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## Heavy metals and metalloids content and enrichment in Gulf Coast sediments in the vicinity of an oil refinery

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### ABSTRACT

The heavy metals and metalloids released by the oil refineries accumulated in the natural lakes may severely endanger the aquatic life. For this purpose the present study was carried out to explore the potential risk posed by the heavy metals and metalloids in the drainage ditch of a large oil refinery located at the southwest of Lake Pontchartrain, Norco, St. Charles Parish, Louisiana, USA. The concentration and enrichment of 24 heavy metals and metalloids (Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Ti, V, and Zn) were determined in sediments at a distance of 5 km from an oil refinery to the Lake Pontchartrain. The results showed that the concentration of 24 metals and metalloids declined gradually with the distance from the refinery to the lake, suggesting the oil refinery as a potential source. The enrichment factors (EFs) for Cd, Sb, V, As, and Se indicated that they were heavily accumulated in the sediments but were insignificant for Zn, Be, Ni, Pb, Co, Cu, and Cr. The results of EDTA and BCR extraction demonstrated that Zn, Cd, Co, Cu, Ni, Be and Pb were the most bioavailable elements in the sediments and would cause potential hazards to the environment. Based on our results, the oil refinery can be presumed as one of the sources responsible for the trace metal pollution of Lake Pontchartrain.

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### 1. Introduction

Petroleum or oil refining is an important industry along the Louisiana Gulf Coast. Petrochemical industries are a potential source of environmental pollution, generating wastewater and solid waste that are heavily contaminated with organic compounds and heavy metals, both of which pose a potentially high threat to human life and the environment (Aloulou et al., 2011; Wake, 2005). Sediments are an important sink and source for heavy metals and play an important role in the remobilization of metals to the aquatic environment (Sprovieri et al., 2007). The transfer of metals from sediments to organisms has been reported as an important metal source for many species (Rosales-Hoz et al., 2003). Sediment quality guidelines developed by Long et al. (1995) are used to assess sediment ecological toxicity to aquatic organisms. These guidelines are based upon a biological effects database for sediments (BEDS) containing the concentrations of contaminants at which adverse biological effects occur. The guidelines refer to contaminant effects range-low (ERL) and effects range-median (ERM). They also describe concentrations at which adverse biological effects occur rarely (<ERL), occasionally (ERL-ERM), or frequently (>ERM). Below the ERL level is not considered

toxic because the adverse effects to organisms occurred in less than 10% of studies that used the database, where concentrations were below the respective ERL values. Above the ERM level is considered toxic because adverse effects to organisms occurred in more than 75% of studies in which concentrations exceeded the respective ERM values. To assess sediments contamination, we employed enrichment factors (EFs) estimated against local preindustrial sediments. The use of EFs is a popular means of identifying and quantifying the anthropogenic origin of certain elements (DeLaune et al., 2008; Karageorgis et al., 2009; Kaushik et al., 2009). For detecting the bioavailable form of heavy metals in sediments the one step EDTA extraction method was used (Arain et al., 2008). To get more information about the heavy metals fractionation and bioavailability in sediments, we also used the European Community Bureau of Reference (BCR) sequential extraction process (Rauret et al., 1999), which is the most acceptable technique. It standardizes not only the diversity of different methods, such as the Tessier method (Tessier et al., 1979), Sposito method (Sposito et al., 1982), and Kersten and Förstner method (Kersten and Förstner, 1986), but also the heterogeneity of the different protocols of previous procedures to probe the speciation of trace elements because the total concentration is not a good parameter for assessing bioavailability (Dundar et al., 2012).

Leakage and insufficient maintenance of petroleum installations may lead to accidental oil spills, which contaminate the environment by organic components as well as heavy metals such as V, Ni, Ba, Cr,

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Pb, and Cd (Fiedler et al., 2009). Apart from V and Ni, which are at highest concentration in crude oil and residual fuel oils, As, Fe, Mn, Mo, Zn are also encountered. In addition, organometallics of Ba, Ca, Mn, Fe, Mn, MnO, Mg, MgO, MgO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub> are used as combustion catalysts/deposit modifiers (Karageorgis et al., 2009). Although, the literature has reported oil refineries a source of heavy metals pollution in water and soil, but less information is reported about the effects on natural lakes (Karageorgis et al., 2009). Lake Pontchartrain is one of the largest lagoons in southeastern Louisiana, and it is reported that the lake has been moderately polluted by some of the trace metals such as Cu (Delaune et al., 2009). To explore the source and impact of selected elements in drainage sediments, drain ditch sediments samples of a large oil refinery located at the southwest of Lake Pontchartrain, Norco, St. Charles Parish, Louisiana, USA, were collected and analyzed. The concentrations of heavy metals were also normalized using Al as conservative element. In addition, the EFs were estimated for the elements. The bioavailability of each trace element was evaluated by ethylene diamine tetra acetic acid disodium salt (EDTA) and the BCR sequential extraction process.

## 2. Materials and methods

### 2.1. Sampling and pre-treatment

Eight sampling sites were established along a ditch at a distance extending to 5 km from an oil refinery (in operation since the 1920s) to the Lake Pontchartrain (Fig. 1). The bold lines marked with 10 stands for the Interstate 10 highway near Lake Pontchartrain. The drainage

ditch, located on the right side of the Lower Guide Levee Road of the Carré Spillway in Louisiana, carries oil refinery wastewater.

The sediments samples were collected in July 2009 at 8 stations using a dipper. All collected sediments samples were stored in an insulated cooler containing ice, were delivered to the laboratory on the same day, and were kept at 4 °C before further processing.

Approximately 80 g of the sediments were transferred to a 100-mL plastic beaker, and the beaker was then covered with two layers of gauze and placed in a freezer at –40 °C for 48 h. The frozen beaker was then moved to the Advantage Freeze Dryer (The VirTis Company), and its contents were pulverized manually with a mortar and pestle and then sieved through a 75- $\mu$ m stainless steel sieve. The powder was stored in polyethylene bottles for trace element analysis.

### 2.2. Trace element determinations

The sediments samples were prepared for metal analysis by acid digestion (U.S. EPA, Method 3050) using the automated sample digestion system DEENA (Thomas Cain, Inc.). In brief, 0.50 g solid sample was transferred to a 50-mL disposable digestion vial (SCP Science), which was then placed in the DEENA rack. The block temperature was preset at 120 °C, which is a high value that ensured that the sample would achieve the desired temperature (95 °C) in the allotted time. The reagents used were deionized (DI) water, concentrated nitric acid (HNO<sub>3</sub>), concentrated hydrochloric acid (HCl), and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) (30%). HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> were added drop-wise to avoid excessive foaming. The final sample volume was ~40 mL. Samples were then filtered with a 0.45- $\mu$ m filter membrane and diluted to 80.0 mL for

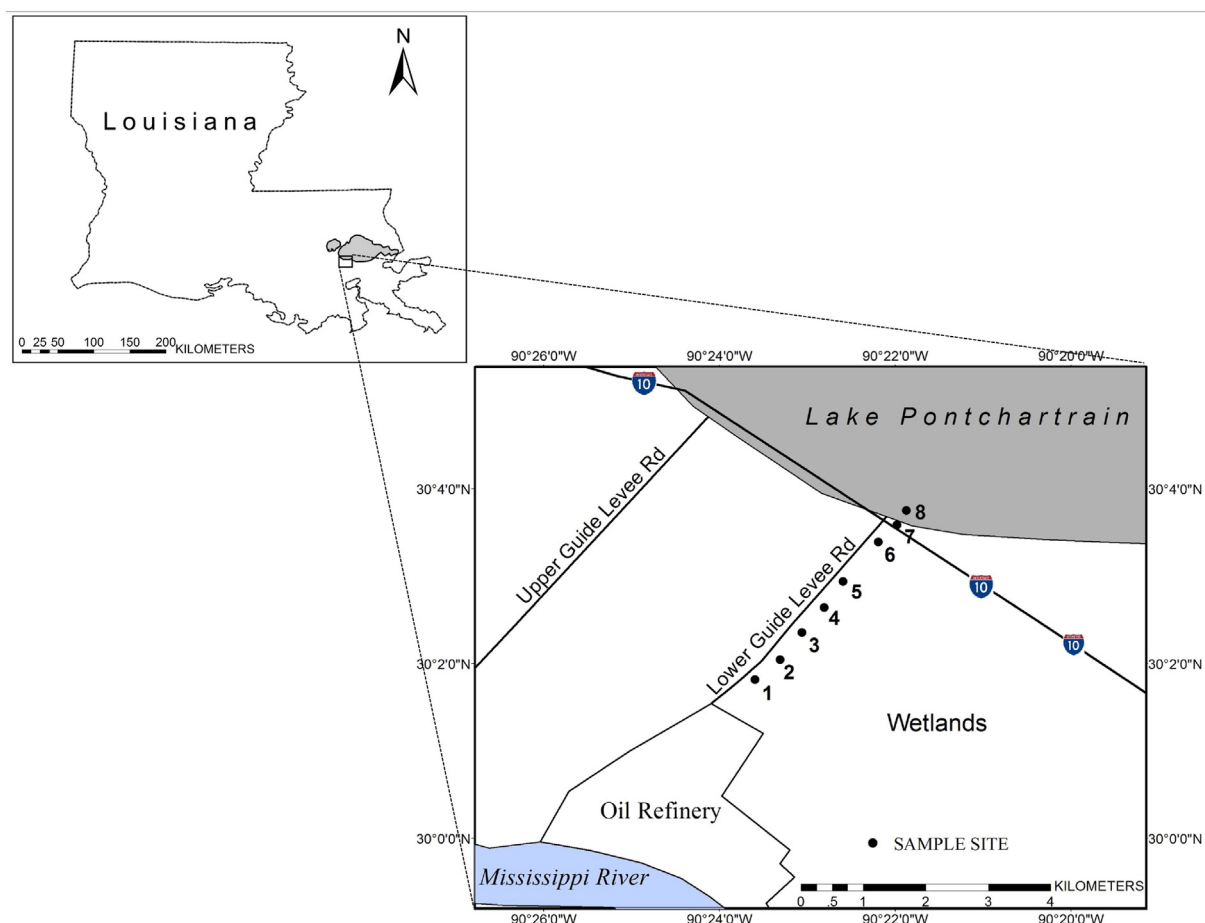


Fig. 1. Sampling stations in the drainage ditch near Lake Pontchartrain.





**Table 3**  
The total trace elements concentration in sediment at different sites (mg kg<sup>-1</sup>).

Sampling site	As	Be	Cd	Cr	Co	Cu	Ni	Pb	Sb	Se	V	Zn
1	69.3	1.08	2.22	109	9.98	50.6	32.0	71.4	48.3	199	87.3	428
2	66.2	1.00	1.94	87.8	8.60	35.7	30.3	70.4	46.0	195	80.2	333
3	63.4	0.981	1.87	53.5	8.29	33.2	29.1	64.2	39.5	167	78.2	323
4	58.7	0.926	1.73	46.2	8.13	23.7	20.9	51.0	39.2	163	75.2	158
5	52.0	0.919	1.50	39.4	7.67	20.8	20.1	42.8	38.5	163	72.4	102
6	48.7	0.821	1.36	30.0	7.08	19.2	19.2	34.1	35.6	144	65.3	88.3
7	38.9	0.659	1.25	25.4	6.25	13.9	15.5	24.2	29.3	120	52.6	64.7
8	35.1	0.605	1.21	14.6	6.17	11.9	14.0	22.2	27.5	115	48.6	52.4
Average	54.0	0.874	1.64	50.7	7.77	26.1	22.6	47.5	38.0	158	70.0	194
STDEV	12.6	0.168	0.363	32.2	1.27	13.0	6.91	19.9	7.22	31.0	13.6	146
MAX	69.3	1.08	2.22	109	9.98	50.6	32.0	71.4	48.3	198	87.3	428
MIN	35.1	0.605	1.20	14.6	6.17	11.9	14.0	22.2	27.5	115	48.6	52.5
BGV	7.2	0.92	0.1	54	9.1	25	19	19	1	0.4	90	60
ERL	8.2	NO	1.2	81	NO	34	20.9	46.7	2	NO	NO	150
ERM	70	NO	9.6	370	NO	270	51.6	218	25	NO	NO	410
LOD (µg L <sup>-1</sup> )	2.1	0.08	0.09	0.18	0.19	0.27	0.32	1.5	2.1	2.7	0.33	0.27

Note: (1) the parameters in the first column have the same meaning as Table 2.  
(2) ERL— refers to Toxic Effects-Range Low; ERM— refers to Toxic Effects-Range Medium.  
(3) NO— These elements have no the ERL and ERM data.

has the highest bioavailability compared with Cr (III) (David et al., 2012). Therefore, more attention should be given to chromium (VI). Only for Sb and Se did the EDTA-extractable state increase from the refinery drain outlet to the inlet of the lake. By contrast, the EDTA-extractable fraction for the other 10 trace elements decreased from the refinery outlet along the drainage ditch, indicating that the 10 trace elements might be from the refinery discharge. The proportion

of the EDTA-extracted portion relative to the total element concentration decreased as Pb (46.1%) > Zn (42.9%) > Cd (41.3%) > Co (28.1%) > Ni (26.0%) > Cu (25.7%) > Se (24.45%) > Sb (19.5%) > V (10.9%) > As (7.03%) > Be (5.56%) > Cr (0%), suggesting that the bioavailability of most of the trace elements is high and would pose potential risks to the ecosystem. This conclusion is in strong agreement with a previous river assessment report (Arain et al., 2008).

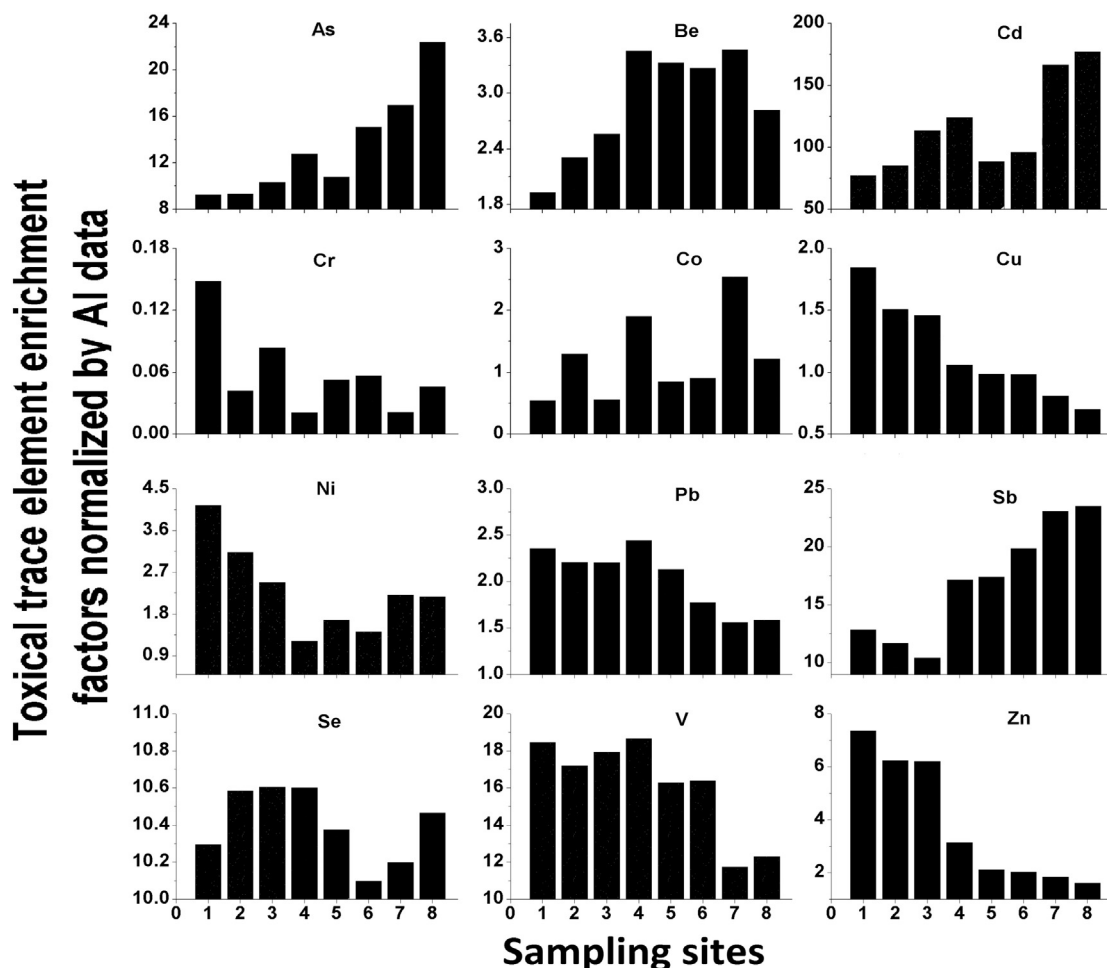


Fig. 2. Toxic trace element enrichment factors normalized with Al.





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