PAPER

Migration, speciation and distribution of heavy metals in an oil-polluted soil affected by crude oil extraction processes

Xiaowen Fu,[a] Zhaojie Cui*[a] and Guolong Zang[b]

Heavy metals are among the major pollutants in the worldwide soil environment. In oilfields, the crude oil extraction process results in the simultaneous contamination of the soil with petroleum and heavy metals. In this work, we investigated the influence of oil extraction on the migration, speciation, and temporal distribution of heavy metals (Cu, Zn, Pb, Cd, Cr, Mn, Ni, V, and Mn) in soils of an oil region of Shengli Oilfield, China. The results showed that oil-polluted soils were contaminated with Cu, Zn, Cd and Ni, with mean concentrations of 27.63, 67.12, 0.185 and 33.80 mg kg^{-1}, respectively (greater than the background values of local surface soils). Compared with the control profile, the vertical distributions of Cu, Zn, Pb, Cd, Ni, and V were affected in oil-polluted soils, particularly those of Cd and Ni. The concentrations of Zn, Cd, Ni, V, and Mn in oil-polluted soils increased with the duration of oil well development, which indicated the levels of these metals in the oil field were enhanced by human activities. Fractionation analysis revealed that the mobility potential of heavy metals in oil polluted soil decreased in the sequence Cd > Mn > Zn > Ni > Pb > Cu > Cr > V. The most important proportion of Cd is ion exchangeable and acid soluble, which indicates that Cd is the most labile, available, and harmful heavy metal among the elements that damage the soil environment in oil-polluted soil.

Environmental impact

Heavy metals are severely toxic and exist widely in the soil environment. Oil pollution in soils will affect the concentration and distribution of heavy metals. Until now, little research has focused on heavy metals in oil-polluted soils. This paper revealed that the concentrations of Cu, Zn, Cd, and Ni in oil-polluted soils were relatively high and exceeded the local background values of Shandong Province. The presence of oil enhanced the concentrations of Cd and Ni in the whole profiles and significantly affected the vertical distributions of all heavy metals except Cr and Mn. The concentrations of Zn, Cd, Ni, V, and Mn increased with increasing oil-well development time, and the mobility potential of heavy metals in oil polluted soil decreased in the order Cd > Mn > Zn > Ni > Pb > Cu > Cr > V. All these results are necessary for contamination assessment, control, and management of pollution in oil-polluted soils.

Introduction

Economic development has caused a significant enhancement in the rate of crude oil extraction and utilization to satisfy the industrial processes of modern society. The crude oil extraction process, similar to many other mining activities, inevitably generates gaseous, liquid and solid pollutants that affect the environment.[1] Heavy metal contamination in oil polluted soils is one of these threats to soil environments.

Numerous studies have reported that heavy metal contamination exists in the soil of oil fields or industries.[1–3] Crude oil contains heavy metals such as Cd, Pb, Ni, and V, and drilling fluid may also contain heavy metals (such as Cr, Pb, and Zn).[2,4–6]

Oil contamination is supposed to be responsible for the higher levels of heavy metals in oil-polluted soils.[7,8]

Petroleum hydrocarbons in soils could also degrade, increase the amount of organic matter and form organo–metallic complexes with heavy metals.[8,9] Meanwhile, crude oil extraction processes, such as drilling and oil spillage, could also change the local soil characteristics.[2,4] Therefore, crude oil extraction processes will very likely affect the distribution and migration of heavy metals in the soil. With the increasing duration of oil-extraction processes, further accumulation of oil and heavy metal contaminants will occur and result in higher environmental risks. Clarifying the distribution, migration, and speciation of heavy metals in crude oil-polluted soils is very important and urgently needed.[10,11] However, studies in this area have not received sufficient attention.

Thus, in this paper, an oil region of Shengli Oilfield was selected to study the concentration and speciation of heavy metals (Cu, Zn, Pb, Cd, Cr, Ni, V, and Mn) in crude oil-polluted

[a]*School of Environmental Science and Engineering, Shandong University, No. 27 South of Shanda Road, Jinan, 250100, China. E-mail: cuizj@sdu.edu.cn; Fax: +86 0531 88361176; Tel: +86 0531 88361176*

[b]*Tianjin Recyclable Resource Institute, Tianjin, 300191, China*

This journal is © The Royal Society of Chemistry 2014

Environ. Sci.: Processes Impacts, 2014, **16**, 1737–1744 | **1737**

soils affected by oil extraction processes. The vertical and temporal distribution patterns were also analyzed to describe the migration and transformation of heavy metals in crude oil-polluted soils.

Materials and methods

Description of the study area

The study area was located in the Gudao oil region of Shengli Oilfield, north of the Yellow River Delta (Fig. 1). Gudao oil region, which covers an area of 1050 km^2 and has approximately 1679 oil wells (until 1995), is the second largest oil region of Shandong Province, China. The area is in the East Asian monsoon region with an average annual temperature of 12.1 °C and precipitation of approximately 580 mm. Saline fluvo-aquic soil and coastal alluvial soil are the major soil categories in this area.

Sampling procedure

In July 2013, soil samples were collected near oil wells where the soils were polluted by crude oil. According to the history of development in the Gudao oil region, the time of the development of the oil wells can be divided into four periods (1970s, 1980s, 1990s, and 2000s). Twelve sampling sites were selected near oil wells developed at different times (three sampling sites for each interval, Table 1). The selected oil wells have been under continuous operation from their development, except for the three oil wells developed in the 1970s (sampling sites 1, 2, and 3) which have been abandoned for about 10 years. The oil-polluted soil profile was sampled 10 m from an oil well exploited in the 1970s. A randomly chosen site was used as the control profile with non-oil-polluted native soil (approximately 1 km away from the study area). The soil profiles, 1 m deep, were sectioned horizontally at 10 cm intervals in the first 60 cm and at 20 cm intervals in the remaining 40 cm. Except for the two soil profiles, all samples were collected from surface soils (0–20 cm). Table 1 shows that fourteen sampling sites were selected in our study area. The sample locations are ordered according to the development time of the nearby oil wells, and the soil profiles are at the bottom. All the sampling locations can be found in Fig. 1, except for the control profile (sample 14).

All soil samples were collected in unvegetated areas, approximately 1 kg of soil was collected using a plastic scoop and a stainless steel shovel, and then stored in a plastic bag. For each sample (but not the soil profiles), five sub-samples with similar weight were collected, mixed together and then decreased to about 1 kg using the Quarter Method.[12] The soil samples were stored in plastic bags. The coordinates of sampling locations were recorded simultaneously through GPS (Garmin eTrex Venture).

Soil chemical analysis

Soil organic matter (OM) concentrations were measured using the Walkley and Black method,[13] and pH values were
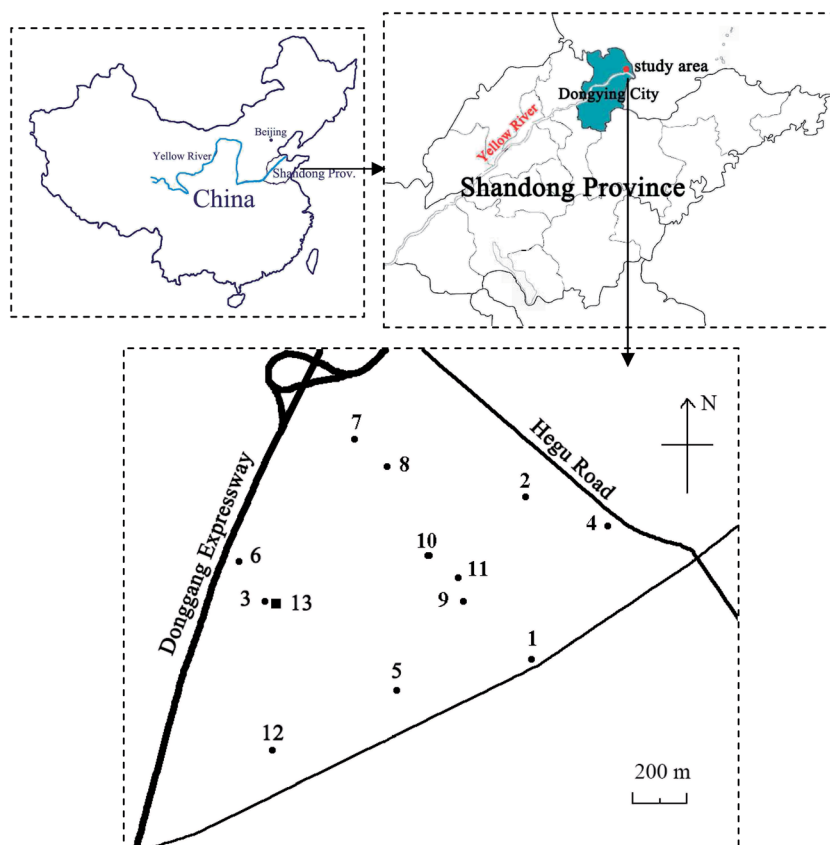

Fig. 1   Sampling locations in this study.

1738 | Environ. Sci.: Processes Impacts, 2014, 16, 1737–1744

This journal is © The Royal Society of Chemistry 2014

Table 1 Descriptions and locations of the sampling sites (the oil well refers to that nearest each sampling site)

Site	Sample type	Year of development of the oil well	Present status of the oil well	Latitude	Longitude
1	Age	1972	Abandoned	37°51′44″ N	118°45′04″ E
2	Age	1971	Abandoned	37°52′00″ N	118°45′05″ E
3	Age	1972	Abandoned	37°51′55″ N	118°44′27″ E
4	Age	1983	Active	37°52′00″ N	118°45′13″ E
5	Age	1983	Active	37°51′42″ N	118°44′44″ E
6	Age	1983	Active	37°51′59″ N	118°44′24″ E
7	Age	1991	Active	37°52′12″ N	118°44′43″ E
8	Age	1994	Active	37°52′07″ N	118°44′50″ E
9	Age	1995	Active	37°51′51″ N	118°44′56″ E
10	Age	2005	Active	37°51′56″ N	118°44′52″ E
11	Age	2005	Active	37°51′54″ N	118°44′55″ E
12	Age	2001	Active	37°51′38″ N	118°44′25″ E
13	Oil-polluted profile	—	—	37°51′50″ N	118°44′46″ E
14	Control profile	—	—	37°51′22″ N	118°43′44″ E

determined at a 1 : 5 (soil : water, w/w) ratio using a digital ion meter (PXS-215, RIDAO Instrument Co., Ltd, China). A TOC-5000A (Shimadzu Corp., Japan) was used to detect total organic carbon (TOC) and water-soluble organic carbon (WSOC). The WSOC was extracted from soil samples with deionized water (1 : 2, w/w) (TOC-V$_{CPH}$, Shimadzu Corp., Tokyo, Japan). Salinity was measured in a deionized water suspension (1 : 5, w/w) using a standard conductivity meter (DDS-11A, INESA, China).[8]

Soil samples were dried at room temperature and impurities such as plant roots and stones were discarded, the samples were then finely ground to pass through a 100-mesh nylon sieve prior to analysis. For each sample, approximately 3.000 g of soil was digested in a high-pressure microwave system (XT-9900A, Xintuo Analytical Instruments Co., Ltd, China). Before the digestion process, 5 mL of HNO_3, 5 mL of HF, and 3 mL of $HClO_4$ were mixed with the soil samples in a polytetrafluoro-ethylene vessel. After the microwave process, the vessel was taken out, uncovered, and heated to expel the acids until the residue was a viscous colorless or light yellow fluid. After adding 10 mL of deionized water, the crucible was then gently heated to dissolve the residues. 1 mL of HNO_3 was added to the final solution and this was made up to 50 mL with deionized water. The solutions of HCl, HNO_3, HF and $HClO_4$ used in the process were all concentrated. All heavy metal concentrations were determined by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS, 7700i, Agilent, USA).

Heavy metal fractionation

The heavy metal fractionation of soil samples was analyzed with the modified BCR sequential extraction procedure.[14–18] Each soil sample was analyzed using approximately 1.00 g of dried specimen (<74 μm), and the reagents and experimental conditions are shown in brief in Table 2. The only difference in the method in this study from the modified BCR method was that after each step of the BCR scheme, the extraction solutions were digested by adding 3 mL concentrated HNO_3 and heating. Each digestion was then made up to 25 mL with 1 M HNO_3.

Statistical analyses

Duplicates, standard reference material (GBW07401 and GBW07437, the Center of National Standard Reference Material of China), and method blanks were used as quality assurance and quality control (QA/QC) methods. The recovery ranged from 97% to 107%, which fit with the requirements of the Technical Specification for Soil Environmental Monitoring HJ/T 166-2004.[19] All statistical analysis in this paper was carried out using SPSS 17.0 software (SPSS Inc., Chicago, USA). The statistical differences in heavy metal concentrations among samples from oil wells of different ages were determined using one-way ANOVA followed by LSD (Least Significant Difference) multiple comparisons, $P < 0.05$.

Results and discussion

Soil properties and oil pollution

Table 3 shows statistical data on the soil properties and heavy metal concentrations of the soil samples. The pH and salinity values demonstrated that the soil in the study area was saline alkali soil. Oil-polluted soils (with high TPHs values) in this study generally had relatively high TOC and WSOC values. TPHs could not be detected in some samples because the samples were obtained from the bottom of the oil-polluted profile or the whole control profile. The maximum and mean values of TPHs revealed that the study area has been contaminated by petroleum hydrocarbons.[20]

Total heavy metal concentrations

To describe the variation in the heavy metal concentrations, the arithmetic mean and maximum values, and standard deviations of all samples were calculated (Table 4). The mean values of total heavy metal concentrations showed that the mean order of their abundance was: Mn ≫ V > Zn > Cr > Ni > Cu > Pb ≫ Cd.

The background value (A horizon) of Shandong Province, China[21] and the Grade II criteria (alkaline soil) of the Chinese environmental quality standard for soil[12] are also shown in

This journal is © The Royal Society of Chemistry 2014

Environ. Sci.: Processes Impacts, 2014, **16**, 1737–1744 | **1739**

Table 2 Extraction conditions for soil fractionation analysis using the modified BCR method

Step	Soil phase	Extractant	Extracting procedure
F1	Exchangeable	40 mL of 0.11 M CH_3COOH	Shaking for 16 h at room temperature
F2	Reducible	40 mL of 0.5 M $HONH_2 \cdot HCl$ (pH = 2)	Shaking for 16 h at room temperature
F3	Oxidisable	10 mL of 8.8 M H_2O_2 (pH = 2) then 10 mL of 8.8 M H_2O_2 (pH = 2) heat, cool and add 50 mL of 1 M NH_4OAc (pH = 2)	Heating for 1 h at room temperature and 1 h at 85 °C, and 1 h at 85 °C; shaking for 16 h at room temperature
R	Residual	5 mL HNO_3, 5 mL HF and 3 mL $HClO_4$	Microwave digestion

Table 3 Statistical data on the soil properties and TPHs of the studied soils (the results represent data obtained from all samples except the control profile)

	Min.	Max.	Mean	SD
pH	7.61	8.37	7.96	0.223
Salinity (g kg^{-1})	1.43	41.3	9.99	8.39
TOC^a (g kg^{-1})	3.10	6.36	4.59	1.01
WSOC^b (mg kg^{-1})	11.1	36.8	15.0	7.52
TPHs^c (g kg^{-1})	Nd^d	56.2	6.43	12.5
Granulometry (%)				
Clay (0–2 μm)	2.04	24.00	10.01	5.98
Silt (2–50 μm)	3.32	65.80	31.87	17.94
Sand (>50 μm)	15.80	94.64	58.12	23.02

^{a} Total organic carbon (TOC). ^{b} Water-soluble organic carbon (WSOC). ^{c} Total petroleum hydrocarbons (TPHs). ^{d} Not detected.

Table 4 Statistical data of total heavy metal concentrations (mg kg^{-1}) in the analysed soils

	Max	Mean	SD	Grade II	Background value
Cu	63.32	27.63	10.35	100	24.0
Zn	98.70	67.12	13.47	300	63.5
Pb	49.76	16.22	9.95	350	25.8
Cd	0.420	0.185	0.108	1.0	0.084
Cr	433.2	61.66	69.42	250	66.0
Ni	66.85	33.80	11.94	60	25.8
V	91.89	75.10	8.56	—	80.1
Mn	708.9	524.2	85.08	—	644

Table 4. None of the concentrations of the seven heavy metals for each soil sample exceeded the Grade II criteria. However, the mean values of Cu, Zn, Cd, and Ni in this study were relatively higher than the background values, which indicated notable enrichment of these metal contaminants in the oil-polluted soil. This finding suggests a potential risk to soil environmental quality from these heavy metal contaminants, and further monitoring and management are required to avoid additional pollution and enrichment.

Vertical distribution of total heavy metals

Fig. 2 shows the vertical distribution patterns of heavy metals (Cu, Zn, Pb, Cd, Cr, Ni, V, and Mn) in the soil profile of the oilfield. Compared with unpolluted soil, the concentrations of Cd and Ni in the whole profile of the oil-polluted soil were enhanced. For all heavy metals (except Cr and Mn) the vertical distribution patterns were also significantly different in the oil-polluted soil profile from that of unpolluted soil.

From the top of the profiles to the bottom, the highest concentrations of Cu, Zn, Pb, Cd, Ni and V generally appeared in the range of 10 to 40 cm. These elements generally decreased with increasing depth below 40 cm. From the surface to a depth of 60 cm, the concentrations of Cu, Zn, Cr and Ni in the soil were all above the local background values (A horizon). This finding suggested that Cu, Zn, Cr, and Ni were enriched in the top of the soil and revealed that they probably arose from anthropogenic sources such as crude oil and drilling fluids. The elements of Mn and Cr showed a fluctuating and downward tendency from the top to the bottom of the soil profiles.

The vertical distribution of WSOC is also shown in Fig. 2. Comparing the distribution pattern of WSOC with that of heavy metals, peak concentrations were found at a depth of 20 to 30 cm for both WSOC and most of the heavy metals. This finding revealed that WSOC probably has an important function in the vertical distribution of heavy metals in oil-polluted soils. The reason could be that petroleum hydrocarbons can be degraded by microorganisms and consequently increase the TOC and WSOC values of soils. Previous studies have reported a similar result, that WSOC in the soil could form stable and soluble complexes with heavy metals, thus affecting the dissolution and migration of heavy metals in the soil profile.[9,22] Therefore, the migration and distribution of heavy metals in oil-polluted soils were influenced by the crude oil extraction process.

Analysis of the correlation between TPHs and heavy metals was carried out to find out if there was any relevance. However, the results showed little correlation between the TPHs and heavy metals. The reason for this phenomenon would be that the relationship between oil and heavy metal contaminants is indirect. The organic compounds of the oil are diminished over time because of their evaporation and degradation by microorganisms, but at the same time, the heavy metals in oil-polluted soils are maintained and enhanced. Besides, drilling fluids, with relatively low TPH values, are also important sources of heavy metals in oil-polluted soils.

Metal fractionation and mobility

The modified BCR method was used to analyze the speciation of heavy metals in oil polluted soils. The mean concentration and standard deviation of each fraction are shown in Table 5. In this

1740 | *Environ. Sci.: Processes Impacts*, 2014, **16**, 1737–1744

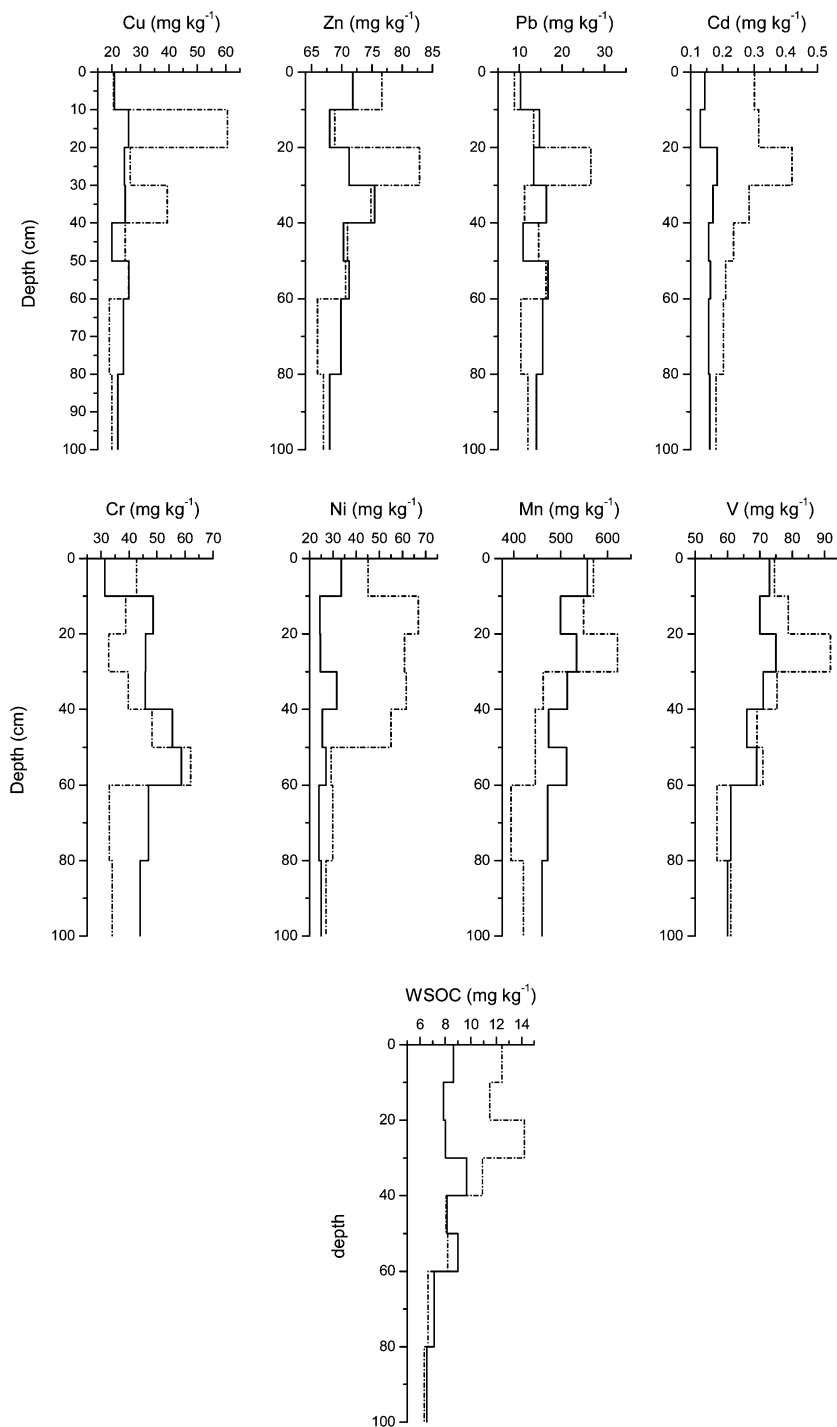This journal is © The Royal Society of Chemistry 2014

Fig. 2 Vertical distribution patterns of heavy metals in the oil polluted soil profile (dotted line) and the control profile (solid line).

method, all heavy metals (except Cd and Zn) were extracted at a higher concentration from the residue than the other fractions. Cd and Zn were found at higher levels (more than 50%, Fig. 3) in soluble fractions than other elements, which indicated an increased possible risk to the environment from these heavy metals. In particular, Cd was found mostly in the exchangeable and acid soluble fraction (approximately 40%). Zn exhibited a uniform distribution over all soil phases. Although Mn was mainly bound to silicates (residual fraction), approximately

30% of this element could be extracted through weak acid and simple ion exchange. Pb was uniformly distributed over each extractable phase. The most important forms of Ni appeared in the insoluble fraction, but it was also found at a relatively high level in the exchangeable fraction.

The mobility of heavy metals in soils depends primarily on their binding forms. Table 6 demonstrates the mobility potential of different heavy metals. Cd evidently has the highest mobility potential and capability to be released from soils by ion

Table 5 Speciation of heavy metals (mean ± SD) in mg kg^{-1} in oil-polluted soils obtained from the modified BCR method

Fractionation	F1	F2	F3	R
Cu	0.83 ± 0.11	1.64 ± 0.2	1.25 ± 0.7	27.0 ± 16.4
Zn	11.1 ± 1.5	11.7 ± 1.7	13.8 ± 3.4	26.9 ± 12.9
Pb	1.44 ± 0.11	2.75 ± 0.61	4.63 ± 0.79	14.7 ± 3.5
Cd	0.026 ± 0.06	0.015 ± 0.002	0.008 ± 0.003	0.016 ± 0.011
Cr	0.29 ± 0.08	0.63 ± 0.09	2.3 ± 1.02	59.3 ± 7.2
Ni	3.51 ± 0.61	1.78 ± 0.46	2.62 ± 1.31	29.7 ± 12.2
V	0.06 ± 0.03	2.72 ± 1.06	0.98 ± 0.58	70.1 ± 9.72
Mn	97.5 ± 18.7	23.3 ± 18.1	9.11 ± 4.68	202 ± 27.8
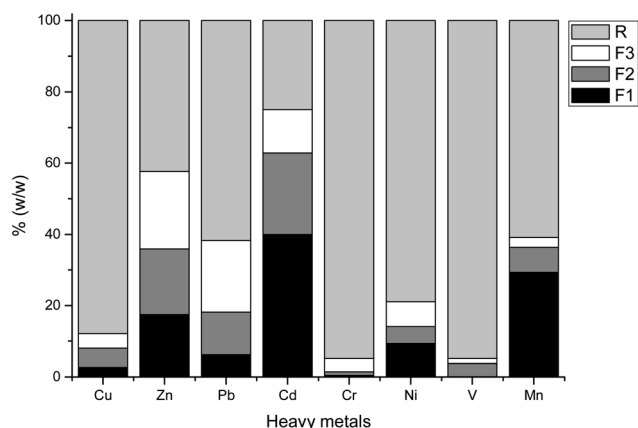
Fig. 3 The percentage speciations of heavy metals (mean values) obtained from the modified BCR method.

exchange and acid dissolution mechanisms. Meanwhile, the percentages of Cd were also highest in the reducible fraction but the lowest in the residual fraction. Considering the high toxicity of Cd, this element could be a severe threat to the local environment. The presence of ion exchangeable and acid soluble fractions of Mn and Pb revealed their sensitivity to acidic conditions and tendency to be leached easily. This finding is in agreement with another study which showed the high mobility of Mn in an acidic environment.[23] Meanwhile, the low percentage of V in this fraction indicated its relative insensitivity.

As revealed by the order of metal mobility under the reduction reaction, Cd, Zn, and Pb were easier to mobilize and release under varied reducing conditions. Meanwhile, compared with other heavy metals, these three elements were absorbed by the OM in soils and appeared to be stable under anaerobic conditions but labile under aerobic conditions.

V and Cr had the highest proportions in the residual fraction. This finding implied that they are the most non-mobile and are the least potentially harmful to the environment.[24,25] The high concentration in the residual fraction and low level in the extracted fraction of heavy metals in soils indicated that the soil was relatively unpolluted.[26,27]

In summary, in this study, Cd was the most mobile and available element, whereas V was the least mobile element. The mobility potential of heavy metals in the oil polluted soils decreased in the sequence of Cd > Mn > Zn > Ni > Pb > Cu > Cr > V.

Temporal distribution of total heavy metals

As shown in Fig. 4, comparing heavy metal concentrations in soisl of different ages, the total heavy metal concentrations in oil-polluted soils were evidently affected by the duration of crude oil extraction processes. The highest concentrations of Zn (69.81 mg kg^{-1}), Cd (0.124 mg kg^{-1}), Ni (49.59 mg kg^{-1}), and V (80.74 mg kg^{-1}) were found in soils near oil-wells developed 40 years ago. Significant differences were found in the concentrations of heavy metals (except Cu and Cr) in oil-polluted soils, according to the ages of oil wells. The concentrations of Zn, Cd, Ni, V, and Mn significantly increased with oil-well age ($P < 0.05$). This result indicated that the total concentrations of these five heavy metals were influenced by the crude oil extraction process. By contrast, no significant difference in Cu or Cr was determined among oil wells of different ages.

For Cd, significant differences were observed among different periods of oil-well development, which indicated that the total concentrations of Cd were affected in each period of the extraction process. Statistically significant differences in Zn and Mn concentrations were found between oil wells developed before the year 1989 and those after 1990. That is, concentrations of Zn and Mn were disturbed in the middle of the oil-well development history. The notable increase in total Ni and V in

Table 6 Mobility of heavy metals in the soil obtained with the BCR method

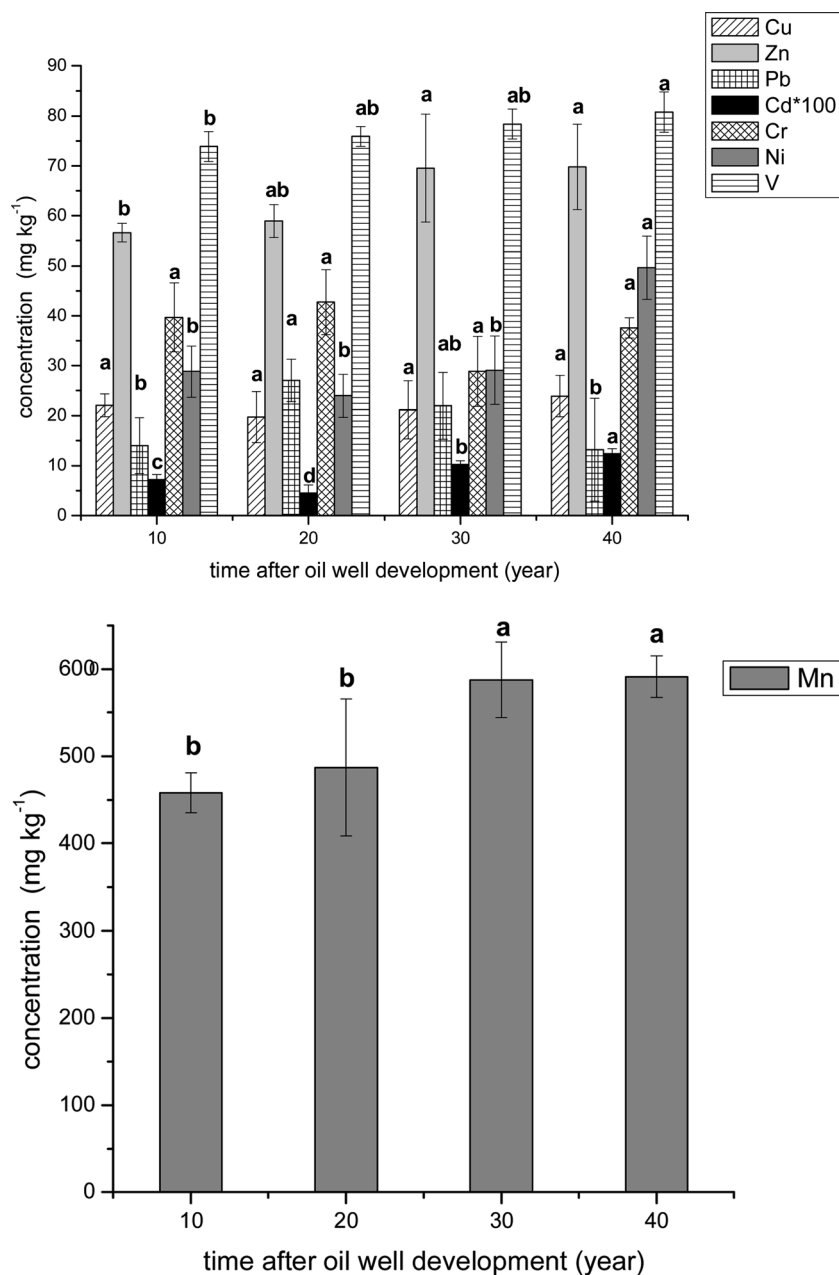| Step	Condition	Mobility
1	Ion exchange and acid dissolution	Cd > Mn > Zn > Ni > Pb > Cu > Cr > V
2	Reduction reaction	Cd > Zn > Pb > Mn > Cu > V > Ni > Cr
3	Oxidation reaction	Zn > Pb > Cd > Ni > Cu > Cr > Mn > V
4	Residual (insoluble)	V > Cr > Cu > Ni > Pb > Mn > Zn > Cd

Fig. 4 Temporal distribution patterns with the time after oil well development of Cu, Zn, Pb, Cd, Cr, Ni, and V (on the top panel) and Mn (on the bottom panel). The different letters (a, b, c, and d) denote significant differences between plots when ANOVA was significant ($P < 0.05$). Because of the high values of Mn, it is separated from the rest of the metals. Values represent mean $\pm$ SD.

the soil in the 1970s revealed that the influence of the crude oil extraction process on these metals has a long-term effect. Total concentrations of Cu remained relatively constant over time, whereas those of Pb and Cr fluctuated. This finding indicated that operating time has a negligible effect on the total concentrations of Cu, Pb, and Cr.

The enhancement of Zn, Cd, Ni, V, and Mn with time could be caused not only by the continuous addition of petroleum and drilling fluids, but also manufacturing activities in the oil well operating processes, such as mechanical equipment and transport vehicles on the oil field. Furthermore, the organic compounds in the oil are diminished over time because of their

evaporation and biodegradation by microorganisms,[28] but at the same time, the levels of heavy metals in oil-polluted soils would be maintained and enhanced.

Conclusions

In this paper, the distribution and fractionation of heavy metals (Cu, Zn, Pb, Cd, Cr, Ni, V and Mn) in oil-polluted soils of Shengli Oilfield, China were investigated. Data on eight heavy metals were collected using ICP-MS, and the fractionations of the heavy metals were determined using the modified BCR sequential extraction procedure. The results showed that the mean

This journal is © The Royal Society of Chemistry 2014

Environ. Sci.: Processes Impacts, 2014, **16**, 1737–1744 | **1743**

concentrations of heavy metals (in mg kg^{-1}) in oil-polluted soils were Cu 27.63, Zn 67.12, Pb 16.22, Cd 0.185, Cr 61.66, Ni 33.80, V 75.10, and Mn 524.2. Cu, Zn, Cd, and Ni were present in relatively high concentrations and exceeded the local background values of Shandong Province. Compared with unpolluted soils, the concentrations of Cd and Ni in the whole profiles of oil-polluted soils were enhanced. For all heavy metals (except Cr and Mn) in the oil-polluted soil profile, the vertical distribution patterns were also significantly different from that of unpolluted soil. The concentrations of Zn, Cd, Ni, V, and Mn increased with increasing oil-well development time, which indicated the influence of the crude oil extraction process on the surrounding soil environment. Among the eight heavy metals, Cd was the most exchangeable, labile, and available heavy metal in oil-polluted soils and furthermore was the most threatening to the surrounding ecosystem. The mobility potential of heavy metals in oil polluted soil decreased in the sequence of Cd > Mn > Zn > Ni > Pb > Cu > Cr > V.

Acknowledgements

Notes and references

1 E. Obiajunwa, D. Pelemo, S. Owolabi, M. Fasasi and F. Johnson-Fatokun, *Nucl. Instrum. Methods Phys. Res., Sect. B*, 2002, **194**, 61–64.

2 E. Carls, D. B. Fenn and S. A. Chaffey, *J. Environ. Manage.*, 1995, **45**, 273–286.

3 C. Oprea, O. Maslov, M. Gustova, A. Belov, P. Szalanski and I. Oprea, *Vacuum*, 2009, **83**, 162–165.

4 I. Kisic, S. Mesic, F. Basic, V. Brkic, M. Mesic, G. Durn, Z. Zgorelec and L. Bertovic, *Geoderma*, 2009, **149**, 209–216.

5 T. F. Yen, *Role of trace metals in petroleum*, Ann Arbor Science Publishers, Ann Arbor, MI, 1975.

6 J. Krzyzanowski, *Environ. Rev.*, 2012, **20**, 122–134.

7 M. Onojake and O. Frank, *Chem. Ecol.*, 2013, **29**, 246–254.

8 M. Nie, N. Xian, X. Fu, X. Chen and B. Li, *J. Hazard. Mater.*, 2010, **174**, 156–161.

9 V. Antoniadis and B. Alloway, *Environ. Pollut.*, 2002, **117**, 515–521.

10 X. L. Ruan, G. L. Zhang, L. J. Ni and Y. He, *Pedosphere*, 2008, **18**, 386–393.

11 Y. F. Zhao, X. Z. Shi, B. Huang, D. S. Yu, H. J. Wang, W. X. Sun, I. Oboern and K. Blomback, *Pedosphere*, 2007, **17**, 44–51.

12 SEPAC, *Environmental Quality Standard for Soils (in Chinese)*, Beijing, 1995.

13 A. Walkley and I. A. Black, *Soil Sci.*, 1934, **37**, 29.

14 K. F. Mossop and C. M. Davidson, *Anal. Chim. Acta*, 2003, **478**, 111–118.

15 G. Rauret, J. Lopez-Sanchez, A. Sahuquillo, R. Rubio, C. Davidson, A. Ure and P. Quevauviller, *J. Environ. Monit.*, 1999, **1**, 57–61.

16 R. Sutherland, F. Tack, C. Tolosa and M. Verloo, *J. Environ. Qual.*, 2000, **29**, 1431–1439.

17 R. A. Sutherland, *Appl. Geochem.*, 2002, **17**, 353–365.

18 R. A. Sutherland and F. M. Tack, *Anal. Chim. Acta*, 2002, **454**, 249–257.

19 SEPAC, *Technical Specification for Soil Environmental Monitoring (in Chinese)*, Beijing, 2004.

20 A. Adeniyi and J. Afolabi, *Environ. Int.*, 2002, **28**, 79–82.

21 CNEPA, *The Background Values of Elements in Soils of China (in Chinese)*, China Environmental Science Press, Beijing, 1990.

22 K. Kalbitz and R. Wennrich, *Sci. Total Environ.*, 1998, **209**, 27–39.

23 S. A. Watmough, M. C. Eimers and P. J. Dillon, *Appl. Geochem.*, 2007, **22**, 1241–1247.

24 K. Nemati, N. K. A. Bakar and M. R. Abas, *Microchem. J.*, 2009, **91**, 227–231.

25 C. D. Stalikas, G. A. Pilidis and S. M. Tzouwara-Karayanni, *Sci. Total Environ.*, 1999, **236**, 7–18.

26 M. Kaasalainen and M. Yli-Halla, *Environ. Pollut.*, 2003, **126**, 225–233.

27 N. Tam and Y. Wong, *Environ. Pollut.*, 1996, **94**, 283–291.

28 Z. Y. Wang, D. M. Gao, F. M. Li, J. Zhao, Y. Z. Xin, S. Simkins and B. S. Xing, *Pedosphere*, 2008, **18**, 707–716.

1744 | *Environ. Sci.: Processes Impacts*, 2014, **16**, 1737–1744

This journal is © The Royal Society of Chemistry 2014