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A time-series of heavy metal geochemistry in sediments of Galveston Bay estuary, Texas, 2017-2019

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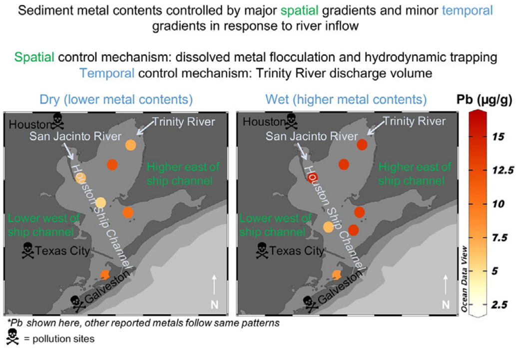
HIGHLIGHTS

- Galveston Bay sediment metal content spatial variability driven by flocculation
- Sediment metal levels have not declined in recent history despite clean-up efforts.
- Galveston Bay sediments may be toxic for As, Cd, Cr, Cu, Ni, Sb, Zn and Hg.

GRAPHICAL ABSTRACT



Sediment metal contents controlled by major spatial gradients and minor temporal gradients in response to river inflow

Spatial control mechanism: dissolved metal flocculation and hydrodynamic trapping
Temporal control mechanism: Trinity River discharge volume

*Pb shown here, other reported metals follow same patterns
☠ = pollution sites

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ABSTRACT

Galveston Bay is an anthropogenic-influenced estuary where industrial runoff, wastewater, and shipping vessel discharges enter the bay alongside natural freshwaters. Here, heavy metal concentrations in Galveston Bay surface sediment (2-year quarterly time-series) and a single sediment core are presented to explore the anthropogenic and geochemical controls on the spatiotemporal distributions, fluxes, sources, and potential toxicity of metals within this estuary. Samples were leached to distinguish authigenic sediment coatings from geogenic crystalline material. Spatial differences dominate the observed concentration variability, with higher metal concentrations in eastern vs. western bay sediments, as the eastern bay is where metals are flocculated from the dissolved phase and/or sediments are hydrodynamically trapped. Temporal variations are a secondary controlling factor, with sediment metal concentrations positively correlated with Trinity River discharge. Core data indicate stable Fe, Pb Ni, Cd and Hg levels during the 20th century but increasing Cu and Zn levels in recent years. Galveston Bay sediments are potentially toxic for As, Cd, Cr, Cu, Ni, Sb, Zn and Hg, based on federal toxicity standards. Enrichment factors and statistical analyses suggest that Ni and Cr originate from natural sources, while anthropogenic sources dominate supply of As, Cd, Hg, Ni, Pb, Sb, and Zn. This unique time-series shows that major flooding events, such as Hurricane Harvey in 2017, affect surface sediment metal distributions in Galveston Bay, but not any more than the natural geochemical controls on spatiotemporal distributions of metals in anthropogenic-influenced estuaries.

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1. Introduction

Galveston Bay, Texas, located southeast of Houston, is an anthropogenic-influenced estuary that is heavily influenced by human activity, making it an ideal location to study how an estuarine system "naturally filters" anthropogenic heavy metals from the environment (Harmon et al., 2003). The Houston Ship Channel (HSC), an extension of the Port of Houston that bisects the estuary, contains ~30-50% of all petrochemical facilities in the United States (Santschi et al., 2001). Heavy metals may enter the bay via atmospheric deposition, urban and industrial runoff, wastewater treatment plant discharges, improper disposal of contaminants at industrial facilities, shipping vessel oil, and chemical leaks. Between 1966 and 1979 the HSC was deemed one of the most polluted waterways in the country. Since then, concerted efforts have been underway to clean up the HSC and greater Galveston Bay (Lester and Gonzalez, 2011; U.S. Environmental Protection Agency, 1980). Despite these changes, pollutant discharges into the bay continue since enormous quantities of chemicals and oil are transported across the bay and processed by industry each year (Santschi et al., 2001; Saleh and Wilson, 1999).

Once emitted, heavy metals persist and accumulate in the natural environment (Wright and Welbourn, 2002). Effects of metal exposure include a variety of detrimental health issues, most notably cancer, neurotoxicity, and mortality (Tchounwou et al., 2012). In natural aqueous environments, processes such as desorption, dissolution, resuspension, precipitation, flocculation, deposition, and biotransformation allow metals to be exchanged between bottom sediments, the water column, and the biota (Turner and Millward, 2002). Previous studies have demonstrated that particle-reactive dissolved heavy metals are largely scavenged by particles removed to sediments within estuaries, thereby reducing metal loadings into coastal waters (Marsan et al., 2014; Ip et al., 2007; Tang et al., 2002; Elbaz-Poulichet et al., 1984). In this way, estuaries naturally filter particle-reactive heavy metals from waters before reaching the ocean. Over time, metals in estuarine/marine sediments accrue; thus, sediment cores become records of metal loadings at a given location over time. Datasets constraining metal fluxes, metal abundances within estuarine pools (waters, sediments, biota), and the mobility of metals between sources and sinks are necessary to improve the understanding of heavy metal biogeochemical cycles and their application to successful estuarine resource management (Lester and Gonzalez, 2011; Rauch and Pacyna, 2009; Morse et al., 1993).

Here, Al, As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sb, and Zn concentrations in Galveston Bay sediments are presented with the goal of exploring heavy metal fluxes and potential toxicity in this anthropogenic-influenced estuary. The heavy metal distributions presented here provide spatial variability of metal concentrations across Galveston Bay sediments from the main bay, the rim of the bay and source waters entering the bay, and they also provide a seasonally-resolved time-series of sedimentary metal loadings. This study will also assess metals in differing sediment fractions of surface and core sediments, with an emphasis on readily exchangeable surface-adsorbed metals that may be most harmful to biota. Data provided by the surface and core sediments will be used in evaluating heavy metal loadings from source waterways, assessing potential heavy metal toxicity, and understanding the history of heavy metal pollution in Galveston Bay.

2. Materials and methods

Seventy-seven Galveston Bay surface sediment samples were acquired on 11 shipboard expeditions on the R/Vs *Lithos* and *Trident* from June 2017 to June 2019 (Fig. 1). Sixty-four samples are from stations within Galveston Bay ("bay stations") and thirteen samples are from tributaries that drain into Galveston Bay ("endmember stations"). A Van Veen grab sampler was used to collect the upper 10 to 15 cm of sediment. Seawater samples were also drawn in the field at the time of sampling at each bay and endmember station; salinity analysis details are in the Supplementary Materials (SM). Twenty-three subsamples were acquired from a Galveston Bay sediment core ("E3" collected July 2016) at 5 cm intervals, with E3-1 representing the core top and E3-23 the core base. In July-August 2018 and June 2019 surface

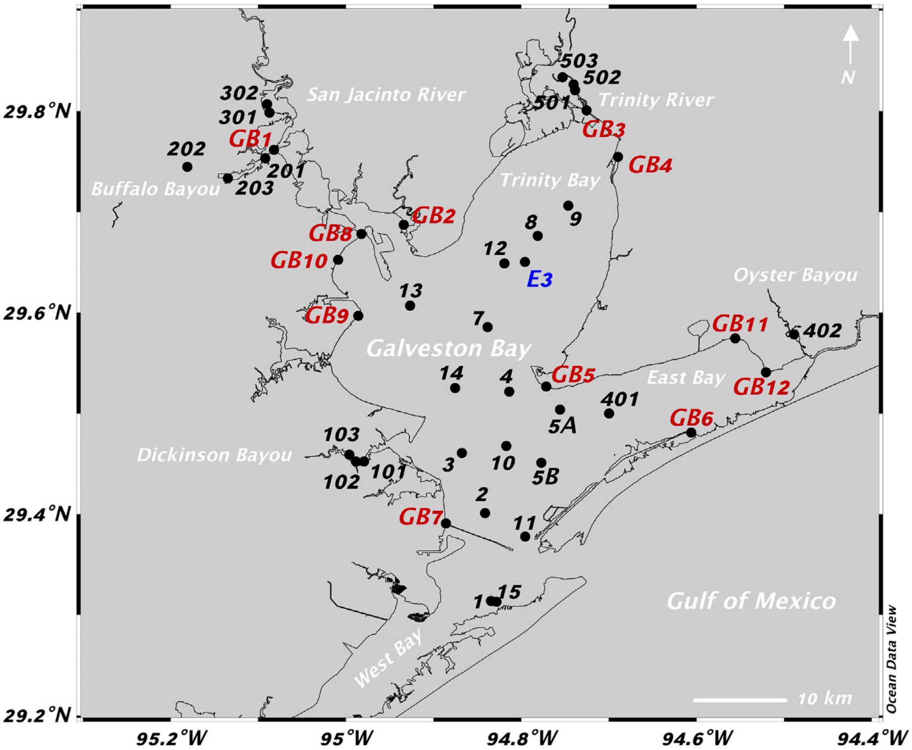


Fig. 1. Sample map showing the location of surface and core sediment samples in this study. Red labels denote shoreline stations, black labels indicate endmember and bay stations, and the blue label designates the E3 sediment core. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

sediment samples were collected along the shoreline of Galveston Bay by hand-scooping with gloved hands (nitrile, Dot Scientific) into acid-cleaned 50 mL centrifuge tubes ("shoreline stations"). After collection, all samples were transported directly to the laboratory and stored at -18 °C to 4 °C until processing was completed. Further details are in Lopez et al. (2021).

The sediments were centrifuged and oven-dried at 60 °C to remove all water. To eliminate the carbonate fraction, visible shell material was removed from the dried sediments. Dry bulk sediments were homogenized using a mortar and pestle. Heavy metals can partition into the surface exchangeable, carbonate, Fe-Mn oxide, organic matter, and the residual fractions in marine sediments (Berger et al., 2008; Tessier et al., 1979). Thus, 20 mg subsamples were leached with 0.02 hydroxylamine hydrochloride in 25% acetic acid to extract the surface exchangeable and Fe-Mn oxide-bound metals. 10 mg subsamples were fully digested in a 3-step procedure of 2:1 hydrofluoric-nitric acid, hydrochloric acid, and dilute hydrochloric acid prior to total sediment concentrations. Separately, 0.5 g subsamples were processed and analyzed for Hg concentrations, as outlined in the SM. These analytical procedures are detailed in Lopez et al. (2021) and outlined in the SM. Procedural blanks (no sediment) and the National Institute of Standards (NIST) 2702, National Research Council Canada (NRCC) MESS-4 and NRCC PACS-3 standard reference materials (SRM) were prepared alongside all samples, and recoveries were good (Table S1). Blank contributions to the samples were negligible.

3. Results

Elemental concentrations measured in Galveston Bay sediment leachates and bulk digests are presented as a function of sample type in Table 1 and are described in detail in the SM (Table S2 and Fig. S2). On average, approximately 3-7% of the Al, Fe and Cr, 19-31% of the As, Cu, Ni, Pb, Sb and Zn, and 46-56% of the Cd and Mn in Galveston Bay sediments exists in the leachable fraction relative to the bulk sediment concentrations. The proportions of Al, Mn, Ni, and Zn in the leachable fractions of Galveston Bay sediments is similar to previous findings; however, further comparison is precluded by differences in leaching methods (Wen et al., 2008; Morse et al., 1993).

Individual metal concentrations were assessed against Al, Fe, and Mn concentrations in the sediments (SM Table S3). The strong linear correlation ($R^2 > 0.96$) between bulk sediment Al and Fe indicates that any Fe (oxyhydr) oxide phases in Galveston Bay sediments co-vary with the lithogenic phases that Al traces. Subsequently, the strong correlations (R^2 between 0.89 and 0.94) between the Ni and Cr concentrations and Al and Fe concentrations in the bulk sediments indicates that these metals are associated with the naturally-sourced lithogenic sediment phase, derived from weathering into rivers, and/or an authigenic Fe (oxyhydr)oxide phase. Weak correlations (R^2 between 0.04 and 0.73) exist between the Pb, Sb, As, Zn, Cd, Cu, and Hg concentrations and Al, Fe, and Mn concentrations in the bulk sediments, indicating that these metals may be anthropogenically sourced or that they are influenced by processes such as flocculation, resuspension, and diagenesis.

3.1. Spatiotemporal variability of surface sediment heavy metal concentrations

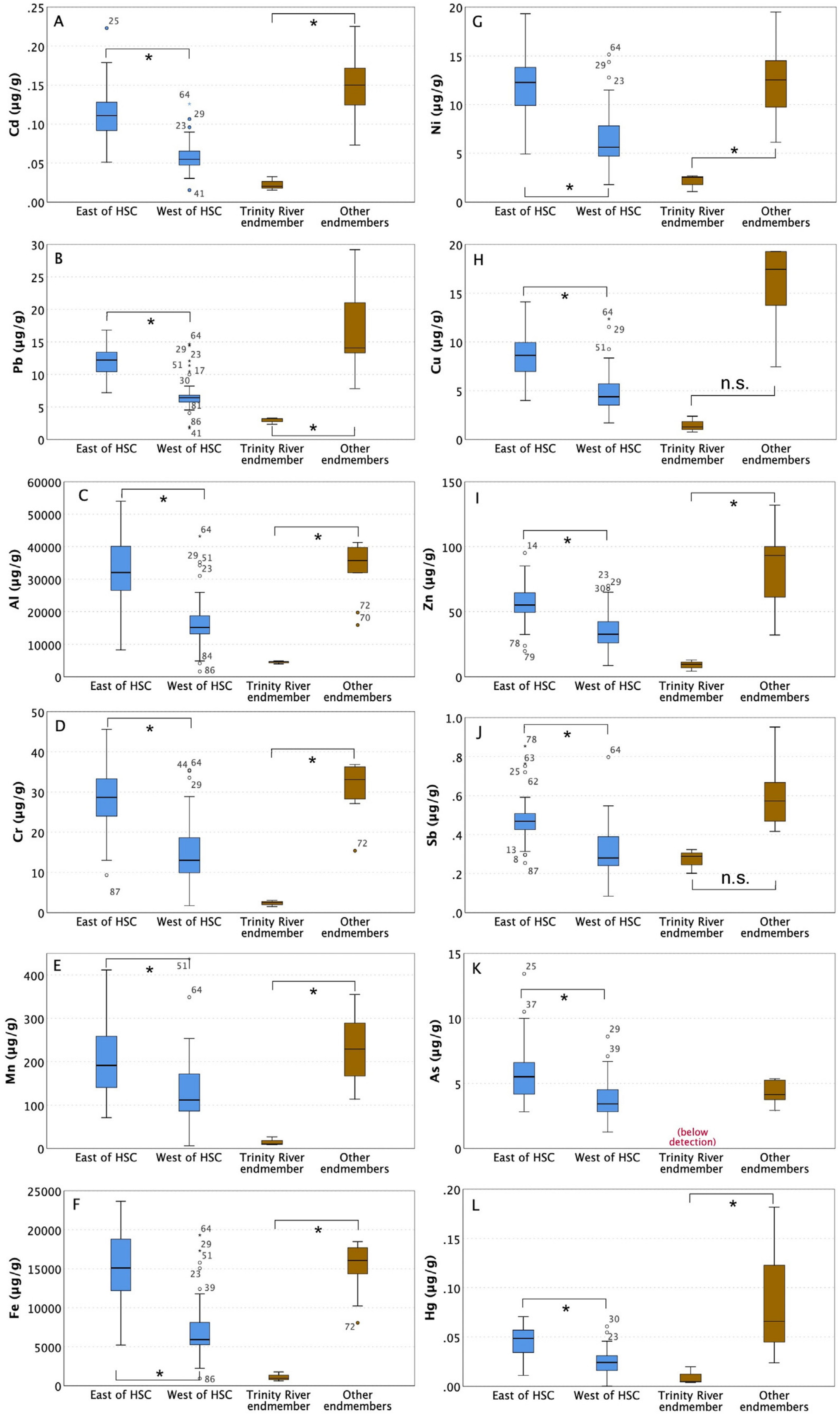
Across all sampling time points, the primary control on sediment metal concentrations in Galveston Bay is their spatial location (Figs. 2, S2–S3), namely their location east or west of the HSC. Stations 4, 5, 7, 8, 9, 12, GB2, GB3, GB4, GB6. GB11, AND GB12 are located to the east of the HSC and possess higher mean ± standard deviation (SD) metal concentrations than stations 1, 2, 3, 11, 13, 14, 15, GB7, GB8, GB9, and GB10, which are located to the west of the HSC (Figs. 2 and S4). The exception to this spatial pattern is Station GB5, which is located on the eastern Galveston Bay shoreline but has low metal concentrations. Station GB1 is also excluded because its northernmost location is not indicative of the main bay. In summary, there is a significant difference in mean metal concentrations for all metals between bay and shoreline stations located to the east of the HSC and stations located to the west of the HSC ($t_{72-73} = 2.5$ to 8.7, $p < 0.014$), based on independent *t*-tests (see SM). Notably Al concentrations follow this spatial pattern (concentrations are statically higher in east compared to west bay regions), indicating that naturally sourced lithogenic fractions drive this trend.

Freshwater endmember sediment metal concentrations often flank the observed bay and shoreline concentrations, with average metal

Table 1
Heavy metal concentrations in Galveston Bay sediment leachates (L) and bulk sediments (D). Minimum ("Min"), maximum ("Max") and mean ("Mean") metal concentrations listed for each metal.

Metal	L/D	Bay stations			Endmember stations			Shoreline stations			E3 core samples		
		Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean
Al	L	85.3	1362.0	333.5	108.4	781.4	405.0	223.7	1019.8	586.4	373.3	6340.5	1234.7
	D	5525.6	54,003.0	26,304.4	3968.7	82,752.3	29,946.1	1634.2.1	40,118.1	13,498.8	30,598.4	53,201.5	38,630.2
As	L	0.4	2.1	0.9	1.2	3.1	1.7	0.4	1.7	0.9	0.9	3.9	1.3
	D	1.3	13.4	5.1	2.9	20.0	5.8	2.1	6.6	3.6	3.5	8.0	6.5
Cd	L	0.01	0.1	0.04	0.01	0.3	0.1	0.01	0.1	0.03	0.02	0.3	0.1
	D	0.02	0.2	0.1	0.02	0.5	0.1	0.03	0.1	0.07	0.06	0.2	0.1
Cr	L	0.3	5.7	0.8	0.2	9.6	2.2	0.4	5.9	1.5	0.7	4.5	1.4
	D	4.5	45.6	23.2	1.5	70.8	27.1	1.7	32.6	13.1	25.3	46.8	33.4
Cu	L	0.3	4.8	1.3	0.3	19.8	4.1	0.5	4.9	1.7	0.8	295.4	20.5
	D	1.7	14.1	7.0	0.8	77.0	17.5	2.1	25.5	7.2	7.3	351.8	34.9
Fe	L	276.3	1473.4	707.7	69.6	1725.7	807.3	50.8	1102.2	481.6	472.0	2317.0	925.4
	D	2359	23,655	11,852	636	50,298	14,350	919.7	17,592.0	6287.2	12,640.4	22,503.3	17,329.6
Hg	D	0.01	0.1	0.04	0.004	0.4	0.08	0.00	0.02	0.01	0.02	0.08	0.05
Mn	L	34.4	420.7	113.2	2.5	269.7	98.3	1.4	113.7	53.5	29.5	354.7	123.3
	D	38.1	540.9	185.8	8.6	694.5	208.2	6.1	209.7	102.0	147.0	310.0	218.8
Ni	L	0.7	13.3	1.7	0.6	11.6	2.6	0.2	2.2	1.0	1.7	8.5	2.6
	D	1.8	19.3	9.7	1.1	30.3	11.1	1.9	13.6	5.3	10.6	18.2	13.3
Pb	L	1.2	4.5	2.8	0.3	13.0	4.8	0.3	12.2	3.0	1.9	14.0	3.5
	D	1.9	16.8	9.7	2.3	29.2	13.5	1.8	15.8	8.3	8.9	18.0	12.5
Sb	L	0.04	0.2	0.1	0.04	3.7	0.4	0.04	0.1	0.07	0.05	0.3	0.08
	D	0.1	0.8	0.4	0.2	1.3	0.6	0.2	1.5	0.5	0.4	0.7	0.5
Zn	L	5.3	39.4	13.5	5.8	302.6	52.4	3.7	36.3	12.0	4.6	211.3	25.4
	D	8.6	194.5	50.4	4.3	132.0	65.9	15.5	71.5	31.4	37.8	336.6	81.4

Results are separated by station types. Stations 1-5 and 7-15 are bay stations, stations 101-103, 201-203, 301-302, 401-402 and 501-503 are freshwater endmember stations, stations GB1-GB12 are shoreline stations. Samples E3-1 thru E3-23 are E3 core sediment subsamples.


A
Cd (µg/g)
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E
Mn (µg/g)
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200
300
400
51
64
*
*
F
Fe (µg/g)
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5000
10000
15000
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64
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Cu (µg/g)
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Zn (µg/g)
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150
14
78
79
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29
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8
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*
J
Sb (µg/g)
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.2
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.6
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1.0
78
63
25
62
13
8
87
64
*
n.s.
K
As (µg/g)
0
5
10
15
25
37
29
39
*
(below detection)
L
Hg (µg/g)
.00
.05
.10
.15
.20
30
23
*
*
East of HSC
West of HSC
Trinity River endmember
Other endmembers

concentrations in Dickinson, Buffalo and Oyster Bayous and the San Jacinto River within the range of concentrations observed at bay stations east of the HSC (Figs. 2 and S5). In contrast, Trinity River bulk sediment metal concentrations are substantially lower than the other endmember stations (and As is even below detection; Figs. 2 and S5). Based on *t*-tests, there is a significant difference in mean metal concentrations between the Trinity River endmember stations and bay and the other endmember stations ($t_{10\text{-}11} = -7.2$ to -2.3, $p < 0.043$). Trinity River is the primary source of freshwater to Galveston Bay, and so northeast Galveston Bay carries the lowest salinity (Guthrie et al., 2012). High riverine concentrations of dissolved metals are flocculated at low salinity in Galveston Bay sediments (Wen et al., 1999). Furthermore, metal concentrations at Trinity River endmember stations 501-503 are among the lowest in the study. Thus, the Trinity River does not supply the high sedimentary metal loads to Galveston Bay; instead, the high heavy metal contents in eastern Galveston Bay are the result of adsorbed metals on sediment surfaces during estuarine flocculation at salinity 0-5. Additionally, it is possible that under certain hydrodynamic conditions, some metal-rich sediments from the San Jacinto River/Buffalo Bayou are transported east of the HSC and are physically trapped there; a good example is the sediments deposited by Hurricane Harvey at Stations 5-12 that account for the observed higher metal contents in these areas (Dellapenna et al., 2021 in review).

A secondary control on the variability of metal concentrations in Galveston Bay sediments is temporal variability in freshwater discharge to the bay, which can carry sediments into the bay directly as well as move the flocculation boundary closer (under dry conditions) or farther (under wet conditions) from the river mouth. The Trinity River supplies about 55%-77% of the total freshwater inflow to Galveston Bay, followed by the San Jacinto River (15%-19%) and Buffalo Bayou (4%-10%) (Du et al., 2019a, 2019b; Guthrie et al., 2012). Metal concentrations in Galveston Bay sediments are positively correlated with riverine discharge into Galveston Bay such that concentrations for some metals are lower during periods of low Trinity River discharge and higher when Trinity River discharge is high (Figs. 3 and S2–S3). Dry conditions (Trinity River discharge <250 m^3/s) occur during the November 2017, June 2018, and September 2018 sampling events. Wet conditions (Trinity River discharge >250 m^3/s) prevail during June 2017, March 2018, November 2018, March 2019, and June 2019 (SM Table S6). From August 26-30, 2017, Hurricane Harvey deposited record-breaking rainfall totals over Texas, which resulted in massive freshwater fluxes through Galveston Bay (Steichen et al., 2020). Consequently, the typical flocculation of dissolved metals did not occur, and the September 2017 bulk sediment metal concentrations resemble samples collected during dry conditions. Independent *t*-tests results indicate that the differences in metal concentration means between wet and dry conditions are only statistically significant for Pb, Al, Cr, Mn, and Sb ($t_{72\text{-}75} = 2.1$ to 2.4, $p < 0.04$) (see SM).

An agglomerative hierarchical cluster analysis (CA) using squared Euclidean distances and Ward's method was applied to individual samples in spatiotemporal space to cluster samples into groups with similar metal concentration trends (Nielsen, 2016; Gaur and Gaur, 2006; IBM SPSS 26.0). The CA ("CA1") results (SM Fig. S6) independently reinforce the spatial and temporal trends suggested above. The Group B sediment samples have the highest average heavy metal concentrations, were collected during mostly wet conditions (Trinity River discharge 340+ m^3/s), and are largely located east of the HSC (i.e., stations 5A, 5B, 7-9, 12). Conversely, Group C sediment samples have the lowest average heavy metal concentrations, were collected during generally dry conditions (Trinity River discharge <170 m^3/s), and are mostly located west of or near the HSC (i.e., stations 1-3, 13-14). Group A sediments have metal concentrations between the Group B and C sediments, were mostly collected during moderately wet conditions (Trinity River discharge 170–340 m^3/s), and are located throughout Galveston Bay (i.e., stations 1, 4-5, 7-14). Group D only contains the sediment sample from Station 402 in Oyster Bayou. This sample clustered separately from all other sediments, indicating the heavy metal influx at this site is independent of the heavy metal loadings at the other sample locations. This CA reinforces that the spatiotemporal patterns in bulk heavy metal concentrations in Galveston Bay are dominated by riverine fluxes of lithogenic materials, overprinted by natural flocculation of particle-reactive metals onto the sediments as well as some sediment focusing within the bay.

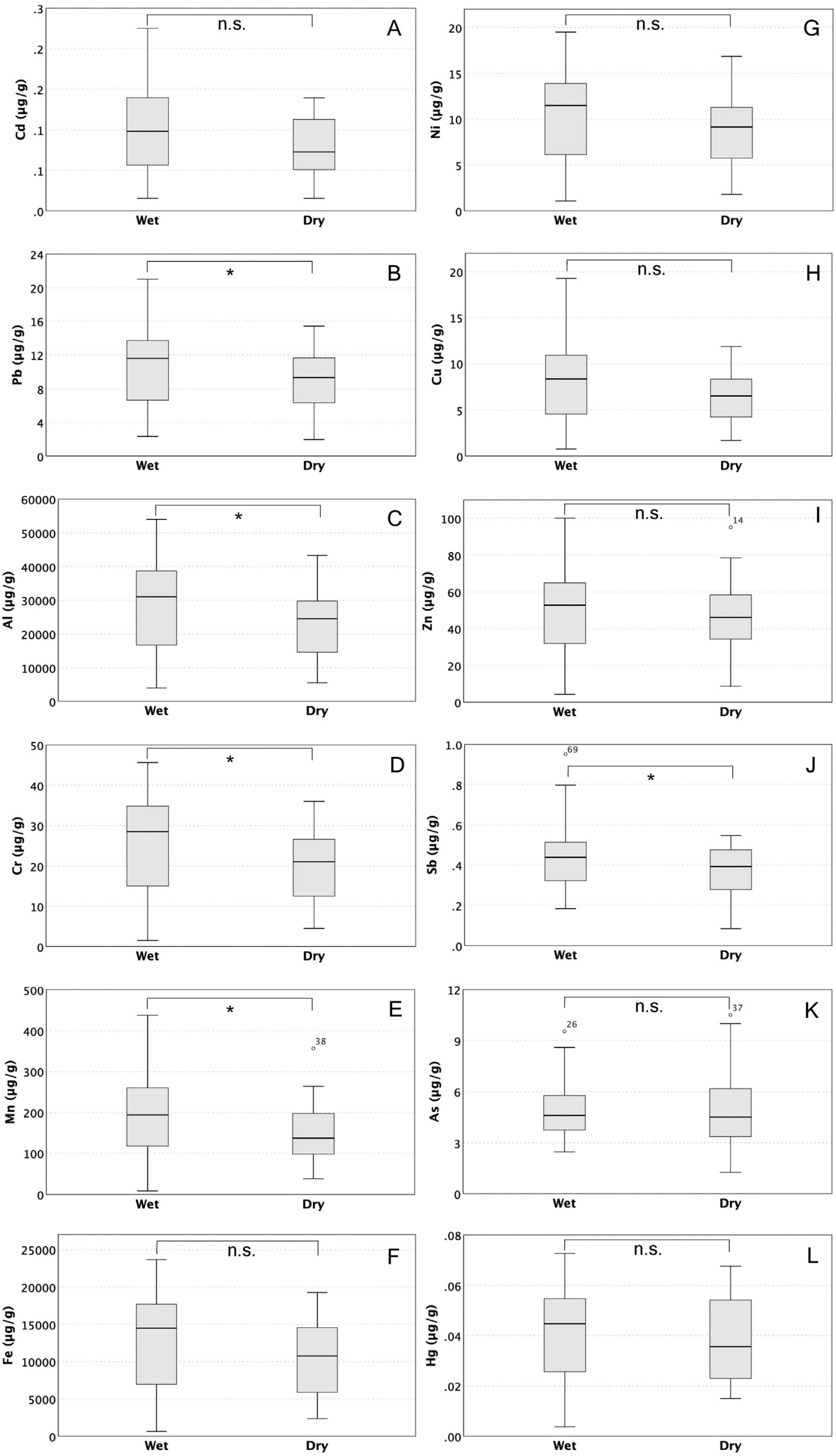
3.2. Long-term temporal variability of core sediment heavy metal concentrations

The E3 core, sampled in Trinity Bay (Fig. 1), presents an opportunity to study the longer-term temporal variability of metal concentrations at a single location in Galveston Bay. Previous ^{210}Pb dating of the E3 core established the year 1968 at a depth of 37 cm and estimated an age model using an average sedimentation rate of 0.41 cm/year for this site and bulk density correction for depth based off of sediment water content (Pekowski, 2017). Pekowski (2017) reported that the x-radiographs from the core showed little evidence of bioturbation. This sedimentation rate is similar to the rate of 0.27 cm/year reported by Al Mukaimi et al. (2018) for a nearby core. However, as noted by Al Mukaimi et al. (2018) and Pekowski (2017), due to the complex subsidence history of Galveston Bay, there is significant spatial heterogeneity of sedimentation rates both to anthropogenically driven subsidence in the upper bay due to groundwater withdraw and due to differential compaction of Holocene sediments due to the existence of buried incised Pleistocene channels in the bay.

Accordingly, the E3-23 subsample approximately represents the year ~1880 and the E3-1 subsample represents the year 2016. To compensate for the natural variability of grain size and mineral content in sediments and elucidate temporal trends within the core sediment data, the core sediment metal concentrations were normalized to Al before temporal trend were assessed (Loring and Prosi, 1986; Schropp and Windom, 1988).There were some metals that had E3 core temporal patterns that are challenging to interpret, including Mn and Sb concentrations that vary sufficiently that no clear interpretation can be made regarding their temporal trends (Fig. 4), especially since sediment focusing and/or scouring during storm events cannot be accounted for by linear approximates of core age; arsenic and Ni levels uniquely remain stable throughout the length of the core (Fig. 4); and the highest Cu (167.71–351.84 μg/g) and Zn (128.65–244.47 μg/g) concentrations of all sediments measured in this study are between ~1880-1914 (core depths 100-111 cm), which may be the result of unique historical pollution or sample contamination. Thus, these data points are thus omitted from further discussion as their validity cannot be confirmed.

Nonetheless, the long-term trends in sediment heavy metal concentrations in the E3 core can be used to approximate whether Galveston Bay sediments are getting cleaner with respect to metals over time. Between 1920 and the 1990s Zn and Cu are generally consistent (except for Zn in 1968) then between 2009 and present day these metals increase (Fig. 4). Iron, Pb, Cd, and Hg concentrations generally increase from the late 1800s to 2016 (Fig. 4), in line with industrialization

Fig. 2. Box and whisker plots showing spatial trends in Galveston Bay Cd (A), Pb (B), Al (C), Cr (D), Mn (E), Fe (F), Ni (G), Cu (H), Zn (I), Sb (J), As (K) and Hg (L) concentrations made using IBM SPSS 26.0. Stations are grouped by spatial heavy metal concentration trends described in the text. Stations east of the HSC are stations 4-5, 8-12, GB2-GB4, GB6, GB11-GB12. Stations to the west of the HSC are stations 1-3, 11, 13-15, GB5, GB7-GB10. Trinity River endmember stations are 501-503, the other endmember stations are 101-103, 201-302, 301-302 and 401-402. Outliers shown as open black circles and black asterisks. Outliers 69 and 74 are removed from most plots for scale, details regarding outliers are provided in the SM. Bracket asterisk = significantly different. Bracket n.s. = not significantly different. The difference between the Cu and Hg means at Trinity River stations and other endmember stations is not statistically significant based on an independent samples *t*-test. All other differences are statistically significant ($p < 0.043$).


A
Cd (µg/g)
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Dry
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Pb (µg/g)
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Cr (µg/g)
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Wet
Dry

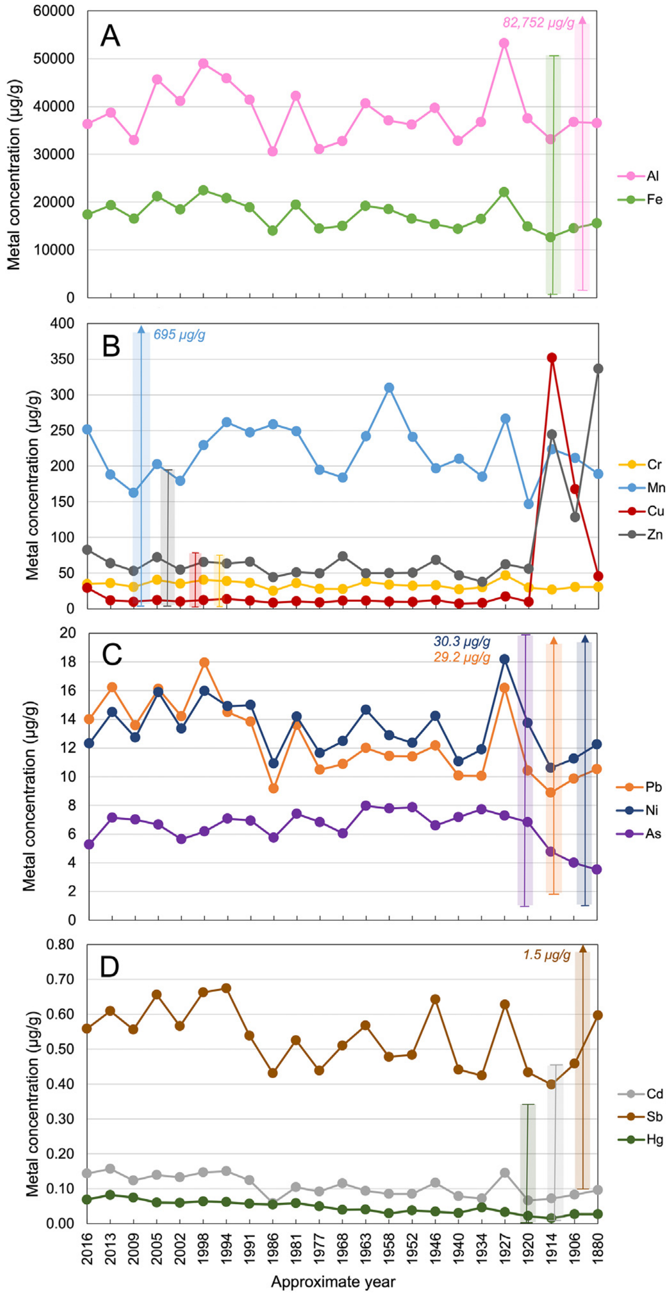


Fig. 4. Temporal variation in bulk sediment E3 core subsample Al-normalized heavy metal contents (metal:Al ratios) as follows, (A) Fe:Al (B) Mn:Al, Cu:Al, and Zn:Al (C) Pb:Al, Ni:Al, As:Al, and Cr:Al (D) Cd:Al, Sb:Al, and Hg:Al. Corresponding surface sediment metal concentration ranges shown for reference using colored, shaded bars. In cases where the surface sediment metal concentration range upper limit is larger than figure scale, the upper limit range value is listed.

increasing their fluxes to bay sediments. Importantly, Fe, Pb, Cd, and Hg concentrations do not clearly level off or decline from the 1990s to present day (Fig. 4). Thus, although the sediment metal concentrations determined by this study are generally lower than previously reported for Galveston Bay, the E3 core data does not clearly demonstrate a decrease in sediment metal concentrations over the past 30 years during which time the bay was being "cleaned up" (Morse et al., 1993). Rather, within the last 30 years the data show an increase in Fe, Cu, Zn, Cr, Pb, Sb, Cd, and Hg deposition, stable Ni and As contents, and variable Mn abundances. Despite pollution reduction measures, continued pollutant fluxes in the 21st century likely contribute to the rising metal concentrations in core sediments (Wen et al., 2008; Harmon et al., 2003; Bollhofer and Rosman, 2001; Santschi et al., 2001; Saleh and Wilson, 1999; Morse et al., 1993).

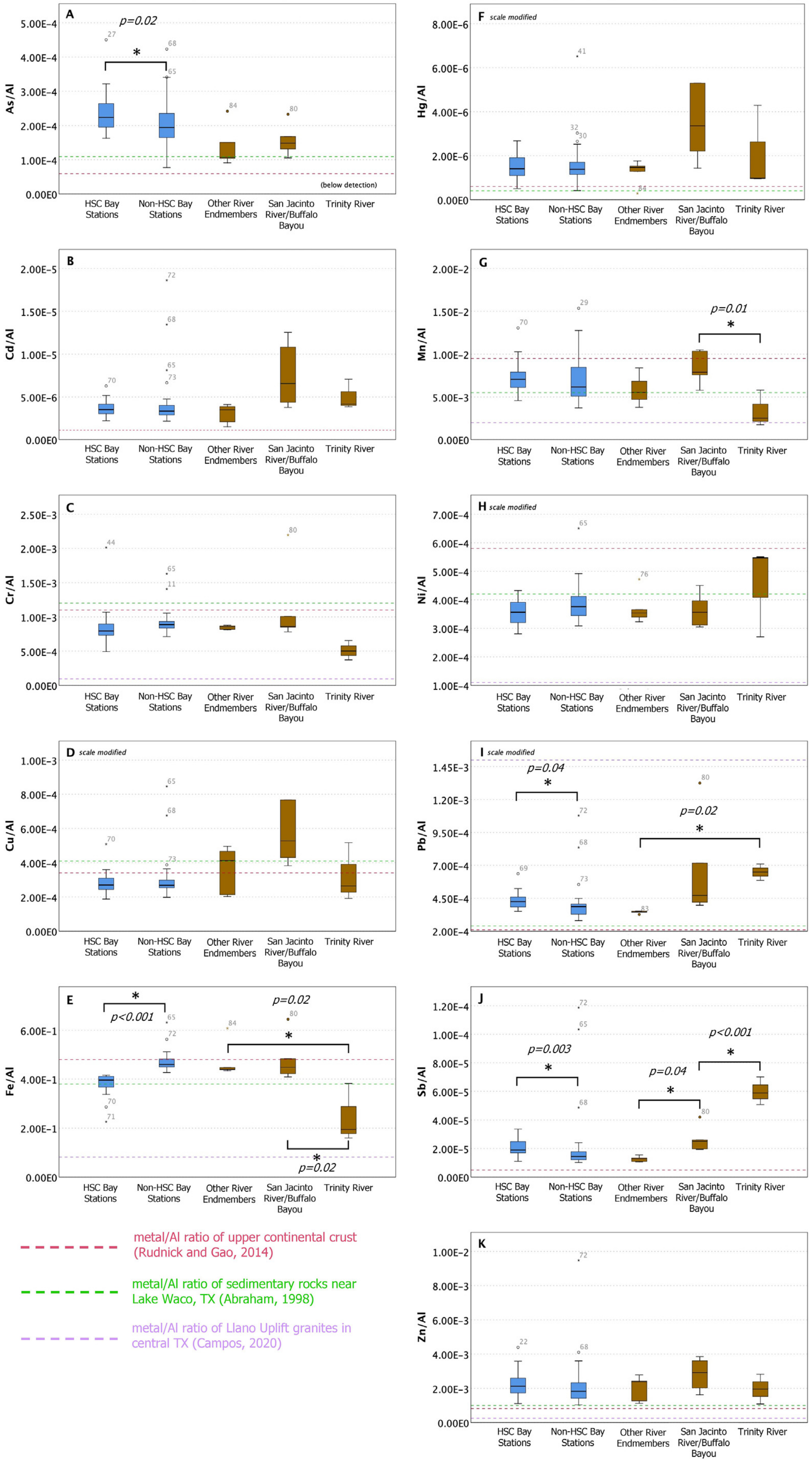
3.3. Spatiotemporal variability of surface sediment Al normalized data

Sediment metal concentrations were normalized to Al concentrations to compensate for the natural variability of grain size and mineral content in sediments (Loring and Prosi, 1986; Windom et al., 1989; Schropp and Windom, 1988). A second CA ("CA2") assesses spatiotemporal trends in the sediment metal/Al ratios, which effectively normalizes out the lithogenic component and allows improved focus on potential anthropogenic patterns. Two clusters of stations containing the bay and shoreline samples were identified by CA2. The first cluster contains Stations 2-4, 13, 14, GB3, GB6, GB7, and GB9 (stations near/within the HSC). The second cluster contains Stations 1, 5A, 5B, 7-10, 12, GB2, GB4, GB5, GB10, GB11, and GB12 (stations outside of the HSC) (Figs. 5 and S7). Results from CA2 also separate three clusters of endmembers stations: the Trinity River stations (501, 502, and 503), the San Jacinto River and Buffalo Bayou stations (201, 202, 203, 301, and 302), and the other river endmember stations (101, 102, 103, 401, and 402) (Figs. 5 and S7). Metal/Al ratios of three natural materials, Llano Uplift Central Texas granites, sedimentary rocks near Waco, TX, and upper continental crust (Campos, 2020; Rudnick and Gao, 2003; Abraham, 1998) are included in Fig. 5 to evaluate how Galveston Bay sediments compare with crustal values. Statistically significant differences in metal/Al ratio between spatial groups was investigated using independent *t*-tests (bay stations groups) and one-way analysis of variance (ANOVA) as applicable (Fig. 5, see SM for additional details).

Bay stations have higher As/Al ratios than endmember stations that are elevated over crustal values indicating that As is acquired within the bay and is likely anthropogenically sourced. The HSC bay stations also have statistically significantly higher As/Al than the other bay stations, indicating that the As is likely acquired near the HSC. Similar to As, the Pb/Al and Sb/Al ratios are also statistically significantly higher at HSC-bay stations compared to other bay stations; however, elevated Pb/Al and Sb/Al ratios in the San Jacinto River, Buffalo Bayou, and Trinity River show that these freshwaters bring Pb and Sb into the bay. This may indicate that some of the anthropogenic metal enrichment of Galveston Bay sediments occurs upstream of the bay in freshwaters and is then carried into the bay, at least for Pb and Sb. The total flow rate and sediment load coming from Trinity River is high despite generally low Trinity River sediment heavy metal concentrations (Fig. 2), which supports this interpretation.

The metal/Al ratios of Cd, Hg, and Zn are also enriched over crustal ratios; however, they do not have significant differences across the bay nor the incoming sediments carried within freshwaters. This indicates that Cd, Hg, and Zn are likely anthropogenically-sourced to sediments within the rivers of the Galveston Bay watershed, but they are not necessarily further contaminated within (nor sufficiently desorbed to the waters of) Galveston Bay. The Cr/Al and Ni/Al ratios are within the range of crustal ratios and do not significantly vary between bay and endmember stations, suggesting that Cr and Ni are lithogenically-

Fig. 3. Box and whisker plots showing temporal trends in Galveston Bay Cd (A), Pb (B), Al (C), Cr (D), Mn (E), Fe (F), Ni (G), Cu (H), Zn (I), Sb (J), As (K) and Hg (L) concentrations made using IBM SPSS 26.0. Stations are grouped by dry (Trinity River discharge <250 m^3/s in November 2017, June 2018, and September 2018) and wet (Trinity River discharge >250 m^3/s in June 2017, March 2018, November 2018, March 2019 and June 2019) conditions. September 2017 is an extreme wet event due to Hurricane Harvey, during which no flocculation of dissolved metals occurred. Thus, September 2017 sample metal concentrations resemble dry condition metal concentrations and are included in the dry category here. Outliers shown as open black circles. Some outliers removed from plots for scale, a list of outliers and their details are provided in the SM. Bracket asterisk = significantly different. Bracket n.s. = not significantly different. Bracket asterisks on Pb, Al, Cr, Mn and Sb panels indicate that the difference between elemental means in wet versus dry samples is statistically significant based on an independent samples *t*-test ($p < 0.04$).


A
p=0.02
As/Al
(below detection)
B
Cd/Al
C
Cr/Al
D scale modified
Cu/Al
E
Fe/Al
p<0.001
p=0.02
p=0.02
F scale modified
Hg/Al
G
Mn/Al
p=0.01
H scale modified
Ni/Al
I scale modified
Pb/Al
p=0.04
p=0.02
J
Sb/Al
p=0.003
p=0.04
p<0.001
K
Zn/Al
HSC Bay Stations
Non-HSC Bay Stations
Other River Endmembers
San Jacinto River/Buffalo Bayou
Trinity River
metal/Al ratio of upper continental crust (Rudnick and Gao, 2014)
metal/Al ratio of sedimentary rocks near Lake Waco, TX (Abraham, 1998)
metal/Al ratio of Llano Uplift granites in central TX (Campos, 2020)

derived. Lastly. Fe/Al and Mn/Al ratios fall within crustal ratios, meaning that if Fe and Mn (oxyhydr)oxides are present they do not overwhelm the lithogenic signal.

Together, the metal/Al ratio data show that many heavy metals (As, Cd, Hg, Sb, and Zn) have concentrations exceeding lithogenic concentrations in sediments of Galveston Bay, indicating that they likely have anthropogenic sources. The difference in station groupings between CA1 and CA2 also indicates that although the ebb and flow in the flux of lithogenic fine sediment fractions dominates the spatiotemporal trend of bulk metal concentrations within the bay (CA1), the industrialized complex near the HSC is an important source of contaminant metals (As, Hg, Cd, Pb, and Zn) to Galveston Bay sediments (CA2).

4. Discussion

4.1. Galveston Bay sediment heavy metal toxicity

The National Ocean and Atmospheric Administration (NOAA) Screening Quick Reference Tables (SQuiRTs) provide T_{20} and T_{50} toxicity thresholds for As, Cd, Cr, Cu, Hg, Ni, Pb, Sb, and Zn in marine sediment (Buchman, 2008). The T_{20} and T_{50} values are the concentrations of a given element above which there is a 20% or 50%, respectively, probability of observing benthic toxicity. The measured heavy metal concentrations for Galveston Bay sediment leachates and digests were compared to the NOAA SQuiRTs T_{20} and T_{50} values to assess potential toxicity in the bay (SM Table S7). In the leachates, very few samples exceed the T_{20} and T_{50} thresholds: only 1.3% of all samples for Sb and Zn. Bulk sediment concentrations exceeded the toxicity thresholds more frequently, though it is unclear whether sediment fractions not accessed by the leach would be biologically accessible. The T_{20} threshold was exceeded by bulk sediment concentrations of Cd, Cr, and Cu (1.0% of samples), Hg (2.0% of samples), Ni and Zn (6.0% of samples), As (10.4% of samples), and Sb (11.0% of samples). Only the As T_{50} threshold was exceeded (at 1.0% of samples). Thus, Galveston Bay sediments may be toxic (Sb, As > Ni, Zn > Hg > Cd, Cr, Cu), though their overall potential toxicity is relatively low.

4.2. Comparison of Galveston Bay to other estuaries

Galveston Bay sediment heavy metal concentrations are on the lower end of the spectrum of concentrations observed in other estuaries around the globe (SM Table S8). This may be explained by low metal input from the relatively pristine Trinity River and/or regulatory efforts to clean up Galveston Bay (Lester and Gonzalez, 2011; Warnken and Santschi, 2009; Harmon et al., 2003), though the E3 sediment core data do not indicate major decreases in sediment heavy metal concentrations resulting from these efforts. For context, the large range in Al concentrations (1634–82,752 μg/g) in Galveston Bay sediments resemble Al concentrations in estuaries worldwide (Enuneku et al., 2018; Liu et al., 2016; Delgado et al., 2010; Ip et al., 2007; Hornberger et al., 1999; Lee et al., 1999; Sharma et al., 1999; Bricker, 1996; Ahn et al., 1995; Attrill and Thomes, 1995; Bricker, 1993; Morse et al., 1993; Van Alsenoy et al., 1993; Subramanian et al., 1988; Sinex and Helz, 1981), indicating similar overall lithogenic particle fluxes across these global estuaries. Most notably, average Galveston Bay sediment metal concentrations have similar average concentrations to the following estuaries: Nueces Bay (Cu, Fe, Ni, Pb), Corpus Christi Bay (Cr, Cu, Ni), Oso Bay (Cu, Fe, Ni, Pb), Narragansett Bay (Fe, Mn), St. Lawrence Estuary (As, Cd, Pb, Hg), Guadiana Estuary (Cd, Cr), Benin River (Cu, Zn), and the Yangtze Estuary (As, Hg) (Enuneku et al., 2018; Liu et al., 2016; Delgado et al., 2010; Lee et al., 1999; Sharma et al., 1999; Bricker, 1996).

4.3. Anthropogenic versus natural heavy metal sources in Galveston Bay sediments

Another way to determine whether Galveston Bay heavy metals were derived from natural or anthropogenic sources is to use enrichment factors (Herut and Sandler, 2006; Loring and Prosi, 1986). Enrichment factors (EF) were calculated by dividing the metal/Al ratio of a bulk sediment sample to the metal/Al ratio of an uncontaminated "natural" material (Herut and Sandler, 2006; Loring and Prosi, 1986). Three "natural" materials were used: Llano Uplift Central Texas granites, sedimentary rocks near Waco, TX, and upper continental crust. Texas rocks are included as they may be more representative of locally-sourced fine sediment fractions to Galveston Bay (SM Table S9-S10, Campos, 2020; Rudnick and Gao, 2003; Abraham, 1998). Based on the EFs, the metals Cd, Hg, Sb, and Zn are generally present above crustal levels (EF ≥ 2, regardless of "crustal" normalizer), suggesting that they are anthropogenically-sourced to the bay. Lead is largely present at crustal (EF = 1) levels (Lopez et al., 2021). In contrast, Cr, Cu, and Ni are crustal or even depleted relative to natural rocks (EF ≤ 1). The As, Fe, and Mn EFs vary depending on the reference material used, making these elements less straightforward to assess. When compared to Central-East Texas sedimentary rocks, As, Fe, and Mn are crustal; however, Fe and Mn are depleted when compared to upper continental crust and potentially anthropogenic when compared to Central Texas granites.

We also completed two principal components analyses (PCA) of our dataset, with varimax rotation with Kaiser Normalization, in order to group metals by source/pattern and shed light on the metal speciation of Galveston Bay sediments (IBM SPSS 26.0; Nielsen, 2016; Lu et al., 2010; Franco-Uria et al., 2009; Gaur and Gaur, 2006). Principal component loadings and communalities from PCA analyses of Galveston Bay sediment leachates and bulk sediments (PCA1) are tabulated in Table 2; principal component loadings and communalities from PCA analyses of Galveston Bay bulk sediment metal/Al ratios (PCA2) are tabulated in Table 3. In addition, a third CA ("CA3") was completed to evaluate the sources of heavy metals in Galveston Bay bulk sediments, which revealed very similar results to the PCA, and so they are discussed together here (SM Fig. S8). The heavy metal concentration data were z-score standardized before CA3 was performed using Ward's method (squared Euclidean distances). Except for Sb in PCA1, communalities are above 0.70 for all metal loadings, indicating that the components extracted by the PCA analyses can explain the majority of the variance observed in Galveston Bay bulk sediment heavy metal concentrations; thus, the PCA1 results for Sb are only cautiously interpreted here.

First, in PCA1, four principal components were identified that could explain 79% of the total variance in observed leachate concentration. Components 1, 2, 3 and 4, respectively, account for 43%, 15%, 12% and 10% of the heavy metal concentration variance in the leachates. The largest loadings of each component on individual metals are: component 1 on Cr, Cd and Pb, component 2 on Sb, Zn and Ni, component 3 on Mn, Fe and As, and component 4 on Cu and Al. Components 1 and 2 distinguish two potential sources of anthropogenic metals in Galveston Bay, with one source being more influential on Cr, Cd and Pb more and the other source being more significant for Sb, Zn and Ni. Component 3 represents the oxide phase and indicates that As is largely controlled by Fe-Mn oxide coatings on sediment grains. Aluminum in

Fig. 5. Box and whisker plots showing spatial trends in Galveston Bay (A) As/Al, (B) Cd/Al, (C) Cr/Al, (D) Cu/Al, (E) Fe/Al, (F) Hg/Al, (G) Mn/Al, (H) Ni/Al, (I) Pb/Al, (J) Sb/Al, and (K) Zn/Al ratios made using IBM SPSS 26.0. The HSC bay stations are stations 2-4, 13, 14, GB3, GB6, GB7, and GB9. The non-HSC bay stations are stations 1, 5A, 5B, 7-10, 12, GB2, GB4, GB5, GB10, GB11, and GB12. The other river endmembers category includes stations 101, 102, 103, 401, and 402. Stations 201, 202, 203, 301, and 302 are the San Jacinto River/Buffalo Bayou stations. Stations 501, 502, and 503 are the Trinity River stations. Outliers shown as black open circles and asterisks. Some outliers removed from plots for scale, a list of outliers and their details are provided in the SM. Statistically significant ($p < 0.05$) differences between spatial areas assessed by independent t-test or ANOVA. Bracket asterisk = significantly different. The metal/Al ratios of Llano Uplift Central Texas granites (purple dashed lines), sedimentary rocks near Waco, TX (green dashed lines), and upper continental crust (red dashed lines) are included for reference (Campos, 2020; Rudnick and Gao, 2003; Abraham, 1998). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 2
Rotated component matrices and communalities for PCA analyses of Galveston Bay sediment leachates (L) and bulk sediments (D). Loadings > 0.5 are bolded.

Element	Component 1		Component 2		Component 3		Component 4		Communalities	
	L	D	L	D	L	D	L	D	L	D
Al	0.463	**0.92**	-0.046	0.228	-0.171	0.182	**0.669**	n/a	0.693	0.932
As	0.44	**0.869**	0.387	0.027	**0.624**	-0.045	0.013	n/a	0.733	0.758
Cd	**0.732**	0.365	0.125	**0.794**	0.396	0.142	-0.059	n/a	0.712	0.784
Cr	**0.744**	**0.87**	0.448	0.38	0.039	0.167	0.116	n/a	0.769	0.929
Cu	-0.202	-0.03	0.141	-0.003	0.234	**0.916**	**0.866**	n/a	0.865	0.839
Fe	0.217	**0.942**	0.253	0.262	**0.764**	0.113	0.291	n/a	0.779	0.969
Mn	0.175	**0.819**	-0.012	0.16	**0.853**	0.089	-0.035	n/a	0.76	0.704
Ni	0.43	**0.912**	**0.643**	0.267	0.294	0.155	-0.008	n/a	0.685	0.927
Pb	**0.817**	**0.676**	0.05	**0.685**	0.396	0.088	0.03	n/a	0.828	0.933
Sb	0.08	**0.519**	**0.951**	**0.552**	0.02	0.047	-0.063	n/a	0.916	0.576
Zn	0.109	0.296	**0.814**	0.208	0.201	**0.817**	0.452	n/a	0.918	0.799
Hg	n/a	0.001	n/a	**0.863**	n/a	0.052	n/a	n/a	n/a	0.747

component 4 points toward a lithogenic phase accessed by the leach and points to a natural source of Cu in Galveston Bay sediments.

Three principal components explaining 82% of the total variance observed were identified in the bulk sediment data. Components 1, 2 and 3 respectively account for 59%, 12%, and 11% the variance in bulk sediment metal abundances. Aluminum, Fe, Mn, Ni, Cr and As are dominated by component 1. Mercury and Cd and to a lesser extent Pb and Sb are primarily influenced by component 2. Component 3 loads heavily on Cu and Zn and to a lesser amount Pb and Sb. Components 2 and 3 have approximately equal loadings on Pb and Sb indicating that the variance observed in these two variables is best explained by two factors rather than one. The presence of Al, Fe and Mn in principal component 1 indicates that this component represents lithogenic and oxide phases. The loading of component 1 on Ni, Cr, and As indicates these metals are associated with natural (i.e., lithogenic aluminosilicates) and/or anthropogenic (i.e., Fe-Mn oxide coatings) sources. The anthropogenic contribution of metals to Galveston Bay bulk sediments is represented by components 2 and 3. Arsenic groups with Fe and Mn in both the leachate and bulk sediment PCA, highlighting this metal's affinity for the oxide phase.

The PCA2 results (Table 3) indicate that three principal components explain 85% of the total variance observed in the bulk sediment metal/Al ratios. Component 1 loads heavily on the Cd/Al, Cr/Al, Fe/Al, Mn/Al, Ni/Al, Pb/Al, Sb/Al, and Zn/Al ratios. Component 2 loads heavily on the As/Al and Hg/Al ratios. The Cu/Al ratio is dominated by component 3. These results suggest that As and Hg (Component 2) are most likely anthropogenically-sourced whereas the other metals are associated with the crustal component and/or Fe and Mn (oxyhydr)oxides.

Results for the CA3 reveal three main clusters of metals that are in agreement with the bulk sediment PCA results (SM Fig. S8). Cluster 1 contains the PCA group 1 metals Al, Fe, Mn, Ni, Cr, and As; cluster 2 contains the PCA group 2 metals Cd, Hg, Pb, and Sb; and cluster 3 contains the PCA group 3 metals Cu and Zn. The CA3 results thus reinforce the bulk sediment PCA analysis assignments that metals Hg, Cd, Cu, Zn, Pb and Sb are similarly anthropogenic-sourced, while Cr and Ni are more naturally-sourced to Galveston Bay sediments.

Table 3
Rotated component matrices and communalities for PCA analyses of Galveston Bay bulk sediment metal/Al ratios. Loadings > 0.5 are bolded.

Metal/Al ratios	Component 1	Component 2	Component 3	Communalities
As/Al	-0.146	**0.812**	0.151	0.704
Cd/Al	**0.901**	-0.194	-0.049	0.852
Cr/Al	**0.905**	0.318	-0.076	0.925
Cu/Al	0.385	0.038	**0.886**	0.935
Fe/Al	**0.828**	0.296	0.07	0.778
Hg/Al	-0.302	**0.828**	-0.043	0.778
Mn/Al	**0.831**	0.399	-0.136	0.867
Ni/Al	**0.828**	-0.424	-0.036	0.867
Pb/Al	**0.945**	0.132	-0.185	0.944
Sb/Al	**0.934**	0.038	-0.23	0.928
Zn/Al	**0.829**	-0.175	0.308	0.812

Based on the EFs alone, Cr, Cu, Ni, and Pb in Galveston Bay sediment are present at depleted to crustal levels whereas Cd, Hg, Sb, and Zn are present at levels suggesting anthropogenic sourcing. This interpretation holds true for Ni and Cr, for which PCA1, PCA2, and CA3 indicate a natural metal source. Furthermore, PCA1, PCA2, and CA3 point to anthropogenic sourcing of Cd, Hg, Sb, and Zn in Galveston Bay sediments in line with EF results. The sources of Cu and Pb to Galveston Bay sediments are the least clear. The bulk sediment PCA1, PCA2, and CA3 indicate anthropogenically sourced Cu; however, the EFs and leachate PCA results suggest that Cu is naturally sourced. Bulk sediment PCA1 and CA3 results along with the Central Texas granite EFs indicate anthropogenically sourced Pb; however, the PCA2 results and remaining EFs point toward naturally sourced Pb. Given the subjectivity associated with EF calculations and sediment leaching methods and the presence of pollutant Cu and Pb in Galveston Bay established by previous work, anthropogenic sources of Cu and Pb in Galveston Bay are considered more likely (Lopez et al., 2021; Sholkovitz, 1989; Presley et al., 1990; Herut and Sandler, 2006).Previous studies have reported Galveston Bay industrial heavy metal inputs from vehicle exhaust, surface runoff, shipping vessel discharge, and atmospheric deposition (Dellapenna et al., 2020; Al Mukaimi et al., 2018; Harmon et al., 2003; Morse et al., 1993). Chemical production and petrochemical activities within the HSC are recognized culprits of anthropogenic metals in Galveston Bay and the Gulf of Mexico (Apeti et al., 2012). A few point sources of Galveston Bay heavy metals have been identified, including a former Chlor-Alkali plant and a paper mill. Located in the San Jacinto River near the HSC, the Chlor-Alkali plant is a known source of Hg to the bay (Dellapenna et al., 2020). Waste leakage from a decommissioned paper mill stored in the San Jacinto Waste Pits at the northern end of Galveston Bay emitted dioxin contamination into the bay (Louchouarn et al., 2018; Yeager et al., 2010; Yeager et al., 2007). Unpublished sediment data show elevated Cd, Cu, Hg and Pb concentrations near the paper mill denoting that this facility may have also released metal contaminants (Presley et al., 1990). Additionally, lead isotope tracing of this study's Galveston Bay sediments reinforces the presence of gasoline- and industrial ore-derived Pb in Galveston Bay and also supports coal as a source of metal contaminants to the bay (Lopez et al., 2021; Al Mukaimi et al., 2018; Allan et al., 2013).

5. Conclusions

The 2-year quarterly time-series of Galveston Bay sediment heavy metal data presented here displays clear spatiotemporal trends in metal concentrations and metal/Al ratios that were corroborated by statistical methods. Galveston Bay bulk sediment heavy metal concentration spatiotemporal trends show the overarching natural ebb and flow of the estuary, as dominated by the river-supplied lithogenic phase.

Spatial differences dominated the variability of bulk heavy metal concentrations, with areas east of the HSC in Trinity Bay and near the entrance of East Bay having higher metal concentrations than areas west of the HSC; high metal contents in eastern Galveston Bay are driven by flocculation of dissolved metals in low salinity regions, in addition to potential sediment trapping mechanisms. Temporal trends were observed secondary driver, with highest sedimentary metal concentrations highest during periods of elevated river discharge. Importantly, these wet/dry differences do not require storms the size of Hurricane Harvey but can change the sediment metal concentrations even on seasonal timescales. Lithogenic-normalized trends (metal/Al ratios) reveal the influence of industrialization in local hotspots. Galveston Bay sediment heavy metal concentrations are among the lowest observed in global estuarine systems, despite the large presence of petrochemical industry in its watershed. Nonetheless, ≤11% of Galveston Bay sediments exceed toxicity thresholds for As, Cd, Cr, Cu, Hg, Ni, Sb, and Zn based on NOAA guidelines. Sedimentary Ni and Cr are likely derived from natural sources, whereas As, Cd, Hg, Ni, Pb, Sb, Zn and possibly Cu stem from anthropogenic inputs. Based on the metal/Al ratios, the San Jacinto River and Buffalo Bayou predominantly supply Cd, Cr, Cu, Hg, and Zn to the bay, whereas the Trinity River largely supplies Ni, Pb, and Sb to the bay. Arsenic is a unique case, which is sourced to the bay itself. Despite recent efforts to reduce pollutant loadings to Galveston Bay, no clear decline in sedimentary metal concentrations is observed in a core sediment time-series over the last century. Instead, over the last 30 Fe, Cu, Zn, Cr, Pb, Sb, Cd, and Hg deposition increased, Ni and As deposition was stable, and Mn deposition was variable. This rich spatiotemporal dataset demonstrates that Galveston Bay sediment metal concentrations are shaped by a combination of local riverine input, flocculation dynamics, and direct anthropogenic fluxes within the bay or along its shoreline. This detailed study can serve as a case study for future comparisons with other local anthropogenic-influenced estuaries.

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CRediT authorship contribution statement

Amanda M. Lopez: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Resources, Writing – original draft, Visualization. **Jessica N. Fitzsimmons:** Conceptualization, Methodology, Validation, Formal analysis, Writing – review & editing, Supervision, Funding acquisition. **Hannah M. Adams:** Investigation, Writing – review & editing. **Timothy M. Dellapenna:** Resources, Writing – review & editing. **Alan D. Brandon:** Conceptualization, Methodology, Resources, Writing – review & editing, Supervision, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Salinity and concentration data methods, data quality details (Table S1 and Fig. S1), Galveston Bay sediment heavy metal concentrations (Table S2), spatial and temporal variation of Galveston Bay bulk sediment metal concentrations in the E3 core and at bay, shoreline and endmember stations (Figs. S2–S3), linear correlations between Galveston Bay sediment As, Cd, Cr, Cu, Hg, Ni, Pb, Sb, Zn and Al, Fe, Mn concentrations (Table S3), Galveston Bay bulk sediment heavy metal concentrations at shoreline stations (Fig. S4), Galveston Bay bulk sediment heavy metal concentrations at endmember stations (Fig. S5), discussion of *t*-tests and Figs. 2, 3, and 5 including outliers (Tables S4-S5), study period Trinity River discharge summary (Table S6), Galveston Bay sediment toxicity screening and toxicity exceedances discussion (Table S7), comparison of heavy metal concentrations in Galveston Bay and other estuarine systems (Table S8), CA1 dendrogram results (Fig. S6), discussion of Galveston Bay bulk sediment enrichment factors (Tables S9-S10), sample location map showing station clusters identified in CA2 (Fig. S7), CA2 dendrogram results (Fig. S8), discussion of Galveston Bay sediment Pb isotope ratios and concentrations. Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2021.150446.

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