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Metal Transport in the Mixing Zone of an Estuarine River to the Northern Gulf of Mexico

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Abstract: To better understand the pollution potential of metals in estuaries heavily concentrated with petrochemical industries, we measured concentrations of total recoverable metals in the lower Calcasieu River in southwestern Louisiana that flows into the northern Gulf of Mexico. Water samples were collected at six sites along the last 88 km reach of the river monthly between May 2013 and November 2015, during which salinity ranged from 0.02 to 29.5 ppt from upstream to downstream. The samples were analyzed for a series of total recoverable metals, including aluminum (Al), arsenic (As), boron (B), cadmium (Cd), calcium (Ca), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), lithium (Li), magnesium (Mg), manganese (Mn), nickel (Ni), silicon (Si), titanium (Ti), vanadium (V), and zinc (Zn), of which only Al, As, B, Ca, Fe, Li, Mg, Mn, Si, Ti, and Zn had a detection rate higher than 30% over the 31-month study period. In the freshwater portion of the river, Si, Ca, Al, Fe, and Mg showed the highest concentration (8, 5, 4, 2, and 2 mg/L, respectively), while Li, As, Zn, Ti, and B had the lowest concentration (6, 16, 27, 34 and 50 μg/L, respectively). The concentrations of Al and Si declined by more than 30% from the freshwater to the river mouth, but the concentrations of Li and B increased by 61 and 66 times, respectively. None of these metals' concentrations were found to exceed US EPA standards, but the rapid increase in Li and B concentrations may indicate a potential anthropogenic influence. On average, the Calcasieu River discharged a total of 35,484 tons of the elements each year (or 8059 kg/km^2/yr), of which Si, Al, Ca, Fe, and Mg contributed 98%. Three major components of factors were extracted explaining 34, 20, and 13% (cumulative 67%) of the total variation in the metal concentrations. Salinity and pH were the major (>0.3) parameters in component 1 explaining the variability of B and Li; TSS was the major (>0.3) parameter in component 2 explaining the variation of Al, Fe, and Ti concentration; and temperature and DO% were the major (>0.3) parameters in component 3 explaining the variation of Mn concentration. Further studies on riverbed sediment metals and their effect on metal concentrations in surface water can help understand the metal sources and their potential effects on coastal aquatic ecosystems.

Keywords: riverine metals; total recoverable metals; metals in mixing zone; estuaries; Calcasieu River; Gulf of Mexico

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1. Introduction

Estuaries are sinks for suspended solids and thus for metals associated with them that originate from natural and anthropogenic influences in their watersheds and along their shores [1,2]. They are often locations of port, urban, industrial, and recreational development, and are also important habitats for many forms of animal life [3]. This makes estuaries highly vulnerable to human activities that produce toxic substances, including heavy metals. The impacted aquatic species by toxic substances can include microorganisms, aquatic plants, benthic macroinvertebrates, zooplankton, fish, reptiles, and amphibians [4,5]. Aquatic-dependent birds and mammals can be also exposed through ingestion of contaminated prey species [6–8]. Consumption of contaminated seafood by humans poses a potential health risk due to the presence of toxic substances that undergo biomagnification in estuarine food chains [3]. Although there are fundamental biogeochemical processes, variances in the time scales of mixing and transport result in significant variations in the routes, cycling, and fate of pollutants within coastal zones.

Estuarine systems face a variety of threats including alterations in land use within a river basin [9,10], increase in nutrient levels within a riverine system [11,12], industrial pollution in coastal areas [13], and sea level rise [14,15]. With rising sea levels, saltwater intrudes upstream, potentially reaching inland tributaries. The rise in salinity and pH levels can significantly influence various chemical and biological processes within estuarine waters. One such process is the adsorption–desorption of trace elements from suspended sediments in estuarine mixing zones. It has been observed that salinity and pH can have a substantial impact on the mobility and flux rates of trace elements as they are transported by rivers to different estuarine and coastal systems worldwide [16,17]. Although it is well-established knowledge that changes in pH can regulate the desorption and absorption of metals from the sediments, field studies are relatively limited on the fluctuation of metals in water along estuarine reaches.

The Calcasieu River in southwest Louisiana, USA, presents a typical low-land, intensively human-affected estuary. The estuary serves as an important navigation channel for petrochemical and fishery industries to the northern Gulf of Mexico. A deep draft channel was created before the 1960s, connecting the Gulf of Mexico to the industrial Lake Charles area. This resulted in the migration of saltwater from the Gulf of Mexico further inland, leading to the collapse of some vulnerable wetland environments within the Calcasieu River Basin. In response to this environmental issue, a dam known as the Calcasieu River Saltwater Barrier was constructed in the 1960s upstream of Lake Charles. The purpose of the barrier was to prevent the intrusion of saltwater into the upstream region [18]. In addition to saltwater intrusion, the river flows through the Lake Charles area that is densely populated with refinery and other petrochemical facilities on its banks and the banks of its tributaries; for instance, Bayou d’Inde, which drains into the Calcasieu River, has been industrialized since oil and natural gas deposits were discovered nearby in the 1920s. Bayou d’Inde has been severely contaminated by numerous industrial and municipal outfalls along its length, and highly elevated levels of toxic metals were found in surface sediment [18,19]. This raised concerns and triggered the U.S. Environmental Protection Agency (EPA) to declare the site as a Superfund site (i.e., a special study site identified through the Comprehensive Environmental Response, Compensation, and Liability Act) in the 1980s. The presence of these two reasons makes the river estuary an excellent site for studying the behavior of metals within salinity gradients.

Because of the concerns of potential contamination of metals from industrial development in the Calcasieu River Estuary, several studies were conducted in the 1980s and 1990s to document heavy metal levels in the estuary waters, such as mercury in the surface sediment and various types of biota from the Calcasieu River/Lake complex [19], the macrobenthic communities in the Calcasieu Estuary [20–22], and the effects of contaminants on macrobenthic communities in the upper Calcasieu Estuary. Beck et al. [23] measured heavy metals Cd, Cr, Cu, Pb, Hg, Ag, and Zn in sediments in the Calcasieu River/Lake complex, and the results showed that sites near sewage and industrial outfalls had increased metal concentrations above the background levels, but the increases were restricted to the regions near the outfalls. The Calcasieu Estuary cooperative site underwent a remedial investigation/feasibility study (RI/FS) starting in 1998 [7]. The site under investigation includes the section of the estuary from the saltwater barrier on the Calcasieu River to Moss Lake. Part of the result of the RI/FS study—a 58-page long baseline ecological risk assessment—was published in 2011 [7–9]. According to the study, the portion of the Calcasieu Estuary from the saltwater barrier to Moss Lake was identified as the area in which environmental contamination posed the greatest potential risks to ecological receptors and, as such, was designated as the primary study area.

Collectively, these studies have helped gain a baseline of the levels of some trace elements in sediments of the Calcasieu River. However, none of them has looked into actual heavy metal levels in the estuarine water. In addition, most data records are of short duration and lack a long-term monitoring program to study metal migration and transformation dynamics in surface waters along the mainstream of the Calcasieu River mouth. To fill in the gap, we conducted this 31-month study with the following specific objectives: (1) to document the level of heavy metals in the estuarine water, (2) to determine spatial trends of these metals along the 88 km freshwater–saltwater mixing reach, (3) to quantify mass transport of the metals from the Calcasieu River to the estuary, and (4) to identify factors with which metal concentration and transport are associated with across the spatiotemporal scale.

2. Methods

2.1. Study Area

This study focused on the lower Calcasieu River in Southwestern Louisiana, USA (Figure 1). This river is one of the three major rivers that flow across the Louisiana Chenier Plain west of the modern Mississippi River Delta. In the research area, the summer season is long, hot, and humid, while the winter season is short and warm. Muck soils and sandy loam soils represent the main soil types in the study area (>65%). Agriculture is the primary activity of the people living in the northern part of the study area (Calcasieu Parish). Cultivated cropland, pastureland, and woodland collectively account for over 65% of the land in the area, with urban land, marshland, and swampland occupying the majority of the remaining acreage. In the southern part of the study area (Cameron Parish), coastal marshland predominates, serving as habitats for wildlife and range land.

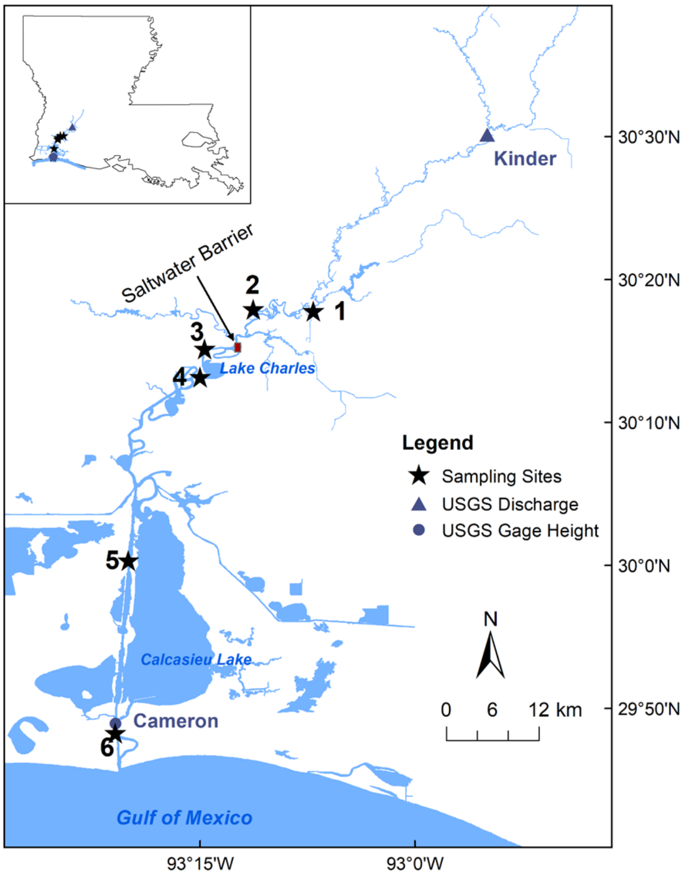

Figure 1. Geographic location of the Calcasieu River in southwestern Louisiana, USA, and the six sampling sites and USGS gage stations. Sites 1 and 2 represent the freshwater reach, while other sites are influenced by saltwater.

2.2. Sample Collection

Six sampling sites were selected directly along the last 88 km reach of the Calcasieu River. We made monthly field trips between May 2013 and November 2015 (except for June 2013, October 2013, November 2014, September 2015, and October 2015) to conduct in-situ measurements and collect surface water samples at these sampling sites (Figure 1). Site 3 was only sampled from August 2014 to November 2015. A saltwater barrier is located approximately 2 km downstream of site 2. All sampling sites below the barrier are affected by tides due to the funding limitation, stratification was not considered in the sampling.

During each trip, a series of ambient water parameters were measured, including water temperature, dissolved oxygen (DO%), pH, salinity, and specific conductance, with a YSI 556 multi-probe meter (YSI Inc., Yellow Springs, OH, USA). Additionally, 250 mL water samples were collected from each site for elemental analysis and 1 L water samples were collected for total suspended solids (TSS) analysis. Water samples were collected using high-density polyethylene (HDPE) bottles, all of which were thoroughly acid washed before use. Water samples are collected approximately 30–50 cm below the surface. Samples were collected from a pier projecting approximately 8–15 m into the river channel using a grab sampler consisting of a 3.7 m aluminum rod with a polyethylene bottle attached to the end of the rod. The water samples were acidified to $\mathrm{pH} < 2$ at the time of field collection. During transport, the samples were stored in coolers with wet ice and refrigerated in the laboratory until analysis. On each trip, duplicate samples were collected at one of the sites; statistical analyses indicated no significant differences (less than 5%) between the duplicate samples, and duplicate data were removed from further analysis.

2.3. Sample Analysis

Water samples were analyzed for total recoverable concentrations, or the combination of dissolved and particulate metals of all elements at the W. A. Callegari Environmental Center, Louisiana State University Agricultural Center using EPA Method 200.7. Therefore, concentrations of the study metals can be affected by total suspended solids in the water samples. Briefly, every 47 mL of sample solution was combined with 1 mL metal-grade concentrated HCl and 2 mL metal-grade concentrated HNO_3 in a 50 mL tube and was digested with a HotBlock (Environmental Express, Charleston, SC, USA) at 115 °C until all but 20 mL of the sample solution evaporated. Yttrium was added to the water samples as an internal standard. Six-point calibration was performed using standard solutions (Exaxol Chemical Corporation, Clearwater, FL, USA) diluted in deionized water. Element concentrations above the calibration curve were diluted by a factor of 10, 20, 50, 100, or 1000 to bring them into the calibration curve. The analyses were conducted using an inductively coupled plasma optical emission spectrometer (ICP-OES, Varian Vista MP-X, Palo Alto, CA, USA).

Field and laboratory blanks, as well as Independent/Continuing Calibration Verification/Blanks, were used for quality control to ensure that the samples were not contaminated and that all sample analyses were within control limits. Analyses of multi-element standards (Exaxol Chemical Corporation, Clearwater, FL, USA) were also routinely included in the quality control. Duplicate analyses of water samples typically yielded an error of less than 5%. The method detection limits for aluminum (Al), arsenic (As), boron (B), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), lithium (Li), manganese (Mn), nickel (Ni), titanium (Ti), vanadium (V), and zinc (Zn) in surface waters are 60, 10, 20, 10, 10, 10, 10, 10, 3.7, 10, 10, 3.8, 10, and 10 μg/L, respectively. The levels of the metals reported in this study were all above the detection limit. For those metal elements whose concentration was too low (the detection rate in most of the sites was lower than 30%), such as Cd, Co, Cr, Cu, Ni, and V, we excluded them from the spatial and temporal variation analysis.

2.4. Other Data Collection

Long-term daily discharge (available since September 1922) and gage height (available since October 1997) data of the Calcasieu River were collected by the U.S. Geological Survey (USGS) in the study area. Stations close to the sampling sites were used to assess flow. Specifically, daily discharge was collected at the Calcasieu River near Kinder, LA (USGS 08015500), and the daily gage height at the Calcasieu River near Cameron, LA (USGS 08017118) was used for this study (Figure 1). These data were utilized for metal transport and river flow condition analysis.

2.5. Data Analysis

Daily discharge values were collected from the U.S. Geological Survey (USGS) to calculate annual metal loads. Daily discharge data were collected on the Calcasieu River near Kinder, LA (USGS 08015500). Total annual load estimates were calculated using the following flow-weighted discharge equation:

$$L_a = \sum_{month} Q \times \left(\frac{\sum L_d}{\sum Q_d} \right) \quad (1)$$

where L_a is the total annual load, L_d is the total daily element load of samples collected, and Q_d is the total daily discharge on days of sample collection.

Statistical analysis was performed with the SAS 9.2 software package. All data were first tested for normality using the Shapiro–Wilk Test. All data proven non-normally distributed were compared using the Wilcox non-parametric one-way comparison of medians. Any data determined normally distributed were compared using Student's paired-samples *t*-test. Regression analysis was performed to identify factors that affect metal transport and spatial trends.

3. Results

3.1. Hydrology and Ambient Conditions

Between 1 May 2013 and 30 November 2015, the average daily discharge of the Calcasieu River was 42 ± 59 m^3/s (cubic meters per second), fluctuating from 5 to 597 m^3/s (Figure 2). The discharge during the 2.5-year study period was notably lower than the long-term average from 1980 to 2009 (72 ± 66 m^3/s; USGS). Seasonally, discharge was higher during the winter and spring months and lower during the summer and fall during the sampling period, consistent with the long-term average trends. April had the highest average discharge (103 m^3/s) and August had the lowest (9 m^3/s). During the 25 days when water levels were collected, the average daily discharge ranged from 5 to 259 m^3/s (Figure 2).

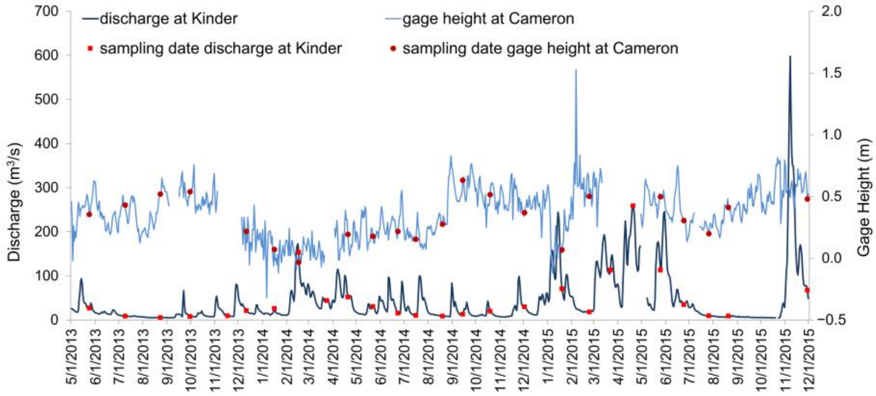

Figure 2. Sampling dates (red squares and dots) and average daily discharge at Kinder, LA (solid black line; USGS Station# 08015500) and tidal gage height at Cameron, LA (solid blue line; USGS Station# 08017118).

The Calcasieu River, near its mouth at Cameron, showed a long-term (October 1997–November 2015) average daily gage height (or tidal stage) of 0.31 m (±0.18) (NGVD29), ranging from −0.48 to 2.31 m. During the 2-year study period, daily gage heights at Cameron fluctuated from −0.32 to 1.53 m (Figure 2), with a mean of 0.36 m (±0.20) (NGVD29). In contrast with the river discharge, the tidal stage at the river mouth was high during the fall months, with September having the highest monthly average (0.48 m, NGVD29), and low during the winter months, with January having the lowest (0.18 m, NGVD29). During the 25 field trips from May 2013 to November 2015, the daily gage heights at the Calcasieu River near Cameron ranged from −0.03 to 0.63 m (NGVD29).

Ambient water conditions at the study sites widely varied (Table 1 and Figure 3). Salinity increased with proximity to the Gulf of Mexico. Salinities at site 6 ranged from 4.8 to 29.5 ppt, averaging 19.7 ppt. There was no clear relationship between salinity and TSS (Table 2). However, the lower two sites (sites 5 and 6) had significantly higher TSS concentrations than the other four sites (Tukey–Kramer's adjustment, Table 1), suggesting that TSS in the lowermost estuary were mainly of marine sources because of turbidity maximum.

As expected, pH was positively correlated to salinity (Table 2). Although sites 1 and 2 had low salinity, the pH largely varied from 4.2 to 8.8. The criterion continuous concentration (CCC) of pH for aquatic life is 6.5 to 9 (EPA, 2016), and the average pH for sites 1, 2, and 3 were 6.3, 6.3, and 6.5, respectively, which means that waters at these three sites were slightly below the threshold for aquatic life. Sites 1 to 4 were grouped together by Tukey–Kramer's adjustment due to their similar pH values. During initial sampling, from May 2013 to March 2014, pH always exhibited large variations. A regular schedule with consistent time-of-day sampling was adhered to after March 2014, and pH subsequently remained fairly stable for the remainder of the sampling. August 2015 had the highest pH for sites 2 to 5, and the second highest for sites 1 and 6 (Figure 3b).

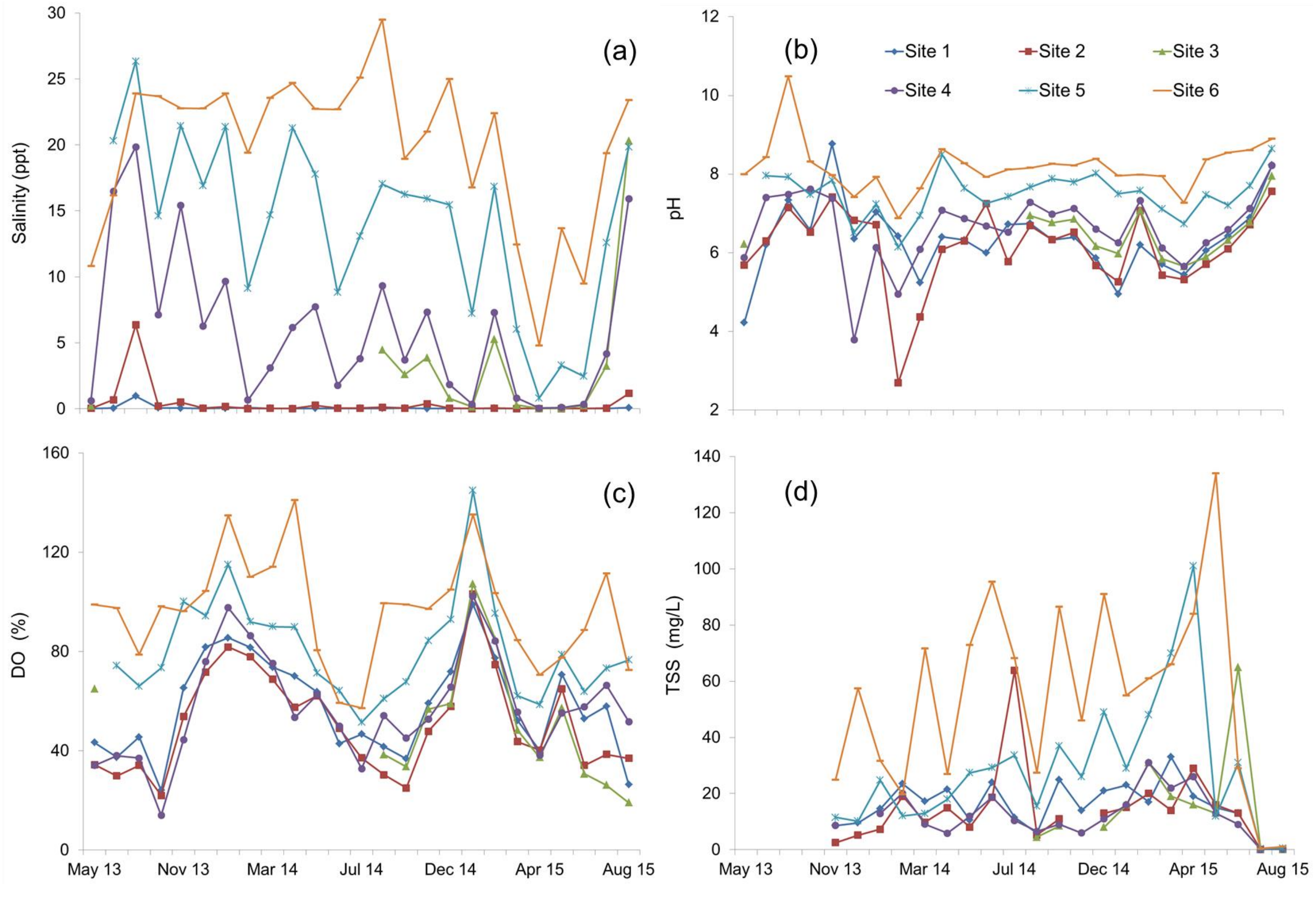

Figure 3. Seasonal trends of salinity (**a**), pH (**b**), dissolved oxygen saturation (DO, (**c**)), and total suspended solids (TSS, (**d**)) at six sampling sites along the Calcasieu River from May 2013 to November 2015. PH data during the February 2014 trip were excluded from all analyses due to instrument malfunction.

Table 1. Means and standard deviations of water quality parameters at six sampling sites along the Calcasieu River between May 2013 and November 2015. Tukey–Kramer's adjustment was performed to group sampling sites when ANOVA shows significant differences among sites. Means with the same letter are not significantly different at the 0.05 level (Tukey groupings).

Site ID	River Distance from Gulf (km)	Temperature (°C)	Salinity (ppt)	pH	DO (%)	TSS (mg/L)
Site 1	87.9	21.58	0.07 ± 0.18 ^{a}	6.34 ± 0.92 ^{a}	58.0 ± 19.2 ^{a}	17 ± 7 ^{a}
Site 2	73.5	21.83	0.40 ± 1.24 ^{a}	6.13 ± 1.03 ^{a}	51.2 ± 20.1 ^{a}	15 ± 131 ^{a}
Site 3	62.6	22.88	3.02 ± 5.30 ^{ab}	6.48 ± 0.62 ^{a}	51.2 ± 23.8 ^{a}	19 ± 16 ^{a}
Site 4	58.1	22.14	5.83 ± 5.71 ^{b}	6.61 ± 0.91 ^{a}	57.3 ± 20.7 ^{a}	14 ± 7 ^{a}
Site 5	27.0	22.51	13.96 ± 6.60 ^{c}	7.47 ± 0.59 ^{b}	81.3 ± 20.3 ^{b}	34 ± 23 ^{b}
Site 6	4.5	22.81	19.71 ± 5.87 ^{d}	8.14 ± 0.68 ^{b}	96.4 ± 21.2 ^{c}	68 ± 43 ^{c}

Table 2. Pearson correlation coefficients between element concentrations and environmental factors in the Calcasieu River. Only significant ($p < 0.01$) correlations are shown.

	Al	As	B	Fe	Li	Mn	Ti	Zn	Temperature	Salinity	pH	DO%	TSS	Discharge
Al	1.00			0.60			0.56		−0.22	−0.28	−0.38		0.24	0.41
As		1.00			0.61									
B			1.00		0.78	−0.38				0.98	0.72	0.56	0.50	
Fe				1.00			0.39			−0.26			0.35	0.36
Li					1.00	0.35				0.78	0.58	0.41	0.42	
Mn						1.00			0.48	−0.31		−0.61		
Ti							1.00						0.56	
Zn								1.00					0.37	
Temperature									1.00		0.29	−0.55		−0.28
Salinity										1.00	0.73	0.52	0.44	−0.26
pH											1.00	0.35	0.37	−0.33
DO%												1.00	0.25	
TSS													1.00	
Discharge														1.00

In general, DO solubility decreases with salinity. However, in this study, the average DO saturation rates at sites 5 and 6, which had much higher salinities, were significantly higher than the other sites (Tukey–Kramer's adjustment, Table 1). Sites 5 and 6 are closer to the Gulf of Mexico and are directly affected by tides and waves, which may have resulted in higher DO saturation rates at sites 5 and 6. Oxygen solubility also is strongly temperature dependent and decreases at higher temperatures. DO saturation rates were higher in the colder winter and spring months and lower in the warmer summer and fall months.

In general, salinity and pH in the Calcasieu River were negatively correlated with discharge at Kinder (Table 2). The Calcasieu River Saltwater Barrier prevents saltwater from flowing around the structure and upriver, and it is only opened when river flow is high (i.e., high discharge at Kinder) and to let ships pass on demand. This explains the negative relationships between discharge at Kinder and salinity and pH in the river. A negative relationship that was found between water temperature and discharge (Table 2) may be due to temperature differences between fresh water and salt water, but this study could not confirm this.

3.2. Spatial Variation in Metal Concentrations

Among the 14 elements analyzed, Cd and Co were not detected at any site and Cr and Ni showed very low detection (0 to 8%) for all the sites. The detection rates of Cu and V were higher than Cd, Co, Cr, and Ni, but the average detection rate in most of the sites was still lower than 30%. Therefore, we excluded Cd, Co, Cr, Cu, Ni, and V from further spatial and temporal variation analysis due to the possible inaccuracy of the ICP-OES method for the detection of metal elements with low detectable concentration.

In the freshwater portion, the following order of the metal concentrations existed: Si > Ca > Al > Fe > Mg > Mn > B > Ti > Zn > As > Li (Table 3). In the saltwater portion, the following order of the metal concentrations was found: Mg > Ca > Si > B > Al > Fe >

Li > Mn > Ti > As > Zn. The concentrations of Al, Fe, and Mn slightly decreased from the freshwater to the saltwater, while the concentration of As, B, and Li largely increased.

Table 3. Means and standard deviations (±) of element concentrations in water samples from six sampling sites along the Calcasieu River. Tukey–Kramer's adjustment was used to group sampling sites when ANOVA shows significant differences among sites. Means with the same letter are not significantly different at the 0.05 level (Tukey groupings).

Site ID	Al (mg/L)	As (μg/L)	B (μg/L)	Ca (mg/L)	Fe (μg/L)	Li (μg/L)	Mg (mg/L)	Mn (μg/L)	Si (mg/L)	Ti (μg/L)	Zn (μg/L)
Site 1	4 ± 3 ^{a}	16 ± 5	50 ± 50 ^{a}	5 ± 6	2170 ± 1010	6 ± 2 ^{a}	2 ± 4	130 ± 60	8 ± 4	34 ± 31	27 ± 47
Site 2	3 ± 2 ^{ab}	14 ± 5	70 ± 90 ^{a}	9 ± 20	1930 ± 840	7 ± 3 ^{a}	12 ± 37	130 ± 80	7 ± 2	26 ± 24	19 ± 11
Site 3	2 ± 1 ^{b}	19 ± 3	320 ± 340 ^{a}	27 ± 26	1400 ± 670	11 ± 7 ^{a}	68 ± 84	130 ± 60	5 ± 2	25 ± 21	17 ± 3
Site 4	2 ± 1 ^{b}	23 ± 13	640 ± 620 ^{a}	43 ± 48	1090 ± 780	24 ± 16 ^{a}	122 ± 134	120 ± 50	5 ± 2	22 ± 18	18 ± 5
Site 5	2 ± 2 ^{b}	23 ± 20	2070 ± 990 ^{b}	184 ± 175	1430 ± 2310	61 ± 40 ^{b}	444 ± 261	90 ± 50	4 ± 3	22 ± 20	18 ± 6
Site 6	3 ± 2 ^{b}	30 ± 41	3070 ± 850 ^{c}	328 ± 377	1630 ± 1240	92 ± 56 ^{c}	627 ± 308	80 ± 50	5 ± 4	44 ± 59	22 ± 14

3.3. Seasonal Variation in Metal Concentrations

During the sampling period, the total recoverable concentrations of all eight elements varied considerably from month to month. For example, Al varied from 3.59 to 16,870 μg/L at site 1, from 326 to 7869 μg/L at site 2, from 249 to 4228 μg/L at site 3, from 293 to 5008 μg/L at site 4, from 682 to 8237 μg/L at site 5, and from 537 to 8895 μg/L at site 6. In general, Al concentrations were higher during spring months (Figure 4a), and the difference in monthly concentration was statistically significant ($p < 0.01$). Considering the sampling site and month, the Al concentration showed no significant difference ($p > 0.01$), suggesting that the monthly difference in Al concentration was consistent for all the study sites. Seasonal trends of B and salinity were extremely similar (Figures 3a and 4c). This matches the fact that salinity and B were highly correlated (Table 2). It is difficult to determine the seasonal trends of As and Zn concentrations due to limited available data (Figure 4b,h) because As and Zn concentrations were below the detection limit for many of the samples. In general, Fe concentration was higher during the spring and early summer months, with one large outlier at site 5 in December 2014 (Figure 4d). However, the difference in monthly Fe concentration was not statistically significant ($p > 0.01$). The total recoverable concentration of Li at sites 5 and 6 largely varied (Figure 4e, site 5: 5–175 μg/L; site 6: 30–207 μg/L), with summer 2014 having higher concentrations. Sites 1 to 4 had much less variability of Li and there was a statistically significant difference among sampling sites ($p < 0.01$). For sites 1 to 4, Mn concentrations were higher during the summer months. There was no clear seasonal pattern in Ti concentration (Figure 4g).

3.4. Metal Loads and Transport

Five elements (Si, Al, Ca, Fe, and Mg) contributed to over 98% of the total mass load of elements from the Calcasieu River to the northern Gulf of Mexico annually (Table 4). Si, Ca, and Al showed the largest annual loads, exceeding 4000 tons per year, while B and Ti represented the smallest metal loads annually (between 20 to 100 tons). River discharge in the second year (05/2014–04/2015) increased by 79% compared with the discharge during the first study year (05/2013–04/2014). Correspondingly, nearly all elements increased in the Calcasieu River. The largest annual load increases were found in Fe, with a median change of 70%, followed by Si, Mn, and Ba at 55, 50, and 47% respectively. Loads of Al, Ca, Ti, and Sr in the Calcasieu River also increased in the second year with an increased rate between 2 and 17%. As the discharge increases, only annual loads of Na, Mg, and B decreased in the Calcasieu River, with an annual change of −15, −4, and −2% respectively.

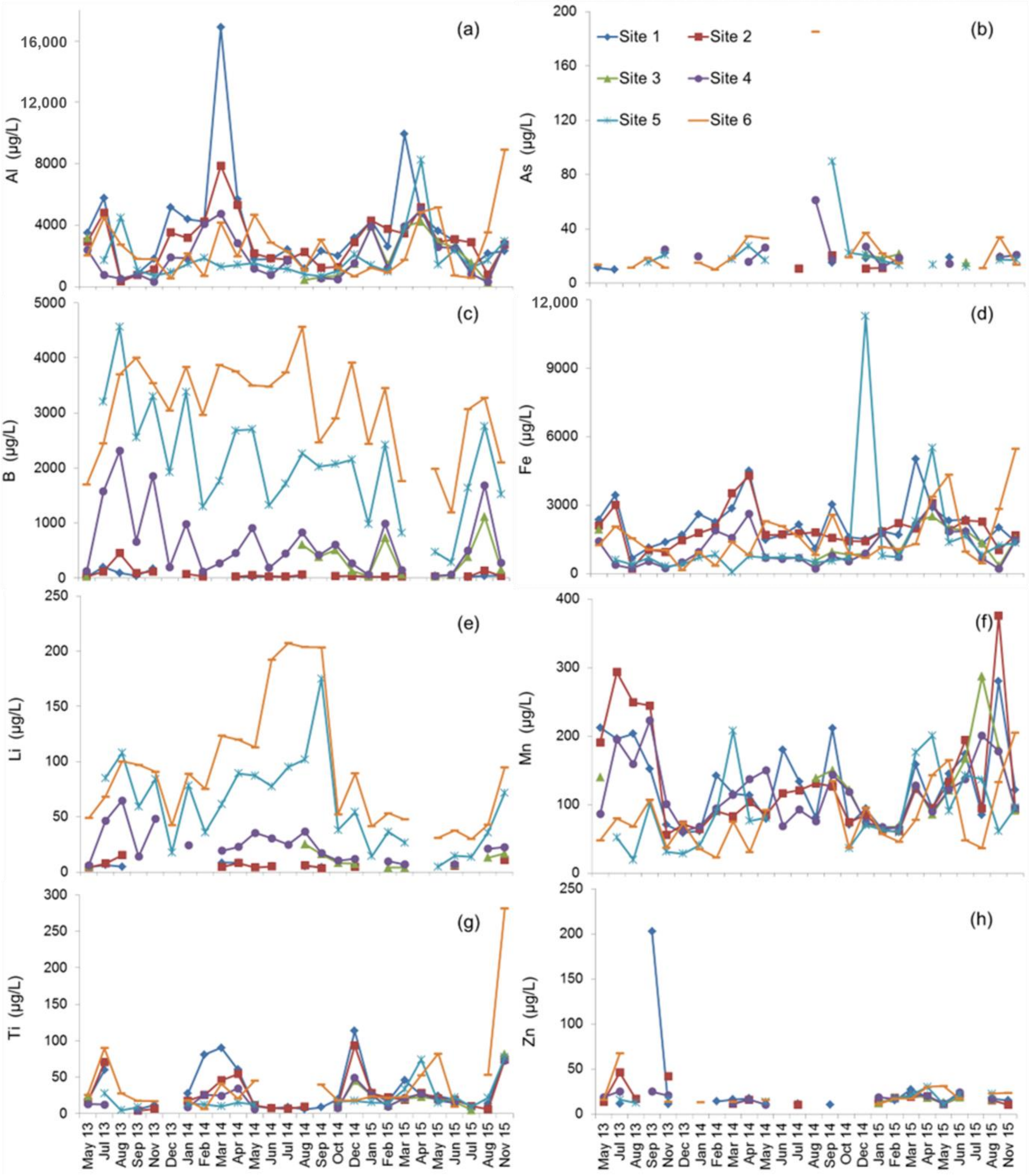

Figure 4. Seasonal trends of Al concentration (**a**), As concentration (**b**), B concentration (**c**), Fe concentration (**d**), Li concentration (**e**), Mn concentration (**f**), Ti concentration (**g**), and Zn concentration (**h**) at six sampling sites along the Calcasieu River.

Table 4. Total annual mass loads (t) and flux (kg km^{-2}) from the Calcasieu River to the northern Gulf of Mexico (in the order of mass).

Parameter	Mass Loads (t yr^{-1})	Flux (kg km^{-2} yr^{-1})	Proportion (%)
Al	5985	1359	22.93
B	40	9	0.15
Ca	4876	1107	18.68
Fe	3163	718	12.12
Mg	1907	433	7.31
Mn	165	37	0.63
Si	9909	2251	37.97
Ti	55	12	0.21
Total	26,100	5928	100

4. Discussion

4.1. Longitudinal and Seasonal Changes in Metal Concentration

The rapid increase in boron, calcium, and magnesium concentrations (Table 3) from upstream to downstream indicates a strong marine influence in the Calcasieu River. This is because of the higher concentration of these three elements in marine water [24–26]. The same is true with the increase in lithium concentration from the freshwater portion to the river mouth, although the increase is much smaller (~15 folds) compared with those of boron (61 folds), calcium (67 folds) and magnesium (314 folds). Previous studies reported that Li concentration in global oceans is about 0.17–0.18 mg L^{-1}, only slightly higher than that in freshwater [27,28]. In our study, the Li concentration in both the freshwater and saltwater portions is lower; however, the large increase from upstream to downstream may suggest a possible external source.

Based on the molar ratios of Al/Si, Fe/Si, and Ca/Mg (Figure 5), freshwater–saltwater mixing in the Calcasieu River is active between site 2 and site 4. These ratios have a clear decreasing trend from site 1 to site 4 and, afterward, show a slightly increasing trend (Figure 5). This result may represent that biological activities are very active between site 4 and site 6. The main Si activities between site 4 and site 6 showed removal, probably caused by the biological uptake and sedimentation of phytoplankton debris [29]. Al and Fe are not nutrients for marine organisms, so they are not directly influenced by biological activities. The biological uptake of Si can contribute to a higher Al/Si and Fe/Si ratio from site 4 to site 6. Compared with Al/Si and Fe/Si ratios, the trend of the Ca/Mg ratio between site 1 to site 6 is similar. The difference is that from site 1 to site 3, the Ca/Mg ratio decreases much faster (65%). Industrial activities are potential reasons for this result. Mg is one of the most common elements in industrial wastewater, especially in the petrochemical industry [30]. Mg is used as a component in various chemical processes, such as catalysts, and wastewater from petrochemical plants can introduce Mg into rivers. Additional Mg from industrial wastewater makes the Ca/Mg ratio from site 1 and site 3 decrease. Seawater typically has a higher Ca/Mg ratio than freshwater because of differences in the solubility and weathering rate of Ca- and Mg-containing minerals [31]. As salinity increases between site 3 and site 6, the Ca/Mg ratio in the estuary water increases to approach that of seawater.

The findings agree with those from other studies. Ball et al. [32] studied the reactive transport of acid mine waters released from the Summitville mine in the San Juan Mountains of southwestern Colorado into the Alamosa River. Their results showed that Al and Fe concentrations rapidly decreased because of the precipitation of Al and Fe during downstream transport when the pH increased. The study that was conducted in the upper Clark Fork River, Montana by Brick and Moore [33] showed that there were negative relationships between Fe, Mn, and Zn with pH. There are numerous studies investigating factors that could potentially control dissolved and particulate element concentrations [16,34], the study by Brick and Moore [33] assessed that temperature, salinity, pH, DO saturation, and TSS concentration factors could potentially control total recoverable trace element concentrations.

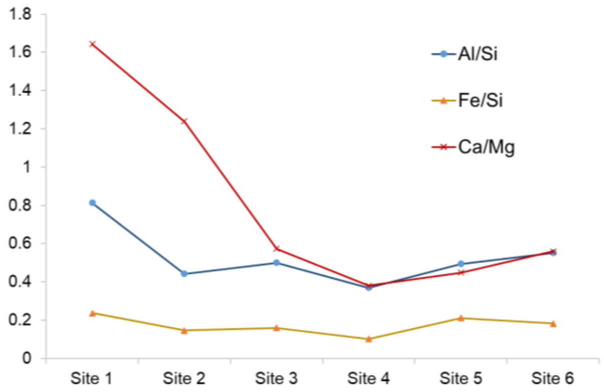

Figure 5. Spatial trends of Al/Si, Fe/Si, and Ca/Mg ratios at six sampling sites along the Calcasieu River.

The highest concentration of Al and Fe found every year in April and May could be related to the increased precipitations (Figure 4). These two months are characterized by an increase in precipitation, and the increased rainfall may lead to enhanced weathering of rocks and soils, which can release Al and Fe into the river water [35]. Additionally, rainwater can mobilize Al and Fe from the surrounding land and transport them to rivers through surface water [36]. The increase in Mn concentration found during the summer months in this study could be explained by increased biological activities. The warmer summer temperatures can enhance biological activity in river water. Microorganisms, particularly bacteria, can contribute to the reduction of manganese oxides (Mn^{4+} or Mn^{3+}) to soluble Mn^{2+} through redox reactions, which can lead to increased dissolved Mn concentrations.

4.2. Correlation between Metal Concentrations and Ambient Water Conditions

Three major component groups were identified by PCA that represent 34, 20, and 13 (cumulative 67%) of the total variance in the data set (Table 5). Salinity, pH, and the concentration of B and Li were the major (>0.3) parameters in component 1, which means that salinity and pH could be used to explain the variability of B and Li (Table 5). The Pearson correlation coefficients between salinity and pH and B and Li were significantly positive (Table 2). Boron displayed a clear positive linear association with salinity, indicating seawater from the Gulf of Mexico is a major source to the Calcasieu River (Figure 6). Lithium increased with salinity (Figure 6), but lithium deviated from the theoretical dilution line, indicating the removal of Li during transport from upstream to downstream. Marine environments are considered a sink of Li [37], which could explain why Li concentrations increased with salinity. In factor 2, TSS, Al, Fe, and Ti are the major (>0.3) parameters, which means that TSS could potentially explain the variability of Al, Fe, and Ti. Concentrations of Al, Fe, and Ti showed a significant correlation with TSS in the study area, suggesting that these elements are possibly transported in particulate form. Temperature, DO%, and Mn are the major (>0.3) parameters in factor 3, which means that temperature and DO% could potentially explain the variability of Mn. The Pearson correlation showed a statistically significant positive relationship between temperature and Mn (0.48), and a negative relationship between DO% and Mn (−0.61).

Table 5. Principal component analysis (PCA) showing factors of three components affecting metal concentration and ambient conditions. Percentage below each factor indicates the variance it explains. Values of the loadings between −0.1 and 0.1 are not shown.

	PCA Factor		
Variable	**1 (33.4%)**	**2 (20.1%)**	**3 (13.7%)**
Temperature		−0.16	0.62
Salinity	0.43	0.14	

Table 5. *Cont.*

	PCA Factor		
Variable	**1 (33.4%)**	**2 (20.1%)**	**3 (13.7%)**
pH	0.35		0.29
DO%	0.25	0.23	−0.43
TSS	0.13	0.46	0.25
Discharge	−0.21	0.26	−0.12
Al	−0.24	0.39	
As	0.24		
B	0.43	0.17	
Fe	−0.19	0.36	0.12
Li	0.38	0.15	
Mn	−0.23		0.44
Ti	−0.12	0.44	
Zn	−0.15	0.29	0.23

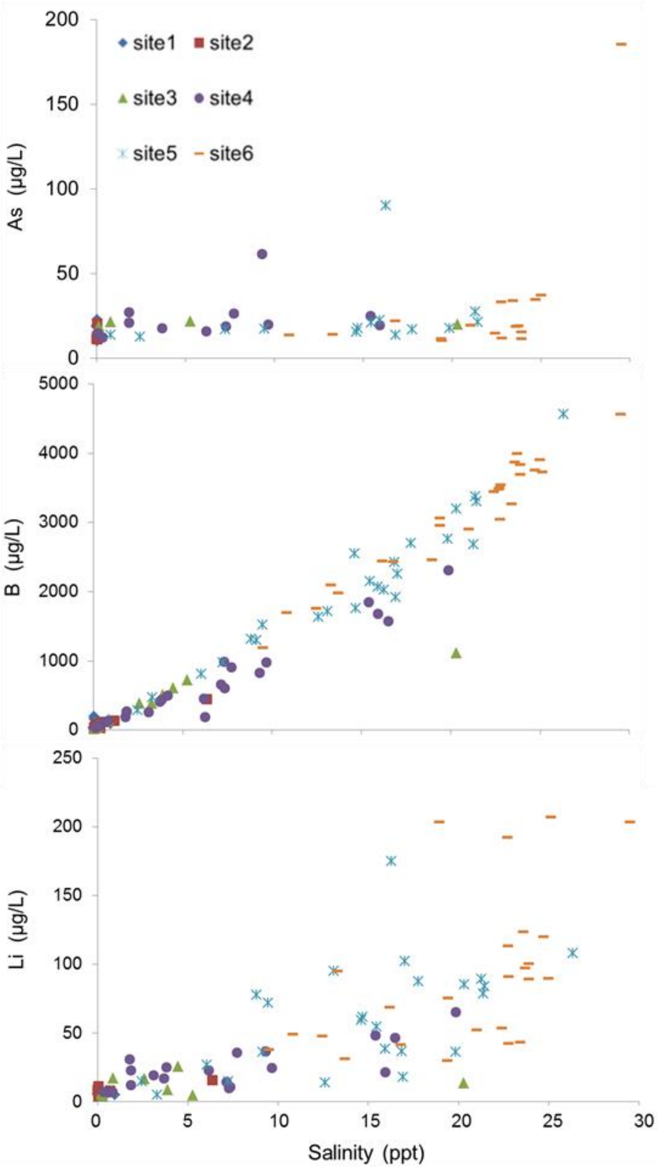

Figure 6. Mixing curves of As, B, and Li concentrations across salinity gradient from freshwater (sites 1 and 2) to mixing zone (sites 3 and 4) and saltwater (sites 5 and 6) along the Calcasieu River.

Pearson correlation of elemental concentrations showed significant correlations among some elements. There were significant correlations between Al and Fe (0.60), Al and Ti (0.56), and Ti and Fe (0.39) (all $p < 0.01$, Table 2). The significant positive correlations between Al, Fe, and Ti indicated that these elements probably had similar sources. The Pearson correlation analysis showed that there were significant positive correlations between As and Li (0.61) and Li and B (0.78) (all $p < 0.01$, Table 2). The significant positive correlations between As, B, and Li indicated that these elements probably had similar sources. According to Pearson correlation analysis, Mn and B were negatively correlated (-0.38, $p < 0.01$, Table 2). The solubility of Mn decreases with increasing pH [38], which means that Mn concentration will decrease from upstream to downstream due to the increased precipitation of Mn. However, seawater is one of the main sources of B due to the abundance of boric acid $B(OH)_3$ and borate ion B(OH)4 in seawater [38]. Therefore, with increasing salinity, Mn concentration decreases and B concentration increases.

In our research, we found abnormally lower concentrations of Mn at sites 5 and 6. Some previous studies have found similar anomalies and attempted to explain them. A review paper on metal and metalloid removal in constructed wetlands by Marchand et al. [39] concluded that metal removal rates in wetlands depend on the type of element (Hg > Mn > Fe = Cd > Pb = Cr > Zn = Cu > Al > Ni > As), their ionic forms, substrate conditions, season, and plant species. Wetlands do not just remove metals and metalloids, but they can also release them. Olivie-lauquet et al. [40] studied the seasonal variability of trace elements release in wetlands and showed marked seasonal changes in dissolved concentration for all elements except Zn and Cu. Combining the results of past studies, we speculate that the dynamics of some elements in our study have been changed because the lower portion of the Calcasieu River is mainly coastal wetlands. For instance, the removal of Mn by coastal wetlands during transport. However, a more detailed study is needed to have a solid conclusion.

We found that although there are relatively clear linear relationships between the concentration of some trace elements and some specific environmental factors, the changes in the concentration of some trace elements over time and space are too complicated, and no corresponding relationship can be found between specific environmental factors and them. The causes for the change in seasonal element concentrations and ratios of a coastal river can be complicated by interrelationships among potential controlling factors [41]. The variability of trace-element concentration may be important even on a diel basis [38]. Brick and Moore [33] have reported that dissolved manganese and zinc concentrations increase two and three-fold at night, while major solutes and water discharge show no evidence of variations. Ten-fold daily to weekly variations of manganese have been described in the Kalic River between winter (minimum concentrations) and snowmelt in May [42]. Due to the mixing of freshwater and saltwater, estuaries are highly dynamic and complex environments. Saltwater intrusion caused by sea level rise will change the mixing point of freshwater and saltwater, which, in turn, may have a significant impact on biogeochemistry within a river. These factors will make explaining the temporal variability of element concentrations in a coastal river extremely challenging.

4.3. Environment Risk of Metals in the Calcasieu River

The concentration of metals found in our study may have been elevated by total suspended solids in the water samples. However, the TSS concentrations in the Calcasieu estuary were generally low (i.e., <20 mg/L), especially in freshwater samples. We compared our findings with the EPA's aquatic life criteria for toxic chemicals that are the highest concentration of specific pollutants or parameters in water that are not expected to pose a significant risk to the majority of species in a given environment, or a narrative description of the desired conditions of a water body being "free from" certain negative conditions [43]. According to the National Recommended Water Quality Criteria—Aquatic Life Criteria Table, the criterion maximum concentration (CMC) and CCC of Al in freshwater are 750 and 87 µg/L, respectively. The average total recoverable concentrations of Al in this study

(1890 µg/L at site 5 to 3730 µg/L at site 1) were at least twice the CMC and 18 times the CCC values (Table 3). Iron is an essential trace element required by both plants and animals. In some waters, it may be a limiting factor for the growth of algae and other plants [44]. However, the Fe concentrations in this study (1090 µg/L at site 4 to 2170 µg/L at site 1) were higher than the CCC of 1000 µg/L [44]. Only sites 5 and 6 had B concentrations above the criterion of B for long-term irrigation on sensitive crops (750 µg/L) [44]. This should not cause any problems because the lower portion of the Calcasieu River is mainly coastal wetlands [45]. Although inhaled manganese dust has been reported to be toxic to humans, manganese normally is ingested as a trace nutrient in food [44]. Only a few manganese toxicity problems have been found throughout the world, and these have occurred under unique circumstances, i.e., a well in Japan near a deposit of buried batteries [46]. To protect against a possible health hazard to humans by manganese accumulation in shellfish, a criterion of 100 µg/L was recommended for marine water [39]. In this study, four out of six sites had average Mn concentrations higher than 100 µg/L. However, these five sites are not marine environments. Therefore, there should be little concern about Mn pollution in the Calcasieu River. The concentrations of As, Cd, Cr, Cu, Ni, and Zn in this study did not exceed EPA standards [43,44]. There were no EPA aquatic life standards for Co, Li, Ti, and V, so we cannot ascertain the potential influence they may have on the coastal ecosystem. Many estuaries around the world are experiencing potential metal pollution. A study from the Yangtze River estuary in China revealed that the highest measured value of dissolved as in the surface water within the study area reached 243 µg/L [47]. The highest measured value of dissolved Zn in the surface water reached 130 µg/L, which is 2 times higher than the highest measured Zn concentration in this study area. Another study on the metal concentration in the Modaomen estuary in China showed that the measured value of dissolved Zn in the surface water within the study area can reach a maximum of 140 µg/L [48]. All the evidence indicates that estuaries are highly vulnerable and susceptible to human activities' impacts. Therefore, we believe that future monitoring of metal concentrations in the Estuarine Calcasieu River and continued research on metal transport will play a crucial role in protecting the coastal environment of Louisiana.

5. Conclusions

This study investigated the concentrations and mass transport of metals from May 2013 to November 2015 in an 88 km long estuarine river. The Calcasieu River, that has been strongly influenced by human activities. The spatial and temporal variations of the concentration of total recoverable metals, including Al, As, B, Ca, Cd, Co, Cr, Cu, Fe, Li, Mg, Mn, Ni, Si, Ti, V, and Zn, were assessed in the estuary with a salinity level ranging from 0.02 to 29.50 ppt. We found that 11 (Al, As, B, Ca, Fe, Li, Mg, Mn, Si, Ti, and Zn) out of the 17 elements had a detection rate higher than 30% over the study period. Five elements (Si, Al, Ca, Fe, and Mg) contributed to over 98% of the total mass load of elements (26,100 tons/yr or 5928 kg/km^2/yr) from the river annually. Longitudinally, from freshwater to saltwater, the concentrations of Al, Fe, and Mn significantly decreased, while the concentrations of As, B, and Li largely increased, indicating a marine influence on the metal dynamics. Seasonally, the concentrations of Al, Li, Fe, and Mn are higher during spring and summer, while the concentrations of B and Ti have no clear seasonal trend. This difference can be partially explained by river water temperature, salinity, pH, DO%, and TSS. Despite the concern over metal pollution in this river draining the petrochemical industrial area, we found no elevated concentration of the study metals. Specifically, the concentrations of As, Cd, Cr, Cu, Ni, and Zn found in this study did not exceed EPA standards. However, the rapid increase in Li (50-fold) and B (15-fold) concentrations from the freshwater to the saltwater reach may indicate a potential anthropogenic influence, although, currently, no EPA aquatic life standards exist for the concentration levels of these elements. Further studies are needed to discern the source of the elements and their potential effects on coastal aquatic ecosystems.

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Data Availability Statement: River discharge and stage data used in this study can be obtained from the United States Geological Survey (https://waterdata.usgs.gov/nwis/sw). Field measurement data during this study are available from the corresponding author upon reasonable request.

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