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An investigation on heavy metals in soils around oil field area

[1*]A. R. Karbassi; [2]S. Tajziehchi; [3]S. Afshar

[1]Graduate Faculty of Environment, University of Tehran, P.O. Box 1455-6135, Tehran, Iran

[2]Department of Environmental Science, Graduate School of the Environment and Energy, Science and Research Branch, Islamic Azad University, Tehran, Iran

[3]Department of Environmental Science, Islamic Azad University, Ahvaz, Khuzestan, Iran

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ABSTRACT: Oil and pollutants resulting from its extraction and exploitation are considered as one of the serious problems for human health. Vast oil fields of Ahvaz City located in southern Iran are known as one of controversial subjects in contamination with heavy metals. In this study, oil fields' soils of Ahvaz city (Ab-Teymour) were chemically analyzed in order to determine the concentration of eight heavy elements (Cu, Ni, V, Co, Cd, Zn, Mo and Pb) and intensity of contamination. The area was divided into 12 plots with respect to proximity to drilled oil wells as well as the existing flares. The results show that concentration of studied metals is higher than earth's crust mean values. According to Muller's geochemical index, intensity of contamination varies from unpolluted to highly polluted ones. These highly polluted areas require methods such as phytoremediation more than ever. By comparing list of local plants with that of heavy metals absorbing plants and given the local climate, a suitable absorbing plant for each of the existing heavy metals was recommended.

Keywords: *Enrichment factor (EF); Environmental pollution; Heavy metals; Index of geo-accumulation (Igeo); Phytoremediation; Soil*

INTRODUCTION

Pollutants resulting from various human activities such as agricultural, industrial, and municipal wastewater has caused environmental, economic and health problems (Xiao-Yong *et al*., 2007). Nowadays with the understanding of environmental problems, there have been significant efforts to clean up the environment and various methods have been developed and applied (Tajziehchi *et al*., 2013). Soil contamination with metals, semi- metals and organic pollutants is one of serious global problems (Nasehi *et al*., 2008). Concerns intensify when the pollutants are moved by groundwater, drainage and dust, and enter into the food chain (Lin *et al*., 2012; Lokeshwari *et al*., 2006; Mehrdadi *et al*., 2009). Pollution with heavy metals is certainly considered as a potential ecological risk (Siegel, 2002).

Oil and gas issues and their pollution in Iran is very complicated especially when it is decided to increase the energy products that can have various impacts on environment components (Karbassi *et al*., 2007).

In recent years, by applying sediment and soil geochemistry, it is possible to estimate the exact amount of pollutions (Nouri *et al*., 2008). Index of geo accumulation (Igeo) defined by Muller in 1979 is one of the indices for determination of soil pollution degree. In a research on the amount of Bamdezh wetland sediments pollution with heavy metals, it was found that Fe, Zn and Ni have natural origin in wetland sediment (Vaezi *et al*., 2015).

In another study performed in the vicinity of the Shirud River located in the west of Mazandaran

*Corresponding Author Email: *akarbasi@ut.ac.ir*
Tel.: (+98) 21 6111 3139; Fax: (+98) 21 6640 7719
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Province of Iran, the total concentration of copper, zinc, lead, vanadium, nickel, manganese and iron was measured and sediments of the area were classified to compare Enrichment factor (EF) and Igeo indices in assessing the environmental pollutions intensity. (Nasrabadi *et al.,* 2010a; Nasrabadi *et al.,* 2010b). In a study on pollution and distribution of heavy metals in soils of South Pars Special Economic Zone using two indices of enrichment factor and geo accumulation, the results showed that heavy metals pollution nearby the industries has higher concentration. In another study on heavy metals in dam reservoirs, sediments samples were collected from Kousar dam reservoir in Kohgiluyeh and Boyer- Ahmad Province. The results showed contamination with nickel, cadmium and lead. Finally, the degree of sediment contamination was evaluated using EF, Igeo and pollution index (I_{PoLL}) (Karbassi *et al.*, 2011).

Afkhami *et al.,* (2013) showed higher concentrations of As, Cd & V are related to oil drilling activities, and also geological structures at different depths.

In another study, the concentrations of heavy metals, in the sediment of Shavoor River in Khuzestan Province in Iran have been investigated. For quantitative assessment of the severity of contamination in the sediments, the geochemical indicators such as EF and the Igeo were used. The results of the experiments showed that the organic matter content has a mean of 2.49% and it ranges from 1.95% to 3.43%. EF was calculated for the elements revealed that heavy metals are classified as non-polluted ones. The Geo-accumulation Index showed similar results as EF did (Karbassi and Pazoki, 2015).

In recent years geochemistry of river bed sediment is studied along with flocculation processes that occurs during estuarine mixing (Vaezi *et al.*, 2015).For instance, impact of salinity, pH and DO on flocculation of Cu, Zn, Pb, Ni, Cd and Mn throughout mixing of Chalus River with Caspian Sea was investigated. The trend of flocculation of Pb (24.32%) < Zn (24.38%) < Cd (40.00%) < Cu (64.71%) < Ni (68.00%) < Mn (76.47%) reveals that among the studied elements Mn and lead experience minimum and maximum flocculation at diverse salinity regimes, respectively. Moreover, flocculation rate of studied metals fluctuates between 24 and 76 percent (Karbassi and Heidari, 2015). It should be noted that given the toxicity and bioaccumulation of heavy metals in biota, metal ions can lead to serious problems (Morillo *et al.,* 2002; Nasrabadi *et al.*, 2009; Rauret *et al.*, 1999). These metal pollutants can be removed from contaminated soil by phyto-remediation (Liphadzi *et al.*, 2005; Chehregania *et al.*, 2009; Weyens *et al.*, 2009; Gerhardt *et al.*, 2009; Yasseen, 2014). One of the critical reasons which distinguishes these metals from other toxic pollutants is that they are biodegradable in the environment (Rouret *et al.,* 1999; Nabi Bidhendi *et al.*, 2007; Nasrabadi *et al.*, 2009; karbassi *et al.*, 2005). Therefore, it is necessary to remove them from the environment (Tajziehchi *et al.*, 2012). Since remediation of soils contaminated with metals through engineering methods and other conventional methods is very costly (Persans and Salt 2013), thus special attention has been paid to the phytoremediation method as an emerging, affordable and practical technology to clean-up soil pollutants, especially when the local plants are used (Hassani *et al.*, 2015). In this study, soils of Ahvaz oil field (Ab-Teymour) were chemically analyzed in order to determine concentration of 8 heavy elements and also the intensity of pollution.

This study has been performed in Ab-Teymour of Ahvaz city, located in southern part of Iran in 2010.

MATERIALS AND METHODS

Soils samples of the studied area namely the area around Ab-Teymour oil field located at 25 km away from Ahvaz-Khorramshahr road were selected. Karun Oil & Gas Production Company as the largest subsidiary of National Iranian South Oilfields Company is limited from the north and northeast to Mollasani and Naft-e-sefid, from the south and southwest to Abadan and Khorramshahr, from the west to Susangerd and from the east to Marun. By producing more than 1,040,000 barrels of crude oil per day from about 475 oil wells in Ahvaz, Asmari, Bangestan, Mansuri, Ab-Teymour and Ramin oil reservoirs, this company plays a critical role in production of oil and gas in Iran. Ab-Teymour production unit is located 25-km of Ahvaz-Khorramshahr road. Oils of Ab-Teymour and Darkhovin oil fields are processed in Ab-Teymour production unit. This area has relatively rich vegetation with agricultural feature and located 4-km west of Karun River.

Locations of soil samples is given in Table 1. The soil samples were dried in room temperature and then passed through 63μm sieve. The soil samples were then powdered using an agate mortar and pestle. Bulk digestion was carried out by HF-HNO_3-HCl-$HClO_4$. The bio-availability of metals was carried out by a mixture of NaOH and acid acetic at a pH equal to 5. Metal contents were measured by atomic absorption spectroscopy (Varian 240 AFF).

To quantify the degree of elemental accumulation in soil, Igeo was calculated according to Muller (Eq. 1) as describe by Radojevic *et al.*, (2008).

$$Igeo = Log2\ \frac{C_n}{1.5\ B_n} \qquad (1)$$

Where C_n is the concentration of the examined element in the soil, B_n is the geochemical background value of a given element in shale and the factor 1.5 is used to account the possible variations in the background values.

RESULTS AND DISCUSSION

Bulk concentrations of the metals are presented in Table 2. As it is seen in all plots, bulk concentration of metals in the studied area is more than that of earth's crust and shale. The variation of metal contents in various plots are shown in Fig. 1 (A to L). The geo-accumulation of metals were computed based on Igeo formulae (Muller, 1979). The Igeo values are given in Table 3. The Muller's classification is also presented in Table 4. These classifications were applied to the data obtained in the present study (Table 5).

In order to determine the pollution intensity of the studied area, Muller's geochemical index was applied. As shown in Tables 3 and 5, the intensity of pollution with heavy metals in various plots ranges from unpolluted to highly polluted ones. Cluster analysis (Fig. 2) showed that Pb, Zn and V join each other at a relatively high similarity coefficient. Since vanadium is considered as an index of oil pollution, one may conclude that Zn and Pb are of the same origin. The other metals do not show any intra relationship with V and this may indicate a different origin for Co, Mo, Cu, Ni and Cd.

In general, the geochemical classification shows that nickel, vanadium, copper, cobalt and zinc are more accumulated than lead, cadmium and molybdenum. As it is shown in Table 2, the mean concentration of

Table 1: Geographical coordinates of sampling stations in Ab-Teymour oil field

Sample	Lat & Long coordinates	Plot	Location	Sample	Lat & Long coordinates	Plot	Location
1	0258434 3456773	A	Well 35	14	0263017 3455095	H	Well 10
2	0259157 3456905	B	Well 7	15	0258065 3452365	I	Next to agricultural land
3	0259543 3456533	B	Well 38	16	0261580 3453136	I	Near the dirt road
4	0261006 3456880	C	Near well 13	17	0263343 3453448	J	Well 17
5	0262235 3459656	D	Well 5	18	0262498 3452511	J	Near the dirt road or vegetation
6	0257921 3457197	E	Well 14	19	6440261 3454828	J	Well 19
7	0258603 3458037	E	Well 27 or 28	20	0262650 3454676	K	Well 18
8	0257887 3452478	E	Next to agricultural land	21	0262357 3454430	K	Inside agricultural land
9	0260450 3454743	F	Behind Ab-Teymour Well 8	22	0262905 3454676	K	Inside agricultural land
10	0260755 3453813	F	Next to agricultural land	23	0264050 3453959	L	Well 20
11	0260910 3456885	F	Next to agricultural land	24	0263738 3453999	L	West of road to well 20
12	0260709 3455239	G	Behind Ab-Teymour	25	0264605 3453809	L	south of road to well 20
13	0262385 3455130	G	Well 37				

Table 2: Concentration of metals in Ab-Teymour oil field's soil (mg/kg)

Station	Pb	Ni	V	Cd	Co	Zn	Mo	Cu
A	21	478	798	0.65	32	175	1.9	156
B	18	552	902	0.52	57	215	2.1	199
C	21	508	697	0.74	95	261	1.9	184
D	29	233	455	0.51	81	242	2.3	123
E	17	244	1126	1.02	56	115	3.2	456
F	22	269	956	0.45	68	100	3.7	238
G	23	238	1248	0.36	97	426	2.3	156
H	26	306	535	0.47	80	325	4.8	485
I	22	213	867	0.27	47	335	3.8	197
J	20	283	947	0.93	87	120	2.6	299
K	82	292	1808	0.57	72	1377	2.8	248
L	34	317	1009	0.62	52	260	2.8	574
Min.	17	213	455	0.27	32	100	1.9	123
Max.	82	552	1809	1.02	97	1378	4.8	574
Average	29	328	946	0.27	69	329	2.8	276
Standard deviation	18	117	354	0.21	20	344	0.87	148
Earth's crust	14	80	160	0.10	20	75	1.5	50
Shale	23	68	130	0.30	19	95	2.6	45ale

Table 3: Soil pollution in Ab-Teymour oil field based on Muller's Geochemical Index

Station	Pb	Ni	V	Cd	Co	Mo	Zn	Cu
A	0	2.2	2.0	0.5	0.15	0	0.3	1.2
B	0	2.4	2.2	0.2	1.01	0	0.6	1.6
C	0	2.3	1.8	0.7	1.75	0	0.9	1.5
D	0	1.2	1.2	0.2	1.52	0	0.8	0.9
E	0	1.3	2.5	1.2	0.97	0	0	2.8
F	0	1.4	2.3	0	1.25	0	0	1.8
G	0	1.2	2.7	0	1.78	0	1.6	1.2
H	0	1.6	1.5	0.1	1.49	0.3	1.2	2.9
I	0	1.1	2.2	0	0.72	0	1.2	1.3
J	0	1.5	2.3	1.1	1.62	0	0	2.2
K	0	1.5	3.2	0.3	1.33	0	3.3	1.9
L	0	1.6	2.4	0.5	0.88	0	0.9	3.1

0 denotes negative values

Table 4: Igeo classification for metals in soil/sediment (Muller, 1979)

Degree of soil contamination	Igeo
Unpolluted	0
Unpolluted to slightly polluted	0-1
slightly polluted	1-2
slightly polluted to highly polluted	2-3
highly polluted	3-4
highly polluted to severely polluted	4-5
severely polluted	< 5

nickel and vanadium is more than the mean concentration of these elements in the earth's crust, and this case is due to nature of the area as well as exploration, drilling and oil producing activities. On the other hand it could be argued that the high amount of concentration of heavy metals and pollution intensity is related to sequestration of oil hydrocarbons resulted from burning of gases associated with oil and hydrocarbon materials in flares of Ab-Teymour oil field. Due to the relatively high concentration of heavy metals in this area, the use of phytoremediation is practically efficient (Liphadzi *et al.*, 2005; Chehregania *et al.*, 2009; Weyens *et al.*, 2009; Gerhardt *et al.*, 2009; Yasseen, 2014). A comparison amongst types of plant species in Ab-Taymour with the list of plants capable of absorbing metals, it could be inferred that some plants of the area have high capability to absorb metals. These plants species are shown in Table 6. The plant species given in Table 6 are purely based on the above mentioned studies and therefore in future studies more attention should be given to proper selection of plant species for the area of study.

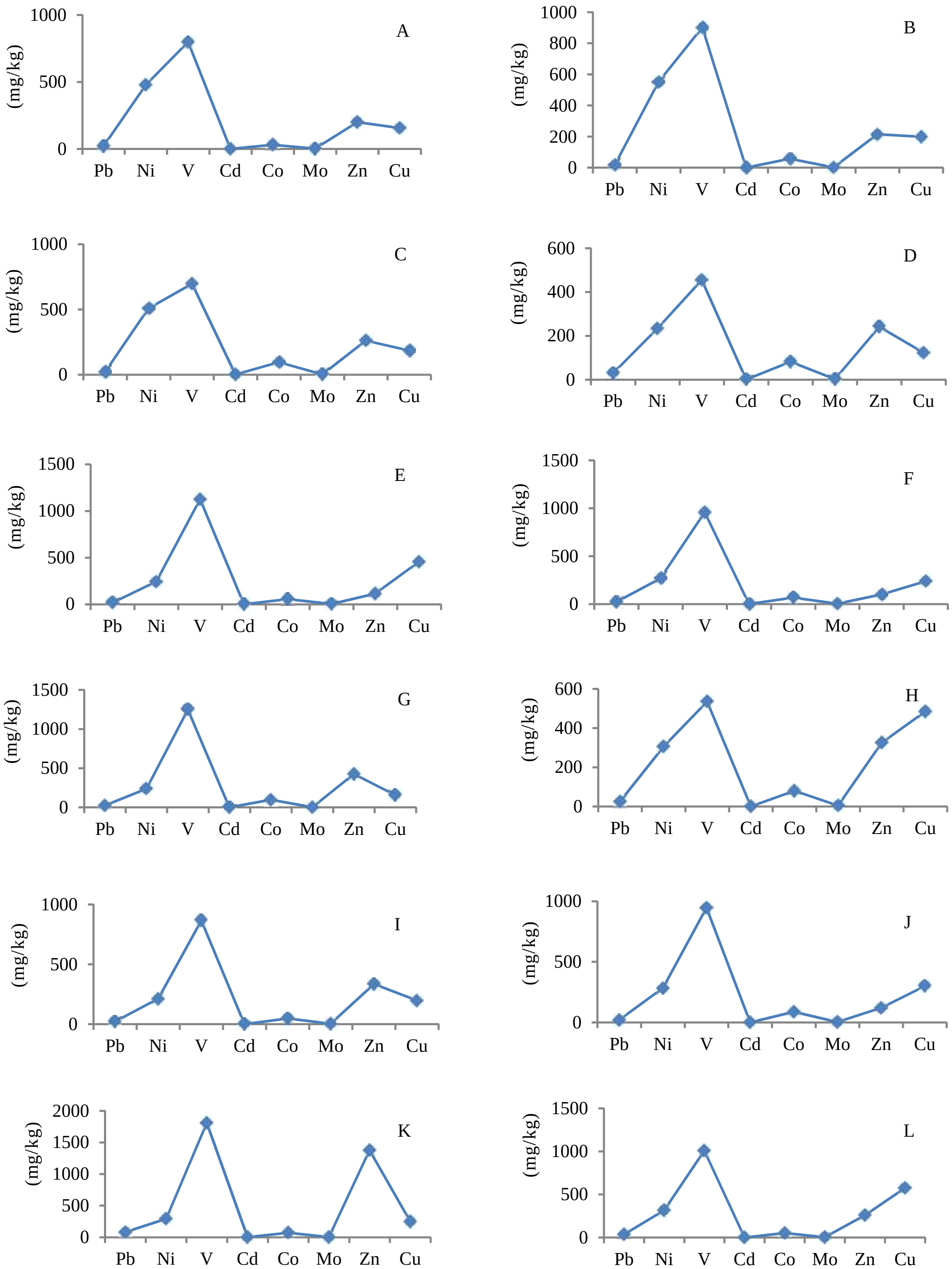

Fig. 1: The variation of metal contents in various plots (A to L)

Table 5: Classification of metal contamination in Ab-Teymour soil based on Muller's Igeo

Element / Station	Pb	Ni	V	Cd	Co	Mo	Zn	Cu
A	1	4	4	1	2	1	2	3
B	1	4	4	1	3	1	2	3
C	1	4	4	1	3	1	2	3
D	1	3	4	1	3	1	2	2
E	1	3	4	4	2	1	1	4
F	1	3	4	2	3	1	1	3
G	1	3	4	1	3	1	3	3
H	1	3	4	2	3	2	3	4
I	1	3	4	1	2	1	2	3
J	1	3	4	4	3	1	2	3
k	1	3	5	2	3	1	2	3
L	2	3	4	2	3	1	2	2

1. Unpolluted; 2. Unpolluted to slightly polluted; 3. Slightly polluted; 4. Slightly polluted to highly polluted and 5. Highly polluted.

Table 6: Local plants of Ab-Teymour area with high capability of metal removal from soil

Item	Plant Species	Item	Plant Species
1	Alpha alpha	8	Erusa sativa
2	Chenopodium album	9	Heliantus annus
3	Wheat (disambiguation)	10	Atriplex sp.
4	Hypecum pendulum	11	Sorghum sp.
5	Teucrium polium	12	Poplous spp.
6	Amaranthus radretroflxus	13	Avena sativa
7	Hordeum vulgare	14	Malva sp.

Table 7: Recommended plant species for cleaning-up metals in Ab-Teymour soil

Heavy metal	Metal absorbing plant
Ni	Eruca sativa,Heliantus annus
Zn	Erusa sativa, Atriplex sp., Heliantus annus, Sorghum sp., Malva sp., Poplous spp., Teucrium polium, Hypecum pendulum, Hordeum vulgare
Cu	Heliantus annus, Alpha alpha, Hordeum vulgare, Avena sativa, Sorghum sp.
Pb	Chenopodium album, Erusa sativa, Heliantus annus, Wheat (disambiguation), Poplous spp., Amaranthus radretroflxus
Cd	Sorghum sp., Erusa sativa, Poplous spp., Amaranthus radretroflxus, Hordeum vulgare, Avena sativa, Heliantus annus,Vulgare
V, Co, Mo	No plant Species has been recommended

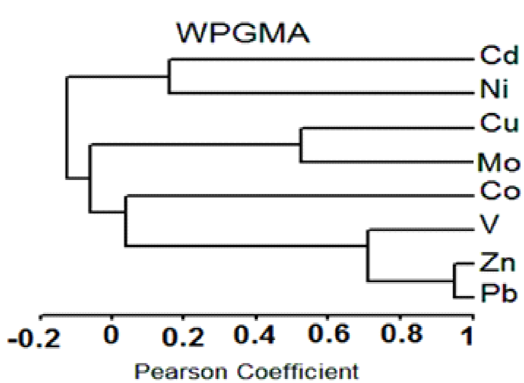

Fig. 2: Cluster analysis amongst Metals

Given the climate conditions and floristic list of the studied area, the plants in Table 7 are recommended for cleaning-up the existing metals.

Despite high concentration of Vanadium, Cobalt and Molybdenum in the soils of the area, no local plants has been approved for monitoring of these elements yet.

CONCLUSION

Vast oil fields in southern Iran are known as one of controversial subjects in contamination with heavy metals. In this study, oil fields' soils of Ahvaz city (Ab-Teymour) were chemically analyzed in order to determine the concentration of eight heavy elements and intensity of contamination. The results show that concentration of studied metals is higher than earth's crust mean values. These highly polluted areas require methods such as phytoremediation more than ever. Except for V, Co and Mo, local plant species can be effectively used as bio-remediation tool. Therefore, further investigation is needed to know about the plant species that could handle V, Co and Mo contamination from Ab-Teymour soil. It is also necessary to control the dispersion of pollutants from its sources. This can include flares as well as oil drilling activities. Thus, introduction of advanced technologies must be carefully studied for this purpose.

CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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AUTHOR (S) BIOSKETCHES

Karbassi, A.R., Ph.D., Associate Professor, Graduate Faculty of Environment, University of Tehran, P.O. Box 1455-6135, Tehran, Iran. Email: *akarbasi@ut.ac.ir*

Tajziehchi, S., Ph.D., Assistant Professor, Department of Environmental science, Science & Research Branch, Islamic Azad University, Tehran, Iran. E-mail: *Tajziehchi.sanaz@gmail.com*

Afshar, S., MSc., Department of Environmental Science, Islamic Azad University, Ahvaz, Khuzestan, Iran. Email: *Afshar@yhaoo.com*

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