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Original Article

Investigation of heavy metals and petroleum hydrocarbons pollution source in agricultural lands in the south of Tehran

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Introduction: As a result of human development and population growth, there is a corresponding need for essential resources for humans. Industrial and agricultural activities have greatly polluted most agricultural lands. Petroleum compounds and heavy metals, both are common pollutants of soils that have been irrigated by untreated wastewater, which pose a potential threat to the environment. Soil pollution of the agricultural lands will lead to a decline in cultivation and finally decrease food production. Agricultural lands in the southern part of Tehran are being irrigated with untreated wastewater for more than 30 years to produce a variety of vegetables, legumes, and cereals.

Material and methods: In this study, the concentration of heavy metals and petroleum compounds were determined in 83 sampling points at two depths (0 to 30 and 30 to 60 cm). The study area was divided into two separate zones, in which 44 points were located in zone 2 and 39 points were located in zone 1. Petroleum hydrocarbons and heavy metals, As, Cd, Co, Cr, Cu, Ni, Pb, V, and Zn, were measured at the top and subsoil by MOOPAM and ICP-AES methods, respectively. ArcGIS and R software were applied to create distribution maps of the pollutants and some statistical analyses.

Results and discussion: The results showed that the soil of agricultural land in the area is highly polluted, as the concentration of Cr, Pb, Co, and Ni has exceeded the standard level e.g. 0.22 mg/kg for Cd and 620 mg/kg

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for Pb. The concentration of petroleum compounds in wastewater irrigated lands in both top and subsoil was higher than that of groundwater irrigated lands. High levels of As, Cr, Cu, Pb, and Zn were observed in groundwater irrigated lands compared with wastewater irrigated lands. Cr and Pb were almost 89 and 8 times higher than the standard limit of agricultural lands in Iran, respectively. The spatial distribution map of petroleum compounds showed that only the southeast of the area falls into the heavily contaminated class. The distribution map of heavy metals also revealed that most parts of the studied area fall into the heavily contaminated class. Soil organic matter has more concentration in the topsoil.

Conclusion: Overall, the south of the studied area has been more affected by wastewater irrigation, agrochemicals and groundwater pollution in terms of heavy metals and petroleum compounds. Our study revealed various anthropogenic pollution sources, which are mostly from wastewater irrigation and the application of agrochemicals. Therefore, a management plan should be applied to the agricultural lands of this region to control and reduce the level of contamination.

Keywords: Agricultural lands, Pollution, Heavy metals, Petroleum hydrocarbons, Wastewater irrigation**.**

Introduction

Nowadays, development and population growth have led to increasing demand for supplying human vital resources. Consequently, industrial and agricultural activities have greatly polluted most agricultural lands (Telysheva *et al.,* 2001). As a result of soil pollution, the environment will deteriorate. Using wastewater for irrigation causes deterioration and accumulation of contaminants like petroleum hydrocarbons and heavy metals in groundwater, which raises concern about public exposure to contaminants in the environment (Chen *et al.,* 2005; Toth *et al.,* 2016). Due to the soil pollution of these productive lands, the decline in cultivation, and food production is undeniable. Agricultural lands in the southern part of Tehran have been irrigated with untreated wastewater for more than 30 years to produce a variety of vegetables, legumes, and cereals (Bayat *et al.,* 2015). On the other hand, the excessive use of agrochemicals and manure by the farmers has risen the possibility of high levels of heavy metals in the soil, as some fertilizers and pesticides contain heavy metals such as Cd, Hg, Pb, and Zn. In addition, the placement of the Tehran oil refinery and storage tanks close to the agricultural land has caused oil pollution in the groundwater. The existence of some heavy metals such as lead and cadmium in the soil can cause biological magnification and enter into the food chain (Wong *et al.,* 2002; Ma *et al.,* 2005). The uptake of carcinogenic hydrocarbons and heavy metals through the soil-to-root system and their accumulation in plant tissues has attracted much attention, particularly for food crops cultivated on wastewater irrigated soils (Zhang *et al.,* 2017). Such compounds are considered persistent organic pollutants (POPs) and are of high environmental and human health concerns. Excessive accumulation of such nondegradable pollutants in soils and plants may pose risks to humans and ecosystems through direct ingestion or contact with contaminated soils, food chains, and drinking of contaminated groundwater.

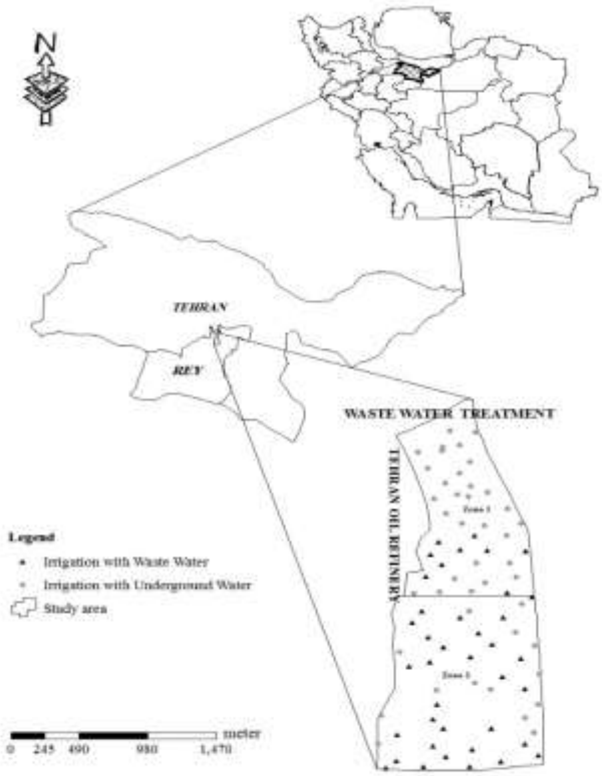
Several previous studies related to petroleum compounds have reported sites polluted by oil refinery activities as well as land irrigation with untreated urban wastewater (Bayat *et al.*, 2015; Bayat *et al.*, 2016). Ravankhah *et al.* (2018) studied the concentration and health risks of heavy metals in surface soil of Kashan city and reported that the soil is polluted by heavy metals due to industrial activities. Wu *et al.* (2018) reported serious risks for Cd, Hg, Pb, and moderate risk for As in agricultural lands in Southwest China. Determining the distribution of hazardous compounds is the key factor in managing such pollutants in the environment. It helps scientists in defining the areas where risks are high and then helps decision-makers in identifying locations where remediation efforts should be focused.

The main objective of this study is to find the area with a high degree of pollution and also monitor the heavy metals and petroleum compounds in agricultural lands in the southern part of Tehran, in terms of accumulation and migration of these hazardous materials in the soil. The research may also be useful in the formulation of strategic sustainable agriculture in the region. The study does not cover aspects like the bioavailability of elements by various plant species.

Material and methods

The study area

The study area is located in Ray city, southeast of the Tehran Oil Refinery, Tehran, Iran. Fig. 1 shows the location of the study area, as well as the sample points. The area is about 2,000 ha (latitude: 35° 49′ to 35° 57′N, longitude: 51° 43′ to 51° 46′ E).



شکل ۱- منطقه مورد مطالعه و نقاط نمونه‌برداری شده

Fig. 1- Study area and sampling points

Soil sample collection and preparation

A total of 166 soil samples were collected in September 2012 at depths of 0–30 cm (depth 1; topsoil) and 30–60 cm (depth 2; subsoil) using systematic random sampling. The study area was divided into two separate zones; zone 1 and 2. Then the region was gridded using ArcGIS 9.3 using the same number of pixels (317×317m). The center of each square was chosen as the sampling point (39 sampling points from zone 1 and 44 from zone 2). Sampling was performed at each point at both depths 1 and 2. Each sampling point represents an average of 10 ha. The weather was almost sunny and no rain occurred during the sampling period. After determining the point positions, the soil samples were collected (roughly 1 kg) and were pooled in an aluminum sheet, and packed in a polyethylene bag. These samples were immediately transferred to the laboratory and air-dried at 25 °C for organic matter and heavy metals analysis and freeze-dried for total petroleum hydrocarbons (TPHs) analysis. They were then ground and sieved through no. 30 mesh to test for organic matter (Ryan *et al.*, 2007), and no. 230 mesh to test for TPHs and heavy metals (MOOPAM, 1999).

Analysis of samples

An Agilent 7890A GC-FID and a splitless injector were used to determine the TPHs concentrations. Separation was done in a fused silica capillary column (HP-5, 30 m, 0.32 mm ID, 0.25µm film thickness). High-purity (99.999%) nitrogen was used as the carrier gas at a flow rate of 1 ml.min$_{-1}$. Calibration graphs were constructed by plotting the peak area against the injected concentration every 3 d; in all cases, a linear relationship at r^2>0.99 was obtained.

To analyze heavy metals, the soil samples were ground down to 75 micrometers. All analyzed elements (As, Cd, Co, Cr, Cu, Ni, Pb, V, and Zn) were determined by ICP-AES (Varian, 715-ES) applying ultrasonic nebulizer CETAC (ICP/U-5000AT) for better sensitivity (Jusufi *et al.*, 2016).

Soil and Plant Analysis Laboratory Manual (Ryan *et al.*, 2001) as well as the Standard and *Walkley-Black* method were used to analyze the organic materials of the soil.

Preparation of spatial distribution maps

To create spatial distribution maps of hazardous materials, the Inverse Distance Weighting method in the ArcGIS 10.4 environment was used. To create these maps, heavy metals and aromatic compounds concentrations were used.

Statistical analysis

Statistical analyses were performed using R software (R Development Core Team, 2014). Statistical tests such as median, range, Spearman correlation, and Mann-Whitney test were employed to find the differences between variables and treatments.

Results and discussion

The soil heavy metal and TPHs assessment showed a quite diverse pattern both for top and subsoil distribution. Table 1 presents the median and range of parameters at two depths. The highest value of organic material (OM) on the surface layer was 3.86% and with regards to the soil type of this area, the amount of OM in the studied area substantially high. This is mostly because of using manure in the area. The amount of OM was higher in the topsoil in both zones compared to the subsoil. Our results were in agreement with Huang *et al*. (2007), who found that long-term fertilization acts to enhance the OM content of agricultural land. There seems to be no special correlation between soil organic material and TPHs in the soil. Percentages of organic material also reveal that zone 2 has less organic matter and there is a significant difference between the two zones, in terms of organic material.

TPHs concentration

Data related to TPHs showed that the concentration of these variables has been detected up to 72 mg/kg and 54.8 mg/kg for top and subsoil, respectively. Also, the amount of TPHs in the topsoil more than that of the subsoil. None of the samples (both top and subsoil) were below the limit of detection, and this shows that agricultural lands are polluted. Groundwater is being polluted with petroleum compounds due to the leakage of storage tanks of the Tehran oil refinery in the region (Anonymous, 2008). On the other hand, agricultural lands are irrigated with urban untreated wastewater (Hani *et al.*, 2010). So, irrigation with untreated wastewater and polluted groundwater is more likely to be the reason for the high concentration of TPHs in the soil of the area. Our findings were similar to some previous studies that more TPHs in surface soils are attributed to frequent human activities (Zhang *et al.*, 2017). Statistical analysis showed a significant and very clear difference between the TPHs concentration in the lands irrigated with untreated wastewater and irrigated with groundwater. A comparison of TPHs concentration in the lands irrigated with untreated wastewater and groundwater indicates that the wastewater irrigated lands have a higher concentration of TPHs. Tao *et al*. (2004) and Zhang *et al*. (2012) in China, by studying aromatic and aliphatic hydrocarbons in agricultural lands, reported the same results. Also, there was no significant difference between the top and subsoil in lands that were irrigated with wastewater in terms of TPHs, and it seems both soil layers was polluted as TPHs have migrated to the lower depth. Since oil compounds including aromatic and aliphatic compounds are inherently different, they can cause health problems for the people in the region. Some aromatic compounds are known as human carcinogens and have been classified by the Environmental Protection Agency (Magi *et al.*, 2002; Yan *et al.*, 2004; Qiao *et al.*, 2006; Hao *et al.*, 2007; Hung *et al.*, 2011; Gonul and Kucuksezgin, 2012). Mann-Whitney test showed that there is no significant difference for the TPHs at both top and subsoil in the whole area, whereas a significant difference between the two zones is obvious in terms of TPHs. The interpolation map of TPHs showed that the southern parts of the region are more polluted. Farmlands in the south of the region have been more irrigated with urban untreated wastewater. Moreover, polluted groundwater due to leakage of the oil refinery caused the agricultural land to be more polluted. The correlation results (Table 2) indicated that there is no correlation between TPHs and soil OM and this is broadly consistent with Chen *et al*. (2005) and Ma *et al*. (2005), who reported similar results with a lack of correlation between petroleum compounds and organic materials. There is a significant and positive correlation between TPHs and nickel, one of the indices used in tracking oil in the environment (Klemt *et al.*, 2020), at the top and subsoil (r=0.33 and 0.22, respectively), which indicates the role of the refinery in polluting the lands. TPHs are found to be negatively correlated with chromium (Cr), copper (Cu), lead (Pb), and zinc (Zn) in topsoil as well as in second depth with arsenic (As) and zinc (Zn). There is no significant relationship between this variable and other metals.

جدول ۱- آمار توصیفی (محدوده تغییرات و میانه) متغیرهای مورد بررسی در دو عمق

Table 1. Descriptive statistics of the studied variables at two sampling depths

پارامترها Parameters	محدوده تغییرات Range		میانه Median										استاندارد فلزات سنگین در زمین‌های کشاورزی Standard threshold of HMs in agricultural lands of Iran (mg/kg)
			کل منطقه Total Area		زمین‌های آبیاری شده با آب چاه Groundwater irrigated lands		زمین‌های آبیاری شده با فاضلاب Wastewater irrigated lands		منطقه ۱ Zone I		منطقه ۲ Zone II		
	0-30 cm	30-60 cm	0-30 cm	30-60 cm	0-30 cm	30-60 cm	0-30 cm	30-60 cm	0-30 cm	30-60 cm	0-30 cm	30-60 cm	
As (mg/kg)	2.4 -12.6	2.4-16.4	6.86	8.15	7.4	8.64	6.28	7.61	6.07	7.47	7.57	8.75	40
Cd (mg/kg)	0.22-0.6	0.22-0.5	0.20	0.26	0.26	0.26	0.25	0.26	0.27	0.27	0.26	0.25	5
Co (mg/kg)	5-65	11-74	12.74	13.63	12.5	14.16	13.07	13.07	12.28	13.13	13.16	14.09	50
Cr (mg/kg)	26-168	56-178	88.63	85.16	97.8	89.44	78.8	80.33	110.31	94.87	69.43	76.57	2
Cu (mg/kg)	13-85	24-74	40.51	38.27	46	42.7	34.2	33.5	53.64	47.21	28.89	30.36	200
Ni (mg/kg)	21-177	37-98	46.01	47.5	45.7	46.74	46.25	48.25	43.13	44.18	48.57	50.43	110
Pb (mg/kg)	8-509	9-620	29.3	86.54	34.2	146.6	24.5	22	40.92	32.26	19	134.66	75
V (mg/kg)	37-107	78-113	91.15	94.79	90	93.76	92.67	95.1	87.44	93.38	94.45	96.05	200
Zn (mg/kg)	36-246	61-189	111.51	99.03	123.95	108.27	98.15	89.1	143.13	117.28	83.5	82.86	500

ادامه جدول ۱- آمار توصیفی (محدوده تغییرات و میانه) متغیرهای مورد بررسی در دو عمق

Table 1. Cont. Descriptive statistics of the studied variables at two sampling depths

پارامترها Parameters	محدوده تغییرات Range		میانه Median: کل منطقه Total Area		زمین‌های آبیاری شده با آب چاه Groundwater irrigated lands		زمین‌های آبیاری شده با فاضلاب Wastewater irrigated lands		منطقه ۱ Zone I		منطقه ۲ Zone II		استاندارد فلزات سنگین در زمینهای کشاورزی Standard threshold of HMs in agricultural lands of Iran (mg/kg)
	0-30 cm	30-60 cm	0-30 cm	0-30 cm	30-60 cm	0-30 cm	0-30 cm	30-60 cm	0-30 cm	0-30 cm	30-60 cm	0-30 cm	
TPHs (mg/kg)	0.25-72	0.5-54.8	13.48	12.86	11.2	8.88	15.86	17.15	7.29	8.8	18.97	16.48	-
OM (%)	0.16-3.86	0.13-3.6	1.9	1.35	2.01	1.22	1.77	1.5	2.14	1.3	1.68	1.4	-

جدول ۲- همبستگی اسپیرمن بین فلزات سنگین، ترکیبات نفتی و ماده آلی در دو عمق

Table 2. The Spearman correlation among HMs, TPHs, and OM at the two depths

Parameters	As	Cd	Co	Cr	Cu	Ni	Pb	V	Zn	TPHs	OM
As	1	$0.26^{*\,a}$	$0.22^{*\,a}$	$-0.19^{ns\,a}$	$-0.21^{*\,a}$	$0.40^{**\,a}$	$-0.19^{ns\,a}$	$0.37^{**\,a}$	$-0.23^{*\,a}$	$-0.12^{ns\,a}$	$-0.26^{*\,a}$
Cd	$0.29^{**\,b}$	1	$0.06^{ns\,a}$	$0.15^{ns\,a}$	$0.30^{**\,a}$	$0.07^{ns\,a}$	$0.24^{*\,a}$	$0.01^{ns\,a}$	$0.21^{*\,a}$	$-0.17^{ns\,a}$	$0.01^{ns\,a}$
Co	$-0.05^{ns\,b}$	$-0.03^{ns\,b}$	1	$-0.06^{ns\,a}$	$-0.21^{ns\,a}$	$0.71^{**\,a}$	$-0.27^{*\,a}$	$0.84^{**\,a}$	$-0.16^{ns\,a}$	$0.19^{ns\,a}$	$-0.21^{ns\,a}$
Cr	$-0.02^{ns\,b}$	$0.20^{ns\,b}$	$-0.09^{ns\,b}$	1	$0.72^{**\,a}$	$-0.13^{ns\,a}$	$0.82^{**\,a}$	$-0.13^{ns\,a}$	$0.79^{**\,a}$	$-0.40^{**\,a}$	$0.29^{**\,a}$
Cu	$-0.16^{ns\,b}$	$0.20^{ns\,b}$	$-0.05^{ns\,b}$	$0.62^{**\,b}$	1	$-0.19^{ns\,a}$	$0.92^{**\,a}$	$-0.23^{*\,a}$	$0.94^{**\,a}$	$-0.44^{**\,a}$	$0.48^{**\,a}$
Ni	$0.36^{**\,b}$	$0.05^{ns\,b}$	$0.14^{ns\,b}$	$0.02^{ns\,b}$	$-0.36^{**\,b}$	1	$-0.31^{**\,a}$	$0.82^{**\,a}$	$-0.14^{ns\,a}$	$0.22^{*\,a}$	$-0.08^{ns\,a}$
Pb	$-0.08^{ns\,b}$	$-0.04^{ns\,b}$	$0.98^{**\,b}$	$-0.08^{ns\,b}$	$-0.01^{ns\,b}$	$0.06^{ns\,b}$	1	$-0.32^{**\,a}$	$0.92^{**\,a}$	$-0.51^{**\,a}$	$0.40^{**\,a}$
V	$0.41^{**\,b}$	$0.11^{ns\,b}$	$-0.03^{ns\,b}$	$-0.13^{ns\,b}$	$-0.37^{**\,b}$	$0.55^{**\,b}$	$-0.13^{ns\,b}$	1	$-0.20^{ns\,a}$	$0.19^{ns\,a}$	$-0.23^{*\,a}$
Zn	$-0.04^{ns\,b}$	$0.29^{**\,b}$	$-0.06^{ns\,b}$	$0.78^{**\,b}$	$0.84^{**\,b}$	$-0.19^{ns\,b}$	$-0.03^{ns\,b}$	$-0.26^{*\,b}$	1	$-0.43^{**\,a}$	$0.48^{**\,a}$
TPHs	$-0.22^{*\,b}$	$-0.19^{ns\,b}$	$0.10^{ns\,b}$	$-0.11^{ns\,b}$	$-0.28^{ns\,b}$	$0.33^{**\,b}$	$0.08^{ns\,b}$	$0.11^{ns\,b}$	$-0.32^{**\,b}$	1	$0.21^{ns\,a}$
OM	$-0.13^{ns\,b}$	$0.06^{ns\,b}$	$-0.21^{ns\,b}$	$0.35^{**\,b}$	$0.11^{ns\,b}$	$-0.02^{ns\,b}$	$-0.15^{ns\,b}$	$-0.25^{*\,b}$	$0.22^{*\,b}$	$0.07^{ns\,b}$	1

*Significant at 0.05 percent, ** Significant at 0.01 percent, ns Not significant, a = 0-30 cm, b = 30-60 cm

جدول ۳- نتایج آزمون من-ویتنی بین دو عمق

Table 3. Results of the Mann-Whitney test between the top- and sub-soil

پارامترها Parameters		As (mg/kg)	Cd (mg/kg)	Co (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Ni (mg/kg)	Pb (mg/kg)	V (mg/kg)	Zn (mg/kg)	TPHs (mg/kg)	OM (%)
بین مناطق آبیاری شده با آب چاه و فاضلاب **Between ground water and wastewater irrigated lands**	**30-60 cm**	960^{ns}	923^{ns}	977^{ns}	905^{ns}	1213**	727^{ns}	1120*	649^{ns}	1218**	369**	673^{ns}
	0-30 cm	1064**	1059^{ns}	604*	1234**	1254**	814^{ns}	1196**	688^{ns}	1285**	554**	1038^{ns}
منطقه آبیاری شده با فاضلاب **Wastewater (2 depths)**		541*	796^{ns}	831^{ns}	60^{ns}	764^{ns}	631^{ns}	826^{ns}	565*	845^{ns}	722^{ns}	976^{ns}
منطقه آبیاری شده با آب چاه **Groundwater (2 depths)**		666*	1037^{ns}	563**	1128^{ns}	1022^{ns}	857^{ns}	1085^{ns}	613**	1183*	1006^{ns}	1519**
منطقه ۲ بین دو عمق **Zone II (2 depths)**		603**	958^{ns}	1054^{ns}	565**	895^{ns}	772^{ns}	819^{ns}	854^{ns}	973^{ns}	1081^{ns}	1226*
منطقه ۱ بین دو عمق **Zone I (2 depths)**		591^{ns}	837^{ns}	373**	1016*	1006*	675^{ns}	1074**	324**	1093**	717^{ns}	1248**
بین دو منطقه در عمق دوم **Between 2 zones (30-60 cm)**		617*	723^{ns}	803^{ns}	100^{ns}	1595**	275**	1406**	573**	1518**	378**	828^{ns}
بین دو منطقه در عمق اول **Between 2 zones (0-30 cm)**		585*	770^{ns}	324**	1586**	1680**	339**	1697**	262**	1657**	267**	1163**
کل منطقه **Total area (2 depths)**		2404**	324^{ns}	2704*	3578^{ns}	3593^{ns}	2996^{ns}	3802^{ns}	2418**	3964^{ns}	3508^{ns}	4942**

^{ns} Not Significant

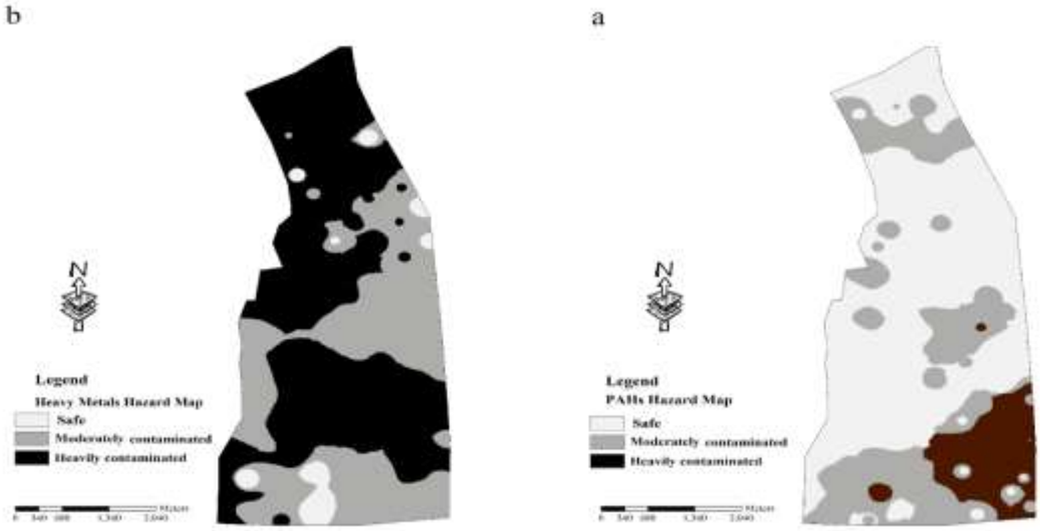
Heavy metals

The results of the analyses of all heavy metals (HMs) were summarized in Table 1. The observed average concentration of Cr in all samples and both depths; Pb, Ni, and Co at top soil exceeded the standard limits of Iran values which are presented in Table 1. On the other hand, As, Cd, Cu, V and Zn were below the standard limits of Iran. Zn, Ni, Cu, and Cd were higher in topsoil whereas others were higher in the subsoil. Cd had the lowest value concentration (0.22 mg/kg) in both the top and subsoil, while the highest contents were recorded for Pb (620 mg/kg) in the subsoil. Cr and Pb were almost 89 and 8 times higher than the standard limits of the agricultural lands of Iran, respectively. Pb is one of the most dangerous HMs and a high concentration of that can accumulate in agricultural plants, because plants have the ability to capture and store it (Bigdeli and Seilsepour, 2008). Although Cd had the lowest concentration in all HMs, its concentration can be accumulated overtimes because of using various agrochemicals, fertilizers, and pesticides that contain heavy metals such as Cd. For example, Cd is found predominantly in phosphatic fertilizers because Cd is commonly present as an impurity in phosphatic rocks (Huang *et al.*, 2007). High levels of HMs in agricultural lands of the region imply the accumulation of HMs in soil due to sources such as using untreated wastewater and oil refinery activities. Bigdeli and Seilsepour (2008) reported a high accumulation of heavy metals (Pb, Zn, and Cd) in agricultural products in an area of land irrigated with sewage. The median of metals showed some HMs in the groundwater irrigated lands have accumulated more in the soil in comparison with wastewater irrigated lands, which reflects the presence of contaminants in the groundwater of the region. The results also showed that the concentration of metals in zone 1 is higher than those in zone 2. As, Co, Pb, and V have much more concentration in the subsoil and probably have a higher risk in terms of groundwater and drinking water pollution.

Co, As and V indicate significant differences between the two depths ($pr<0.01$), while other metals do not show significant differences. Between the two zones, there are significant differences among heavy metal compounds at both depths (except Cd at topsoil, and Cd, Cr, and Co at subsoil). In zone 1 As, Cd, and Ni and in zone 2 all metals except As and Cr did not show a significant difference between the two depths. In terms of irrigation water, in groundwater irrigated lands As, Co, V, and Zn and in wastewater irrigated lands, As and V illustrated a significant difference between top and subsoil. From Table 3, most metals in the surface layer in the areas irrigated with groundwater showed significant differences with the lands irrigated with untreated wastewater. Besides, there was no significant difference between top and subsoil for most of the metals in the lands irrigated with wastewater which reflects the impact of land plowing in the migration of HMs to the deep soil.

Spatial distribution of hazardous materials

The spatial distribution (Fig. 2) of hazardous HMs and TPHs was established in three classes according to the standard threshold of the agricultural land of Iran. The maps were created only for the topsoil. The interpolation map of petroleum compounds (Fig. 2a) showed that most parts of the area fell into the safe class. According to Fig 2, zone 2, compared to zone 1, contains highly polluted areas. Carcinogenic petroleum compounds are highest in the southeast of the studied region. Moreover, the statistical analysis also indicated that the concentration of TPHs in zone 2 was much more than in zone 1 at both sampled depths. The spatial distribution map (Fig. 2b) showed that HMs in both zones fell into the heavily contaminated class which is remarkably risky and dangerous. The enrichment of these metals in the area is probably caused by human activity in association with the oil refinery. Our results are in accordance with other research in Iran and other countries (e.g., Huang *et al.*, 2007; Parizanganeh *et al.*, 2010; Nekoeinia *et al.*, 2016; Wu *et al.*, 2018; Ravankhah *et al.*, 2018). Agricultural lands in this area are the main source of vegetables' supply in Tehran city (Hani *et al.*, 2010); hence, HMs can pose a risk to people, who consume vegetables and other cultivated products. Irrigation with untreated wastewater and polluted groundwater over thirty years has led to the accumulation of HMs and TPH in agricultural soils. Li *et al.* (2007) also reported the same results regarding the accumulation of hazardous materials due to irrigation with untreated wastewater in agricultural lands. Previous studies in the region (Anonymous, 2008; Hani *et al.*, 2010) have shown that besides the contamination of soil and plants, animal milk has also been contaminated with HMs. Since HMs and some petroleum hydrocarbons such as aromatics are persistent in the environment, they can be accumulated in animals' and plants' tissue, passing from one to the next through the food chain. As a result of the risk of cancer or genetic mutations in animals and humans will increase (Chandra *et al.*, 2013). Although other studies have shown that the contamination levels of TPHs are higher in the northern part of the studied area, in this study it was found that the southern parts of the area have the highest TPHs pollution.



شکل ۲- نقشه پهنه‌بندی ترکیبات نفتی و فلزات سنگین در منطقه مورد مطالعه

Fig. 2- Spatial distribution of TPHs (a) and HMs (b) in the studied area

Conclusion

The present study examined the distribution of HMs and TPHs contents in topsoils and subsoils of the agricultural lands in the south of Tehran city, Iran. The concentration of measured variables indicated that the immense majority of agricultural lands in the studied area can be considered as heavily polluted, so the implementation of a special management program is necessary to control and reduce pollution in the area. While TPHs have more concentration in the topsoil, HMs polluted both the top and subsoil. Hydrocarbons accumulation in the topsoil can be absorbed by cultivated plants, resulting in bioconcentration and biomagnification. Besides, a higher concentration of HMs can lead to underground water pollution in terms of HMs in the long run. Spatial distribution maps of the variables showed that almost all parts of the area fell into the heavily contaminated class and may pose a risk to wildlife and human populations as well in the area. Irrigation with untreated wastewater has more impact on TPHs accumulation in the agricultural lands in the region as it contains higher concentrations of hazardous materials. Many of these compounds are dangerous and carcinogens and may cause irreparable damage to the population. Since almost all of the studied area has a risk for people's health, we propose a monitoring program that simultaneously considers TPHs and HMs in irrigation water, soil, air, plants, animals, and people for hazardous substances. Demonstrating the role of each of these sources on hazardous pollution in the region is critical. Our work provides useful information for other researchers to address sampling from polluted soil in the vicinity of oil refineries and also farmlands that are irrigated with wastewater to monitor the hazardous material and to correct their sampling points.

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مقاله پژوهشی

مطالعه آلودگی فلزات سنگین و ترکیبات نفتی در زمین‌های کشاورزی جنوب شهر تهران

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سابقه و هدف: به‌دلیل توسعه و رشد جمعیت انسان، نیاز انسان به منابع ضروری افزایش یافته است. فعالیت‌های مربوط به صنایع و همچنین فعالیت‌های کشاورزی به‌طور گسترده‌ای زمین‌های کشاورزی را آلوده کرده است. ترکیبات نفتی و فلزات سنگین هر دو از آلاینده‌های رایج موجود در خاک‌هایی هستند که با فاضلاب تصفیه نشده آبیاری شده‌اند و سلامت محیط زیست را با خطر مواجه می‌کنند. آلودگی خاک زمین‌های کشاورزی می‌تواند سبب کاهش امکان زراعت، و در نهایت کاهش تولید غذا برای انسان شود. زمین‌های کشاورزی در جنوب شهر تهران تقریبا به مدت ۳۰ سال است که به وسیله فاضلاب تصفیه نشده برای تولید سبزیجات، غلات و حبوبات آبیاری می‌شوند.

مواد و روش‌ها: در این مطالعه غلظت فلزات سنگین و ترکیبات نفتی در ۸۳ نقطه نمونه‌برداری در دو عمق (صفر تا ۳۰ سانتی‌متری و ۳۰ تا ۶۰ سانتی‌متری) اندازه گیری شد. منطقه مورد مطالعه به دو ناحیه، ناحیه شماره ۱ و ناحیه شماره ۲، تقسیم شد که ۴۴ نقطه نمونه‌برداری در ناحیه شماره ۲ و ۳۹ نقطه نمونه‌برداری در ناحیه شماره یک قرار گرفت. هیدروکربن‌های نفتی و فلزات سنگین (آرسنیک، کادمیم، کبالت، کروم، مس، نیکل، سرب، وانادیم و روی) در لایه سطحی و عمقی اندازه‌گیری شدند. ترکیبات نفتی با روش استاندارد MOOPAM و فلزات سنگین نیز به روش ICP-AES مورد آنالیز قرار گرفتند. برای تهیه نقشه‌های پراکنش آلاینده‌ها از نرم افزار ArcGIS و برای آزمون‌های آماری از نرم افزار R استفاده شد.

نتایج و بحث: نتایج نشان داد که خاک زمین‌های کشاورزی در منطقه به شدت آلوده شده به‌طوری‌که غلظت کروم، سرب، کبالت و نیکل در خاک از میزان استاندارد تعیین شده تجاوز کرده است. محدوده تغییرات فلزات سنگین از ۰/۲۲ میلی‌گرم بر کیلوگرم برای کادمیم و ۶۲۰ میلی‌گرم بر کیلوگرم برای سرب متغیر بود. غلظت ترکیبات نفتی در زمین‌های آبیاری شده با فاضلاب خام، در سطح و عمق، بیشتر از غلظت آن در زمین‌های آبیاری شده با آب چاه بود. غلظت قابل توجهی از فلزات آرسنیک، کروم، مس، سرب و روی در زمین‌های آبیاری شده با آب چاه مشاهده شد. غلظت کروم و سرب به ترتیب تقریبا ۸۹ برابر و ۸ برابر بیشتر از حد استاندارد تعیین شده برای زمین‌های کشاورزی ایران بود. نقشه‌های پراکندگی ترکیبات نفتی نشان داد که قسمت جنوبی منطقه به شدت آلودگی بیشتری دارد. همچنین نقشه‌های پراکندگی فلزات سنگین مشخص کرد که کل منطقه آلودگی زیادی دارد. داده‌های مربوط به مواد آلی خاک نیز نشان دهنده غلظت بالاتر

مواد آلی در سطح خاک، در مقایسه با لایه عمقی، است.

نتیجه‌گیری: در کل غلظت ترکیبات نفتی و فلزات سنگین نشان داد که قسمت‌های جنوبی منطقه مورد مطالعه بیشتر تحت تاثیر آبیاری با فاضلاب تصفیه نشده، کودهای شیمیایی مورد استفاده در کشاورزی و آبیاری با آب چاه بوده است. این مطالعه نشان داد که منابع مختلف انسانی، به‌خصوص آبیاری با فاضلاب تصفیه نشده و به‌کارگیری کودهای شیمیایی، سبب آلودگی در زمین‌های کشاورزی منطقه شده است. بنابراین به‌کارگیری برنامه مدیریتی صحیح برای کنترل و کاهش این آلاینده‌های خطرناک در زمین‌های کشاورزی ضروری است.

واژه‌های کلیدی: آلودگی زمین‌های کشاورزی، فلزات سنگین، ترکیبات نفتی، آبیاری با فاضلاب.