

Final Paper

Zhenwei Wu

Title

Metals in riparian surface sediment of an estuarine channel surrounded by petrochemical industries near the Northern Gulf of Mexico

Abstract

Heavy metal contamination in estuarine environments presents significant environmental and human health challenges, particularly in regions affected by industrial activities. This study investigates heavy metal accumulation in the riparian sediments of the Calcasieu River in Louisiana, an area heavily impacted by petrochemical operations. The research aims to assess spatial and temporal variations in metal concentrations, determine pollution levels, and identify potential contamination sources. Using contamination indices and ecological risk assessment methods, the findings will help inform environmental management practices and regulatory policies. The study's results are crucial for protecting aquatic ecosystems and local communities from the adverse effects of heavy metal pollution.

1. Introduction

Estuaries and coastal areas often receive substantial urban and industrial pollutants, making them highly susceptible to anthropogenic impacts, including hazardous materials like metals. The rising contamination of water bodies by metals is a significant concern, driven by industrial and urban development. This contamination poses threats to marine ecosystems and human health, as noted by Krasnići et al. (2013) and Jordanova et al. (2018). Metals can accumulate in estuarine sediments, persisting over time and entering the food chain (Micó et al., 2006; Zhuang et al., 2009). The bioaccumulation of metals in aquatic organisms can result in toxic effects across trophic levels, affecting fish, birds, and humans consuming contaminated seafood, thereby impacting health through the water and food chain (Bryan and Langston, 1992; Birch and Taylor, 1999; Wan and

Rainbow, 2008). Monitoring and assessing metal concentrations in sediments is crucial for identifying and managing pollution sources.

Sediments typically contain metal concentrations several orders of magnitude higher than the overlying water, making them reliable indicators of pollution (Łuczyńska et al., 2018). This is particularly true for estuaries near petrochemical industries, a major source of metal pollution. Petrochemical industries, which produce chemicals from petroleum and natural gas, release metals as by-products and waste materials, contaminating nearby environments, including water sediments (Nobi et al., 2010). However, studies on metal pollution in estuarine environments near petrochemical hubs remain limited.

The Calcasieu River in southwestern Louisiana, USA, exemplifies this issue. As a critical navigational route for the national petrochemical industry, the river passes through the heavily industrialized Lake Charles area, home to numerous refineries and chemical plants, particularly near Bayou d'Inde. Industrial activities in Bayou d'Inde began in the 1920s with oil and natural gas discoveries, leading to severe contamination from industrial and municipal discharge. Alarming high concentrations of toxic metals in surface sediments have been documented (Redmond et al., 1996; Hardaway et al., 1999, 2002). The contamination prompted the U.S. Environmental Protection Agency to designate Bayou d'Inde as a Superfund site in the 1990s, necessitating remediation. Despite cleanup efforts, research on metal concentrations in the main channel of the Calcasieu River remains scarce. This gap is critical to understanding the potential migration of metals from upstream areas to downstream estuarine zones.

This study aims to provide baseline data on metal concentrations along the Calcasieu River banks. The objectives are threefold: first, to evaluate spatial and temporal changes in levels of arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), silver (Ag), and zinc (Zn) in riverbank sediments; second, to assess pollution extent and conduct an ecological risk assessment of individual and combined metals; and third, to identify sources and factors influencing metal concentrations and spatial patterns.

2. Methods

2.1 Research area and sampling method

This study was conducted in the lower part of Calcasieu River that enters the northern Gulf of Mexico in southwestern Louisiana, USA (Figure 1). The river drains a total surface area of 9780 km² with an approximate 260 km long freshwater reach and a 60 km long saltwater-freshwater mixing zone. The drainage basin is predominantly covered by forests (51%), followed by agricultural land (26%) and wetlands (12%) (Rosen and Xu, 2011). The river ranks among the three principal rivers traversing the Louisiana Chenier Plain to the west of the contemporary Mississippi River Delta. The Chenier Plain is characterized by a series of beach ridges (i.e. cheniers) separated by marshy areas. The Louisiana Chenier Plain were formed over thousands of years from marine materials and sediment deposited by the changing course of the Mississippi River (Owen, 2008; Yao et al., 2020). The lower Calcasieu River serves as an important marine transportation corridor and infrastructure for the petrochemical industries concentrated in the region. As such, the channel requires regular dredging every other year in its last 45 km reach (USACE, retrieved May 12, 2023, <https://www.mvn.usace.army.mil/About/Projects/Calcasieu-River-Pass-LA/>).

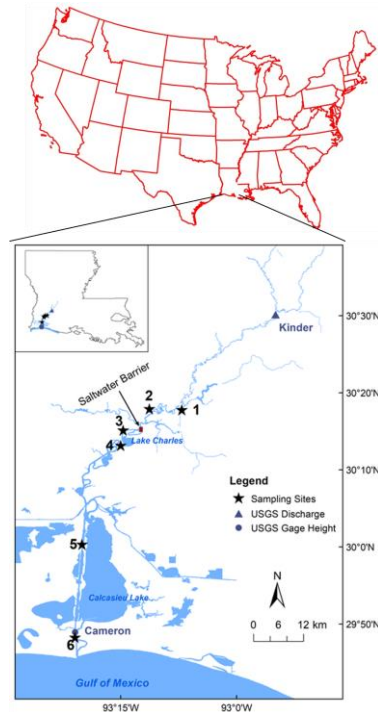


Figure 1. Geographic location of the lower Calcasieu River in Southwestern Louisiana, USA and the six sampling sites and USGS gage stations. Sites 1 and 2 are within the freshwater research, and sites 3, 4, 5 and 6 show an increasing salinity in relation with river discharge. Daily discharge was recorded by U.S. Geological Survey at Kinder.

2.2 Laboratory analysis

To measure total metal content, sediment samples were processed following EPA Method 3050 with the aid of a DEENA automated digestion system provided by Thomas Cain, Inc. The procedure began by accurately weighing 0.50 grams of the dry sediment sample and placing it into a 50 mL single-use digestion vial from SCP Science. This vial was then positioned in the DEENA rack. The system's block temperature was preset at 120°C. The digestion reagents consisted of deionized water, high-purity nitric acid (HNO₃), hydrochloric acid (HCl), and 30% hydrogen peroxide (H₂O₂). Both HNO₃ and H₂O₂ were carefully added in a controlled manner to prevent over-foaming. The temperature setting was adjusted to a high range to ensure the sample reached the target temperature of 95°C within the specified duration. The volume post-digestion was approximately 40 mL. The DEENA system was utilized for all stages of this process. Post-digestion, the samples were filtered using a 0.45 µm membrane filter and then diluted to a final volume of 80 mL in preparation for analysis. The diluted samples were then quantitatively assessed using an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES), specifically the SPECTRO Ciros-CCD model from SPECTRO Analytical Instruments GmbH, located in Kleve, Germany.

2.3 Evaluation of Metal Pollution and Contamination Levels

The selection of reference baseline values is pivotal in the analysis of geochemical data. Due to the absence of uncontaminated sediment samples (USS) as a baseline in this study, we resorted to employing Beck's (1990) standard metal concentrations: arsenic (As) at 0.60 mg/kg, cadmium (Cd) ranging from 0.3 to 1.4 mg/kg, chromium (Cr) at 25 mg/kg, copper (Cu) at 10 mg/kg, lead (Pb) at 15 mg/kg, silver (Ag) at 0.07 mg/kg, and zinc (Zn) at 40 mg/kg. To assess the extent of metal pollution in the Calcasieu River's surface sediments, we employed two different indices: the contamination factor (CF), pollution load index (PLI).

2.3.1 Contamination Factor (CF)

The contamination factor (CF), as proposed by Hakanson (1980), was adopted in this research. CF is calculated by dividing the measured concentration of each metal found in the sediment by

its corresponding baseline or background level (concentration in sediment presumed to be uncontaminated):

$$CF = \frac{C_{metal}}{C_{background}}$$

CF values are categorized into four distinct grades to track the pollution levels of a single metal over time, as established by Turekian and Wedepohl (1961) and further utilized by Loska et al. (1997): a low degree of contamination is indicated by a CF value less than 1, a moderate degree is noted for values between 1 and less than 3, a considerable degree for values from 3 up to less than 6, and a CF value of 6 or greater signifies a very high degree of contamination. Therefore, these CF values serve as indicators of the progressive enrichment of a specific metal within sediments as time advances.

2.3.2 Pollution load index (PLI)

To evaluate the quality of the sediments, we adopted an integrated approach using the pollution load index (PLI) for the six studied metals, based on the methodology proposed by Suresh et al. (2011). The PLI is calculated by taking the n th root (where n represents the number of metals analyzed) of the product of the contamination factors (CF) for each metal:

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \dots \times CF_n)^{1/n}$$

This empirical index is a straightforward tool for comparing the extents of metal pollution across different sites. A PLI value greater than 1 indicates the presence of pollution, while a PLI less than 1 suggests no significant metal pollution, as stated by Tomilson et al. (1980). This index is particularly useful for providing a single figure that represents the overall level of metal contamination at a given site.

3. Results

3.1 Longitudinal distribution of metal contents

Fig 2 shows the mean total metal content varies across sites, with Site-6 having the highest value and Site-4 the lowest. Sites 1, 2, 3, and 5 show intermediate levels of contamination. The data indicates significant variability in metal accumulation among the sites.

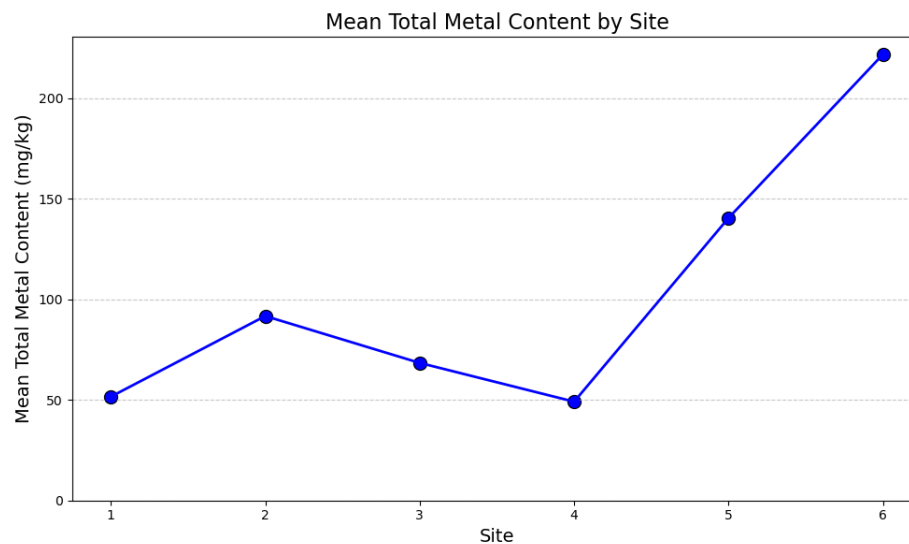


Fig 2. Mean Total Metal Content Change Through Sites

Table 1 illustrates the concentrations of metals in sediment samples. Notably, sites 5 and 6 exhibited significantly elevated levels of these metals compared to the other locations, which can be attributed to their proximity to the petrochemical industrial zone and the prevalent discharge of untreated industrial effluents. The average concentrations of the metals in the sediment samples were found to follow this descending order: zinc (Zn) > chromium (Cr) > copper (Cu) > lead (Pb) > arsenic (As) > silver (Ag) > cadmium (Cd).

Table 1. Heavy metal contents in the lower Calcasieu River

Sites	Heavy metal content (mg/kg)							Sum
	As	Cd	Cr	Cu	Pb	Ag	Zn	
Site 1	5.30	0.40	3.41	3.93	10.52	2.45	27.61	53.62
Site 2	6.70	0.34	22.44	6.71	12.91	0.54	43.85	93.50
Site 3	7.30	0.44	8.03	7.32	9.04	0.19	38.18	70.50

Site 4	6.80	0.40	5.93	10.22	7.76	0.93	19.17	51.22
Site 5	8.70	0.41	11.37	46.15	9.44	0.51	67.63	144.21
Site 6	10.50	0.57	102.32	26.91	19.10	0.21	62.25	221.86
Mean	7.55	0.43	25.58	16.88	11.46	0.80	43.12	105.82

Figure 3 shows the mean concentrations of metals across six sites. Arsenic (As) is highest at Site-6 and consistent across other sites. Cadmium (Cd) peaks at Site-6 and is lowest at Sites-1 and 2. Chromium (Cr) remains low except for a significant increase at Site-6. Copper (Cu) is variable, with a maximum at Site-5. Lead (Pb) shows low levels across sites, slightly higher at Site-6. Silver (Ag) is highest at Site-1, with variability among other sites. Zinc (Zn) peaks at Site-5, with intermediate levels across sites. Site-6 generally has the highest concentrations of most metals.

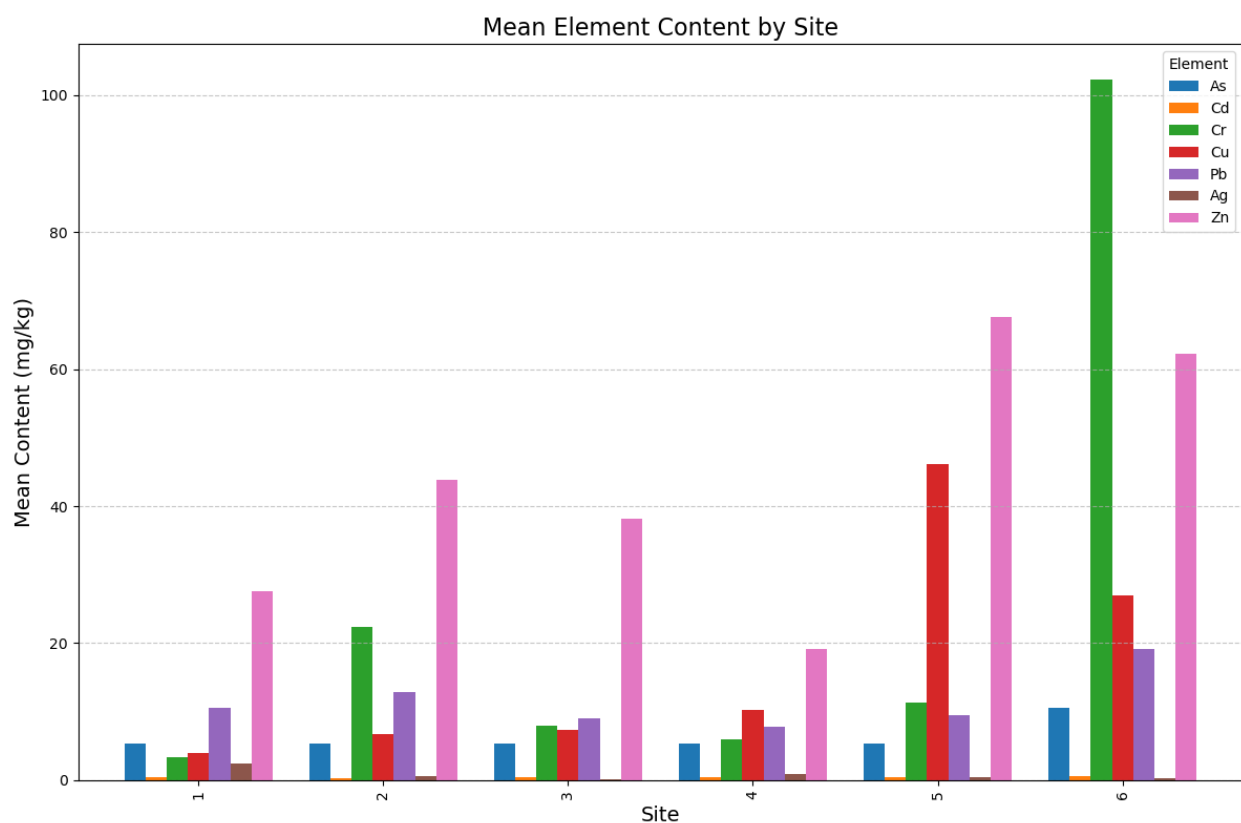


Fig 3. Different Metal Content Change Through Sites

3.2 Accumulation of heavy metals in the estuary mouth

The results of contamination factors (CFs) and pollution load index (PLI) are presented in Table 2 and Fig 4. The results of CF (Table 2) clearly showed that the pollution of As at all 6 sites are under very high level ($CF > 6$). And from site 1 to site 6, the level of pollution progressively increases. The CF value of As at the site 6 ($CF = 17.49$) has already doubled that of the site 1 ($CF = 8.83$). The levels of Cd pollution at all 6 sites are moderate. However, their levels are just slightly above the standard ($CF=1$). The level of Ag pollution is at a very high degree at all sites except for site 3. The maximum CF value at site 1 is 17 times the minimum CF value at site 3. All metals have accumulated at sites 5 and 6, i.e., in the river mouth. The accumulation was strongest with As followed by Ag, Cu, Cr, Cd, Zn, and Pb. Judging from the PLI values, they are continuously increasing from site 1 to site 6, and pollution is present at all sites.

Table 2. Metal contamination factors (CFs) and pollution load indices (PLIs) for sediments of all sites studied in the Calcasieu River

Sites	Contamination factors (CFs)							PLI
	As	Cd	Cr	Cu	Pb	Ag	Zn	
site-1	8.83	1.33	0.14	0.39	0.70	35.05	0.69	1.40
site-2	11.17	1.13	0.90	0.67	0.86	7.68	1.10	1.77
site-3	12.17	1.46	0.32	0.73	0.60	2.67	0.95	1.30
site-4	11.33	1.35	0.24	1.02	0.52	13.28	0.48	1.43
site-5	14.50	1.37	0.45	4.61	0.63	7.26	1.69	2.28
site-6	17.49	1.90	4.09	2.69	1.27	3.06	1.56	3.01

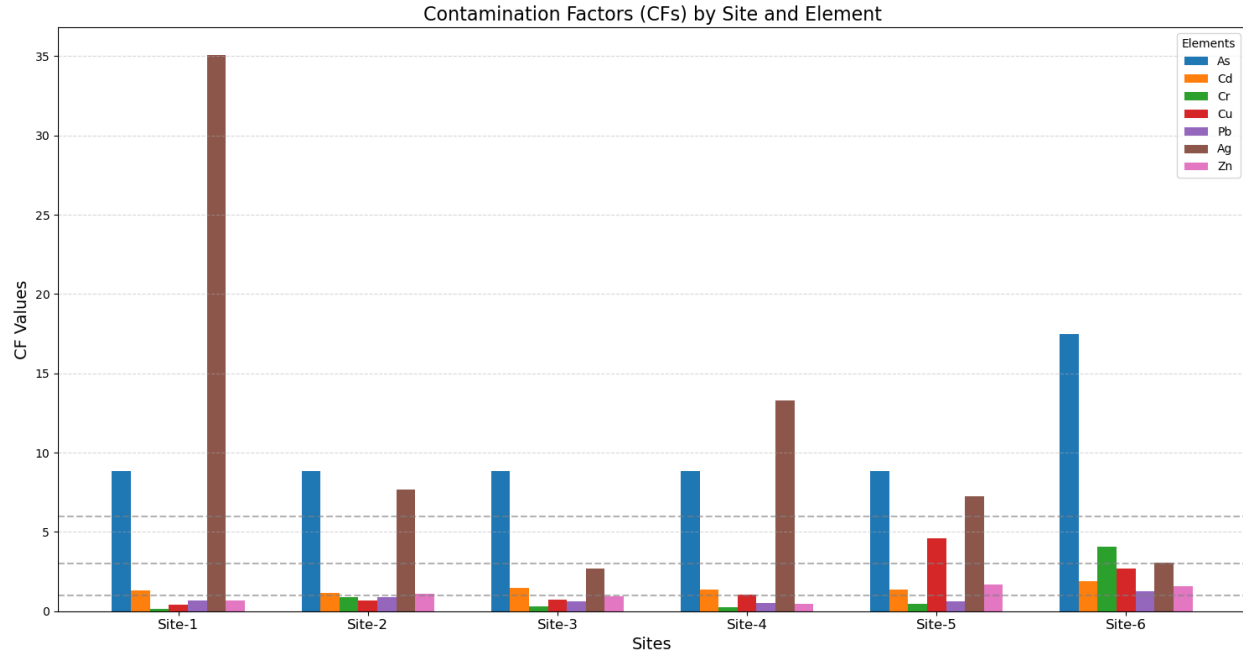


Fig.4 Contamination Factors (CFs) by Site and Element

4. Discussion and Conclusion

Our analysis indicated that the concentrations of zinc (Zn) and chromium (Cr) in the sediment were more pronounced than those of other metals, which may be a result of the direct release of untreated effluent from industries such as petroleum, fertilizer production, and textiles (Facetti et al., 1998; Islam et al., 2015a). Additionally, we observed that the level of arsenic (As) is likely attributable to human-induced activities. These include the usage of arsenical compounds in fertilizer and pesticide formulations (Fu et al., 2014; Ahmed et al., 2016), the application of copper arsenate in wood preservation processes (Singare et al., 2012; Baeyens et al., 2007), and the use of certain chemicals in the tanning industry, particularly arsenic sulfide (Bhuiyan et al., 2011).

The CF values indicate severe pollution of As at all six sites. In aquatic environments, As can have toxic effects on aquatic organisms such as fish, invertebrates, and algae. Arsenic can accumulate in the food chain, leading to bioaccumulation and biomagnification, where higher-level organisms may be exposed to higher concentrations of arsenic. When it comes to human health, exposure to high levels of arsenic can have severe health effects. Ingesting or inhaling arsenic-contaminated soil, dust, or water can lead to both acute and chronic health problems. Acute poisoning can cause

symptoms such as nausea, vomiting, abdominal pain, and diarrhea. Long-term exposure to lower levels of arsenic can increase the risk of various health conditions, including skin lesions, cardiovascular diseases, respiratory problems, and certain types of cancer, such as lung, bladder, and skin cancer. For Cr, the content at site 6 is very high, indicating a potential risk of Cr pollution at this site. In soil, Cr can affect plant life by inhibiting growth and reducing productivity, especially if present in high concentrations. It can interfere with plant metabolic processes, causing oxidative stress and damage to cellular structures. Furthermore, in coastal environments, if Cr-contaminated soil is eroded and ends up in the water, it can harm marine life. Cr can accumulate in aquatic organisms, affecting their survival and reproduction. Prolonged exposure to Cr can be lethal to many forms of marine life, and it can also move up the food chain, impacting larger aquatic creatures and eventually humans who consume seafood. However, some microorganisms and plants can tolerate and even remediate Cr pollution to some extent through processes such as phytoremediation and bioremediation.

For Ag, although its content is high at all six sites, Ag in sediments hardly causes damage to the estuarine environment or human health, and it does not accumulate rapidly in aquatic organisms. Therefore, we believe that there is no notable Ag pollution issue within this study area. As for the remaining metals that we analyzed (Cd, Cu, Pb, and Zn), their contents are at a lower pollution level based on CF values. Therefore, we can conclude that there are no pollution issues related to them within the study area.

In light of the evidence above, we believe there is no serious metal pollution issue in the study area at present. However, due to ongoing pollution from coastal industrial activities and shipping lanes, we believe that maintaining long-term monitoring of metal elements, especially As and Cr, can make a significant contribution to protecting the coastal environment of South Louisiana. It could also better inform policymakers to manage the sediment load of the Calcasieu River.

Reference

- Ahmed, M. K., Shaheen, N., Islam, M. S., Habibullah-Al-Mamun, M., Islam, S., Islam, M. M., ... & Bhattacharjee, L. (2016). A comprehensive assessment of arsenic in commonly consumed foodstuffs to evaluate the potential health risk in Bangladesh. *Science of the*
- Beck, J. N., Ramelow, G. J., Thompson, R. S., Mueller, C. S., Webre, C. L., Young, J. C., & Langley, M. P. (1990). Heavy metal content of sediments in the Calcasieu River/Lake Complex, Louisiana. *Hydrobiologia*, 192, 149-165.
- Birch, G.F., & Taylor, S.E. (1999). Source of heavy metals in sediments of the Port Jackson estuary, Australia. *Science of The Total Environment*, 227(2-3), 123-138.
[https://doi.org/10.1016/S0048-9697\(99\)00003-0](https://doi.org/10.1016/S0048-9697(99)00003-0).
- Franco-Uría, A., López-Mateo, C., Roca, E., & Fernández-Marcos, M. L. (2009). Source identification of heavy metals in pastureland by multivariate analysis in NW Spain. *Journal of hazardous materials*, 165(1-3), 1008-1015.
- Héberger, K., Milczewska, K., & Voelkel, A. (2005). Principal component analysis of polymer–solvent and filler–solvent interactions by inverse gas chromatography. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 260(1-3), 29-37.
- Islam, M. S., Ahmed, M. K., Habibullah-Al-Mamun, M., & Hoque, M. F. (2015). Preliminary assessment of heavy metal contamination in surface sediments from a river in Bangladesh. *Environmental earth sciences*, 73, 1837-1848.
- Jordanova, M., Hristovski, S., Musai, M., Boškovska, V., Rebok, K., Dinevska-Kovkarovska, S., & Melovski, L. (2018). Accumulation of heavy metals in some organs in barbel and chub from Crn Drim River in the Republic of Macedonia. *Bulletin of environmental contamination and toxicology*, 101, 392-397.
- Krasnići, N., Dragun, Z., Erk, M., & Raspor, B. (2013). Distribution of selected essential (Co, Cu, Fe, Mn, Mo, Se, and Zn) and nonessential (Cd, Pb) trace elements among protein fractions from hepatic cytosol of European chub (*Squalius cephalus* L.). *Environmental Science and Pollution Research*, 20, 2340-2351.

- Łuczyńska, J., Paszczyk, B., & Łuczyński, M. J. (2018). Fish as a bioindicator of heavy metals pollution in aquatic ecosystem of Pluszne Lake, Poland, and risk assessment for consumer's health. *Ecotoxicology and environmental safety*, 153, 60-67.
- Nduka, J. K., & Orisakwe, O. E. (2011). Water-quality issues in the Niger Delta of Nigeria: a look at heavy metal levels and some physicochemical properties. *Environmental science and pollution research*, 18, 237-246.
- Ouyang, Y., Higman, J., Thompson, J., O'Toole, T., & Campbell, D. (2002). Characterization and spatial distribution of heavy metals in sediment from Cedar and Ortega rivers subbasin. *Journal of Contaminant Hydrology*, 54(1-2), 19-35.
- Owen, D.E., 2008. Geology of the Chenier Plain of Cameron Parish, southwestern Louisiana. *Geological Society of America Field Guide* 14, 27–38.
- Qu, W., & Kelderman, P. (2001). Heavy metal contents in the Delft canal sediments and suspended solids of the River Rhine: multivariate analysis for source tracing. *Chemosphere*, 45(6-7), 919-925.
- Rosen, T., & Xu, Y. J. (2011). Riverine sediment inflow to Louisiana Chenier Plain in the northern Gulf of Mexico. *Estuarine, Coastal and Shelf Science*, 95(2-3), 279-288.
- Sany, S. B. T., Salleh, A., Sulaiman, A. H., Sasekumar, A., Rezayi, M., & Tehrani, G. M. (2013). Heavy metal contamination in water and sediment of the Port Klang coastal area, Selangor, Malaysia. *Environmental earth sciences*, 69(6), 2013-2025.
- Singare, P. U., Trivedi, M. P., & Mishra, R. M. (2012). Sediment heavy metal contaminants in Vasai Creek of Mumbai: pollution impacts. *American journal of chemistry*, 2(3), 171-180.
- Tansel, B., & Rafiuddin, S. (2016). Heavy metal content in relation to particle size and organic content of surficial sediments in Miami River and transport potential. *International Journal of Sediment Research*, 31(4), 324-329.
- USACE (2023). Calcasieu River & Pass. Retrieved May 12, 2023, <https://www.mvn.usace.army.mil/About/Projects/Calcasieu-River-Pass-LA/>

Zhang, W., Feng, H., Chang, J., Qu, J., Xie, H., & Yu, L. (2009). Heavy metal contamination in surface sediments of Yangtze River intertidal zone: an assessment from different indexes. *Environmental Pollution*, 157(5), 1533-1543.

Zhuang, P., McBride, M. B., Xia, H., Li, N., & Li, Z. (2009). Health risk from heavy metals via consumption of food crops in the vicinity of Dabaoshan mine, South China. *Science of the total environment*, 407(5), 1551-1561.