNO₃.

Results

Radium isotope activities from the main channel and four branches are presented in Table 1. In general, the highest activities were observed at the upstream end of each of the branches and the lowest activities in the main channel at the outlet to lower Chesapeake Bay. All stations were signifi-

cantly enriched in Ra relative to the open North Atlantic, where ²²⁸Ra and ²²⁶Ra average 1.5 and 8.0 dpm (disintegrations per minute) 100 L⁻¹ (Kaufman et al. 1973) and unsupported ²²³Ra and ²²⁴Ra average near zero (Moore 2000; Rasmussen 2003). The lowest average Ra activities were found in the Main Channel (²²⁴Ra, 20.7; ²²³Ra, 2.0; ²²⁶Ra, 16.4; ²²⁸Ra, 45.9; all values are dpm 100 L⁻¹), and the highest average activities were found in the Lafayette River (²²⁴Ra, 98.5; ²²³Ra, 8.8; ²²⁶Ra, 30.0; ²²⁸Ra, 99.8). The ²²⁸Ra/²²⁶Ra activity ratio (AR) ranged from an average of 2.4 in the Southern Branch to 3.3 in the Lafayette River. Dissolved inorganic nutrient concentrations from the same stations are also presented in Table 1. Levels of dissolved inorganic nitrogen (DIN = NO₃⁻/NO₂⁻ + NH₄⁺) were quite high for an enclosed estuary in late spring.

Groundwater concentrations of nutrients, trace metals, and Ra isotopes are presented in Table 2. Groundwater Ra activities were as much as 10 times more enriched relative to surface waters. The highest observed values were 278, 25, 244, and 175 dpm 100 L⁻¹ for ²²⁴Ra, ²²³Ra, ²²⁶Ra, and ²²⁸Ra, respectively. The ²²⁸Ra/²²⁶Ra AR ranged from 0.5 to 2.6 and averaged 1.3 among the nine samples. Groundwater nutrient concentrations were as much as two orders of magnitude more enriched relative to surface waters. Groundwater Cu ranged from 9.4 to 58 nmol L⁻¹, which is in the range of values reported by Montlucon and Sanudo-Wilhelmy (2001) for groundwater in a similar coastal plain setting. We measured Cu at four stations within the main channel, and Cu increased linearly with distance from 47 nmol L⁻¹ near the mouth of the estuary to 79 nmol L⁻¹ at the intersection of the southern and eastern branches. The relatively high surface water Cu concentrations are due mainly to large inputs from antifouling paints on ship's hulls, including both naval and recreational vessels (Johnson et al. 1998).

Discussion

Groundwater sources to the estuary—Groundwater Ra activities were often high despite low salinity, perhaps a result of Ra release from reduction of Mn and Fe oxides rather than cation exchange processes (e.g., Rama and Moore 1996). This is in contrast to previous studies where the highest Ra values were observed in brackish groundwater

Table 2. Dissolved nutrient and copper concentrations and radium activities in groundwater from the Elizabeth River watershed.

Station ID	Salinity	NO ³⁻ / NO ²⁻				Cu (nmol L ⁻¹)	²²⁴ Ra	²²³ Ra	²²⁶ Ra	²²⁸ Ra	²²⁸ Ra/ ²²⁶ Ra AR	²²³ Ra/ ²²⁸ Ra _{ex} AR
		NO ³⁻	NH ₄ ⁺	DIN	PO ₄ ³⁻							
GW1	0.17	745	0.5	745	0.3	39.3	213	25	244	124	0.5	0.208
GW2	16.26	BDL	74.2	74.2	15.8	20.8	57.9	2.7	21.1	54.4	2.6	0.051
GW3	0.29	28.0	137	165	2.0		21.2	1.9	17.0	13.7	0.8	0.158
GW4	10.34	0.1	11.6	11.7	21.0	23.6	228	22	131	164	1.2	0.137
GW5	0.43	BDL	101	101	1.0		52.7	9.5	87.0	44.6	0.5	0.220
GW6	0.27	0.5	79.1	79.6	3.6	9.4	27.4	0.5	16.1	33.5	2.1	0.017
GW7	1.35	BDL	205	205	2.4	41.3	39.1	2.1	46.1	42.5	0.9	0.052
GW8	2.09	BDL	393	393	5.3		278	10	116	175	1.5	0.059
GW9	1.62	BDL	182	182	17.0	57.9	92.9	3.2	47.3	74.5	1.6	0.044
Average		193	131	217	7.6	32	112	8.6	81	81	1.3	0.10
±		368	120	226	8.0	17	99	9.3	75	59	0.7	0.08

(Moore 1996; Krest et al. 2000; Charette et al. 2001). The majority of the wells were high in NH₄⁺ relative to NO₃⁻, which suggests that reducing conditions in groundwater are common in this area. Since Ra has a high affinity for Mn oxides, the release of Mn and associated Ra in reducing groundwater may partially explain the observed high Ra activities at low salinity. Similarly, the strong relationship between P and Fe oxides (e.g., Charette and Sholkovitz 2002) may explain the relatively high DIP concentration in groundwater.

The enrichment of uranium relative to thorium in calcium carbonate (e.g., limestone) provides a mechanism whereby the sources of radium in aquifers abundant with this material can be distinguished. This is because ²²⁶Ra and ²²³Ra are U series daughters and ²²⁸Ra and ²²⁴Ra are ²³²Th series daughters. The occurrence of low ²²⁸Ra/²²⁶Ra ARs in several groundwater samples, often significantly less than the average crustal AR of 1 (Table 2; GW1, GW3, GW5, GW7), suggests that it was in contact with aquifer solids enriched in uranium relative to thorium. Also, whereas there is only a weak correlation between groundwater ²²⁸Ra and ²²⁶Ra, both the thorium-derived Ra isotopes (²²⁴Ra and ²²⁸Ra) and the uranium-derived Ra isotopes (²²³Ra and ²²⁶Ra) are highly correlated (Fig. 2). These results are consistent with Meng and Harsh (1988), who characterized the Yorktown aquifer as abundant in carbonaceous material, leaky, and therefore likely hydraulically connected to surface waters via the shallow unconfined Columbia aquifer.

The low groundwater ²²⁸Ra/²²⁶Ra ARs (0.5–2.6) relative to that observed in the surface waters (2.4–3.3) of the Elizabeth River system suggest that the Yorktown aquifer was not the sole source of Ra to the estuary. Tidally driven input from the coastal ocean is another possibility, however; ²²⁸Ra/²²⁶Ra ARs on the Mid-Atlantic Bight shelf are always <2 and typically <1 (Rasmussen 2003). Therefore, we infer that the groundwater we sampled was not the only groundwater source to the estuary. As the undeveloped portions of the estuary are characterized by salt marshes, it is likely the groundwater in these areas is enriched in Ra, in particular ²²⁸Ra relative to ²²⁶Ra (Rama and Moore 1996; Krest et al. 2000; Charette unpubl. data). Rama and Moore (1996) reported marsh groundwater Ra activities of 100 and 1,000

dpm 100 L⁻¹ for ²²⁶Ra and ²²⁸Ra, respectively (²²⁸Ra/²²⁶Ra AR = 10). Krest et al. (2000) observed Ra activities of 80–110 dpm 100 L⁻¹ (²²⁶Ra) and 590–860 dpm 100 L⁻¹ (²²⁸Ra), which translates to ²²⁸Ra/²²⁶Ra ARs of 7.3–7.8. In Rhode Island and Massachusetts salt marshes, the Ra activities were similarly high, with ²²⁸Ra/²²⁶Ra ARs often exceeding ~15 (Charette unpubl. data).

Because two endmembers, groundwater and coastal ocean, do not explain the given high surface water ²²⁸Ra/²²⁶Ra ARs, we assume there was a third source in marsh groundwater influencing Ra activities in the Elizabeth estuary. We therefore attempt to quantify their relative importance with a three-endmember mixing model (Fig. 3). The first endmember is coastal ocean (*co*) seawater, which is introduced to the estuary through tidal mixing. The second endmember is the semiconfined Yorktown aquifer (*yk*), which is characterized by low ²²⁸Ra/²²⁶Ra ARs due to U-enriched aquifer solids. The last endmember is the surficial aquifer (*marsh*), which we assume is the Columbia aquifer driving groundwater flow through the salt marsh sediments. The following three equations,

$$f_{co} + f_{marsh} + f_{yk} = 1 \quad (1)$$

$$\begin{aligned} {}^{228}\text{Ra}_{co} \times f_{co} + {}^{228}\text{Ra}_{marsh} \times f_{marsh} \\ + {}^{228}\text{Ra}_{yk} \times f_{yk} = {}^{228}\text{Ra}_{surf} \end{aligned} \quad (2)$$

$$\begin{aligned} {}^{226}\text{Ra}_{co} \times f_{co} + {}^{226}\text{Ra}_{marsh} \times f_{marsh} \\ + {}^{226}\text{Ra}_{yk} \times f_{yk} = {}^{226}\text{Ra}_{surf} \end{aligned} \quad (3)$$

containing three unknowns (f_{co} , f_{marsh} , f_{yk}), are linear and can therefore be solved by substitution. The terms f_{co} , f_{marsh} , and f_{yk} are the fractions of water derived from the coastal ocean, salt marsh groundwater, and Yorktown aquifer, respectively, in a given sample. The endmember Ra activities are indicated by the subscripts, and ²²⁸Ra_{surf} and ²²⁶Ra_{surf} are the activities in the surface water (*surf*) sample of interest. The endmember activities we used were as follows (all units are dpm 100 L⁻¹): ²²⁸Ra_{co} = 16 and ²²⁶Ra_{co} = 8 (Rasmussen 2003), ²²⁸Ra_{marsh} = 1,000 and ²²⁶Ra_{marsh} = 100 (Rama and Moore 1996), and ²²⁸Ra_{yk} = 125 and ²²⁶Ra_{yk} = 250 (Table 2, GW1). The coastal ocean endmember was chosen as a

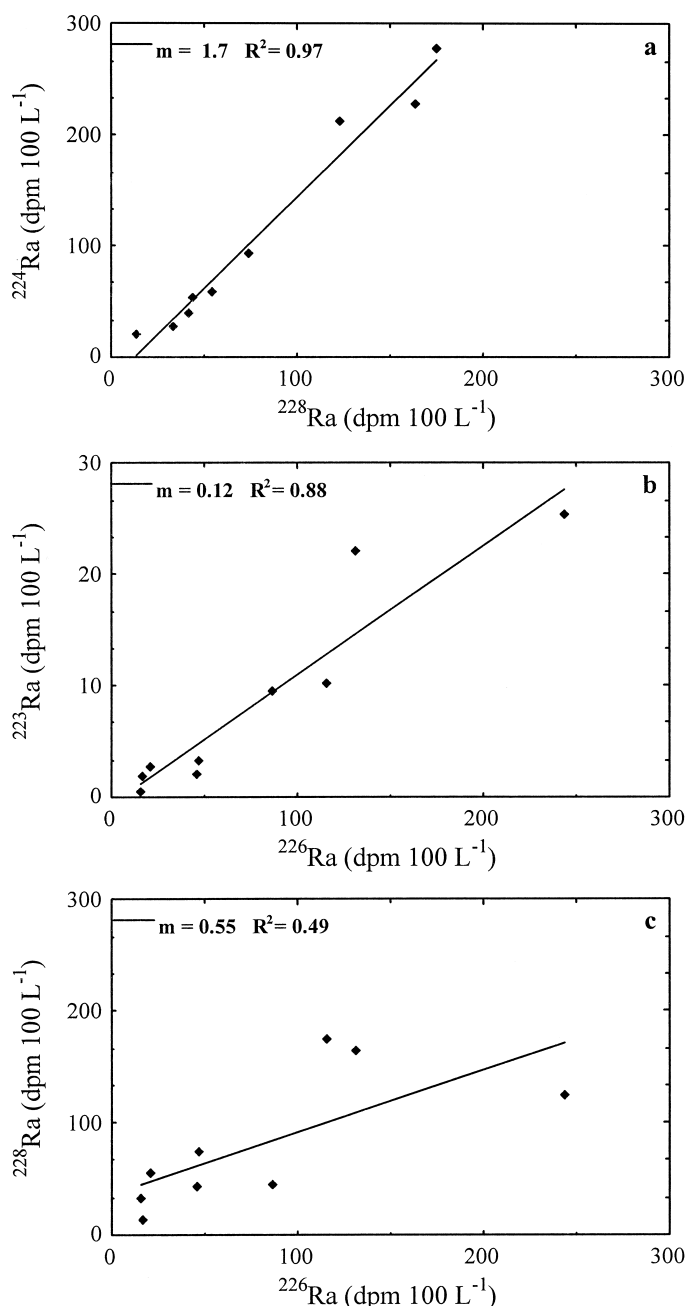


Fig. 2. Radium isotope relationships in groundwater from the Elizabeth River watershed: (a) ^{224}Ra and ^{228}Ra , (b) ^{223}Ra and ^{226}Ra , and (c) ^{228}Ra and ^{226}Ra .

station near the mouth of Chesapeake Bay in Rasmussen (2003). The Yorktown aquifer Ra endmember was chosen as the sample with both the highest ^{226}Ra activity and lowest $^{228}\text{Ra}/^{226}\text{Ra}$ AR (0.5). This sample also has the lowest salinity. Finally, by using upper limit estimates of Ra activity for the two groundwater endmembers (as opposed to the averages), we are calculating a conservative, lower limit estimate of the groundwater input to the estuary.

As would be expected, the locations most influenced by groundwater had the highest Ra activities (Table 3). These include the Lafayette River and the Western Branch, where

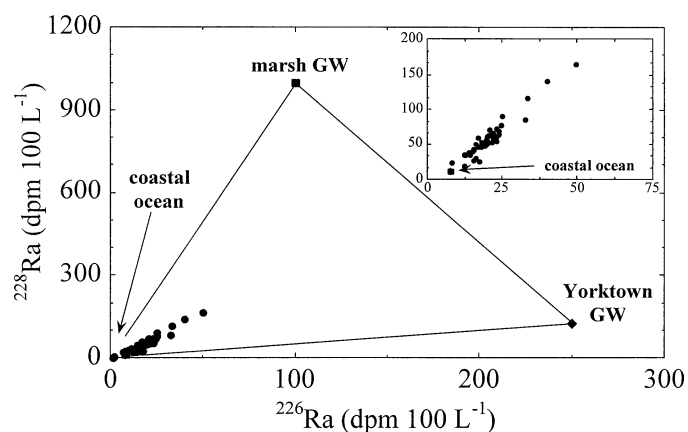


Fig. 3. Surface water ^{228}Ra and ^{226}Ra for all stations including Ra activities used for the three-endmember mixing model. The inset graph illustrates the surface water data only.

the sum of the average groundwater fractions ($f_{\text{marsh}} + f_{\text{yk}}$) was 14% and 9%, respectively. The Main Channel stations were the least influenced by groundwater Ra sources ($f_{\text{marsh}} + f_{\text{yk}} = 5\%$). Model results also indicate that the marsh groundwater and Yorktown aquifer sources of Ra to the estuary were about equally important. The contribution of Ra from the marsh groundwater was at most ~ 10 – 20% greater than the Yorktown aquifer source. The $\sim 50\%$ surficial/deep aquifer flux of Ra to the Elizabeth River system is consistent with the results of Crotwell and Moore (pers. comm.), who performed a similar study for the Port Royal Sound system in South Carolina.

Since this model relies on assumed Ra activities for the marsh endmember, we tested the sensitivity of the mixing model to variation in the $^{228}\text{Ra}/^{226}\text{Ra}$ AR ranging from 7.5 to 15 (with the ^{226}Ra activity fixed at $100 \text{ dpm } 100 \text{ L}^{-1}$); these ARs encompass the range of literature values mentioned earlier. For the surface water Ra activities, we used the average of the entire data set. Figure 4 presents the marsh groundwater contribution as a fraction of the total for the stated range in ARs. As the $^{228}\text{Ra}/^{226}\text{Ra}$ AR decreases below 10, the marsh groundwater becomes a greater source of SGD to the estuary—63% of the total. Conversely, as the AR increases from 10 to 15, the Yorktown aquifer becomes the major source of SGD, with a marsh groundwater fraction of $\sim 38\%$. Though the model is most sensitive to lower marsh groundwater $^{228}\text{Ra}/^{226}\text{Ra}$ ARs, the difference in these activity ratios only changes the fraction of marsh groundwater Ra flux by $\pm 13\%$ of the total.

Calculating groundwater fluxes using radium isotopes—If we assume that groundwater and tidal exchange with the coastal ocean are the dominant sources of Ra in our study area (Rama and Moore 1996; Moore 1997; Hussain et al. 1999; Krest et al. 2000; Charette et al. 2001; Scott and Moran 2001), we can apply our three-endmember mixing model in calculating the groundwater flux for each portion of the Elizabeth River (at steady state):

$$\text{SGD} = [(f_{\text{marsh}} + f_{\text{yk}}) \times V_{\text{sw}}]/T_w \quad (4)$$

where $(f_{\text{marsh}} + f_{\text{yk}})$ is the sum of the groundwater fractions

Table 3. Three end member mixing model for the Elizabeth estuary and its tributaries.

Station ID	f_{co}	f_{marsh}	f_{yk}
Main Channel			
1	0.97	0.02	0.01
2	0.96	0.02	0.02
3	0.96	0.02	0.02
4	0.95	0.03	0.03
5	0.95	0.02	0.02
6	0.95	0.03	0.02
7	0.95	0.03	0.03
8	0.95	0.03	0.03
9	0.91	0.04	0.05
10	0.94	0.03	0.03
11	0.94	0.03	0.03
12	0.94	0.03	0.03
16	0.94	0.03	0.03
17	0.93	0.04	0.03
58	0.96	0.02	0.02
59	0.94	0.04	0.02
60	0.95	0.03	0.02
61	0.97	0.02	0.01
62	0.96	0.02	0.02
Average	0.95	0.03	0.02
±	0.01	0.01	0.01
Southern Branch			
13	0.93	0.03	0.04
14	0.92	0.03	0.05
15	0.93	0.03	0.04
30	0.86	0.06	0.08
31	0.94	0.03	0.04
32	0.92	0.03	0.04
33	0.84	0.09	0.07
34	0.96	0.01	0.03
35	0.97	0.01	0.03
36	0.98	0.00	0.02
37	0.96	0.00	0.04
Average	0.93	0.03	0.04
±	0.04	0.03	0.02
Western Branch			
18	0.93	0.03	0.04
19	0.92	0.04	0.04
20	0.92	0.04	0.04
21	0.91	0.05	0.04
22	0.91	0.05	0.04
23	0.90	0.06	0.05
Average	0.91	0.05	0.04
±	0.01	0.01	0.00
Eastern Branch			
24	0.91	0.04	0.05
25	0.94	0.03	0.03
26	0.93	0.04	0.03
27	0.93	0.04	0.04
28*	0.99	0.01	0.00
29	0.93	0.04	0.03
Average	0.93	0.04	0.04
±	0.01	0.01	0.01

Table 3. Continued.

Station ID	f_{co}	f_{marsh}	f_{yk}
Lafayette River			
46	0.90	0.05	0.05
47	0.92	0.04	0.03
48	0.92	0.05	0.03
49	0.80	0.12	0.09
50	0.74	0.14	0.12
51	0.89	0.07	0.04
Average	0.86	0.08	0.06
±	0.07	0.04	0.03

* Possible poor Ra extraction efficiency on Mn fiber; data not used in calculating averages.

from Table 3, V_{sw} is the water volume of the region of interest (in cubic meters), T_w is the water residence time (in days), and SGD is groundwater flux (in cubic meters per day).

The water residence time is an important term in Eq. 4, and we calculated it using a method based on decay of the short-lived ^{223}Ra ($t_{1/2} = 11.4$ d) as it mixes through the estuary (Charette et al. 2001). In order to correct for mixing effects, the short-lived Ra isotope is normalized to one of its long-lived counterparts, in this case ^{228}Ra , and solved for T_w via the decay law:

$$\left(\frac{^{223}\text{Ra}_{ex}}{^{228}\text{Ra}_{ex}}\right)_{surf} = \left(\frac{^{223}\text{Ra}}{^{228}\text{Ra}}\right)_i \times e^{-\lambda_{223}T_w} \quad (5)$$

where $\left(\frac{^{223}\text{Ra}}{^{228}\text{Ra}}\right)_i$ is the activity ratio of the endmember groundwater, $\left(\frac{^{223}\text{Ra}_{ex}}{^{228}\text{Ra}_{ex}}\right)_{surf}$ is the average AR in the region of interest, and λ_{223} is the decay constant for ^{223}Ra . Since the open ocean contains measurable activities of ^{228}Ra (but not $^{223}\text{Ra}_{ex}$), we normalize the short-lived isotope to $^{228}\text{Ra}_{ex}$, which is simply the observed ^{228}Ra activity minus the open (Atlantic) ocean endmember (we use 1.5 dpm 100 L $^{-1}$; Kaufman et al. 1973). The main assumptions with this approach are that the endmember AR is at steady state and that there are minimal inputs of these isotopes other than

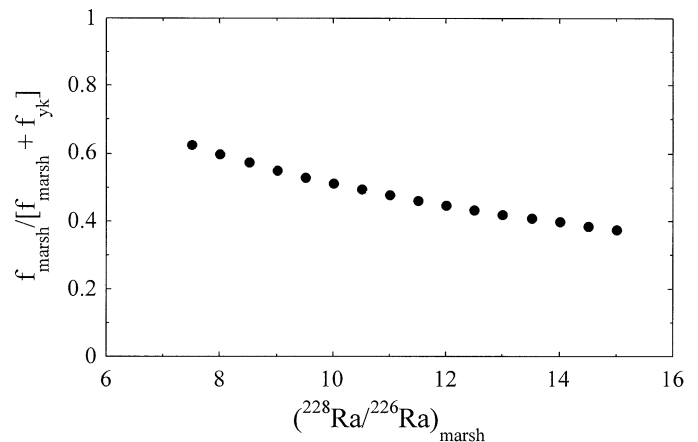


Fig. 4. The fraction of Ra derived from the marsh groundwater relative to the Yorktown aquifer as a function of the marsh groundwater $^{228}\text{Ra}/^{226}\text{Ra}$ activity ratio. The Yorktown aquifer $^{228}\text{Ra}/^{226}\text{Ra}$ activity ratio is held constant at 0.5.

Table 4. Radium-derived submarine groundwater discharge rates for branches of the Elizabeth estuary.

Branch	Volume (10^6 m^3) [a]	Surface area (10^6 m^2) [b]	Residence time (d) [c]	f_{marsh} [d]	f_{yk} [e]	SGD ($10^3 \text{ m}^3 \text{ d}^{-1}$) [f] = [(d + e) × (a)]/c	SGD (cm d^{-1}) [g] = f/b
Main Channel	136	20.3	20	0.03	0.02	360	1.8
Southern Branch	37.5	8.87	16	0.03	0.04	170	1.9
Western Branch	11.7	6.19	5.9	0.05	0.04	170	2.8
Eastern Branch	11.7	5.89	8.6	0.04	0.04	100	1.7
Lafayette River	9.50	6.18	6.7	0.08	0.06	200	3.2

from SGD. If other sources were important, such as diffusion from the sediments, our T_w would represent a lower limit estimate. Since we have assumed there exists a second source of groundwater to the system, our average groundwater ($^{223}\text{Ra}/^{228}\text{Ra}_{\text{ex}})_i$ of 0.10 (Table 2) is weighted toward the deeper aquifer and therefore introduces uncertainty to the T_w estimates. For a surficial aquifer system, Charette et al. (2001) measured an average ($^{223}\text{Ra}/^{228}\text{Ra}_{\text{ex}})_i$ of 0.20. Therefore, we will use the mean of the two estimates (0.15) in our T_w calculation.

We calculated the average T_w for the main channel of the Elizabeth River and its four branches. The average water residence time for the subestuaries of the Elizabeth River ranged from a minimum of 5.9 d in the Western Branch to a maximum of ~ 20 d in the main channel (Table 4). In general, T_w increased with increasing estuary volume. The long T_w for the main channel is consistent with the fact that tidal flushing is minimal in this estuary (Nichols and Howard-Strobel 1991). In addition, the long T_w and contaminant inputs from industrial activity have combined to make this one of the more contaminated estuaries in the world (Rule 1986; Bender et al. 1988; Mitra et al. 1999; Diaz et al. 2003).

Using the T_w estimates and the three-endmember mixing model for radium input, we calculated SGD rates for each of the branches of the estuary (Eq. 4; Table 4). The greatest uncertainty in the Ra-derived SGD estimate is the uncertainty on the endmember activities, which is dictated by our assumed marsh groundwater AR. SGD in general scaled with the estuary volume, ranging from $100,000 \text{ m}^3 \text{ d}^{-1}$ in the Eastern Branch to $360,000 \text{ m}^3 \text{ d}^{-1}$ in the main channel (Table 4). The one exception was the Lafayette River, which had the highest SGD ($200,000 \text{ m}^3 \text{ d}^{-1}$) of the four branches, driven mainly by the large excess Ra activities we observed there. In order to compare these rates with other local studies, we normalized the SGD rates according to the surface area of each estuary (Table 4). In these units, the SGD ranged from 1.7 cm d^{-1} for the Eastern Branch to 3.2 cm

d^{-1} for the Lafayette River. In a tidal estuary on Virginia's Eastern Shore, Robinson et al. (1998) observed SGD rates of $1.2\text{--}7.9 \text{ cm d}^{-1}$ using seepage meters. Using a similar approach in the same region, Reay et al. (1992) reported a range of $0.1\text{--}8.8 \text{ cm d}^{-1}$. Schwartz (2003) estimated a SGD range of $5\text{--}10 \text{ cm d}^{-1}$ for the Delaware estuary, where the groundwater is derived from a coastal plain aquifer similar to our study site. In normalizing our rates to surface area, we are assuming that SGD equally distributed over the entire estuary. In reality, it is likely that discharge occurs mostly along the boundaries. Therefore, our results are in good agreement with the seepage meter-based estimates considering that they would likely be somewhat higher if we knew the effective surface area of seepage.

Hussain et al. (1999), using an approach based on ^{222}Rn , estimated an SGD rate for the entire Chesapeake Bay system of $17 \times 10^6 \text{ m}^3 \text{ d}^{-1}$. Given the sum of our estimates ($\sim 1 \times 10^6 \text{ m}^3 \text{ d}^{-1}$), the Elizabeth estuary is $\sim 6\%$ of that value (Table 5). In comparison with the James River, a major source of freshwater to the lower Chesapeake Bay, Elizabeth River SGD makes up a similar fraction ($\sim 5\%$). Burnett et al. (2001) reviewed global SGD in relation to riverine discharge and concluded that many of the estimates were in the range of $5\text{--}10\%$ SGD: river discharge, which is consistent with our findings for the Elizabeth estuary.

Groundwater-derived nutrient and trace metal fluxes— Given our Ra-derived estimate of SGD, we can estimate the groundwater-derived input of nutrients and trace metals to the Elizabeth estuary (Table 6). Based on the average groundwater concentrations in Table 2, SGD accounted for $4.5 \text{ mmol m}^{-2} \text{ d}^{-1}$ of DIN and $0.16 \text{ mmol m}^{-2} \text{ d}^{-1}$ of DIP. Using the Reay and Simmons (1992) average groundwater DIN of $500 \mu\text{mol L}^{-1}$ for this region, which is an average of many hundreds of measurements, our DIN flux would be a factor of ~ 2 higher. For a South Carolina salt marsh, Krest et al. (2000) reported similar fluxes, with SGD supplying 2.4

Table 5. SGD rates for the Elizabeth estuary compared with other water flux estimates for the Chesapeake Bay region.

	Water flux ($10^6 \text{ m}^3 \text{ d}^{-1}$)	Fraction of Chesapeake rivers	Source
Elizabeth River SGD	1.0 ± 0.1	0.6%	This study
Chesapeake Bay SGD	17	10%	Hussain et al. (1999)
James River	20	12%	Johnson et al. (1998)
Chesapeake Bay rivers	170	—	Hussain et al. (1999)

Table 6. SGD-derived nutrient and Cu fluxes to the Elizabeth estuary.

	Avg GW concentration (mmol m ⁻³)	Flux (mol d ⁻¹)	Flux (kg yr ⁻¹)	Flux (mmol m ⁻² d ⁻¹)
DIN	217	2.1×10 ⁵	1.1×10 ⁶	4.5±4.6
SRP	7.6	7.4×10 ³	8.5×10 ⁴	0.16±0.17
Cu	0.032	32	7.3×10 ²	(6.7±3.6)×10 ⁻⁴

mmol m⁻² d⁻¹ of DIN and 0.9 mmol m⁻² d⁻¹ of DIP. Given the entire Chesapeake Bay N- and P-loading estimates (from all sources) of ~150 and 8 × 10⁶ kg yr⁻¹ and a surface area for the bay of 11.4 × 10⁹ m², the aerially averaged N and P inputs are 2.6 and 0.06 mmol m⁻² d⁻¹, respectively (Chesapeake Bay Program 1999). Thus, the area-adjusted SGD-derived N and P loading estimates for the Elizabeth estuary are comparable to the average for the entire Chesapeake Bay.

The cycling of Cu in the Elizabeth River is of particular importance, given the presence of U.S. Naval operations in the estuary. Johnson et al. (1998) reported total Cu inputs of ~26,000 kg yr⁻¹, with Navy hull leachate representing nearly half of the total. However, they noted in their report that SGD may be an important but unconstrained source of Cu to the estuary. Using an average groundwater Cu concentration of 32 nmol L⁻¹ (Table 2), we estimate that ~730 kg yr⁻¹ (Table 6) may be derived from SGD. Using the highest observed groundwater Cu concentration (58 nmol L⁻¹), this estimate would increase by a factor of ~2. It is important to note that, though we analyzed only a limited number of groundwater samples for Cu, the variability was quite low relative to DIN and DIP. Thus, we have confidence that the inclusion of an SGD component to the Johnson et al. (1998) Cu budget would increase the annual input by ~3–6% at most.

These estimates are similar to those reported by Montlucón and Sanudo-Wilhelmy (2001), who estimated an SGD-derived Cu flux of 120–1,200 kg yr⁻¹ for Flanders Bay, New York, an estuary similar in size to the Elizabeth estuary. However, in contrast with our study site, SGD supplied as much as 60% of the total Cu inputs to the Flanders Bay, the major difference being a lack of leaching from antifouling paints associated with naval operations. Though SGD may not be the dominant source of Cu to the estuary, it is likely significant in comparison with other benthic-derived sources. Donat and Burdige (2001) estimated the diffusive input of Cu from sediments at two stations within the contaminated portion of the estuary's main channel. Their fluxes ranged from 12 nmol m⁻² d⁻¹ at a station near Hampton Roads to 6,500 nmol m⁻² d⁻¹ at a more contaminated location further upstream. In comparison, when normalized to the area of the entire estuary, the SGD-derived Cu flux is 670 nmol m⁻² d⁻¹. That these two estimates are of the same order of magnitude highlights the importance of considering advective inputs of trace metals through permeable sediments (as derived from SGD) as well as diffusive inputs from fine-grained, less permeable sediments in coastal areas.

We used naturally occurring Ra isotopes to examine SGD

and associated elemental fluxes in an urban estuarine setting. Ratios of the long-lived ²²⁶Ra and ²²⁸Ra provided insight into the sources of groundwater to the estuary, specifically that the surface (marsh) aquifer and deep aquifer Ra signatures were equally imparted to surface waters. Radium activities were high in fresh groundwater, likely as a result of redox processes, suggesting that Ra may be partially tracing the freshwater component of SGD as well brackish groundwater in this region. The Ra-derived SGD estimates were low in comparison with a major local (James River) surface runoff. However, groundwater nutrient concentrations were often highly enriched relative to surface waters, making SGD an important component of the DIN and DIP budgets for the Elizabeth estuary. In contrast, SGD was a relatively small source of Cu given that surface water inputs, such as anti-fouling paints associated with naval operations, are a major component of the Cu budget for this system.

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