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Concentrations and ratios of Sr, Ba and Ca along an estuarine river to the Gulf of Mexico – implication for sea level rise effects on trace metal distribution

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Received: 28 October 2015 – Accepted: 4 November 2015 – Published: 16 November 2015

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Published by Copernicus Publications on behalf of the European Geosciences Union.

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Abstract

Strontium and barium to calcium ratios are often used as proxies for tracking animal movement across salinity gradients. As sea level rise continues, many estuarine rivers in the world face saltwater intrusion, which may cause changes in mobility and distribution of these metals upstream. Despite intensive research on metal adsorption and desorption in marine systems, knowledge of the spatiotemporal distribution of these elements along estuarine rivers is still limited. In this study, we conducted an intensive monitoring of Sr and Ba dynamics along an 88 km long estuary, the Calcasieu River in South Louisiana, USA, which has been strongly affected by saltwater intrusion. Over the period from May 2013 to August 2015, we collected monthly water samples and performed in-situ water quality measurements at six sites from the upstream to the river mouth, with a salinity range from 0.02 to 29.50 ppt. Water samples were analyzed for Sr, Ba, and Ca concentrations. In-situ measurements were made on salinity, pH, water temperature, dissolved oxygen concentration, and specific conductance. We found that the Sr and Ca concentrations and the Sr / Ca ratio all increased significantly with increasing salinity. The average Sr concentration at the site closest to the Gulf of Mexico (site 6) was $46.21 \mu\text{mol L}^{-1}$, which was about 130 times higher than that of the site furthest upstream (site 1, $0.35 \mu\text{mol L}^{-1}$). The average Ca concentration at site 6 was 8.19 mmol L^{-1} , which was about 60 times higher than that of site 1 (0.13 mmol L^{-1}). The average Sr / Ca ratio at site 6 ($8.41 \text{ mmol mol}^{-1}$) was about 3 times the average Sr / Ca ratio at site 1 ($2.89 \text{ mmol mol}^{-1}$). However, the spatial variation in Ba concentration was marginal, varying from $0.36 \mu\text{mol L}^{-1}$ at site 6 to 0.47 at site 5. The average Ba / Ca ratio at site 1 ($4.82 \text{ mmol mol}^{-1}$) was about 54 times the average Ba / Ca ratio at site 6 ($0.09 \text{ mmol mol}^{-1}$), showing a clear negative relation between the Ba / Ca ratio and increasing salinity. All the elemental concentrations and ratios had considerable seasonal variations, with significant differences among sampling months for the Sr, Ba concentrations and the Ba / Ca ratio ($p < 0.01$). The results from this study suggest that concentrations of Sr and Ca in the world's estuaries will very likely increase

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in the future as sea level rise continues. For low-gradient estuarine rivers such as the Calcasieu River in South Louisiana, USA, water chemistry upstream would experience substantial Sr and Ca enrichment, which could affect aquatic environments and biological communities.

1 Introduction

Estuarine systems face a variety of threats ranging from regional anthropogenic factors, such as river basin land use change (e.g. Birch et al., 2015; Dorado et al., 2015), riverine nutrient enrichment (e.g. Scavia et al., 2003; Ferreira et al., 2015), and coastal industrial pollution (e.g. Pinto et al., 2015), to global stressors such as climate change and sea level rise (e.g. Geselbracht et al., 2015; Wang et al., 2015). This is especially true for lowland estuarine rivers where any rise in sea level can have a far-reaching impact on the community. Over the past century, the global mean sea level has increased by nearly 200 mm (e.g. IPCC, 2007; Church and White, 2011) due to an increase in 20th century ocean heat content (Munk, 2002) and mass increase (Miller and Douglas, 2004). The rise rate was found to be accelerating in the past two decades, averaging 3.2 mm per year in a range between 2.8 and 3.6 mm (IPCC, 2013).

As sea level rise continues, saltwater intrudes upstream inland, which can cause changes in water chemistry, especially salinity and pH. Salinity and pH are two important factors affecting many chemical and biological processes in estuarine waters. One of the processes is the adsorption - desorption of trace metals in estuarine mixing zones. Salinity and pH have been found to strongly affect mobility and flux rates of trace metals (e.g., Turner, 1996) when they are carried by rivers to various estuarine/coastal systems around the world; for instance, in the Galveston Bay estuary in Texas (Wen et al., 1999), the San Francisco Bay Estuary in California (Sanudo-Wilhelmy et al., 1996), the Changjiang Estuary in China (Edmond et al., 1985; Zhang et al., 2008), the Bang Pakong Estuary in Thailand (Windom et al., 1989), the Scheldt estuary in the Netherlands (Zwolsman and van Eck al., 1999), and the Conwy estuary in North Wales

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(Zhou et al., 2003). The ongoing saltwater intrusion in the world's estuaries may shift metal mobilization and precipitation landwards, the occurrence and effects of which are not well investigated. Such knowledge can be useful for future coastal resource management especially in low-lying, flat areas such as South Louisiana where the estuaries extend 30 to 70 kilometers inland.

The fate of trace metals in estuaries has been a great concern for aquatic life systems. Studies reported that high levels of strontium (Sr) and barium (Ba) concentrations could be toxic for marine embryos (abnormal shell calcification and embryo morphology) (Spangenberg and Cherr, 1996), benthic biota (Lira et al., 2011), and photosynthetic microorganisms (Polonini et al., 2014). In addition to their natural occurrence, the level of trace metals in waterways could be elevated from petrochemical industry (Fiedler et al., 2009). Offshore oil and gas drilling use two primary types of drilling fluids: water-based fluids and non-aqueous drilling fluids. Both of these fluids contain Ba as a major component (Melton et al., 2000; OGP, 2003). Lira et al. (2011) concluded that oil and gas drilling activities may potentially have important implications for meiobenthos through the toxicity of Ba. South Louisiana is a national center of the US oil and petrochemical industry, and many processing plants are located along the estuaries. It is unknown if there is any elevated level of Ba in the estuarine waters in this region.

Determining movements and migrations of aquatic animals between environments is important, especially if we want to understand the life history characteristics of these animals. In complicated environments, such as estuaries, the movements and migrations of animals are affected by multiple factors (Elsdon and Gillanders, 2005). Instead of using conventional tags, many animals have natural tags that can be used to answer ecological questions regarding their life histories. For instance, the elements present within otoliths (earbones) of fish are ideally suited to be used as natural tags, because elements, such as Sr and Ba, can be incorporated into their calcium carbonate matrix (CaCO_3) through either substitution (e.g., BaCO_3 or SrCO_3) or binding within the lattice matrix (Nielson and Christoffersen, 1982; Elsdon and Gillanders, 2003). Studies have shown that the ambient Sr/Ca and Ba/Ca ratios and environmental conditions, includ-

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ing salinity, influence the Sr/Ca and Ba/Ca ratios in fish otoliths and scales (e.g., Bath et al., 2000; Wells et al., 2000). For instance, fish with otolith Ba / Ca $\leq 5 \mu\text{mol mol}^{-1}$ were classified as resident in salt water, and those with $\geq 6 \mu\text{mol mol}^{-1}$ as resident in fresh water (Elsdon and Gillanders, 2005). Therefore, Sr/Ca and Ba/Ca ratios have been used as proxies across salinity gradients to detect aquatic animal (such as fish) movements.

Louisiana's coast of the northern Gulf of Mexico experienced rapid land subsidence and land loss in the past century (Britsch and Dunbar, 1993; Törnqvist et al., 2008; Morton and Bernier, 2010). As a result, the Louisiana Gulf coast has had one of the highest relative sea-level rises in the United States (e.g. Dixon et al., 2006; Ivins et al., 2007). Saltwater intrusion has been observed in many coastal rivers in the region, and the Calcasieu River is a prime example. This river flows through the Chenier Plain comprising an area of approximately 5000 km² with a west–east coastline of about 200 km (Gammill, 2002), stretching geographically from approximately 29.5 to 33.2° N and from 91.3 to 94.0° W. The Calcasieu River is 322 km long with a drainage area of 9780 km² (Nichol et al., 1992), discharging into the Calcasieu Lake before the northern Gulf of Mexico. During the past half century, this river was hydrologically altered. For instance, along the Calcasieu River, two dams were constructed in its upper reach, and prior to the 1960s, a deep draft channel in the Calcasieu River from the Gulf of Mexico to Lake Charles allowed saltwater from the Gulf to migrate further inland. The saltwater, which kills many types of vegetation, began to destroy some of the sensitive wetlands of the Calcasieu River Basin. To solve the saltwater intrusion problem, the Calcasieu River Saltwater Barrier was constructed in the 1960s to prevent saltwater from traveling north further upstream as well as to regulate freshwater outflow (US Army Corps of Engineers). In addition to saltwater intrusion, the lower Calcasieu River is a heavy shipping channel for petrochemical industry concentrated on the river banks. These two problems make the river estuary an ideal location to study the Sr and Ba dynamics across salinity gradients, as the aforementioned hydrological alterations may have had considerable effects on water quality and riverine metal transport.

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Intensive studies have been conducted on trace metals for the Mississippi River, which has a high volume of freshwater discharge pushing into the far-shore open water. On the other hand, little is known about trace metal dynamics in Louisiana's small estuarine rivers like the Calcasieu that has low freshwater discharge and is strongly affected by tides and saltwater intrusion. Due to its highest rate of relative sea-level rise among all regions in the United States, the study of saltwater impacts on metal dynamics in South Louisiana can provide information that will have global relevance. The ultimate goal of this study is to investigate the impacts of saltwater intrusion on trace metal distribution. Specifically, this study is to quantify spatial and temporal variations of Sr, Ca, Ba, Sr/Ca, and Ba/Ca in the Calcasieu River and to assess mixing dynamics across salinity gradients for these same constituents.

2 Methods

2.1 Study area

The study area is the lower reach of the Calcasieu River that enters the northern Gulf of Mexico in Southwest Louisiana. Six sampling sites were selected along the 88 km reach and they are all within the Calcasieu Parish (north) and the Cameron Parish (south). In the study area, the main soil types (> 65 %) are: Arat mucky silt loam (AR), Bancker muck (BA), Creole mucky clay (CR), Clovelly muck (CO), Crowley–Vidrine (Cr), Guyton–Messer silt loams (Gy), Gentilly muck (GC), Kinder–Gist complex (Kd), Mowata–Vidrine complex (Mt), Edgerly loam (Mr), Scatlake mucky clay (SC), and Udi-fluvents (UA) (USDA, 2014).

The climate of the study area is characterized by long, hot, and humid summers and generally short, mild winters. Land use in the north part of the study area (Calcasieu Parish) is primarily agriculture. More than 65 % of the land is used as cultivated cropland, pastureland, and woodland, and most of the remaining acreage is used as urban land, marshland, or swampland (USDA, 1988). Most of the south part of the study area

(Cameron Parish) is coastal marshland. These marshes are used mainly as habitats for wildlife, rangeland, and oil and gas fields (USDA, 1995).

2.2 Data collection

Long-term daily discharge (available since September 1922) and gage height (available since October 1997) data of the Calcasieu River was collected from the US Geological Survey (USGS). The gage stations were chosen based on their proximity to the sampling sites for optimal representation. Specifically, daily discharge was collected at the Calcasieu River near Kinder, LA (USGS 08015500), and the daily gage height was collected at the Calcasieu River near Cameron, LA (USGS 08017118) (Fig. 1).

2.3 Water sample collection

From May 2013 to August 2015, monthly field trips (except June 2013, October 2013 and November 2014) were made to conduct in-situ measurements and collect water samples at six sampling sites along the Calcasieu River (Fig. 1). Note that site 3 was only sampled from August 2014 to August 2015. The saltwater barrier is located approximately 2 kilometers downstream of site 2, below which all sampling sites are affected by tidal water. During each trip, field measurements, including water temperature, dissolved oxygen (DO) concentration, pH, salinity, and specific conductance were measured using an YSI 556 multi-probe meter (YSI Inc., Yellow Springs, OH, USA). In addition, a 250 mL water sample was collected from each site for elemental analysis. To preserve the samples, 375 μ L nitric acid was added to each sample bottle before use. A one liter water sample was collected from each site for total suspended solids (TSS) analysis. All the water samples were stored in a cooler with wet ice during the transportation for later laboratory analysis. Table 1 shows the sampling sites' information.

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2.4 Water sample analysis

Water samples were analyzed for all elements at the W. A. Callegari Environmental Center, Louisiana State University Agricultural Center using EPA Method 200.7. Briefly, water samples were digested using metals-grade concentrated HCl and HNO₃. Yttrium was added to the water samples as an internal standard. Element concentrations above the calibration curve were diluted by factors of 10, 20, 50, 100, or 1000 to bring them into the calibration curve. Finally, the analyses were conducted using an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, Varian Vista MP-X, Palo Alto, CA). Although this method is designed to detect total recoverable analytes, the measurements of Sr, Ca and Ba in our study can be considered as dissolved because our water samples had very low levels of total suspended solids (TSS, mostly lower than 30 mg L⁻¹). Field and lab blanks, and Independent/Continuing Calibration Verification/Blanks were used for quality control to insure that the samples were not contaminated, and that all sample analyses were within control limits. Duplicate analyses of water samples typically yielded an error less than 0.05 %.

2.5 Statistical analyses

Multivariate analysis of variance (MANOVA) was performed for all element concentration/ratio for main and interactive effects of sampling site and month on differences in concentrations/ratios. Two-way analyses of variance (ANOVAs) comparing water sample values were calculated separately for each of the five measured element concentrations and ratios according to sampling site and month of collection. Pearson correlations were compared between dissolved element concentrations and ratios and environmental parameters, including salinity, pH, temperature, specific conductance, dissolved oxygen (DO), and TSS, to investigate potential relationships. Backward stepwise linear regression was performed between every element concentration/ratio and environmental parameters, and the analysis was conducted for all sites together. To note, specific conductance was eliminated for the multiple regression model because

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of the high correlation of salinity and specific conductance. All statistical analyses were performed with the SAS Statistical Software package. All statistical tests and confidence intervals are reported at $\alpha = 0.01$ critical level.

3 Results

3.1 Hydrology and ambient conditions

From 1 May 2013 to 31 August 2015, the Calcasieu River showed an average daily discharge of $39 \text{ m}^3 \text{ s}^{-1}$ (SD: ± 46), ranging from 5 to $259 \text{ m}^3 \text{ s}^{-1}$. The discharge during the sampling period was notably lower than the long-term average from 1980 to 2009 ($72 \pm 66 \text{ m}^3 \text{ s}^{-1}$; He and Xu, 2015). Seasonally, the Calcasieu River showed higher discharge during the winter and spring months and lower discharge during the summer and fall months in the period from 1980 to 2009 (He and Xu, 2015). During the sampling period, the river exhibited the same seasonal pattern as in the period from 1980 to 2009, with April having the highest average discharge ($103 \text{ m}^3 \text{ s}^{-1}$) and August the lowest ($9 \text{ m}^3 \text{ s}^{-1}$). During the 25 field sampling days from 1 May 2013 to 31 August 2015, the discharges ranged from 5 to $259 \text{ m}^3 \text{ s}^{-1}$ with an average of $44 \text{ m}^3 \text{ s}^{-1}$ (SD: ± 59) (Fig. 2).

The Calcasieu River near its mouth at Cameron showed a long-term (October 1997–August 2015) average daily gage height (or tidal stage) of 0.31 m (± 0.18), ranging from -0.48 to 2.31 m. Over the past eight years, the tidal stage showed a clear increasing trend (Fig. 3a). During the 2 year sampling period, the average daily gage height at Cameron ranged from -0.32 to 1.53 m, with an average of 0.34 m (± 0.19). Seasonally, in contrast with the river discharge, the tidal stage at the river mouth was high in the fall months, with September having the highest monthly average (0.48 m), and low in the winter months, with January having the lowest (0.18 m). During the sampling period, the monthly average gage heights at the Calcasieu River near Cameron were similar to the historical monthly average gage heights, and the seasonal trend of gage height was

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similar to the historical trend, with larger variance (Fig. 3b). During the 25 field trip days from May 2013 to August 2015, the average daily gage height at the Calcasieu River near Cameron ranged from -0.03 to 0.63 , averaging 0.31 (SD: ± 0.18). The average daily gage heights at the Calcasieu River near Cameron were well represented by the average daily gage heights during the 25 field trip days (Fig. 2).

The ambient conditions at the six sampling sites varied largely (Table 2). Salinities at site 6 ranged from 4.80 to 29.50 ppt, with an average of 19.91 , which is more than 280 times higher than the average salinity at site 1. Salinity increased with the decrease of distance from the Gulf of Mexico. Overall, specific conductance, pH, DO concentration, and water temperature showed similar trends to salinity. During the 25 sampling trips, the average specific conductance ranged from 0.14 mS cm^{-1} at site 1 to 31.84 mS cm^{-1} at site 6. The average pH at all the sampling sites ranged from 6.08 at site 2 to 8.18 at site 6, while the average DO concentration ranged from 4.64 mg L^{-1} at site 3 to 7.77 mg L^{-1} at site 6. The average water temperature at site 3 was higher than other sites, which is attributed to a different sampling schedule for site 3. TSS concentration varied from site 1 to site 6, but there was no clear trend in terms of the distance to the Gulf. All six sites had higher salinity and specific conductance during summer and fall months (Fig. 4a and d), and correlation analysis showed that salinity and specific conductance were positively highly correlated (Table 3). From March to November, pH exhibited an increasing trend (Fig. 4b). As expected, June, July, and August had higher water temperatures, while December, January, and February had lower (Fig. 4c). The dissolved oxygen (DO) concentration had the opposite trend from water temperature (Fig. 4e). Correlation analysis showed that temperature and DO concentration were negatively highly correlated (Table 3). Sites 5 and 6 had higher TSS variation seasonally, but there was no clear trend (Fig. 4f).

3.2 Strontium, Ca concentrations and Sr/Ca ratio

During the sampling period, the Sr concentration showed a considerable variation among sampling sites, with sites closer to the Gulf having much higher concentrations

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(Table 4). The average Sr concentration at site 6 was $46.21 \mu\text{mol L}^{-1}$, about 130 times higher than that at the stream site 1 ($0.35 \mu\text{mol L}^{-1}$). The spatial difference in Sr concentration was statistically significant (both $p < 0.01$, Tables 5 and 6). Seasonally, there was also a large variation in Sr concentration at each site: from not detected (n.d.) to $1.71 \mu\text{mol L}^{-1}$ at site 1, from n.d. to $7.19 \mu\text{mol L}^{-1}$ at site 2, from 0.23 to $18.26 \mu\text{mol L}^{-1}$ at site 3, from 0.34 to $35.61 \mu\text{mol L}^{-1}$ at site 4, from 1.60 to $63.00 \mu\text{mol L}^{-1}$ at site 5, and from 10.61 to $74.18 \mu\text{mol L}^{-1}$ at site 6. In general, all six sites had higher Sr concentrations during the summer and fall months (Fig. 5a), and the difference in monthly Sr concentration was statistically significant (both $p < 0.01$, Tables 5 and 6). In the interactive effect of sampling site and month, the Sr concentration showed no significant differences (both $p > 0.01$, Tables 5 and 6).

The Ca concentration was significantly different among sampling sites (both $p < 0.01$, Tables 5 and 6), with sites closer to the Gulf having much higher concentrations (Table 4). The average Ca concentration at site 6 was 8.19mmol L^{-1} , about 60 times higher than site 1 (0.13mmol L^{-1}). The Ca concentration varied largely at all the sampling sites: from 0.06 to 0.92mmol L^{-1} at site 1, from 0.07 to 2.64mmol L^{-1} at site 2, from 0.07 to 2.07mmol L^{-1} at site 3, from 0.08 to 5.51mmol L^{-1} at site 4, from 0.24 to 18.25mmol L^{-1} at site 5, and from 1.22 to 45.76mmol L^{-1} at site 6. Seasonally, the Ca concentration had a large variation, with August having the highest concentration of all six sites except site 6 (Fig. 5b). Furthermore, there was no statistically significant difference in the interactive effect of sampling site and month ($p > 0.01$, Table 6). In the interactive effect of sampling site and month, the Ca concentration showed no significant differences (both $p > 0.01$, Tables 5 and 6).

The Sr/Ca ratio increased with the decrease of distance to the Gulf and the spatial difference in the Sr/Ca ratio was statistically significant (both $p < 0.01$, Tables 5 and 6). The average Sr/Ca ratio at site 6 ($8.41 \text{mmol mol}^{-1}$) was about 3 times the average Sr/Ca ratio at site 1 ($2.89 \text{mmol mol}^{-1}$). Seasonally, the Sr/Ca ratio varied largely at all sampling sites: from 0 to $4.14 \text{mmol mol}^{-1}$ at site 1, from 0 to $6.48 \text{mmol mol}^{-1}$ at site 2, from 2.46 to $8.82 \text{mmol mol}^{-1}$ at site 3, from 4.32 to $20.83 \text{mmol mol}^{-1}$ at site 4, from

2.92 to 34.16 mmol mol⁻¹ at site 5, and from 1.23 to 28.53 mmol mol⁻¹ at site 6. There was no clear seasonal trend of the Sr/Ca ratio at sites 1 and 2, while the other four sites had large variations, with July having the highest Sr/Ca ratio for sites 4, 5, and 6 (Fig. 5c). There was no statistically significant difference among sampling months ($p > 0.01$, Table 6).

3.3 Barium concentration and Ba/Ca ratio

Overall, spatial variation in Ba concentration was small among the six sites, from 0.36 $\mu\text{mol L}^{-1}$ at site 6 to 0.47 $\mu\text{mol L}^{-1}$ at site 5. However, there was significant difference in Ba concentration among sampling sites (both $p < 0.01$, Tables 5 and 6). Temporal variation of Ba concentration was larger (from 1 to 3 fold), but relatively smaller when compared with the spatial variation of Sr and Ca concentrations (Table 4 and Fig. 5d). There was significant difference of Ba concentration among sampling months (both $p < 0.01$, Tables 5 and 6), with winter months having lower Ba concentrations (Fig. 5d). There was no statistically significant difference in the interactive effect of sampling site and month (both $p > 0.01$, Tables 5 and 6).

Unlike the Sr/Ca ratio, the Ba/Ca ratio decreased with decreasing distance to the Gulf of Mexico, and the spatial difference in the Ba/Ca ratio was statistically significant (both $p < 0.01$, Tables 5 and 6). The average Ba/Ca ratio at site 1 (4.82 mmol mol⁻¹) was about 54 times the average ratio at site 6 (0.09 mmol mol⁻¹). Temporally, the Ba/Ca ratio varied largely at all sampling sites: from 0.55 to 9.21 mmol mol⁻¹ at site 1, from 0.16 to 7.24 mmol mol⁻¹ at site 2, from 0.11 to 5.96 mmol mol⁻¹ at site 3, from 0.09 to 5.68 mmol mol⁻¹ at site 4, from 0.02 to 2.15 mmol mol⁻¹ at site 5, and from 0.01 to 0.36 mmol mol⁻¹ at site 6. Seasonally, the Ba/Ca ratio had large variation and there was significant difference among sampling months (both $p < 0.01$, Tables 5 and 6). In general, all six sites had higher Ba/Ca ratios during spring and fall months (Fig. 5e). The Ba/Ca ratio was no significantly different in the interactive effect of sampling site and month (both $p > 0.01$, Tables 5 and 6).

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3.4 Relationships between concentrations and ratios of Sr, Ba, and Ca and environmental parameters

The Sr and Ca concentrations were positively correlated to salinity, pH, specific conductance, DO, and TSS, while no clear correlation of these concentrations with water temperature was found (Table 3). The Sr/Ca ratio was positively correlated to salinity, pH, and specific conductance, but not correlated to temperature, DO, and TSS (Table 3). In contrast with other element concentrations and ratios, the Ba concentration was positively correlated to temperature and negatively correlated to DO, while no correlation was found between Ba concentration and salinity, pH, specific conductance, and TSS (Table 3). The Ba/Ca ratio was negatively correlated to salinity, pH, and specific conductance, but not correlated to temperature, DO, and TSS (Table 3).

Multiple regression analysis (Table 7) for all sites together showed that the Sr and Ca concentrations were significantly correlated to both salinity and TSS concentration at the 0.01 level, with salinity having higher contribution. For the Sr/Ca and Ba/Ca ratios, salinity was the only variable left in the model for all sites together. According to the multiple regression analysis for all sites together, the Ba concentration was only significantly correlated to DO concentration.

4 Discussion

Dissolved Sr loads in the world's river waters have been reported by Gaillardet et al. (2003) to have the largest variation when compared with other trace metals. These loads ranged from a few ngL^{-1} to nearly $100\mu\text{gL}^{-1}$, with an average of $60\mu\text{gL}^{-1}$. On the other hand, dissolved Ba loads in the world's river waters are among the least variable, ranging between 10 and nearly $100\mu\text{gL}^{-1}$ with an average of $23\mu\text{gL}^{-1}$ (Gaillardet et al., 2003). Similar to Sr, dissolved Ca concentrations in freshwaters can be highly variable, potentially reaching very low levels, e.g. $< 1\text{--}20\text{mgL}^{-1}$ (Hem, 1985; Hamer et al., 2015). In this study, we found a very similar trend: dissolved

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Sr and Ca loads in river water samples collected above the saltwater barrier (freshwater) varied largely ($0.35\text{--}0.77\ \mu\text{mol L}^{-1}$ or $31\text{--}67\ \mu\text{g L}^{-1}$ for Sr, $0.13\text{--}0.23\ \text{mmol L}^{-1}$ or $5.21\text{--}9.22\ \text{mg L}^{-1}$ for Ca), both spatially and temporally, while dissolved Ba loads showed little change ($0.42\text{--}0.46\ \mu\text{mol L}^{-1}$ or $58\text{--}63\ \mu\text{g L}^{-1}$) in the same samples. The variations of element concentrations will in turn result in variations of element ratios. Variations of element concentrations and ratios include spatial and temporal variations. We discuss spatial and temporal variations separately below.

4.1 Spatial variation

The Sr and Ca concentrations in marine waters are significantly higher than in freshwaters due to different geological compositions of marine and fresh water systems (Brown and Severin, 2009; Walther and Nims, 2015). Brown and Severin (2009) reported average marine water Sr and Ca concentrations of $7.64 \pm 0.53\ \text{mg kg}^{-1}$ ($87.19 \pm 6.05\ \mu\text{mol L}^{-1}$) and $405.87 \pm 27.49\ \text{mg kg}^{-1}$ ($10.13 \pm 0.68\ \text{mmol L}^{-1}$), respectively. The Sr and Ca concentrations in the Calcasieu River were lower than the average marine water Sr and Ca concentrations (Table 4). However, the Sr/Ca ratio in our study was fairly close to the average marine Sr/Ca ratio ($8.61\ \text{mmol mol}^{-1}$, range: 8.17 to 8.87), and was much higher than the median river water Sr/Ca ratio ($2.39\ \text{mmol mol}^{-1}$, range: 0.27 to 19.18) (Brown and Severin, 2009) (Table 4). According to Brown and Severin (2009), the Sr/Ca ratio varied across a wider range in river environments than in marine environments, with less than 3% of the 786 rivers reviewed having median Sr/Ca levels that exceeded minimum marine levels. In the Calcasieu River, two (sites 5 and 6) out of six sampling sites had Sr/Ca ratios that exceeded the minimum marine levels.

The Ba concentrations found in the Calcasieu River were higher than those found in the majority of surface and municipal water supplies in the US ($\leq 0.03\ \text{mg L}^{-1}$ or $\leq 0.22\ \mu\text{mol L}^{-1}$) (Moffett et al., 2007). New and expanded industrial Ba uses are studied in Kravchenko et al., 2014. For instance, BaSO_4 is commonly used as a contrast agent in medical imaging studies (X-ray). Because of its high molecular weight, approximately 94% of barite mined today is used as a wetting agent or component of drilling

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mud for oil and gas drilling (USGS, 2006). In this study, however, there is no evidence suggesting any effect from the surrounding petrochemical industry on the higher-than average concentration level of Ba. Sites 1 and 2, which are located above the saltwater barrier and petrochemical plants, showed a similar or even slightly higher level of Ba concentration than the other sites that are close to the chemical plants and the Gulf (Table 4). Previous studies found that dissolved Ba in natural waters is largely determined by the geological composition of the streambed and weathering processes (Gailardet et al., 2003). For instance, Ba is often rich in the geographic areas characterized by volcanic terrains, specifically alkaline-rich volcanic products or detrital (sedimentary) volcanic by-products (e.g., black shales) (e.g., Chakrabarti et al., 2009; Cuoco et al., 2013). The levels of Ba concentration found in this study strongly indicate the role of geological origin of Ba.

Unlike Sr and Ca, the level of Ba concentration in this study was not related with salinity or pH. However, because of a close positive relation of Ca concentration with salinity and because of the large mass portion of Ca in dissolved solids, there was a strong negative relation between Ba/Ca ratio and salinity (Tables 3 and 7). In their study on trace metals in coastal waters along the Texas coast, Walther and Nims (2015) reported a wide range of the Ba/Ca ratio, 62 to 973 $\mu\text{mol mol}^{-1}$, similar to the Ba/Ca ratios found in our study at the two sites closest to the Gulf of Mexico. The fact that higher Ba/Ca ratios were found at other sites upstream suggests that freshwater discharge plays an important role in this elemental ratio. This finding may further suggest that large river systems with high fresh flows will not be chemically affected by sea level rise as much as small coastal rivers with low freshwater flow will.

Strontium has been the most widely used trace metal to study aquatic animal movements between freshwater and marine habitats (Secor and Rooker, 2000), and most studies of fish migration with otolith chemistry have used the Sr/Ca ratio. Recent studies have found that the Ba/Ca ratio may also be a sensitive indicator of freshwater residency (Milton and Chenery, 2001; Elsdon and Gillanders, 2005; Martin and Thorold, 2005). However, not all constituents are equally effective as proxies. For instance,

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Walther and Nims (2015) concluded that in Texas systems, the capacity to detect animal movements across salinity gradients using the Sr/Ca ratio as a proxy will be more difficult compared to other systems, while using the Ba/Ca ratio as a proxy would be highly useful for tracking animal movements. In the Calcasieu River, the large spatial variations of the Sr/Ca and Ba/Ca ratios, and the clear relationships between these ratios and salinity indicate that both would be very useful as proxies for tracking animal movement.

4.2 Temporal variation

Understanding the causes of seasonal dissolved element concentrations and ratios in a coastal river can be complicated by interrelationships among potential control factors (Shiller, 1997). Shiller (1997) showed that changes in suspended particulate matter, pH, and discharge appear unable to account for the observed dissolved element seasonal variability, but redox processes remained as the likely candidate for causing the most significant element seasonal variability. In our study, as mentioned above, pH had an increasing trend from March to November. However, no element concentration or ratio showed the same trend. Therefore, pH itself was unable to explain the seasonal variability of element concentrations and ratios even though pH was significantly correlated to all the studied element concentrations and ratios except the Ba concentration.

Linear or nearly linear mixing of Sr and Ca across salinity gradients has been reported in estuaries worldwide (e.g., Andersson et al., 1992; Surge and Lohmann, 2002; Walther and Nims, 2015). In our study, mixing curves of both the Ca and Sr concentrations across the salinity gradient in the Calcasieu were linear (Fig. 6). Salinity and specific conductance are highly correlated to the Sr concentration, and may be the driving factors for the seasonal variability of the Sr concentration. The seasonal trends of salinity and specific conductance were basically the same as the seasonal trend of the Sr concentration (Figs. 4 and 5), and multiple linear regression analysis for all sites together showed that the linear relationship between the Sr concentration and salinity were very strong. Salinity and specific conductance may not be the driving factors for

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the seasonal variability of the Ca concentration and the Sr/Ca, Ba/Ca ratios because of differences in seasonal trends. Therefore, for the Ca concentration and the Sr/Ca, Ba/Ca ratios, salinity and specific conductance were the essential control factors of seasonal variability, but with interactions with other environmental factors including pH, DO and TSS.

In natural aquatic systems, the concentration of Ba depends on the mineral matrix of aquifer lithologies (e.g., sulfates, carbonates, granodiorite, and shale) as well as the physicochemical conditions (e.g., pH, temperature, and redox state) of the groundwater (Kravchenko et al., 2014). In general, Ba solubility increases with decreasing pH (EPA, 1985). However, this was not the case in our study. The lack of or weak relationship between Ba concentration and environmental factors strongly indicate the role of geological origin of Ba.

Based on an examination of variability in mean dissolved trace element concentrations in the Mississippi River, Shiller (1997) suggested that hydrologic factors may be important in determining trace element variability. This is, however, not the case in our data analysis. The reason for the lack of a relationship between discharge variability and element concentration and ratio variability might be due to the fact that the discharge records for the Calcasieu River come from a gauge station that is much further upstream than all the sampling sites. Future studies with nearby discharge measurements can be used to test the impact of discharge on variations of element concentrations and ratios, and also to calculate freshwater loadings of dissolved Sr and Ba to the Gulf of Mexico.

Due the mixing of freshwater and saltwater, estuaries are extremely dynamic and complex environments. Sea level rise, which causes saltwater intrusion, will change the mixing point of freshwater and saltwater, which in turn, may have significant impact on biology. Due to its historic saltwater intrusion problem and the existence of the Calcasieu Saltwater Barrier, studies of metal dynamics in the Calcasieu River will provide crucial information on metal dynamics in similar systems worldwide. Current estimates of riverine metal fluxes are based entirely on measurements of dissolved

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metal concentrations, and neglect the impact of riverine particulate dissolution in seawater (Jones et al., 2014). However, the riverine particulate dissolution in seawater could have considerable influence on the overall metal chemistry. For instance, the weathering of riverine particulate material upon arrival in coastal areas makes a significant contribution to the overall Sr chemistry of seawater over geological timescales (Odum, 1951; Jones et al., 2014). Dissolved metal concentrations were used in this study, and riverine particulates were not included. Further studies of water and sediment interaction are needed to better understand metal dynamics.

5 Conclusions

This study investigated dissolved strontium, barium, and calcium concentrations and their ratios in an 88 km long estuarine reach with a salinity range from 0.02 to 29.50 ppt over two years. It is the first assessment on the spatial and temporal variations of these metals in an estuary for such a large salinity range and long period of time. The study found considerable spatiotemporal variation in the element concentrations and their ratios. Salinity strongly affects spatiotemporal distributions of dissolved Sr and Ca concentrations and their elemental ratios. Total suspended solids concentration also plays a role in the element distribution. In contrast, salinity has no effect on Ba concentration, which appears mainly geochemically controlled. These results indicate that concentrations of Sr and Ca in the world's estuaries will very likely increase in the future as sea level rise continues, and that the extent of these increases will depend on the extent of saltwater intrusion. For low-gradient estuarine rivers with low freshwater discharge, such as the Calcasieu River, water chemistry upstream would experience substantial Sr and Ca enrichment, which could affect aquatic environments and biological communities.

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Data availability

The long-term river discharge and gage height data are available at United States Geological Survey website.

Acknowledgements. This study was financially supported through grants from the National Fish and Wildlife Foundation (Project #: 8004.12.036402) and the United States Department of Agriculture Hatch Funds (Project #: LAB94230). Thanks also go to the United States Geological Survey for making the long-term river discharge and gage height data available for this study and Jeff Corkern for laboratory metal analysis at the Louisiana State University W.A. Calle-gari Environmental Center. The authors are grateful to many students including, among others, Paula Castello Blindt, Kaci Fisher, Sanjeev Joshi, and Zhen Xu for their outstanding field assistance.

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Table 1. Geographical location of six sampling sites along the Calcasieu River and their distance to the northern Gulf of Mexico.

Site ID	Latitude	Longitude	River Distance from Gulf (km)
Site 1	30.297	−93.118	87.9
Site 2	30.299	−93.188	73.5
Site 3	30.253	−93.245	62.6
Site 4	30.219	−93.250	58.1
Site 5	30.006	−93.334	27.0
Site 6	29.805	−93.349	4.5

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Table 2. Means and standard deviations of water quality parameters at six sampling sites along the Calcasieu River during May 2013 and Aug 2015.

Site ID	<i>n</i>	Salinity (ppt)	pH	Temperature (°C)	Specific conductance (mScm ⁻¹)	DO (mgL ⁻¹)	TSS (mgL ⁻¹)
Site 1	25	0.07 ± 0.18	6.30 ± 0.96	21.61 ± 7.09	0.14 ± 0.36	5.40 ± 2.52	16.36 ± 7.66
Site 2	25	0.40 ± 1.24	6.08 ± 1.06	21.90 ± 7.45	0.75 ± 2.21	4.78 ± 2.64	14.28 ± 13.71
Site 3	13	3.05 ± 5.29	6.45 ± 0.64	23.01 ± 6.97	5.29 ± 8.55	4.64 ± 2.91	16.48 ± 18.43
Site 4	25	5.89 ± 5.67	6.59 ± 0.92	22.17 ± 7.53	10.07 ± 9.21	5.20 ± 2.69	12.37 ± 7.97
Site 5	24	14.15 ± 6.67	7.51 ± 0.57	22.55 ± 7.67	23.15 ± 10.35	6.75 ± 2.70	28.53 ± 23.63
Site 6	25	19.91 ± 5.73	8.18 ± 0.64	22.89 ± 7.31	31.84 ± 8.54	7.77 ± 2.56	54.79 ± 33.78

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Table 3. Pearson correlation between dissolved Sr, Ba, Ca and environmental factors in the Calcasieu River. Significant ($p < 0.01$) correlations using Pearson Correlation Coefficients are indicated in bold.

	Salinity	pH	Temperature	Specific conductance	DO	TSS
Sr	0.98	0.67	0.05	0.98	0.29	0.42
Ca	0.83	0.53	0.02	0.83	0.25	0.47
Sr/Ca	0.58	0.48	0.03	0.59	0.16	0.23
Ba	-0.05	0.02	0.33	-0.04	-0.42	-0.17
Ba/Ca	-0.69	-0.63	-0.12	-0.70	-0.17	-0.24
Salinity	1.00	0.70	0.07	1.00	0.27	0.37
pH		1.00	0.34	0.70	0.04	0.26
Temperature			1.00	0.08	-0.79	-0.02
Specific Conductance				1.00	0.27	0.36
DO					1.00	0.15
TSS						1.00

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Table 4. Means and standard deviations of element concentrations and ratios in water samples from six sampling sites along the Calcasieu River.

Site ID	Sr ($\mu\text{mol L}^{-1}$)	Ca (mmol L^{-1})	Sr Ca ⁻¹ (mmol mol^{-1})	Ba ($\mu\text{mol L}^{-1}$)	Ba/Ca (mmol mol^{-1})
Site 1	0.35 ± 0.31	0.13 ± 0.17	2.89 ± 0.80	0.46 ± 0.11	4.82 ± 1.75
Site 2	0.77 ± 1.42	0.23 ± 0.53	3.49 ± 1.51	0.42 ± 0.09	3.94 ± 1.74
Site 3	5.13 ± 5.72	0.68 ± 0.67	6.06 ± 1.93	0.41 ± 0.11	2.10 ± 1.93
Site 4	9.91 ± 9.58	1.10 ± 1.24	8.11 ± 3.38	0.43 ± 0.11	1.22 ± 1.41
Site 5	30.85 ± 15.24	4.66 ± 4.56	8.67 ± 6.01	0.47 ± 0.09	0.30 ± 0.49
Site 6	46.21 ± 14.94	8.19 ± 9.89	8.41 ± 5.07	0.36 ± 0.07	0.09 ± 0.10

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Table 5. Results from factorial multivariate analysis of variance (MANOVA, Wilks' Lambda) performed for all element concentration/ratio for main and interactive effects of sampling site and month on differences in concentrations/ratios.

	Value	Num DF	Den DF	<i>F</i>	<i>P</i>
Site	0.02	25	153.81	10.76	< 0.0001
Month	0.08	55	193.37	2.49	< 0.0001
Site × Month	0.05	240	209.57	0.73	0.9910

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Table 6. Results from two-way analyses of variance (ANOVAs) performed separately for each element concentration/ratio for main and interactive effects of sampling site, year, and month on differences in concentrations/ratios.

		Num DF	Den DF	<i>F</i>	<i>P</i>
Sr	Site	5	54	76.40	< 0.0001
	Month	11	54	3.14	0.0024
	Site × Month	54	54	0.60	0.9701
Ca	Site	5	51	22.06	< 0.0001
	Month	11	51	1.81	0.0767
	Site × Month	50	51	0.65	0.9374
Sr/Ca	Site	5	51	38.42	< 0.0001
	Month	11	51	1.91	0.0594
	Site × Month	50	51	0.79	0.8012
Ba	Site	5	42	4.83	0.0014
	Month	11	42	4.61	0.0001
	Site × Month	52	42	1.00	0.5055
Ba/Ca	Site	5	40	70.98	< 0.0001
	Month	11	40	7.58	< 0.0001
	Site × Month	47	40	1.34	0.1710

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Table 7. Linear relationships between dissolved element concentrations/ratios and water quality parameters for all sites together using backward stepwise regression. Slope and intercept estimates are presented ± SE. Only statistically significant relationships are reported ($p < 0.01$). Variables left in the model are significant at the 0.01 level.

Element	Water quality parameters	Regression	r^2	F	p
Sr	Salinity			3036	< 0.0001
	TSS			14.11	0.0003
Ca	Salinity + TSS	$Sr = -1.34(\pm 0.48) + 2.17(\pm 0.04)Salinity + 0.052(\pm 0.014)TSS$	0.97	1849	< 0.0001
	Salinity			188.0	< 0.0001
	TSS			7.90	0.0059
	Salinity + TSS	$Ca = -0.30(\pm 0.23) + 0.27(\pm 0.02)Salinity + 0.019(\pm 0.007)TSS$	0.72	134.9	< 0.0001
Sr/Ca	Salinity	$\frac{Sr}{Ca} = 6.01(\pm 0.15) + 0.82(\pm 0.05)Ln(Salinity)$	0.69	229.0	< 0.0001
Ba	DO	$Ba = 0.54(\pm 0.02) - 0.017(\pm 0.003)DO$	0.22	27.05	< 0.0001
Ba/Ca	Salinity	$\frac{Ba}{Ca} = 2.08(\pm 0.10) - 0.81(\pm 0.04)Ln(Salinity)$	0.85	517.0	< 0.0001

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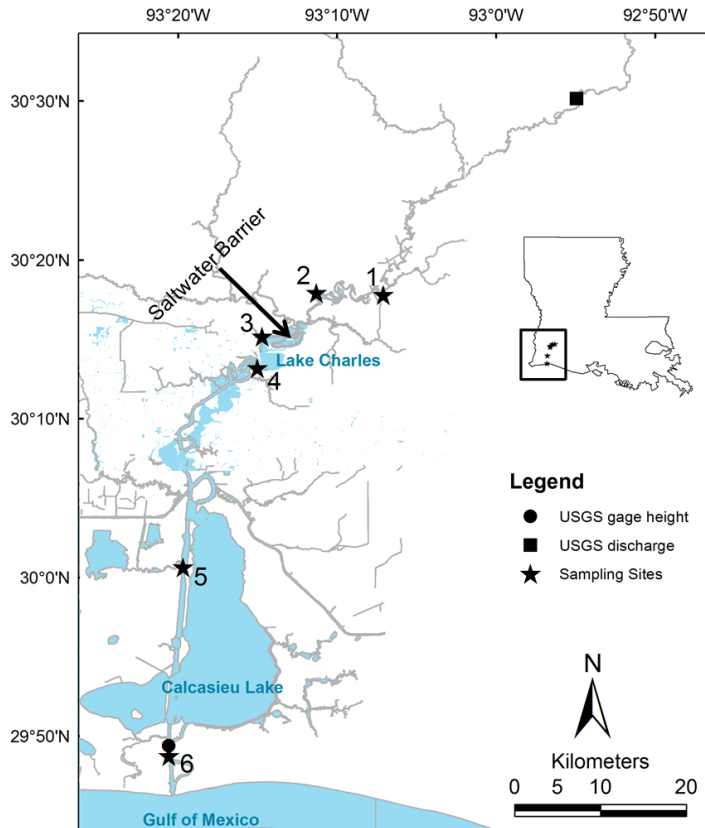


Figure 1. Geographic location of the Calcasieu River entering the Northern Gulf of Mexico, and the locations of six sampling sites and USGS discharge and tidal gaging sites.

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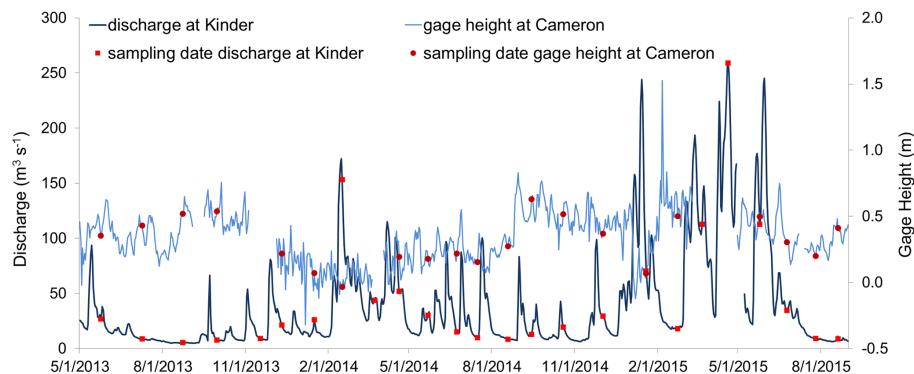


Figure 2. Discharge at Kinder, LA (USGS Station# 08015500) and tidal gage height at Cameron, LA (USGS Station# 08017118).

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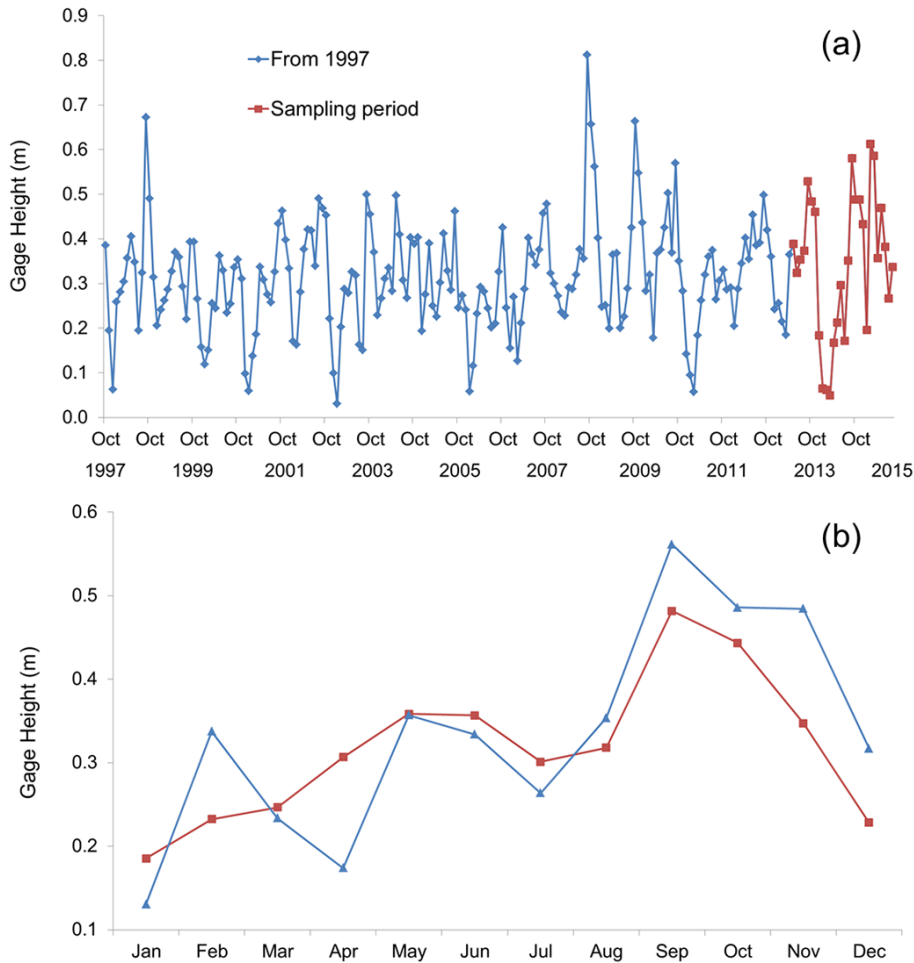


Figure 3. Seasonal trend of tidal gage height at Cameron, LA (USGS Station# 08017118).

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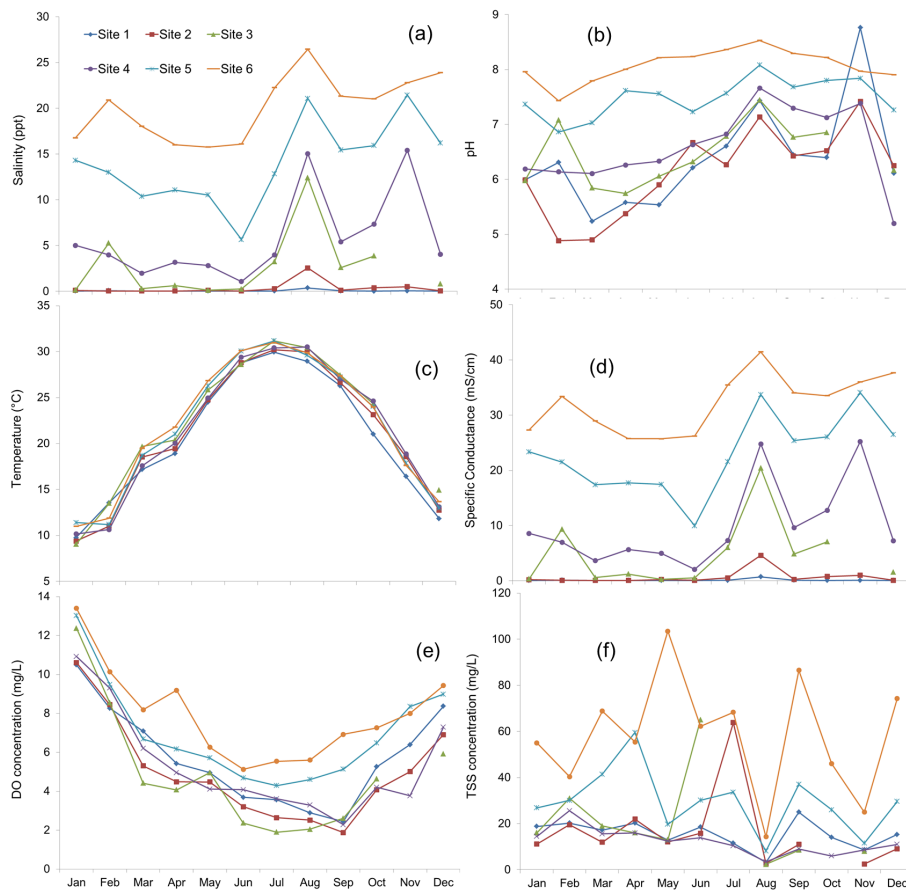


Figure 4. Seasonal trends of salinity (a), pH (b), temperature (c), specific conductance (d), dissolved oxygen (DO, e), and total suspended solids (TSS, f) at six sampling sites along the Calcasieu River.

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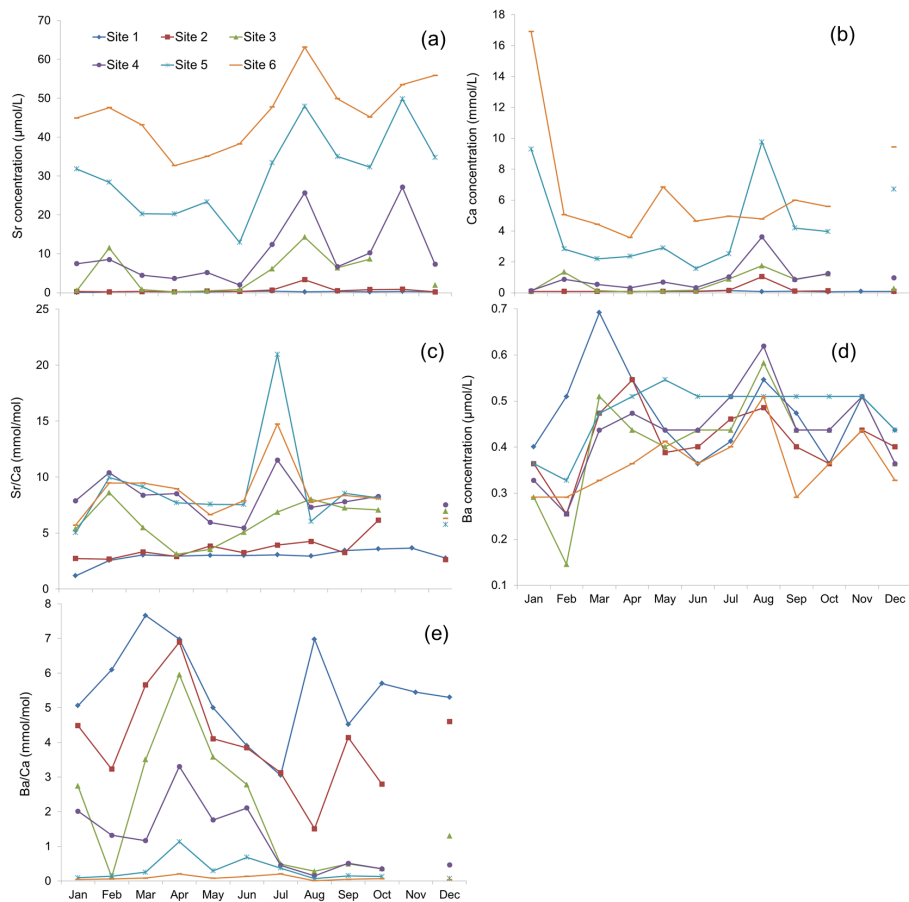


Figure 5. Seasonal trends of Sr concentration (a), Ca concentration (b), Sr/Ca ratio (c), Ba concentration (d), and Ba/Ca ratio at six sampling sites along the Calcasieu River.

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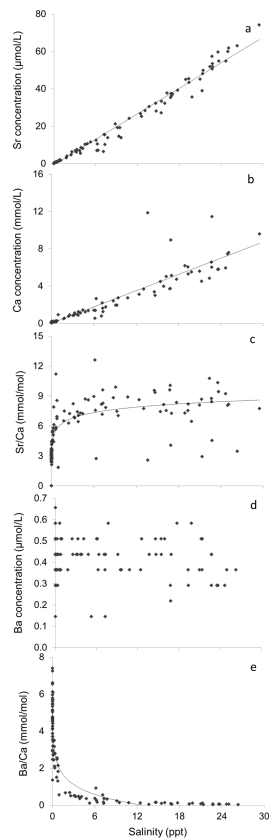


Figure 6. Mixing curves of Sr concentration **(a)**, Ca concentration **(b)**, Sr/Ca ratio **(c)**, Ba concentration **(d)**, and Ba/Ca ratio **(e)** across salinity gradient along the Calcasieu River.

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