



The interactive effects of petroleum-hydrocarbon spillage and plant rhizosphere on concentrations and distribution of heavy metals in sediments in the Yellow River Delta, China

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ABSTRACT

In order to understand how petroleum-hydrocarbon spillage and plant rhizosphere interact to affect concentrations and distribution of heavy metals, nine metals were analyzed from four different types of sediments (i.e. petroleum-hydrocarbon spilled rhizosphere, pristine rhizosphere, petroleum-hydrocarbon spilled unvegetated, and pristine unvegetated) in the Yellow River Delta, China. Our results showed that petroleum-hydrocarbon spillage together with rhizosphere effects were responsible for the significantly higher levels of metals in these four types of sediments. Compared to unvegetated sediments, rhizosphere sediments were well grouped into petroleum-hydrocarbon spilled and pristine sites on the basis of the concentrations of heavy metals by the correspondence analysis (CA). Furthermore, analysis of the transfer factors indicated that the capacity of rhizosphere sediments to stabilize heavy metals increased with increasing petroleum-hydrocarbon spillage, which might be due to the changes of sediment profiles by plant rhizosphere. Our results suggested that interactive effects of petroleum-hydrocarbon spillage and plant rhizosphere played an important role in determining concentrations and spatial distribution pattern of heavy metals.

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1. Introduction

Riverine deltas are often the most densely populated, economically important and industrial or agricultural areas. Sediments in the deltas are highly valued for maintenance of water cycle, ecosystem functions and biodiversity [1]. Unfortunately, sediments are becoming increasingly polluted with inorganic and organic compounds, primarily as a result of intense human activities [2,3].

Heavy metals are common toxic pollutants, and enter the sedimentary surface through different activities such as industries and mining [4]. There are extensive surveys on effects of either biotic or abiotic factors on concentrations and distribution of heavy metals but little is known about the interactive effects of both biotic and abiotic factors [5–8]. The biotic factors, such as plant roots, can modify the fixation, mobility, and bioavailability of heavy metals in soils [9]. The abiotic factors, such as petroleum-hydrocarbon spillage, have strong impact on quantity of soil heavy metals which exist in crude oil as non-hydrocarbon compounds

[10], and, thus petroleum-hydrocarbon spillage may potentially intensify pollution of heavy metals in sediments [11,12]. Increasing evidence suggests that plants may employ a range of strategies to minimize the negative effects of rhizosphere toxic pollutants through releasing root exudates [13,14]. Therefore, the plant processes may change the behavior of heavy metals in response to petroleum-hydrocarbon toxicity [15]. To date, few studies have reported the interactive effects of plant rhizosphere (biotic factor) and petroleum-hydrocarbon spillage (abiotic factor) on concentrations and distribution of heavy metals.

The objective of the present study was to examine the interactive effects of petroleum-hydrocarbon spillage and plant rhizosphere on the concentrations and distribution of heavy metals in the Yellow River Delta. The information obtained from this study may be of value to assess metal behavior in contaminated sediments.

2. Materials and methods

2.1. Study site and sediment sampling

This study was conducted in the Yellow River Delta, located in the northeast of Shandong Province, China (36°55′–38°12′N,

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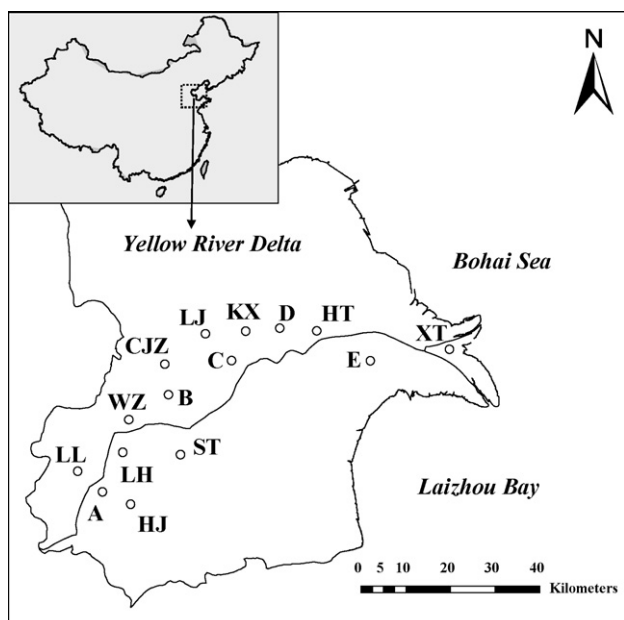
Table 1The crude oil concentrations of rhizosphere and unvegetated sediments (mg kg^{-1}) with the history of oil exploitation (year).

Site	Rhizosphere sediment	Unvegetated sediment	History of oil exploitation	Site	Rhizosphere sediment	Unvegetated sediment	History of oil exploitation
Shengtuo (ST)	8649.7	5399.6	1964	Hetan (HT)	5434.7	4515.9	1985
Haojia (HJ)	6404.3	4703.3	1968	Luojia (LJ)	574.0	4119.7	1987
Kenxi (KX)	4385.3	7639.3	1971	Chenjiazhuang (CJZ)	5750.0	6166.7	1990
Lijin (LL)	3037.4	9720.3	1977	Xintan (XT)	1159.6	3203.2	1996
Ninghai (LH)	7157.6	11173.5	1981	Wangzhuang (WZ)	155.7	261.3	2001

118°07'–119°18'E). Since oil exploitation from 1964, an important environmental problem with the petroleum industry is the spillage and transportation of petroleum and related products that cause severe sediment contamination in the Delta [16]. In September 2007, 10 areas of oil exploitation (ST, HJ, KX, LL, LH, HT, LJ, CJZ, XT, and WZ) and five pristine areas (A, B, C, D, and E) were chosen as sampling sites, with checking out to confirm there was no obvious disturbance from agricultural and grazing activities (Fig. 1). Below-ground zone of *Phragmites australis* was selected as rhizosphere sediments so as to make a comparison with surrounding unvegetated sediments, because of wide distribution, high tolerance, and dense roots of this plant species [17,18]. The petroleum concentrations and the history of oil exploitation in these areas were given in Table 1. Consequently, there were four types of sediments in this study, i.e. petroleum-hydrocarbon spilled rhizosphere (PSR), pristine rhizosphere (PR), petroleum-hydrocarbon spilled unvegetated (PSU), and pristine unvegetated (PU) sediments. A total of 90 sediment samples were collected from *P. australis* rhizosphere and neighboring unvegetated sediments from 15 sites. Briefly, each site (about 1–1.5 km^2) was evenly divided into three sub-sites, i.e. three replicates. For each replicate, we randomly sampled 10–15 pairs of soil cores from the top 15 cm soil using a 2.5-cm diameter auger, and then mixed well. All sediments were stored at 4 °C and analyzed within one week after collection.

2.2. Sediment analysis

Samples were oven-dried at 50 °C to constant weight, weighed to determine dry weight, and then ground to fine powder, and passed through 100 mesh sieve prior to metal analysis. For sediment digestion sieved samples were digested in an acid mixture of

**Fig. 1.** Map showing the 15 sampling sites in the Yellow River Delta, China.

concentrated HNO_3 – HClO_4 – HF . The sample (0.1000 g) was put into a PTFE crucible to which 10 ml of concentrated HCl was added. The crucible was allowed to stand still for 12 h at room temperature to allow for slow oxidation of organic matter. The solution was gently heated and evaporated to 1–2 ml. After being cooled, an acid mixture (5 ml of concentrated HNO_3 , 5 ml of concentrated HF and 3 ml of concentrated HClO_4) was added and the covered crucible was heated in a heating plate at about 150 °C for 2–3 h. The crucible was then uncovered and heated continuously until appearance of white fumes. This acid-digesting process was repeated until the sample was decomposed completely and white crystals remained. Finally, the residual solution was filtered to a 50 ml volumetric flask by 2% HNO_3 solution. All used chemicals were suprapur or ultra-pure grade (Merck, Germany) and water was obtained through a Milli-Q water purification system (Millipore, Billerica, US). Concentrations of chromium (Cr), copper (Cu), manganese (Mn), nickel (Ni), plumbum (Pb), and zinc (Zn) were measured by ICP-AES (HITACHI P-4010, Japan), and those of arsenic (As), cadmium (Cd), and cobalt (Co) were measured by atomic absorption spectrophotometry using graphite tube (HITACHI Z-5000, Japan). Triplicate controls were also measured without sample, following the same acid-digesting processes.

The oxidation–reduction potential (ORP) and pH values were measured using calibrated Hanna HI 9025 portable meter (Hanna Instruments, Laval, Quebec, Canada) and IQ-150 pH meter (IQ Scientific Instruments Inc., Carlsbad, CA) *in situ*, respectively. Salinity was measured with a standard conductivity meter (S30 SevenEasy Conductivity, Mettler-Toledo, Switzerland) after soil was mixed with deionized water (1:10, w/w). Dissolved organic carbon (DOC) was extracted from the samples using 0.5 M K_2SO_4 (1:4, w/v) and quantified by TOC/TN-analyzer (Shimadzu TOC-VCPH/TN, Kyoto, Japan). The above soil profiles are generally selected as indexes to study rhizosphere effects on concentrations and distribution of heavy metals [19–21]. For total content of petroleum hydrocarbon (TPH), the samples were extracted three times in an ultrasonic bath (15 min for each extraction) with dichloromethane–acetone (1:1, v/v) and quantified by infrared method [22].

2.3. Data analysis

t-tests were used to examine the differences in metal concentrations and sediment profiles of paired (rhizosphere and unvegetated) sediments using SPSS 13.0. Correspondence analysis (CA) is an unconstrained ordination method that allows exploration of the variability in a data set related to metal concentrations by Canoco for Windows (version 4.5). Canonical correspondence analysis (CCA) is a direct constrained ordination method to explore the variability in a data set related to the environmental variables (e.g., DOC, pH, etc.) by Canoco. The linear regression was used to test the effects of petroleum-hydrocarbon spillage on the ability of plant roots to stabilize heavy metals by SPSS 13.0.

The transfer factor reflecting the ability of plant roots to stabilize heavy metals was calculated using following equation [8]:

$$Tf\% = \left[\frac{C_{ir}/C_{rtotal}}{C_{iu}/C_{utotal}} - 1 \right] \times 100$$

Table 2
Metal concentrations (mean \pm SD) for four types of sediments (mg kg^{-1}).

	Rhizosphere sediment		Unvegetated sediment	
	Petroleum-hydrocarbon spilled	Pristine	Petroleum-hydrocarbon spilled	Pristine
Cr	61.59 \pm 25.87	41.58 \pm 8.00	54.21 \pm 19.62	40.32 \pm 9.53
Cu	37.04 \pm 3.95	29.23 \pm 4.96	33.49 \pm 3.90	28.16 \pm 3.88
Mn	501.3 \pm 37.90	498.39 \pm 77.71	496.01 \pm 27.81	464.93 \pm 33.77
Ni	27.75 \pm 4.33	30.53 \pm 4.32	26.88 \pm 2.94	28.42 \pm 6.30
Pb	39.67 \pm 14.43	20.51 \pm 3.72	30.16 \pm 8.58	18.66 \pm 3.59
Zn	194.08 \pm 29.89	159.26 \pm 28.94	173.85 \pm 26.63	156.6 \pm 20.54
As	15.36 \pm 5.26	33.26 \pm 3.60	15.84 \pm 4.82	24.99 \pm 5.86
Cd	0.26 \pm 0.29	0.77 \pm 0.10	0.25 \pm 0.28	0.766 \pm 0.06
Co	8.71 \pm 1.76	10.97 \pm 4.36	8.22 \pm 1.37	9.60 \pm 2.35
Total	885.75	824.49	838.90	772.43

where C_{ir} is the concentration of metal i in the rhizosphere sediment; $C_{r\text{total}}$ is the total concentration of heavy metals in the rhizosphere sediment; C_{iu} is the concentration of metal i in the unvegetated sediments; and $C_{u\text{total}}$ is the total concentration of heavy metals in the unvegetated sediments.

The contamination/pollution index (C/PI) was used to interpret the level of heavy metal contamination in sediments, and it is calculated using following equation [23]:

$$\frac{C}{PI} = \frac{\text{concentration of metals in soil}}{\text{target value}}$$

where target value is the reference value from the Environmental Quality Standard for Soils of Chinese National Standards (GB 15618-1995). Values of C/PI greater than 1 can be used to define the pollution range; and those lower than 1 to define the contamination range. The two ranges were divided into categories of values that define a very slight (<0.10), slight ($0.10\text{--}0.25$), moderate ($0.26\text{--}0.50$), severe ($0.51\text{--}0.75$) and very severe ($0.76\text{--}1.00$) contamination, and slight ($1.1\text{--}2.0$), moderate ($2.1\text{--}4.0$), severe ($4.1\text{--}8.0$), very severe ($8.1\text{--}16.0$) and excessive (>16.0) pollution, respectively.

3. Results and discussion

3.1. Metal concentration

Mean metal concentrations for the four types of sediments (PSR, PR, PSU, and PU) are summarized in Table 2. In all types of sediments, the mean concentrations of Mn, Zn and Cr were the first three highest, and the mean concentrations of Cd and Co the low-

est among the nine metals. Other four metals (Cu, Ni, Pb and As) had medium concentrations, but had different orders in the four types of sediments (Table 2). In general, the highest mean total concentration of heavy metals occurred in PSR, followed by PSU > PR > PU. The results suggest that petroleum-hydrocarbon spillage had potentially aggravated metal pollution in the sediments of the Yellow River Delta. The mean total concentrations of metals were higher in petroleum-hydrocarbon spilled sediments (PSR and PSU) than in pristine sediments (PR and PU). The higher mean concentrations of Cr, Cu, Mn, Pb, and Zn were found in petroleum-hydrocarbon spilled sediments compared to those in pristine sediments.

As shown in Table 2, the results also suggest that the mean total concentrations of metals in rhizosphere sediments were higher than those in corresponding unvegetated sediments (PSR > PSU; PR > PU). The paired t -tests showed that the total concentrations of heavy metals in rhizosphere sediments were also higher than those in unvegetated sediments ($P < 0.05$), but there was no significant difference in TPH between rhizosphere and unvegetated sediments (Table 3). Zn and Pb concentrations were significantly higher in rhizosphere sediments.

Based on the paired t -tests (Table 3), rhizosphere sediments trended to have significantly higher DOC content, higher water, lower salinity and higher pH in comparison to those of unvegetated sediments. Abundant DOC in rhizosphere sediments has great potential of sequestering heavy metals from surrounding unvegetated sediments through forming organo-metallic complexes [24,25], high water content and low salinity have great potential of increasing absorbable volume of metals in soil solution [26], and alkalization of rhizosphere sediments decreases metal's mobility and increases the ability of rhizosphere sediments to stabilize metals [27,28]. These may be the reasons why rhizosphere

Table 3
Comparison of metal concentrations and soil profiles (mean \pm SD) of rhizosphere and unvegetated sediments by paired t -test.

	Rhizosphere sediment	Unvegetated sediment	Difference	t	P
Cr (mg kg^{-1})	54.92 \pm 23.32	49.58 \pm 17.87	5.34 \pm 11.59	1.78	0.096
Cu (mg kg^{-1})	34.44 \pm 5.62	31.71 \pm 4.57	2.73 \pm 5.37	1.97	0.069
Mn (mg kg^{-1})	500.33 \pm 51.48	485.65 \pm 32.45	14.68 \pm 56.58	1.01	0.332
Ni (mg kg^{-1})	28.68 \pm 4.39	27.39 \pm 4.18	1.28 \pm 3.24	1.53	0.147
Pb (mg kg^{-1})	33.29 \pm 15.01	26.32 \pm 9.08	6.96 \pm 11.81	2.28	<0.05
Zn (mg kg^{-1})	182.48 \pm 33.20	168.10 \pm 25.44	14.38 \pm 21.42	2.60	<0.05
As (mg kg^{-1})	21.32 \pm 9.89	18.90 \pm 6.68	2.43 \pm 7.65	1.23	0.238
Cd (mg kg^{-1})	0.43 \pm 0.34	0.42 \pm 0.34	0.01 \pm 0.09	0.25	0.809
Co (mg kg^{-1})	9.47 \pm 2.94	10.15 \pm 6.54	-0.68 \pm 6.54	-0.41	0.692
Total Metals (mg kg^{-1})	865.33 \pm 88.87	818.21 \pm 56.54	47.12 \pm 71.34	2.56	<0.05
TPH (mg kg^{-1})	2837.52 \pm 2992.87	3194.52 \pm 3217.66	357.00 \pm 1182.58	-1.17	0.261
DOC (mg kg^{-1})	117.24 \pm 23.44	101.89 \pm 28.36	15.35 \pm 24.78	2.40	<0.05
Water Content (%)	19.07 \pm 2.85	16.82 \pm 1.89	2.25 \pm 1.93	4.51	<0.001
Salinity (mg g^{-1})	7.73 \pm 3.68	13.88 \pm 7.24	6.14 \pm 4.89	-4.87	<0.001
pH	7.32 \pm 0.25	7.07 \pm 0.35	0.24 \pm 0.36	2.63	<0.05
ORP (mV)	47.96 \pm 20.99	43.46 \pm 23.27	4.50 \pm 9.06	-1.92	0.075

TPH: total petroleum hydrocarbon; ORP: oxidation-reduction potential; DOC: dissolved organic carbon. The bold values show significant differences between rhizosphere and unvegetated sediments ($P < 0.05$).

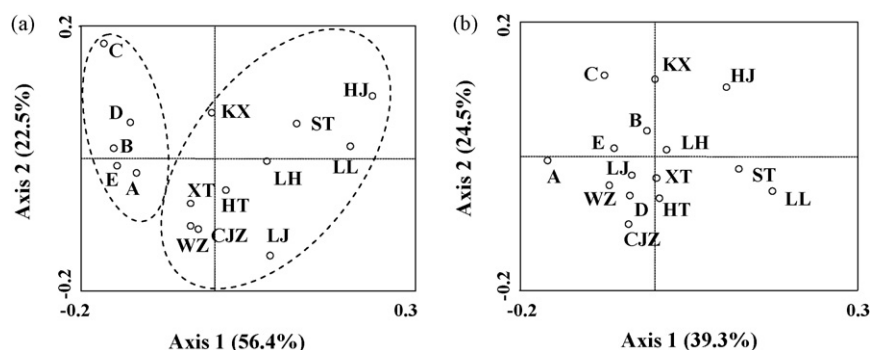


Fig. 2. Ordination plots of correspondence analysis (CA) of metal concentrations of rhizosphere (a) and unvegetated (b) sediments. Ten exploitation areas of crude oil (ST, HJ, KX, LL, LH, HT, LJ, CJZ, XT, and WZ) and five pristine areas (A, B, C, D, and E) are shown.

Table 4

Regional background and ambient sedimentary metal concentrations (mg kg^{-1}) in the Yellow River Delta described by Rui et al. [29].

Heavy metals	1996	2006	Percent increment
Mn	223.91	344.15	53.70%
Cu	6.82	12.48	83.00%
Zn	24.87	39.18	57.50%
As	13.07	18.16	38.94%
Cd	0.021	0.046	116.30%
Pb	8.84	10.99	24.30%
Cr	10.47	21.77	107.90%

sediments had higher levels of heavy metals than unvegetated sediments in this study.

Metal pollution in the Yellow River Delta is increasingly severe due to continuous input from human activities and sediment movements. Previous data on metal concentrations were used to provide reference for those in newly reclaimed sediments in the Yellow River Delta [29]. The results of the present study showed that the concentrations of heavy metals (Mn, Cu, Zn, As, Cd, Pb and Cr) were significantly higher in 2006 than those in 1996 (Table 4). In comparison with the previous study, significantly higher concentrations of these metals were detected in early-reclaimed sediments, especially in PSR and PSU. These observations indicate that the Yellow River Delta has been gradually influenced by human activities.

In order to classify sediment quality based on heavy metal concentrations, the contamination/pollution index (C/PI) was used to rank the sediments: five contamination classes and five pollution classes. Contamination (C/PI value is less than 1.0) indicates that the metals have not or will not have immediate negative effects on plant growth and development or on other environmental components. However, 'pollution' (C/PI value is greater than 1.0) indicates that the metals have negative effects on some or all of the environmental components [23]. Table 5 shows that PSR are 'slightly polluted' with regard to Cu, Pb, Zn, As and Cd. PSU are 'slightly polluted' with regard to Zn, As and Cd, and 'very severely con-

Table 5

Schematic presentation of contamination/pollution index (C/PI) for metals based on the Environmental Quality Standard for Soils of Chinese National Standards (GB 15618-1995).

Metal	PSR		PR		PSU		PU	
	C/PI	Significance	C/PI	Significance	C/PI	Significance	C/PI	Significance
Cr	0.68	Severe contamination	0.46	Moderate contamination	0.60	Severe contamination	0.45	Moderate contamination
Cu	1.06	Slight pollution	0.84	Severe contamination	0.96	Very severe contamination	0.80	Very severe contamination
Ni	0.69	Severe contamination	0.76	Severe contamination	0.67	Severe contamination	0.71	Severe contamination
Pb	1.13	Slight pollution	0.59	Severe contamination	0.86	Very severe contamination	0.53	Severe contamination
Zn	1.94	Slight pollution	1.59	Slight pollution	1.74	Slight pollution	1.57	Slight pollution
As	1.02	Slight pollution	2.22	Moderate pollution	1.06	Slight pollution	1.67	Slight pollution
Cd	1.30	Slight pollution	3.85	Moderate pollution	1.25	Slight pollution	3.83	Moderate pollution

Petroleum-hydrocarbon spilled rhizosphere (PSR), pristine rhizosphere (PR), petroleum-hydrocarbon spilled unvegetated (PSU), and pristine unvegetated (PU) sediments.

taminated' with regard to Cu and Pb. Cu and Zn are essential micronutrients for plant growth [30,31], but both can be phytotoxic at high concentrations, and, thus may have potentially harmful impacts on plants and soil biota. For Pb, As and Cd, these metals are regarded highly toxic to plants and soil environments. Hence, the presence of these metals at the levels of 'very severe contamination' and (or) 'slight pollution' might have great potential to cause adverse biological effects. In PR and PU, Zn, As and Cd 'slightly polluted' and (or) 'moderately polluted' unvegetated sediments. The presence of these metals may make habitat restoration difficult.

3.2. Spatial distribution of heavy metals

To assess spatial distribution patterns, CA analysis was performed to characterize variations of metal concentrations among study sites relative to petroleum-hydrocarbon spillages. The CA of rhizosphere sediments explained up to 78.9% of the variation, while the data of unvegetated sediments explained only 63.8% of the variation in the first two axes (Fig. 2). Fig. 2a shows two main groups can be clearly identified, namely one group contains the sediments collected from petroleum-hydrocarbon spilled sites, and the other comprises the sediments collected from pristine sites. However, the score plot (Fig. 2b) shows that CA using the data from unvegetated sediments failed to group study sites in relation to petroleum-hydrocarbon spillage. It seems that petroleum hydrocarbon plays an important role in shaping spatial distribution pattern of rhizosphere heavy metals. From CCA analysis, the strongest determinants of distribution patterns of heavy metals were TPH for rhizosphere sediments and DOC for unvegetated sediments, as indicated by the greater lengths of the environmental variable arrows in the CCA plots (Fig. 3). Although there was no significant difference in TPH between rhizosphere and unvegetated sediments (Table 3), TPH had greater influences on the metal distribution in rhizosphere sediments.

Petroleum pollution has multiple toxic effects on plants [15]. However, plant roots employ a range of strategies to up-regulate

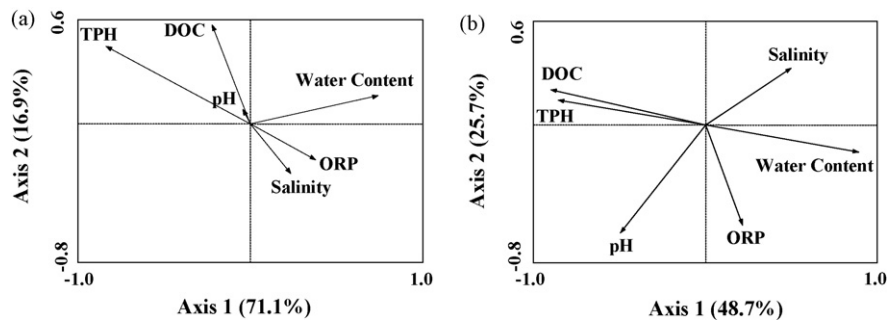


Fig. 3. Ordination plots of CCA results for rhizosphere (a) and unvegetated (b) sediments. The direction of an arrow indicates the steepest increase in the variable, and the length indicates the strength relative to other variables. TPH, total petroleum hydrocarbon; ORP, oxidation–reduction potential; DOC, dissolved organic carbon.

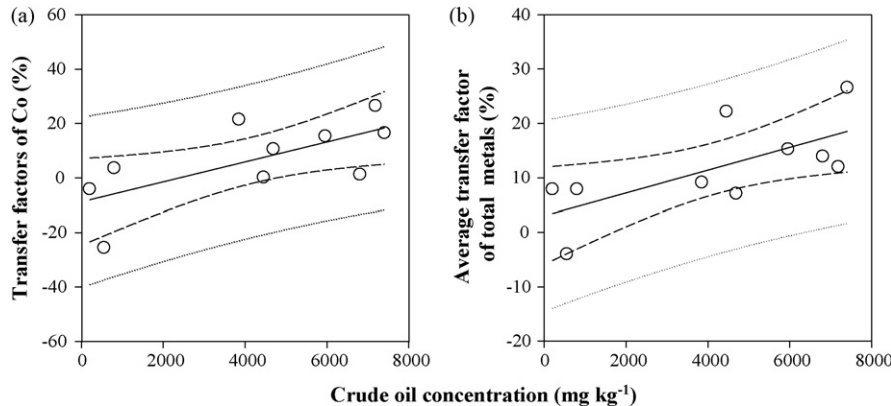


Fig. 4. The linear regression of crude petroleum hydrocarbon concentration with the transfer factor of Co (a) and average transfer factor of all heavy metals (b). The fitted equations are (a) $y = -8.797 + 0.00367x$ ($R = 0.682$, $P = 0.030$), and (b) $y = 3.038 + 0.00209x$ ($R = 0.688$, $P = 0.028$).

to alleviate the stresses from petroleum-hydrocarbon pollution through significantly increasing the rate of root exudation as a result of loss of membrane integrity or a breakdown in normal cell metabolism [14,32–34], which may have considerable effects on the plant's ability of transferring metals [35,36]. Regression analysis suggested that the transfer factors of Co consistently increased with increasing petroleum-hydrocarbon spillage in rhizosphere sediments (Fig. 4a). More importantly, mean transfer factors of nine heavy metals were also positively correlated with TPH of rhizosphere sediments (Fig. 4b), although other eight metals did not display this relationship. The data of the study showed that DOC content which increased with TPH concentration in rhizosphere sediments (Pearson correlation coefficient = 0.775, $P < 0.01$) may play an important role in enhancing the plant's ability of metal fixation and stabilization with the extent of petroleum-hydrocarbon spillage, because more DOC could originate from root exudates in response to underground stress from petroleum pollution [14,32,34–37], and more organo-metallic complexes would form to fix heavy metals in heavy petroleum-hydrocarbon polluted sediments [24,25]. This implies that rhizosphere sediments with root exudates may maintain great capability of immobilizing heavy metals at high level of petroleum hydrocarbon.

4. Conclusions

Petroleum-hydrocarbon spillage is responsible for the significantly higher levels of metals in the affected sediments, especially Cr, Cu, Mn, Pb, and Zn. Moreover, the higher concentrations of metals in rhizosphere sediments are attributable to the fact that plant roots play an important role in shaping spatial distribution patterns of heavy metals and can mobilize and sequester heavy metals from surrounding unvegetated sediments. As a whole, the transfer fac-

tors indicate that plant roots might enhance the ability of metal fixation and stabilization with increasing petroleum-hydrocarbon spillage.

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References

- [1] P.M. Groffman, P.J. Bohlen, Soil and sediment biodiversity—cross-system comparisons and large-scale effects, *Bioscience* 49 (1999) 139–148.
- [2] J.B. Culbertson, I. Valiela, M. Pickart, E.E. Peacock, C.M. Reddy, Long-term consequences of residual petroleum on salt marsh grass, *J. Appl. Ecol.* 45 (2008) 1284–1292.
- [3] B.O. Ekpo, U.J. Ibok, Seasonal variation and partition of trace metals (Fe, Zn, Cu, Mn, Cr, Cd and Pb) in surface sediments: relationship with physico-chemical variables of water from the Calabar River, South Eastern Nigeria, *Environ. Geochem. Health* 20 (1998) 113–121.
- [4] J. Ridgway, G. Shimmield, Estuaries as repositories of historical contamination and their impact on shelf seas, *Estuar. Coast. Shelf Sci.* 55 (2002) 903–928.
- [5] A.H. BuOlayan, M.N.V. Subrahmanyam, Accumulation of copper, nickel, lead and zinc by snail, *Lunella coronatus* and pearl oyster, *Pinctada radiata* from the Kuwait coast before and after the Gulf War oil spill, *Sci. Total Environ.* 197 (1997) 161–165.
- [6] L.C. Osuji, C.M. Onojake, Trace heavy metals associated with crude oil: a case study of Ebocha-8 oil-spill-polluted site in Niger Delta, Nigeria, *Chem. Biodivers.* 1 (2004) 1708–1715.
- [7] R. Prego, A. Cobelo-Garcia, J. Marmolejo-Rodriguez, J. Santos-Echeandia, Trace elements in the Prestige fuel-oil spill: levels and influence on Laxe Ria sediments (NW Iberian Peninsula), *Ceinc. Mar.* 32 (2006) 179–186.
- [8] J. Wang, C.B. Zhang, Z.X. Jin, The distribution and phytoavailability of heavy metal fractions in rhizosphere soils of *Paulownia fortunei* (seem) Hems near a Pb/Zn smelter in Guangdong, PR China, *Geoderma* 148 (2009) 299–306.

- [9] E. Smits, J.L. Freeman, Environmental cleanup using plants: biotechnological advances and ecological considerations, *Front. Ecol. Environ.* 4 (2006) 203–210.
- [10] J. Santos-Echeandia, R. Prego, A. Cobelo-García, Influence of the heavy fuel spill from the *Prestige* tanker wreckage in the overlying seawater column levels of copper, nickel and vanadium (NE Atlantic ocean), *J. Mar. Syst.* 72 (2008) 350–357.
- [11] S. AlMuzaini, P.G. Jacob, The distribution of V, Ni, Cr, Cd, and Pb in topsoils of the Shuaiba industrial area of Kuwait, *Environ. Toxicol. Water Qual.* 11 (1996) 285–292.
- [12] M.S. Reddy, S.B. Basha, H.V. Joshi, B. Jha, Evaluation of the emission characteristics of trace metals from coal and fuel oil fired power plants and their fate during combustion, *J. Hazard. Mater.* 123 (2005) 242–249.
- [13] E. Pilon-Smits, Phytoremediation, *Annu. Rev. Plant Biol.* 56 (2005) 15–39.
- [14] P.R. Ryan, E. Delhaize, P.J. Randall, Malate efflux from root apices and tolerance to aluminum are highly correlated in wheat, *Aust. J. Plant Physiol.* 22 (1995) 531–536.
- [15] R.A. Dowty, G.P. Shaffer, M.W. Hester, G.W. Childers, F.M. Campo, M.C. Greene, Phytoremediation of small-scale oil spills in fresh marsh environments: a mesocosm simulation, *Mar. Environ. Res.* 52 (2001) 195–211.
- [16] W.X. Liu, Y.M. Luo, Y. Teng, Z.G. Li, L.H. Wu, A survey of petroleum contamination in several Chinese oilfield soils, *Soils* 39 (2007) 247–251.
- [17] W.M. Cai, Land Use Changes and its Sustainable Assessment in the Yellow River Delta College of Resources and Environmental Sciences, PhD China Agricultural University, Beijing, 2004.
- [18] I. Kufel, L. Kufel, Chemical-composition of reed (*Phragmites Australis* Trin Ex Steudel) in relation to the substratum, *Bulletin De L Academie Polonaise Des Sciences-Serie Des Sciences Biologiques* 28 (1980) 563–568.
- [19] Y.M. Chen, M.K. Wang, S.Y. Zhuang, P.N. Chiang, Chemical and physical properties of rhizosphere and bulk soils of three tea plants cultivated in Ultisols, *Geoderma* 136 (2006) 378–387.
- [20] R.E. Hamon, S.E. Lorenz, P.E. Holm, T.H. Christensen, S.P. McGrath, Changes in trace-metal species and other components of the rhizosphere during growth of radish, *Plant Cell Environ.* 18 (1995) 749–756.
- [21] L.D. Lacerda, C.E.V. Carvalho, K.F. Tanizaki, A.R.C. Ovalle, C.E. Rezende, The biogeochemistry and trace-metals distribution of mangrove rhizospheres, *Biotropica* 25 (1993) 252–257.
- [22] F. Nadim, S.L. Liu, G.E. Hoag, J.P. Chen, R.J. Carley, P. Zack, A comparison of spectrophotometric and gas chromatographic measurements of heavy petroleum products in soil samples, *Water Air Soil Pollut.* 134 (2002) 97–109.
- [23] R. Lacutusu, Appraising levels of soil contamination and pollution with heavy Metals, European Soil Bureau Research Report No. 4, 2000.
- [24] V. Antoniadis, B.J. Alloway, The role of dissolved organic carbon in the mobility of Cd, Ni and Zn in sewage sludge-amended soils, *Environ. Pollut.* 117 (2002) 515–521.
- [25] K. Kalbitz, R. Wennrich, Mobilization of heavy metals and arsenic in polluted wetland soils and its dependence on dissolved organic matter, *Sci. Total Environ.* 209 (1998) 27–39.
- [26] S. Ehlken, G. Kirchner, Environmental processes affecting plant root uptake of radioactive trace elements and variability of transfer factor data: a review, *J. Environ. Radioact.* 58 (2002) 97–112.
- [27] J. Pichtel, H.T. Sawyerr, K. Czarnowska, Spatial and temporal distribution of metals in soils in Warsaw, Poland, *Environ. Pollut.* 98 (1997) 169–174.
- [28] S.M. Ullrich, M.H. Ramsey, E. Helios-Rybicka, Total and exchangeable concentrations of heavy metals in soils near Bytom, an area of Pb/Zn mining and smelting in Upper Silesia, Poland, *Appl. Geochem.* 14 (1999) 187–196.
- [29] Y.K. Rui, L.C. Qu, X.B. Kong, Effects of soil use along Yellow River basin on the pollution of soil by heavy metals, *Spectrosc. Spect. Anal.* 28 (2008) 934–936.
- [30] T.C. Fox, M.L. Guerinot, Molecular biology of cation transport in plants, *Ann. Rev. Plant Physiol. Plant Mol. Biol.* 49 (1998) 669–696.
- [31] R.S. Pacovsky, Micronutrient uptake and distribution in mycorrhizal or phosphorus-fertilized soybeans, *Plant Soil* 95 (1986) 379–388.
- [32] P.N. Chiang, M.K. Wang, C.Y. Chiu, S.Y. Chou, Effects of cadmium amendments on low-molecular-weight organic acid exudates in rhizosphere soils of tobacco and sunflower, *Environ. Toxicol.* 21 (2006) 479–488.
- [33] D.L. Jones, Organic acids in the rhizosphere—a critical review, *Plant Soil* 205 (1998) 25–44.
- [34] G. Neumann, V. Römheld, The Release of Root Exudates as Affected by the Plant's Physiological Status, Marcel Dekker Inc., New York, 2001.
- [35] P. Audet, C. Charest, Allocation plasticity and plant-metal partitioning: meta-analytical perspectives in phytoremediation, *Environ. Pollut.* 156 (2008) 290–296.
- [36] M. Mench, J.L. Morel, A. Guckert, B. Guillet, Metal-binding with root exudates of low-molecular weight, *J. Soil Sci.* 39 (1988) 521–527.
- [37] D.L. Jones, A. Hodge, Y. Kuzyakov, Plant and mycorrhizal regulation of rhizodeposition, *New Phytol.* 163 (2004) 459–480.