ARTICLE IN PRESS

Journal of Geochemical Exploration xxx (2015) xxx-xxx

Contents lists available at ScienceDirect

Journal of Geochemical Exploration

journal homepage: www.elsevier.com/locate/jgeoexp



اللو دکننده مقالات علم freepaper.me paper

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

Zengqiang Zhang ^{a,b,*}, Jim J. Wang ^b, Cilai Tang ^c, Ronald D. DeLaune ^d

- ^a College of Natural Resources and Environment, Northwest A&F University, Yangling, Shaanxi, 712100, China
- ^b School of Plant, Environmental, and Soil Sciences, Louisiana State University AgCenter, Baton Rouge, LA 70803, USA
- ^c Department of Environmental Engineering, College of Hydraulic & Environmental Engineering, China Three Gorges University, Yichang, Hubei 443002, China
- ^d Wetland Biogeochemistry Institute, Department of Oceanography and Coastal Sciences, Louisiana State University, Baton Rouge, LA 70803-7511, USA

ARTICLE INFO

Article history: Received 31 March 2015 Revised 20 July 2015 Accepted 21 August 2015 Available online xxxx

Keywords:
Heavy metal
Metalloid
Sediment
Oil refinery
Enrichment factor
Pollution

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.

© 2015 Elsevier B.V. All rights reserved.

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

E-mail address: zhangzq58@126.com (Z. Zhang).

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,

http://dx.doi.org/10.1016/j.gexplo.2015.08.008 0375-6742/© 2015 Elsevier B.V. All rights reserved.

 $^{^{*}}$ Corresponding author at: College of Natural Resources and Environment, Northwest A&F University, Yangling, Shaanxi 712100, China.

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, MgO₂, and Al₂O₃ 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 $-40\,^{\circ}\text{C}$ 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- μ 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 (HNO₃), concentrated hydrochloric acid (HCl), and hydrogen peroxide (H₂O₂) (30%). HNO₃ and H₂O₂ were added drop-wise to avoid excessive foaming. The final sample volume was ~40 mL. Samples were then filtered with a 0.45-µm filter membrane and diluted to 80.0 mL for

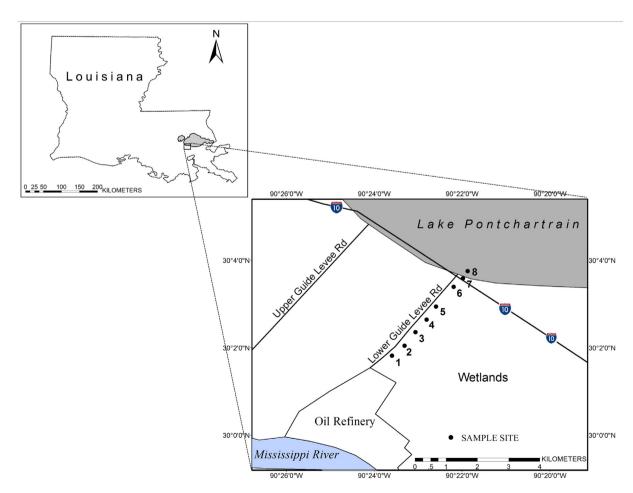


Fig. 1. Sampling stations in the drainage ditch near Lake Pontchartrain.

دائلو دکننده مقالات علم freepaper.me

Z. Zhang et al. / Journal of Geochemical Exploration xxx (2015) xxx-xxx

measurement with an inductively-coupled plasma-optical emission spectrometer (ICP-OES, SPECTRO Ciros-CCD, SPECTRO Analytical Instruments GmbH).

2.3. EDTA extraction

One gram of predetermined sediment sample was transferred to a 200-mL polypropylene bottle, to which 50 mL of 0.05 mol L^{-1} EDTA was added. The bottle was then put in a mechanical rotary tumbler shaker at 30 rpm for 1 h at room temperature. The suspension was centrifuged at 3000 rpm for 30 min. The supernatant liquid was filtered and stored in polyethylene bottles at 4 °C before analysis by ICP-OES.

2.4. Modified BCR extraction methods

A modified BCR sequential extraction procedure was used to extract trace elements with different speciation. The procedure is described as follows:

Step 1 (I: Exchangeable): 0.5 g sediment was mixed with 20 mL of 0.11 mol L^{-1} acetic acid (pH 2.85) overnight (16 h). The mixture was then centrifuged to separate the extractant for measurement. Step 2 (II: Reducible): 20 mL of 0.5 mol L^{-1} of hydroxyl ammonium chloride, pre-adjusted to pH 1.5 with nitric acid, was added to the residue from step 1 and extraction was performed as above.

Step 3 (III: Oxidizable): the residue from step 2 was heated at 85 °C with 5.0 mL of 8.8 mol L^{-1} H₂O₂ for 2 h. Then, 25 mL of 1.0 mol L^{-1} ammonium acetate, pre-adjusted to pH 2 with nitric acid, was added and digested for 16 h.

Step 4 (IV: Residual): the remaining solid after 3 steps of extraction was digested in 10 mL aqua regia on a hot plate nearly to dryness. Then, the mixture was transferred to a 25.0-mL volumetric flask, and DI water was added to the mark for analysis.

Details of the experimental protocol are available elsewhere (Dundar et al., 2012). The trace elements in the extractant in each step obtained from the BCR procedure were determined using ICP-OES.

2.5. Quality control

For quality control, analytical blanks and certified samples with known concentrations of elements were analyzed using the same procedures and reagents. The accuracy of the measured total acid digestion of the sediments was confirmed by using two certified reference materials from the National Institute of Standards & Technology (NIST), 8704 and 2704. The obtained results shown in Table 1, indicated that our determination was acceptable except for Cr. The high recoveries of Cr need correction in data.

2.6. Enrichment factor

Enrichment factor (EF) is a useful tool to determine the degree of heavy metals pollution (Nemati et al., 2011). Here we selected Al as the normalize reference element for calculation of the heavy metals enrichment factor, because Al is present in higher concentrations and stable in the environment. The EF values were interpreted as: EF < 1 indicates no enrichment; EF 1–3 minor enrichment; EF 3–5 moderate enrichment; EF 5–10 moderately severe enrichment; EF 10–25 severe enrichment; EF 50 very severe enrichment; and EF 50 extremely severe enrichment (Sakan et al., 2009). EF value is calculated as below:

$$EF_i = (C_x/C_{Al})_{sediment}/(C_x/C_{Al})_{background}$$

Where: $(C_x/C_{Al})_{sediment}$ is the ratio of concentration of an element X in mg kg⁻¹ in the analyzed sample and $(C_x/C_{Al})_{background}$ is the same ratio in the background material (Alomary and Belhadj, 2007).

The data were statistically analyzed to test the significance of differences using a *t*-test, and correlation coefficients were determined using the SPSS8.0 software package.

3. Results and discussion

3.1. Total trace elements in the sediments

The total concentrations of 24 elements (i.e., 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) in the

Table 1Analytical results of certified reference materials.

Element	Buffalo river sedimen	t		Buffalo river sediment SRM 2704 (mg kg ⁻¹)					
	SRM 8704 (mg kg ⁻¹)								
	Certified values	Observed values	Recovery (%)	Certified values	Observed values	Recovery (%)			
Al	61,000 ± 1800	63,200 ± 1600	104	61,100 ± 1600	63,500 ± 1800				
As	_	21.6 ± 0.8	-	23.4 ± 0.8	24.3 ± 0.6	104			
В	_	8.11 ± 0.25	-	-	8.18 ± 0.23	-			
Ba	413 ± 13	420 ± 8.0	102	414 ± 5.0	421 ± 6.5	102			
Be	_	0.697 ± 0.15	_	-	0.720 ± 0.16	-			
Ca	$26,410 \pm 830$	$26,320 \pm 850$	99.6	$26,000 \pm 1200$	$25,800 \pm 1300$	99.2			
Cd	2.94 ± 0.29	2.89 ± 0.04	98.3	3.45 ± 0.22	3.35 ± 0.05	97.1			
Co	13.57 ± 0.43	13.46 ± 0.09	99.2	-	14.01 ± 0.12	-			
Cr	121.9 ± 3.8	162.3 ± 2.6	133.2	135 ± 5	192.0 ± 2.0	142			
Cu	_	83.4 ± 1.2	-	98.6 ± 5.0	93.1 ± 1.2	94.5			
Fe	$39,700 \pm 1000$	$38,600 \pm 1200$	97.2	$41,100 \pm 1000$	$40,200 \pm 1200$	97.8			
K	$20,010 \pm 410$	$19,850 \pm 450$	99.2	$20,000 \pm 120$	$19,800 \pm 130$	99.0			
Li	_	45.8 ± 5.0	-	47.5 ± 4.1	52.3 ± 2.3	110			
Mg	$12,000 \pm 180$	$12,230 \pm 200$	102	$12,000 \pm 1100$	$12,200 \pm 1200$	102			
Mn	544 ± 21	548 ± 23	101	555 ± 19	561 ± 18	101			
Mo	_	1.97 ± 0.25	-	_	2.16 ± 0.24	-			
Na	5530 ± 150	5620 ± 160	102	5470 ± 160	5570 ± 150	102			
Ni	42.9 ± 3.7	43.6 ± 0.7	101.7	44.1 ± 3.0	45.0 ± 0.4	102			
Pb	150 ± 17	147.8 ± 2.5	98.5	161 ± 17	161.2 ± 5.5	100			
Se	_	1.07 ± 0.05	-	-	1.13 ± 0.06	-			
Sb	3.07 ± 0.32	3.04 ± 0.43	99.0	3.79 ± 0.23	3.65 ± 0.24	96.3			
Ti	4570 ± 200	4560 ± 210	99.7	4570 ± 180	4540 ± 160	99.3			
V	94.6 ± 4.0	93.8 ± 5.4	99.2	95.0 ± 4.0	92.5 ± 3.0	97.4			
Zn	408 ± 15	399.0 ± 7.2	97.8	438 ± 12	448.6 ± 5.0	102.4			

ARTICLE IN PRESS

Z. Zhang et al. / Journal of Geochemical Exploration xxx (2015) xxx-xxx

sediments were determined. All the metals and metalloids were observed to be at their highest concentration in the location near the oil refinery. These concentrations decreased gradually along the drainage ditch to the inlet of the lake, clearly demonstrating that they originated from the oil refinery discharge. The enrichment of these elements in the ditch sediments near the oil refinery poses potential risks to the biota (Tiwari et al., 2011). The biota will also transfer the contaminants downstream with the water and impact the whole ditch ecosystem. Different elements pose different risks to the environment. Some elements may benefit rather than be toxic to biota. The 24 metals and metalloids for the study were categorized into less toxic and toxic (12 metals each). We selected for 12 elements (Al, B, Ba, Ca, Fe, K, Li, Mg, Mn, Mo, Na, and Ti) with relatively low toxicity to the environment. Their average, maximum, minimum, and background values are shown in Table 2.

Table 2 shows that the content of B and Mg are higher than their background levels, especially B, clearly indicating that enrichment occurred. The average values of Mo, Mn, and Li were found to be similar to their background level values (Shacklette and Boerngen, 1984), showing that no enrichment had occurred. In contrast, the average values of Al, Ba, Ca, Fe, Na, and Ti were far below their background level values, showing that some of the elements in the sediments were removed by the oil refinery before discharge by some special mechanism that requires further study. According to a comparison of their background level values and their ecological toxicity, the 12 elements mentioned above are of no concern to the environment. We focus the rest of our discussion on the other 12 common contaminant elements (As, Be, Cd, Co, Cr, Cu, Ni, Pb, Sb, Se, V, and Zn), which are highly toxic and endangers the environment. The parameters of total, average, maximum, minimum, background values (Shacklette and Boerngen, 1984), ERL, and ERM values (Long et al., 1995) are shown in Table 3.

The average values for Be, Cr, Co, and V were lower than their background values, indicating that they had not been enriched in the sediments, although they were present in the oil refinery discharge (Khaitan et al., 2005). The average values of Cd, Cu, Ni, Pb, and Zn were higher than their background levels but 4 times less than those values, showing moderate enrichment in the sediments. The sediments concentrations of Cd at all sample locations were higher than the ERL but lower than the ERM. The sediments concentrations of Cu at 2 sample locations were higher than the ERL but lower than the ERM. Four samples each for Ni and Pb were higher than the ERL but lower than the ERM. Four samples for Zn were higher than the ERL, and 1 sample level was higher than the ERM. Accordingly, we conclude that these five elements showed moderate contamination in the sediments and may be a potential risk to biota in the ditch. The average values of As, Sb, and Se were higher, with values 7.55, 38, and 395.5 times greater than their background, respectively, demonstrating that their enrichment was severe. The enrichment of these elements may pose environmental hazards. The concentrations of all samples for As were higher than the ERL and lower than the ERM, indicating moderate contamination of this element in sediments. The concentrations of all samples for Sb were higher than the ERM, indicating high toxicity of this element in sediments. The concentration of Se in all sediments samples is very high compared to its background value. Although, selenium is an essential nutrient with diverse physiological and metabolic actions (Fernández-Martínez and Charlet, 2009). A deficiency or overabundance of Se may result in serious health problems, including cancer (Clark et al., 1996; Hartikainen, 2005).

3.2. Trace element enrichment factors

Twelve toxic elements (As, Be, Cd, Co, Cr, Cu, Ni, Pb, Sb, Se, V, and Zn) were selected to assess their potential contamination in the sediments by means of EFs.

As illustrated in Fig. 2, all of the 12 trace elements show enrichment to some degree. The average EFs decreased in the order of Cd > Sb > V > As > Se > Zn > Be > Ni > Pb > Co > Cu > Cr. Among the 12 elements, the EFs values for Cd, Sb, V, As, and Se are higher than 10, especially for Cd and As ranging from 77.3–177 and 9.23–22.4, respectively. All the remaining elements showed relatively low enrichment (<10). Due to the high EFs value as well as high risk to biota, much attention should be paid to Cd and As accumulation in sediments. Sb, V, and Se may endanger the aquatic organisms due to their high EFs, even though their low toxicity (Sprovieri et al., 2007). For As, Be, Cd, Co, and Sb, higher EF values were observed at the location closer to the inlet of lake, which indicates the possible accumulation of these metals in the lake. In contrary, the EFs value of Cr, Cu, Pb, V and Zn showed a decreasing trend with respect to the distance, which showed the accumulation of these elements close to the oil refinery. Whereas, the EFs values of Ni and Se showed very close differences with respect the distance from the oil refinery to lake.

3.3. EDTA-extractable (bioavailable) trace elements in sediments

EDTA is a popular extractant for assessing the bioavailability of trace elements in sediments (Arain et al., 2008). The percentage of EDTA-extractable elements with respect to the total number of elements in the sediments samples at the eight locations is shown in Table 4.

There was no direct relationship between the total concentrations and the bioavailable concentrations for trace elements because metal bioavailability is related to metal solubility and the extractable metal concentration. The order of the EDTA-extractable metal concentration rankings was not the same as the order of the total metal concentrations. This means that the extractable fraction was better for assessing an element's ecological toxicity, not its total concentration.

The average concentration of EDTA extraction for the 12 trace elements decreased in the order of Zn (95.45 mg kg $^{-1}$) > Se (37.20 mg kg $^{-1}$) > Pb (22.28 mg kg $^{-1}$) > V (7.710 mg kg $^{-1}$) > Sb (7.113 mg kg $^{-1}$) > Cu (6.712 mg kg $^{-1}$) > Ni (5.588 mg kg $^{-1}$) > As (3.823 mg kg $^{-1}$) > Co (2.110 mg kg $^{-1}$) > Cd (0.664 mg kg $^{-1}$) > Be (0.050 mg kg $^{-1}$) > Cr (0 mg kg $^{-1}$). Among these elements, the EDTA-extractable portion was high for most of the trace elements, except for Be and Cr. No EDTA-extractable Cr was detected, probably due to the existence of Cr as Cr $_2$ O $_7^2$ /CrO $_4^2$, which has a negative charge and is thus not easily extracted by the negative EDTA. It is well known that Cr (VI)

Table 2 The concentrations and standard deviations of different elements in the sediment ($mg kg^{-1}$).

	Al	В	Ba	Ca	Fe	K	Li	Mg	Mn	Mo	Na	Ti
Average	46,540	99.2	203	3719	19,005	11,552	17.6	12,138	564	0.993	6766	139
MAX	75,072	126	352	5063	33,230	15,037	21.8	16,488	881	6.56	10,805	152
MIN	15,664	71.1	120	1632	6169	7167	10.8	7899	368	0.023	4067	127
STDEV	21,852	19.2	79.5	1303	9767	2521	3.90	2926	156	2.26	2399	9.95
BGV	72,000	20	580	24,000	26,000	15,000	24	9000	600	0.98	12,000	2900
LOD ($\mu g L^{-1}$)	0.04	0.45	0.03	1.2	0.20	0.60	0.02	0.01	0.02	0.47	0.08	0.15

Note: (1) these elements are not toxic, even at high concentrations;

- $(2)\ MAX-maximum\ value,\ MIN-minimum\ value,\ STDEV-standard\ deviation,\ BGV-background\ value;\ and\ STDEV-standard\ deviation,\ SGV-background\ value;\ and\ value;\ and\ SGV-background\ value;\ and\ SGV-background\ valu$
- (3) the background value comes from reference of Shacklette and Boerngen (1984).
- (4) LOD means the Limits of Detections.

Table 3The total trace elements concentration in sediment at different sites (mg kg⁻¹).

Sampling site	As	Ве	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 ($\mu g L^{-1}$)	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).

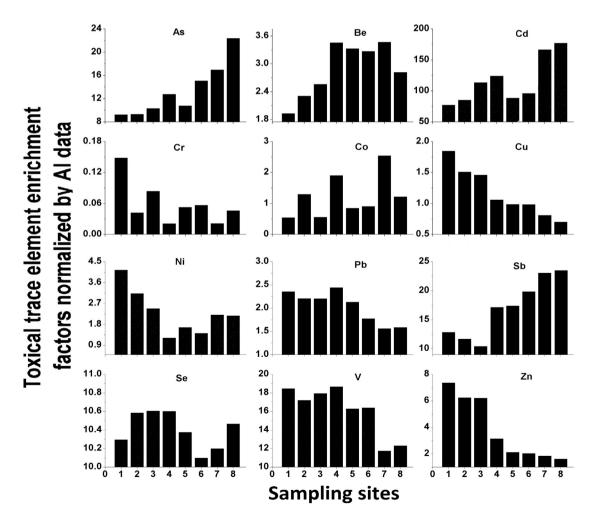


Fig. 2. Toxic trace element enrichment factors normalized with Al.

Z. Zhang et al. / Journal of Geochemical Exploration xxx (2015) xxx-xxx

Table 4 EDTA-extracted metals and their proportion relative to total metals in the sediment samples ($mg kg^{-1}$).

Samp statio	-	As	Ве	Cd	Co	Cr	Cu	Ni	Pb	Sb	Se	V	Zn
1	EMª	4.60	0.06	0.68	1.99	ND ^c	16.9	7.11	33.9	1.16	11.0	8.78	157
	% ^b	6.63	5.78	50.1	20.0	0	33.4	23.5	47.4	2.41	5.53	10.1	36.6
2	EM	4.55	0.06	0.58	1.40	ND	6.73	4.87	31.3	3.18	20.1	8.83	190
	%	6.86	5.77	33.5	16.3	0	18.9	16.7	48.7	8.04	12.0	11.0	57.1
3	EM	6.11	0.07	0.82	2.50	ND	8.73	6.80	33.4	6.87	35.4	11.8	241
	%	9.63	7.19	42.2	30.2	0	26.2	21.3	47.4	17.8	21.7	15.2	74.5
4	EM	3.42	0.06	0.81	1.47	ND	2.01	4.39	25.1	12.3	61.8	8.19	68.3
	%	5.83	6.29	36.4	18.1	0	8.52	21.0	49.2	26.7	31.7	10.9	43.3
5	EM	3.45	0.05	0.60	2.77	ND	5.35	6.08	19.3	10.3	53.3	7.99	49.2
	%	6.63	5.21	32.0	36.1	0	25.7	30.3	45.2	26.3	32.8	11.0	48.1
6	EM	3.76	0.04	0.82	2.44	ND	6.90	6.00	16.0	9.89	47.7	6.80	26.4
	%	7.70	5.33	54.4	34.4	0	36.0	31.2	47.0	27.8	33.2	10.4	30.0
7	EM	1.63	0.03	0.53	1.73	ND	2.10	4.64	9.92	6.09	33.0	4.67	21.2
	%	4.18	4.33	42.0	27.7	0	15.1	30.0	41.1	20.8	27.6	8.88	32.8
8	EM	3.09	0.02	0.48	2.57	ND	4.97	4.80	9.41	7.14	35.3	4.56	10.9
	%	8.81	4.61	39.6	41.7	0	41.9	34.3	42.4	26.0	30.7	9.40	20.9

^a EDTA-extractable metals.

c Not detectable.

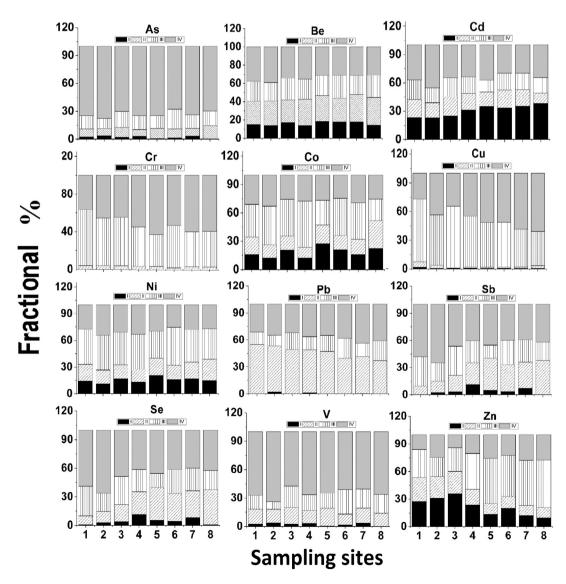


Fig. 3. Trace element distributions in the sediment according to the BCR fractionation scheme.

^b % of extractable metals relative to total metals.

Z. Zhang et al. / Journal of Geochemical Exploration xxx (2015) xxx-xxx

3.4. Trace element speciation distribution in sediments extracted by BCR

The distribution of trace elements in sediments following the BCR sequential extraction process is shown in Fig. 3.

sequential extraction process is shown in Fig. 3. The obtained results reveal that the proportion of each speciation depends on the specific trace element. For the exchangeable form of each element, the percentage contribution decreased in the order of Cd > Zn > Co > Ni > Be > Se > Sb > V > As > Cu > Pb > CrPb > Be > Sb > Se > Ni > Co > Zn > Cd > V > As > Cr > Cu for the reduciblefraction, Cu > Cr > Zn > Ni > Co > Sb > Se > Be > V > Pb > Cd > As for theoxidizable fraction, and As > V > Cr > Se > Sb > Cu > Cd > Be > Pb > Ni > Co > Zn for the residual fraction. Approximately onethird of Cd (23.21-38.46%) was present as an exchangeable fraction, implying relatively high bioavailability, consistent with the EDTA extraction results in Table 3. The similarity of the EDTA extraction results and the exchangeable forms in the BCR process have also been proven in previous studies (Pertsemli and Voutsa, 2007; Yuan et al., 2004). Be, Co, Ni, and Zn were present in all four fractions, and a significant amount of their exchangeable fractions was found (Be 14.03–18.6%; Co 12.18-27.49%; Ni 11.18-20.43%; Zn 9.50-35.75%). The sums of exchangeable forms and another two potential bioavailable forms (i.e., reducible and oxidizable fractions) were 66.07%, 72.05%, 70.53%, and 77.64% for Be, Co, Ni, and Zn, respectively, indicating very high bioavailability. This is similar to results in Lakes Doirani and Kerkini, in northern Greece (Pertsemli and Voutsa, 2007). Cr and Cu dominate in oxidizable and residual forms. The oxidizable and residual fractions for Cr and Cu were 34.06-59.93%, 36.10-62.74%, and 35.54-65.62%, 26.98-60.97%, respectively. The percentages of oxidizable form for Cr and Cu decreased from the oil refinery outlet to the inlet of the lake, and vice versa in case of residual form. The high proportion of oxidizable Cu might be due to its relatively easy and strong interaction with dissolved organic matter (Mossop and Davidson, 2003), as well as with sulfide. The high percentage of oxidizable Cr indicates that Cr predominantly occurred as Cr (VI), which is consistent with the results of the EDTA extraction (David et al., 2012). The exchangeable fractions of As, Pb, Sb, Se, and V were 0.11-3.88%, 0.05-2.05%, 0.12-11.41%, 0.84-11.43%, and 0.11-3.64%, respectively. This indicated the lowest fractions among the four fractions, implying relatively low bioavailabilities of these elements. An insignificant variation in different As fractions was observed at different sampling locations. The residual As reached 72.88%, of which only 2.07% was present in the exchangeable form. This is consistent with the EDTA extraction results. As is associated with the residual fraction, which represents metals largely embedded in the crystal lattice of the sediments fraction, and is not available for remobilization except under extreme conditions (Vicente-Martorell et al., 2009). Although the EF of As is high, its bioavailability is low. The reducible Pb decreased with distance along a gradient from the industrial site extending to Lake Pontchartrain. By contrast, the oxidizable and residual Pb increases from the outlet of the oil refinery to the inlet of the lake. The reducible and oxidizable Pb represented 36.66-54.70% and 12-22.41% of the total Pb, respectively, which implies that Pb is a potential risk to the ecosystem. This is inconsistent with a report regarding the Kerkini and Doirani Lakes in northern Greece (Pertsemli and Voutsa, 2007), which showed Pb to be dominated by the oxidizable fraction (69–94%). Similar to Sb, four speciations of Se did not vary from different sampling locations. For Sb and Se, the reducible forms were 9.45-35.65% and 9.32-36.65, the oxidizable forms were 20.52-32.30% and 14.60-30.84%, and the residual fractions were 39.09-64.65% and 39.87-66.02%, respectively. Reducible Sb and Se increased from the refinery outlet to the inlet of the lake; however, their oxidizable and residual fractions showed the reverse trend. The reducible and oxidizable V showed insignificant variations at different sampling points. The oxidizable, reducible, and residual fractions were constant, whereas the residual fraction occupy nearly 65%, indicating that most of the V was not bioavailable.

4. Conclusions

Results showed that 12 elements (Al, B, Ba, Ca, Fe, K, Li, Mg, Mn, Mo, Na, Ti) in the sediments would not impact the environment, although most of them showed enrichment. Total Cd, Cu, Ni, Pb, and Zn implied moderate contamination in the sediments. EFs demonstrated higher accumulation of Cd, Sb, V, As, and Se in the sediments. EDTA and BCR methods demonstrated that Zn, Cd, Co, Cu, Ni, Be and Pb were the most bioavailable elements in the sediments. Based on our results, the oil refinery may be one of the sources, which should be responsible for trace metal pollution in Lake Pontchartrain.

Acknowledgment

The project was conducted at School of Plant, Environmental and Soil Sciences, Louisiana State University AgCenter. This work was partly supported by a grant through the Lake Pontchartrain Basin Foundation (#06-07NOAA-06-A3). The anonymous reviewers and editor are gratefully acknowledged for their valuable comments and suggestions that helped to substantially improve this article.

Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.gexplo.2015.08.008. These data include Google map of the most important areas described in this article.

References

- Alomary, A.A., Belhadj, S., 2007. Determination of heavy metals (Cd, Cr, Cu, Fe, Ni, Pb, Zn) by ICP-OES and their speciation in Algerian Mediterranean Sea sediments after a five-stage sequential extraction procedure. Environ. Monit. Assess. 135, 265–280.
- Aloulou, F., Kallell, M., Belayouni, H., 2011. Impact of oil field-produced water discharges on sediments: a case study of Sabkhat Boujemal, Sfax, Tunisia. Environ. Forensic 12, 290–299.
- Arain, M.B., Kazi, T.G., Jamali, M.K., Jalbani, N., Afridi, H.I., Shah, A., 2008. Total dissolved and bioavailable elements in water and sediment samples and their accumulation in *Oreochromis mossambicus* of polluted Manchar Lake. Chemosphere 70, 1845–1856.
- Clark, L.C., Combs Jr., G.F., Turnbull, B.W., Slate, E.H., Chalker, D.K., Chow, J., 1996. Effects of selenium supplementation for cancer prevention in patients with carcinoma of the skin. A randomized controlled trial. Nutritional Prevention of Cancer Study Group. J. Am. Med. Assoc. 276, 1957–1963.
- David, J.B., Koch, I., Zhang, J., Reimer, K.J., 2012. Chromium speciation in river sediment pore water contaminated by tannery effluent. Chemosphere 89, 838–843.
- Delaune, R.D., Jugsujindaa, A., Gambrella, R.P., Miao, S., 2008. Metal concentrations and trace metal Al and Fe ratios in soil of the Chenier Plain, Southwest Louisiana coastal zone. J. Environ. Sci. Health A Tox. Hazard. Subst. 3, 300–312.
- Delaune, R.D., Wang, J.J., Jugsujindaa, A., 2009. Copper in Lake Pontchartrain bottom sediment: relationship to sediment properties. Aquat. Ecosyst. Health Manag. 12, 456–460.
- Dundar, M.S., Altundag, H., Eyupoglu, V., Keskin, S.C., Tutunoglu, C., 2012. Determination of heavy metals in lower Sakarya river sediments using a BCR-sequential extraction procedure. Environ. Monit. Assess. 184, 33–41.
- Fernández-Martínez, A., Charlet, L., 2009. Selenium environmental cycling and bioavailability: a structural chemist point of view. Crit. Rev. Environ. Sci. Technol. 8, 81–110.
- Fiedler, S., Siebe, C., Herre, A., Roth, B., Cram, S., Stahr, K., 2009. Contribution of oil industry activities to environmental loads of heavy metals in the Tabasco Lowlands, Mexico. Water Air Soil Pollut. 197, 35–47.
- Hartikainen, H., 2005. Biogeochemistry of selenium and its impact on food chain quality and human health. J. Trace Elem. Med. Biol. 18, 309–318.
- Karageorgis, A.P., Katsanevakis, S., Kaberi, H., 2009. Use of enrichment factors for the assessment of heavy metal contamination in the sediment of Koumoundourou Lake, Greece. Water Air Soil Pollut. 204, 243–258.
- Kaushik, A., Kansal, A., Meena, S., Kumari, S., Kaushik, C.P., 2009. Heavy metal contamination of river Yamuna, Haryana, India: assessment by metal enrichment factor of the sediment. J. Hazard. Mater. 164, 265–270.
- Kersten, M., Förstner, U., 1986. Chemical fractionation of heavy metals in anoxic estuarine and coastal sediments. Water Sci. Technol. 18, 121–130.
- Khaitan, S., Kalainesan, S., Erickson, L.E., Kulakow, P., Martin, S., Karthikeyan, R., Hutchinson, S.L.L., Davis, L.C., Illangasekare, T.H., Ng'oma, C., 2005. Remediation of sites contaminated by oil refinery operations. Environ. Prog. 1, 20–31.
- Long, E.R., MacDonald, D.D., Smith, S.L., Calder, F.D., 1995. Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. Environ. Manag. 19, 81–97.

Z. Zhang et al. / Journal of Geochemical Exploration xxx (2015) xxx-xxx

- Mossop, K.F., Davidson, C.M., 2003. Comparison of original and modified BCR sequential extraction procedures for the fractionation of copper, iron, lead, manganese and zinc in soils and sediments. Anal. Chim. Acta 478, 111–118.
- Nemati, K., Abu Bakar, N.K., Bin Abas, M.R., Sobhanzadeh, E., Low, K.H., 2011. Comparison of unmodified and modified BCR sequential extraction schemes for the fractionation of heavy metals in shrimp aquaculture sludge from Selangor, Malaysia. Environ. Monit. Assess. 176, 313–320.
- Pertsemli, E., Voutsa, D., 2007. Distribution of heavy metals in Lakes Doirani and Kerkini, Northern Greece. J. Hazard. Mater. 148, 529–537.
- Rauret, G., Lopez-Sanchez, J.F., Sahuquillo, A., Rubio, R., Davidson, C.M., Ure, A.M., Quevauviller, Ph., 1999. Improvement of the BCR three step sequential extraction procedure prior to the certification of new sediment and soil reference materials. J. Environ. Monit. 1, 57–61.
- Rosales-Hoz, L., Cundy, A.B., Bahena-Manjarrez, J.L., 2003. Heavy metals in sediment cores from a tropical estuary affected by anthropogenic discharges: Coatzacoalcos estuary, Mexico. Estuar. Coast. Shelf Sci. 58, 117–126.
- Sakan, S.M., Đorđević, D.S., Manojlović, D.D., Predrag, P.S., 2009. Assessment of heavy metal pollutants accumulation in the Tisza river sediments. J. Environ. Manag. 90, 3382–3390.
- Shacklette, H.T., Boerngen, J.G., 1984. Element Concentrations in Soils and Other Surficial Materials of Conterminous United States: An Account of the Concentrations of 50 Chemical Elements in Samples of Soils and Other Regoliths. U.S. Government Printing Office, Washington DC.

- Sposito, G., Lund, L.J., Chang, A.C., 1982. Trace metal chemistry in arid-zone field soils amended with sewage sludge: I. Fractionation of Ni, Cu, Zn, Cd, and Pb in solid phases. Soil Sci. Soc. Am. J. 46, 260–264.
- Sprovieri, M., Feo, M.L., Prevedello, L., Manta, D.S., Sammartino, S., Tamburrino, S.,
 Marsella, E., 2007. Heavy metals, polycyclic aromatic hydrocarbons and polychlorinated biphenyls in surface sediments of the Naples harbour (southern Italy). Chemosphere 67, 998–1009.
 Tessier, A., Campbell, P.G.C., Bisson, M., 1979. Sequential extraction procedure for the
- Tessier, A., Campbell, P.G.C., Bisson, M., 1979. Sequential extraction procedure for the speciation of particulate trace metals. Anal. Chem. 51, 844–851.
- Tiwari, J.N., Chaturvedi, P., Ansari, N.G., Patel, D.K., Jain, S.K., Murthy, R.C., 2011. Assessment of polycyclic aromatic hydrocarbons (PAH) and heavy metals in the vicinity of an oil refinery in India. Soil Sediment Contam. 20, 315–328.
- Vicente-Martorell, J.J., Galindo-Riaño, M.D., García-Vargas, M., Granado-Castro, M.D., 2009. Bioavailability of heavy metals monitoring water, sediments and fish species from a polluted estuary. J. Hazard. Mater. 162, 823–836.
- Wake, H., 2005. Oil refineries: a review of their ecological impacts on the aquatic environment. Estuar. Coast. Shelf Sci. 62, 131–140.
- Yuan, C., Shi, J., He, B., Liu, J., Liang, L., Jiang, G., 2004. Speciation of heavy metals in marine sediments from the East China Sea by ICP-MS with sequential extraction. Environ. Int. 30. 769–783.