Submarine groundwater discharge and alkaline earth element dynamics in a deltaic coastal setting

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ABSTRACT

Submarine groundwater discharge is a process that is often considered negligible in deltaic systems given their low gradient and fine-grained sediment. However, hydrologic budgets and radon surveys indicate that it may be a significant component of the Mississippi River Delta system. To more concretely indicate groundwater's contribution to the local environment, we conducted an analysis of estuarine water chemistry. We focused on the mid-weight alkaline earth metals, which differ significantly in the system's three end-members: river, ocean, and groundwater. We found an anomaly of barium in the estuaries, which could not be completely explained by desorption. Through the construction of a three-end-member mixing model, groundwater was estimated to comprise 14–28% of Terrebonne and Barataria Bay estuarine water, which corresponds to a combined discharge of 160–480 m^3/s. This groundwater discharge helps explain the hydrologic budget of the system, and could influence the chemistry of these large deltaic estuaries.

Key words | barium, deltas, groundwater, mixing ratio, sorption

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INTRODUCTION

Deltas are ecologically and economically important environments. The habitats they support are some of the most productive ecosystems in the world and provide a multitude of ecosystem services such as storm protection, food production, and nursery habitat for commercially important species (Barbier *et al.* 2011; Kirwan & Megonigal 2013). Their high productivity supports industry and major population centers (Day *et al.* 2007; Syvitski & Saito 2007). Despite their importance, our understanding of the processes governing water flow in deltaic systems is still lacking. For example, hydrologic budgets of the lower Mississippi River Delta (MRD) point to a large flow of water, about 1,000 m^3/s, that is lost from the river and a corresponding inflow of freshwater to the coastal bays (Allison *et al.* 2012; Kolker *et al.* 2013). One proposed explanation for this 'missing water' in deltaic environments is extensive submarine groundwater discharge or SGD (Kolker *et al.* 2013).

Because groundwater can be a major part of a delta's hydrologic budget, it is no surprise that it can have a significant influence on the local ecosystem. The salinity of groundwater, for example, has been shown to play a major role in determining local floral and faunal species (Johannes 1980; Shapouri *et al.* 2016). Additionally, SGD can play a major role in nutrient cycling, such as acting as an external source of nitrate (Johannes 1980). In a similar fashion, SGD has been shown to be a source of various toxins and pollutants, such as arsenic in the Ganges-Brahmaputra Delta (Sankar *et al.* 2014). Typically, however, SGD is often overlooked in deltaic systems because of their high clay content, but groundwater flowing through sandy, buried paleochannels could have a significant influence on the coastal ecosystem (Kolker *et al.* 2013). There have been a few studies that address submarine groundwater in deltas, with some arguing that groundwater is negligible (McCoy *et al.* 2007) and others that support substantial SGD (Moore & Krest 2004; Kolker *et al.* 2013; Joung & Shiller 2014). The implications of this controversy are profound;

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the volume of freshwater that is hypothesized to flow from the Mississippi River to the coastal zone has the potential to substantially alter our understanding of the ecology and biogeochemistry of North America's largest delta, and potentially, deltas in general.

Chemical tracers are often used to track the sources (see Currell *et al.* 2013) and fate (see Peterson *et al.* 2008) of groundwater. For example, groundwater is often enriched in alkaline earth metals including strontium, barium, and radium, which allows these elements to be used to trace and quantify the magnitude of SGD (Cable *et al.* 1996; Shaw *et al.* 1998; Moore & Krest 2004; Négrel *et al.* 2004; Dimova *et al.* 2013). However, such analyses must be analyzed with care as these elements can desorb from sediments' particles with the transition from freshwater to estuarine environments (Hanor & Chan 1977; Li & Chan 1979). The goal of this study was to quantify the contribution of SGD to an estuary using mid-weight alkaline earth elements. By analyzing groundwater-tracer alkaline earth metals (strontium and barium) and alkaline earth metals abundant in marine waters (magnesium and calcium), we can define a chemical signature for different water types. From this, we can create a mixing model, which incorporates desorption, to determine the proportion of each end-member water type (river water, seawater, groundwater) that would be required to produce the observed chemical signature of estuarine water.

We conducted our study in the MRD in southeastern Louisiana, USA, which houses the seventh largest river on earth by discharge: approximately 530 km^3 of freshwater to the world's oceans every year (McKee *et al.* 2004). Specifically, we focused on Barataria and Terrebonne Bays, which feature nearly 5,700 km^2 of marsh (Couvillion *et al.* 2011). The importance of SGD has been debated for this region (Moore & Krest 2004; McCoy *et al.* 2007; Kolker *et al.* 2013). We tested the hypothesis that all mid-weight alkaline earth metals would behave similarly in the MRD; any differences between these metals are likely indicative of differential sources.

METHODS

This study was conducted in Barataria and Terrebonne Bays, two of the largest interdistributary bays of the MRD, and the adjacent offshore regions (Figure 1) during the early summer, which is typically hot and wet, of 2013. Barataria Bay has almost no surface freshwater inputs, while Terrebonne Bay has moderate freshwater inputs from the Atchafalaya River and Intercoastal Waterway, which enter from the west. These systems are both shallow (~2 m typical depth), and have an average tidal range of about 30 cm. For all water sampling, we avoided collecting immediately following large rain events to limit dilution effects. We collected the estuary samples in June near *Spartina alterniflora*-dominated salt marshes in the northern portions of Barataria and Terrebonne Bay by small boat (Figure 1(a)). The river samples were collected in May from the main stem of the Mississippi River during average high discharge. The ocean samples were collected in June from a CTD rosette from the R/V Pelican. We used a YSI water quality probe to measure salinity of these samples. To obtain groundwater samples, we extracted pore waters from sediment cores taken in June from the Lac Des Allemandes region, which is in the northern part of the Barataria basin (Figure 1(b)). Sediment from approximately 4 m deep was centrifuged to obtain samples. Owing to the small volume of water, we used a refractometer to measure salinity in the groundwater samples.

After the water was collected, it was taken back to the laboratory and frozen until processing. For all water types except for river samples, processing consisted of creating solutions of a 0.5 mL water sample and a 9.5 mL 2% nitric acid solution. The river samples were diluted by a factor of 5.6 to 6.7 based on mass of the sample as opposed to the 1:20 volume dilution of the other water samples, and this difference was adjusted for in the calculations. We analyzed the samples with an inductively coupled plasma mass spectrometer (ICP-MS) with the focus elements being the mid-weight alkaline earth metals: Mg, Ca, Sr, and Ba. To address whether ions mixed conservatively, we plotted the molality of each alkaline earth metal against the salinity.

RESULTS

Generally, the different water types had non-overlapping ranges for each element with the exception of Ca in groundwater samples (2.08–5.99 mmol/kg) and estuarine samples

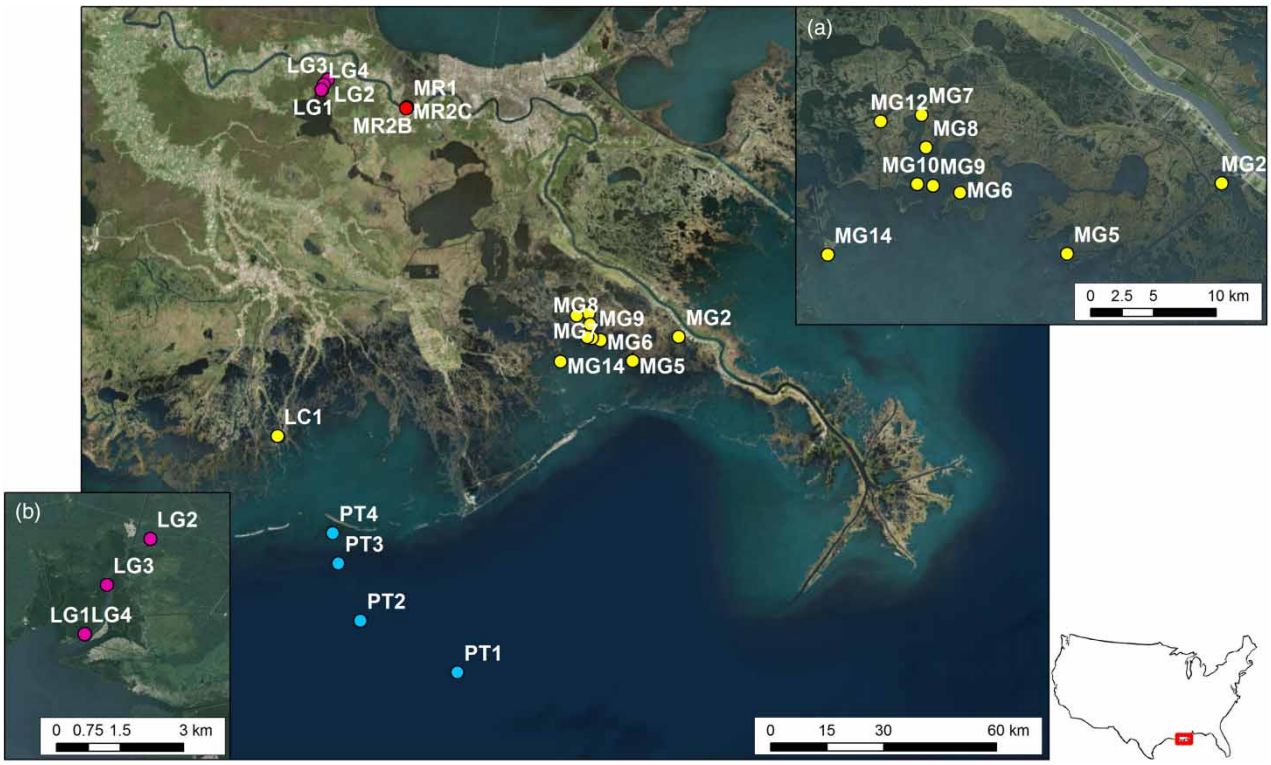

Figure 1 | Site map where river water sites are designated MR, ocean sites are designated PT, groundwater sites are designated LG, and estuary sites are designated MG and LC. Inserts show more detailed distribution of (a) Barataria estuary sites and (b) groundwater sites. Bottom right shows location of study site with respect to USA in the box.

(2.74–6.21 mmol/kg; Table 1). The system-wide average ($\pm 1\sigma$) Mg concentration was 25.3 ± 35.0 mmol/kg, with a maximum in seawater (114 mmol/kg), and a minimum in river water (0.266 mmol/kg; Table 1). Ca ranged from a maximum of 22.9 mmol/kg for seawater to a minimum of 0.312 mmol/kg for a river sample (Table 1), with a system-wide average of 6.19 ± 6.74 mmol/kg. The maximum Sr concentration was 213 μmol/kg in a seawater sample and the minimum was 0.845 μmol/kg in a river sample (Table 1), with a system-wide average of 49.3 ± 63.9 μmol/kg. Finally, Ba ranged from 7.14 μmol/kg in a groundwater sample to 0.132 μmol/kg in a river sample (Table 1), with a system-wide average of 1.81 ± 1.72 μmol/kg.

As salinity increased, Sr, Mg, and Ca all increased in a linear fashion with a strong correlation ($R^2 > 0.95$, $p < 0.01$; Figure 2). Barium, on the other hand, did not show a correlation with salinity ($R^2 = 0.102$, $p > 0.10$) and instead showed definite clustering of the types of water (Figure 2). Mid-salinity waters had concentrations of Ba higher than either the river or ocean waters.

DISCUSSION

In this study, Mg, Ca, and Sr all showed a positive, conservative relationship with salinity, suggesting that the primary source of these elements was seawater. On the other hand, Ba appears to not show a conservative relationship with salinity in the surface waters. For conservative mixing along a salinity gradient, the points would ideally fall along a straight line, similar to Mg, Ca, and Sr trends (Figure 2). However, when looking at surface waters only, Ba shows a concave downward curve with mid-salinities having higher concentrations than low or high salinities. Furthermore, the overall trend indicates that seawater is a sink, rather than a source of Ba, which is to be expected given the low concentration of Ba in seawater. The concavity in the Ba curve is likely explained by either sorptive/precipitation processes or SGD. In the former, Ba is predicted to desorb from particles at low/mid-salinities (Hanor & Chan 1977; Coffey *et al.* 1997 and references therein) and precipitate in seawater. This would cause a

Table 1 | The raw data for all water samples, with average values shown in bold

	ID	Latitude	Longitude	Depth (m)	Salinity (‰)	Mg (mmol/kg)	Ca (mmol/kg)	Sr (μmol/kg)	Ba (μmol/kg)
River	MR1	29 56′18″	90 21′17″	22.1	0.0	0.281	0.332	0.884	0.131
	MR2A	29 56′10″	90 21′22″	0.0	0.0	0.279	0.331	0.893	0.137
	MR2B	29 56′10″	90 21′22″	13.7	0.0	0.274	0.323	0.867	0.128
	MR2C	29 56′10″	90 21′22″	24.7	0.0	0.266	0.313	0.849	0.133
Average					**0.0**	**0.275**	**0.325**	**0.873**	**0.132**
Ocean	PT1	28 45′36″	90 14′01″	0.0	19.0	66.395	13.954	126.985	0.961
	PT2	28 52′06″	90 27′57″	16.5	35.8	114.266	23.051	212.899	0.472
	PT3	28 59′18″	90 31′06″	7.5	35.0	112.998	22.903	207.071	0.419
	PT4	29 03′06″	90 31′54″	3.0	21.7	79.251	16.442	145.145	0.804
Average					**27.87**	**93.227**	**19.088**	**173.025**	**0.664**
Groundwater	LG1	29 58′27″	90 33′29″	4	2.0	7.511	5.997	21.246	4.902
	LG2	29 59′40″	90 32′39″	4	1.0	5.483	5.996	21.009	7.145
	LG3	29 59′05″	90 33′12″	4	0.0	2.697	2.090	8.204	4.235
	LG4	29 58′27″	90 33′29″	4	0.0	3.826	3.147	8.185	2.709
Average					**0.75**	**4.879**	**4.307**	**14.661**	**4.748**
Estuary	MG2	29 27′40″	89 42′16″	0.0	7.45	27.373	6.229	53.349	2.182
	MG5	29 24′37″	89 48′56″	0.0	5.47	20.293	4.978	40.653	1.797
	MG6	29 27′15″	89 53′32″	0.0	3.75	13.868	3.563	28.341	1.529
	MG7	29 30′37″	89 55′11″	0.0	3.89	13.630	3.587	27.948	1.675
	MG8	29 29′12″	89 55′00″	0.0	3.92	14.212	3.840	28.646	1.736
	MG9	29 27′33″	89 54′42″	0.0	3.34	11.957	3.216	25.168	1.698
	MG10	29 27′37″	89 55′23″	0.0	3.00	10.171	2.754	21.634	1.456
	MG12	29 30′19″	89 56′58″	0.0	2.59	9.579	2.826	19.438	1.905
	MG14	29 24′34″	89 59′14″	0.0	8.46	32.407	7.174	63.182	1.582
	LC1	29 15′14″	90 39′50″	0.0	1.35	10.038	3.249	21.077	1.954
Average					**4.3**	**16.353**	**4.141**	**32.944**	**1.751**

rise in Ba after the salinity rises above fresh, followed by a decline in Ba after some threshold salinity. In the latter, the advective flux of SGD is predicted to transport sedimentary Ba into the estuary. A possible Ba pattern is highest concentrations in the groundwater, intermediate in the region experiencing SGD (e.g., the estuary), and lower in the other water types. Either explanation could, in theory, explain the distinctive curve we observed for Ba, so we examined both via an analysis of the data.

Desorption

To address the issue of desorption, we compared our results to Hanor & Chan (1977). By determining the amount of Ba caused by desorption in their study, we were able to determine the amount of excess Ba found that is not explainable by desorption. First we determined the amount of excess Ba Hanor & Chan (1977) found that was above the line of conservative mixing. At the peak of their Ba curve, they observed a cluster of 75 μg/l of dissolved Ba which ranged in concentration of dissolved chloride from about 5 to 10 g/L. If Ba followed the line of conservative mixing from their river samples to their gulf samples, which has a negative slope, then a concentration of about 45 μg/L of dissolved Ba would be expected, meaning an excess Ba of roughly 30 μg/L (Equation (1)):

$$Ba_{observed} - Ba_{expected} = Ba_{excess} \quad (1)$$

where $Ba_{observed}$ is the values farthest from the line of conservative mixing and $Ba_{expected}$ is based on the line of conservative mixing. This results in total expected Ba of 0.33 μmol/kg and an excess Ba of 0.22 μmol/kg (molecular mass of Ba = 137.327 g/mol). Likewise, we converted their salinity units to the ones in this study, using Equation (2). Their brackish samples therefore have a salinity of about 9

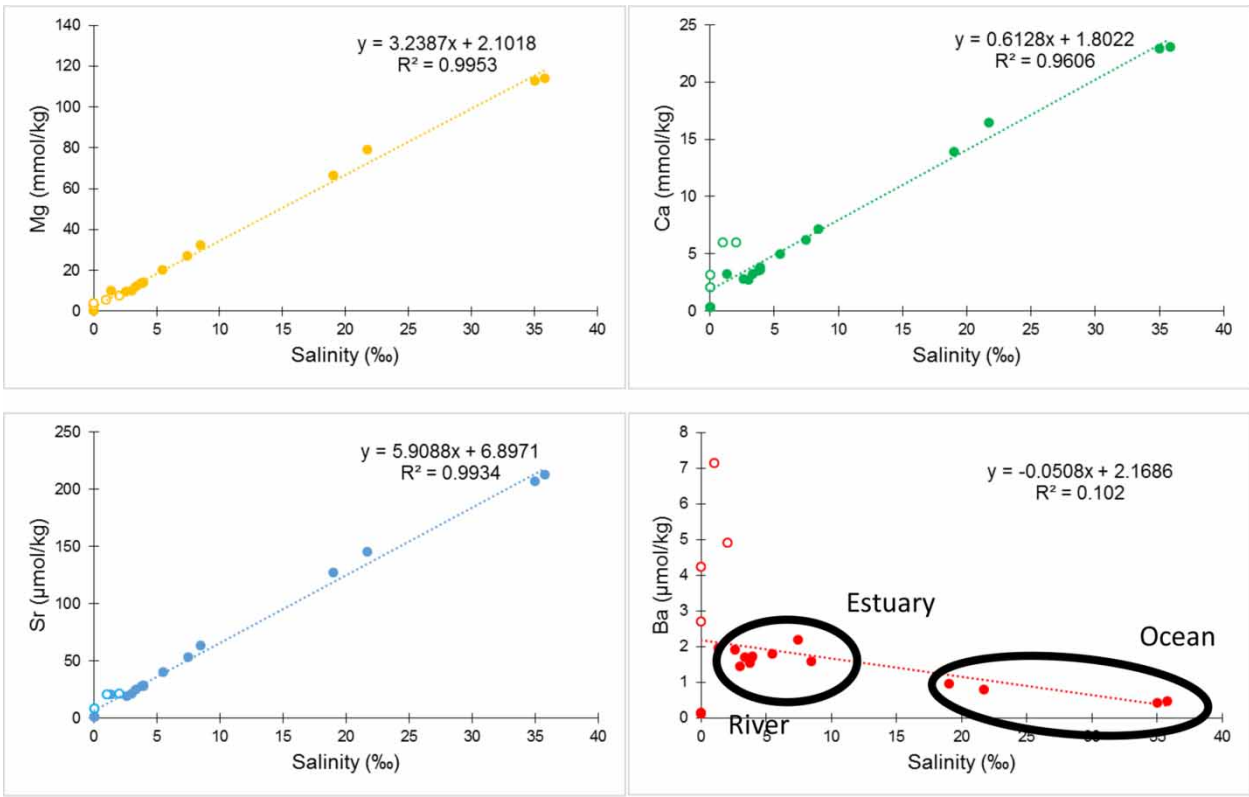

Figure 2 | Graphs of alkaline earth metal abundance versus salinity show a strong linear trend for Mg, Ca, and Sr but not for Ba. Open circles represent groundwater and closed circles signify surface waters. Water-type clustering is labeled on Ba vs. salinity graph.

to 18, averaged to be 13.5:

$$\text{Salinity} = 0.0018066 * [Cl^-] \text{ (in mg/l)} \quad (2)$$

Hanor & Chan's (1977) data indicate that at a salinity of 13.5 the concentration of Ba should be 0.33 µmol/kg of dissolved Ba, and that there is an addition of 0.22 µmol/kg in their study that can be attributed to desorption.

To compare Hanor & Chan's (1977) results to our study, we first determined the total Ba measured over the salinity range of likely desorption. Our data points closest to a salinity of 9 and 18 (actual = 8.46 and 19) have a Ba concentration of 1.58 µmol/kg and 0.96 µmol/kg, respectively. Taking a simple average of these ranges yields a Ba concentration of 1.27 µmol/kg for a salinity of 13.73. Next, we calculated the Ba expected from conservative mixing using a line of conservative mixing from our river and ocean samples:

$$y = 0.0128x + 0.2195 \quad (3)$$

where y is [Ba] in µmol/kg and x is salinity. Solving the conservative mixing equation for $x = 13.73$ gives a value of $y = 0.40$ µmol/kg of Ba. Using Equation (1), indicates an excess of Ba of about 0.87 µmol/kg for our study. Therefore, at comparable salinities (13.5 and 13.73), our study has found 0.72 µmol/kg (from 1.27 to 0.55) more total Ba and 0.65 µ/kg (from 0.87 to 0.22) more excess Ba, which is not explained by desorption. These findings are similar to those of Joung & Shiller (2014), who also found non-conservative mixing of Ba in Gulf of Mexico surface waters, and that desorption was not a significant source of Ba to these systems. Instead, they stated that benthic inputs, of which SGD was one suggested source, was a major factor. We therefore attribute this additional 0.65 µmol/kg of Ba to SGD. This flux is 13.7% of the average Ba concentration determined for groundwater (4.75 µmol/kg), which offers an initial estimate of the amount of groundwater in the system. Interestingly Hanor & Chan's (1977) study also found desorption of Sr, which is notably absent in the present study.

Groundwater discharge

Including groundwater samples on the plot of Ba vs. salinity suggests groundwater may be the source of increased Ba in estuaries. By including groundwater samples, the Ba curve no longer has an overall concave downward shape. This suggests Ba only appears to behave non-conservatively if one looks at surface waters alone, and not all waters in the system. Salinity alone appears not to be an adequate predictor of Ba concentration; contributions of groundwater must also be included. We therefore attempted to quantify the flux of fresh SGD entering these estuaries. We created a three end-member mixing model using essentially a weighted-average Equation (4) which is also seen in Bianchi *et al.* (2011):

$$C_{\text{est}} = C_{\text{ocean}}(F_{\text{ocean}}) + C_{\text{river}}(F_{\text{river}}) + C_{\text{ground}}(F_{\text{ground}}) \quad (4)$$

where C is the concentration of an element and F is the percentage of each water type. First, we determined the fraction of ocean water found in the estuaries based on a salinity balance. The average salinity of the estuary was 4.32, the salinity of LA shelf water, which is significantly diluted by river inputs, was 27.87‰, indicating that the estuary was 15.50% seawater. To approximately account for desorption, we subtracted 0.22 μmol/kg of Ba, as determined from the data of Hanor & Chan (1977), from the average estuarine Ba concentration. With the fraction of ocean water and the known concentration of Ba in each end-member, we calculated the fraction for groundwater, and river water, which are 28.52% and 55.97%, respectively.

We then checked the feasibility of our calculations using the other mid-weight alkaline earth metals. Using the percentages for the water types determined above, we calculated hypothetical estuarine values for the remaining elements using Equation (4), with C being the molal value for a given element in each water type. We then compared these hypothetical values to measured concentrations. With 15.50% ocean water, 28.52% groundwater, and 55.97% river water, expected estuarine values were for Sr of 31.49 μmol/kg, for Mg of 16.00 mmol/kg, and for Ca of 4.37 mmol/kg. These values are all well within one standard deviation of the average molal values experimentally determined for the estuary waters (Table 1). Therefore, mixing of 15.50% ocean water, 28.52% groundwater, and 55.97% river water results in the observed estuarine salinity and concentration of all elements analyzed. Our study was conducted in June which typically has higher discharge than October (waterdata.usgs.gov 2016), which is when Hanor & Chan (1977) conducted their study. With an increased discharge, we would expect to see increased desorption; however, desorption alone would not account for the concentrations of all of the alkaline earth metals in a similar way to which groundwater addition does.

We are then able to bracket the amount of groundwater entering Barataria and Terrebonne Bays to be about 14–28%. These values are in line with, although slightly higher than, estimates by Kolker *et al.* (2013), who suggested that groundwater contributes about 5–15% of the freshwater entering Louisiana's estuaries, and work by Moore & Krest (2004) who found that SGD accounts for about 7% of the water along the Louisiana shelf. During the study period of June to August 2013, USGS hydrologic data indicate an average main stem river water loss of 1,648 m^3/s between Baton Rouge and Belle Chase, while discharge was about 17,000 m^3/s, suggesting that about 10% of the Mississippi River was transferred to SGD. Terrebonne and Barataria Bays contain 1.93×10^9 m^3 of water (Feng & Li 2010), which corresponds to 0.27×10^9 to 0.54×10^9 m^3 of groundwater (14–28%) in both bays combined. Given a summer water residence time of 13–19 days (Li *et al.* 2011), submarine groundwater discharges at 160–480 m^3/s (via Equations (5) and (6)).

$$\frac{0.27 \times 10^9 \text{ m}^3}{19 \text{ days}} * \frac{1 \text{ day}}{24 \text{ hr}} * \frac{1 \text{ hr}}{3600 \text{ s}} = 160 \text{ m}^3/\text{s} \quad (5)$$

Low-end calculation

$$\frac{0.54 \times 10^9 \text{ m}^3}{13 \text{ days}} * \frac{1 \text{ day}}{24 \text{ hr}} * \frac{1 \text{ hr}}{3600 \text{ s}} = 480 \text{ m}^3/\text{s} \quad (6)$$

High-end calculation

During different river conditions, we may expect different SGD rates. This groundwater discharge is for only two of the many coastal bays in the MRD; assuming similar fluxes for other bays, we would expect SGD similar to Kolker *et al.* (2013). The magnitude of SGD is also consistent

with the global average of terrestrial sourced groundwater to the coastal ocean, which is estimated to be ~6% of the total annual river water input to the ocean (Zekster & Loaiciga 1993). Peterson *et al.* (2008) found that SGD in the Yellow River Delta, China, is 2–3 times the magnitude of the Yellow River itself, which further supports that SGD is an important factor in deltas globally, not just in the MRD.

Our study suggests that groundwater affects estuarine water chemistry presumably through leaching. Barium, which is often present in the environment in sediment and sedimentary rocks (Brobst & Pratt 1973), can be leached from aquifer sediment by saline-induced desorption or through sediment diagenesis (Shaw *et al.* 1998). Given the documented saltwater intrusion in portions of the MRD (Shaffer *et al.* 2009) and the large sediment flux of the Mississippi River (McKee *et al.* 2004), both are likely here. The patterns in Ba and SGD observed are also similar to those of Joung & Shiller (2014), who also measured Ba in the northern Gulf of Mexico. If sedimentary leeching is driving Ba concentrations, then groundwater is likely transporting other dissolved constituents from the delta sediments into the estuarine environment, potentially including other elements, environmental toxins, and nutrients. For example, a study in the Yeoja Bay system in South Korea found a link between nutrients being transported by SGD and red tides (Lee & Kim 2007). Other studies have found SGD to be a significantly high source of nitrogen (Slomp & Van Capellen 2004; Peterson *et al.* 2008) and trace metals (Jeong *et al.* 2012) to coastal waters. SGD has a strong transport potential and ability to affect the local environment, making it deserving of further study both in the MRD and other deltaic and estuarine environments around the world.

CONCLUSION

Chemical analysis of different source waters revealed anomalously high levels of Ba in the estuaries. Of the possible explanations for this increase in Ba, the influence of groundwater seems more likely than desorption alone. In order to account for the Ba level in the estuarine water, a volume of 14–28% and corresponding discharge of 160–480 m^3/s of groundwater is required, which makes it a significant component of the system. Groundwater has been shown to be important in a variety of deltas around the world but is still often overlooked because of deltaic geology. More work is needed to understand the importance of groundwater in muddy coastal environments; however, our data suggest it can be significant.

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