



RESEARCH PAPER

Evaluation of Urban Soil Pollution: A Combined Approach of Toxic Metals and Polycyclic Aromatic Hydrocarbons (PAHs)

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Abstract

Overcrowded urban areas are exposed to quotidian loads of toxic metals and PAHs. Simultaneous analysis of mentioned pollutants in surface soil samples of a crowded urban area in Tehran City is considered in this study. A total number of 112 samples were collected from pollution hotspots including gas stations, construction sites, bus terminal and waste recovery centers in summer 2016. Total, anthropogenic and bioavailable concentrations of metals, cadmium, cobalt, chromium, copper, manganese, nickel, lead and zinc, as well as ecological risk index (RI) values were calculated. Rather than Cd, the concentration of other metals was not remarkably different from reference values. The descending order of anthropogenic and bioavailable fractions in metals was proved to be as follows: Cd (87.87%) > Cr (40.14%) > Ni (38.64%) > Pb (37.40%) > Co (8.42%) > Cu (7.98%) > Zn (5.57%) > Mn (3.94%) and Cu (6.84%) > Zn (6.47%) > Pb (3.98%) > Ni (3.97%) > Cr (1.99%) > Cd (1.98%) > Mn (1.45%) > Co (1.39%), respectively. The results of the RI values also indicated that around 80% of total samples lie within a considerable ecological risk level. The total concentration of 16 EPA-approved PAHs was detected to be within the range of 0.62 and 3.51 mg/kg. The majority of PAHs detected in all samples was those with relatively higher molecular weights (higher number of aromatic rings). Accordingly, the major source of PAHs in surface soils was determined to be petroleum/gas combustion due to traffic loads and heating systems. The synergy observed in spatial distribution of toxic metals and PAHs confirms relatively identical pollution sources and at the same time exacerbates the adverse effects on human and ecological health.

Article Highlights

- The combined approach of toxic metals and PAHs in urban soil analysis is considered.
- The source detection of PAHs in urban soils is determined.
- The source detection of toxic metals in urban soils is investigated.
- The fractionation of toxic metals in bulk, anthropogenic and bioavailable fractions is performed.

Keywords Toxic metals · PAHs · Soil pollution · Megacity · Risk index · Synergy

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Introduction

Industrialization and urbanization may impose adverse effects on concentration, mobility and bioavailability of toxic metals in soils (Afkhami et al. 2013; Karbassi et al. 2014; Nasrabadi et al. 2016). Soil pollution in metropolitan cities occurs as a result of various human activities that can be somehow considered complex. The degree of soil contamination might be tracked when the measurements are continuously compared with those of the previous years (Galitskova and Murzayeva 2016). Increase in the elemental

(Pb, Zn, Cu and Cd) contents of soils in the Eastern district of Moscow correlated with the growth of industrial and vehicles' emission over a time span of about 21 years (Kosheleva and Nikiforova 2016). The elemental concentration in urban soil may have adverse health effects on children and therefore it is proposed to find suitable playgrounds by means of GIS (Delahaye et al. 1998). An investigation of the hazardous metal contents of soil in 13 parks of urban areas revealed that shaded areas within parks contained higher concentrations than the open areas (Galušková et al. 2011). Furthermore, bioaccessibility and human health risk from heavy metals in exposed lawn soils from 28 urban parks in southern China's largest city, Guangzhou, were evaluated in a series of studies (Gu et al. 2016a, b; Gu and Gao 2018). Many studies have shown that the metal contents of soils within the urban area are higher in the vicinity of industrial parks than at other sites; nevertheless, wind could disperse the pollution within the whole area (Tume et al. 2008; Li et al. 2013; Lü et al. 2018). Some studies have reported the use of various methods including chemical stabilization, phytoremediation and microbial techniques to control pollution within soil columns (Saffari 2018; Usman et al. 2018; Adetitun et al. 2018; Abbaslou and Bakhtiari 2017). Treatment of soil pollution should take into account various aspects such as reducing health risk, furnishing cultivable soil and so on. These in turn depend on the chemistry and physical characteristics of soil (Wuana and Okieimen 2011).

In terms of organic pollutants, polycyclic aromatic hydrocarbons (PAHs) are among the most notorious compounds found in urban areas. Due to their hydrophobicity, PAHs have a high tendency to get adsorbed by particles and consequently be transported to remote distances from their source of generation (Tu et al. 2018). Being persistent due to their low biodegradation potential (Feng et al. 2016), a certain number of PAHs are also proved as carcinogens/mutagens (Kim et al. 2013). They may be easily exposed to humans directly through dermal (dusts in urban areas, soils in playgrounds, etc.) and inhalation routes. Indirect exposure is also inevitable through the digestion route when considering the entry of PAHs into the food chain (Li et al. 2015; Xia et al. 2015). Concerning concentration of PAHs have recently been detected in urban areas due to oil/coal combustion, traffic-related emissions, waste combustion and urban wastewater drainage in Kaohsiung City, Taiwan (Tu et al. 2018); Aracaju City, Brazil (Souza et al. 2018); Shanghai, China (Liu et al. 2016; Huang et al. 2017) and Guangzhou, China (Ke et al. 2017).

The main goals of this study are (1) to determine the total, bioavailable and anthropogenic concentrations of toxic metals, as well as 16 PAHs in surface soil samples collected from hotspots of an intensified urban district in Tehran City and (2) to find any probable coherence between the distribution pattern of toxic metals and PAHs.

Study Area

District 6 of Tehran municipality covers some of the most overcrowded areas in central to northern parts of the city. More than 8% of total urban trips evolve in this district whose surface area is around 3% of the total Tehran urban areas. Intensive road networks as well as administrative buildings, educational centers, commercial buildings, hospital and military land use are considered as the main reasons for such remarkable everyday commute demand (Fazeli et al. 2018). To consider the worst scenario of urban soil pollution due to traffic load, the sampling locations are selected in a way to have the maximal exposure. Accordingly, 14 sampling stations were selected, namely Valfajr CNG station (1), Yousefabad gas station (2), Beyhaghi bus terminal (3), Beyhaghi municipal waste recovery center (4), Beyhaghi CNG station (5), Valiasr St., Sae Park gas station (6), Chamraan and Ale-ahmad highways junction (7), Mirzaye Shirazi St., gas station (8), North Karegar St. gas station (9), Valiasr, Zartosht St., gas station (10), Valiasr Square, subway construction site (11), vicinity of Imam Khomeini hospital (12), Enghelab St., gas station (13) and Gharani St., gas station (14). Location details of sampling points as well as the location of District 6 in Tehran City and Iran are shown in Fig. 1.

Materials and Methods

Sampling Campaign

A total number of 112 surface soil samples (56 samples for detection of toxic metals and 56 samples for detection of PAHs) were collected from 14 stations. Soil samples were collected by a hand auger to a maximum depth of 50 cm. Four sub-samples (Z grid) from each station were collected and mixed to generate 28 composite samples for further analysis. Sampling campaign was performed in summer 2016. All plant and anthropogenic leftovers were removed before sampling was done by spiral auger. Samples for metal detection were kept in plastic bags, while those for PAHs detection were wrapped in aluminum foils.

Toxic Metal Detection

Samples for detection of metals were dried at room temperature and sieved through 63 μm mesh size for further analysis. To detect the total concentration of metals, 0.5 g of the sample was digested with a mixture of aqua regia (HNO_3 and HCl with a volumetric ration of 3:1) and

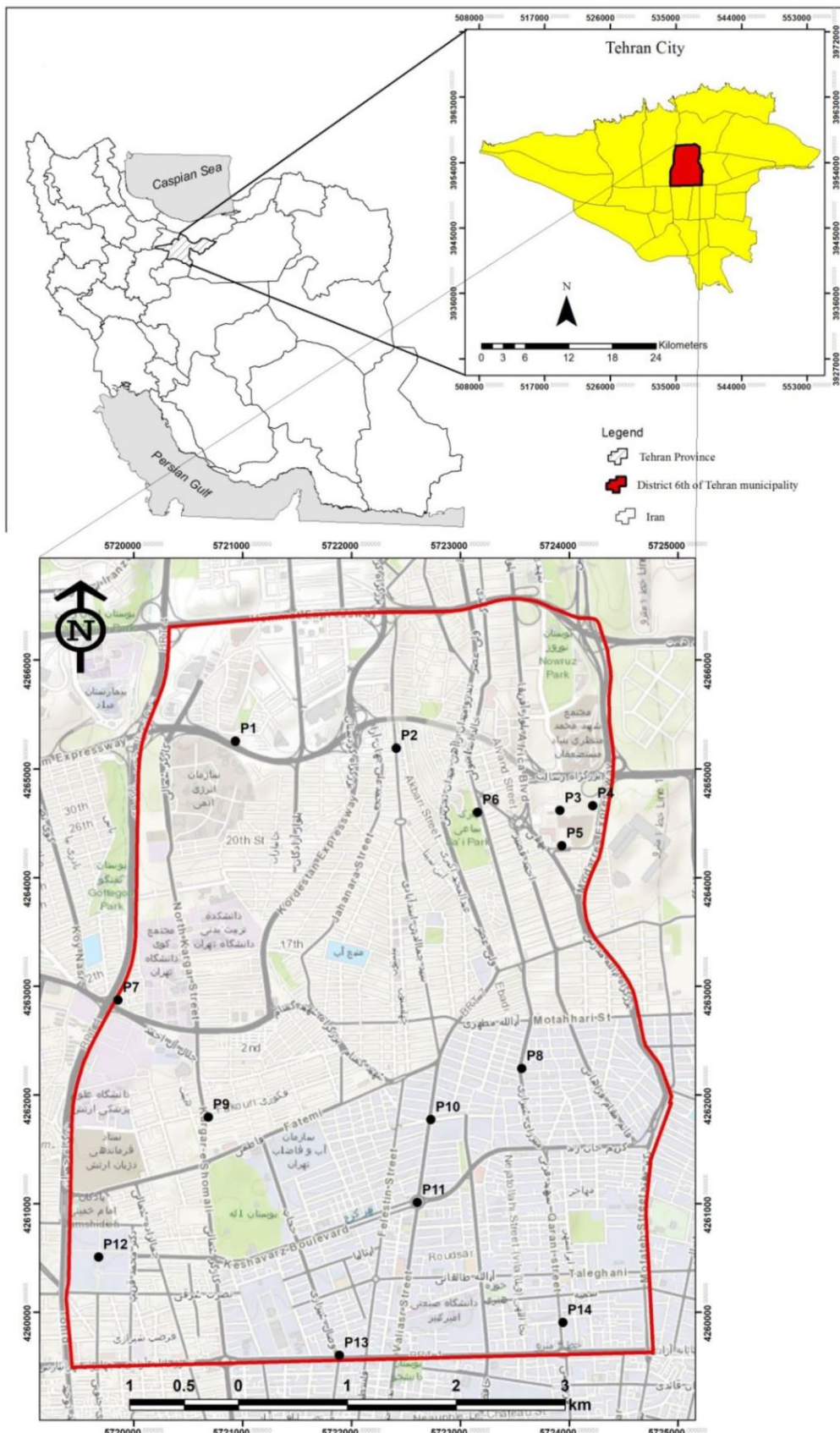


Fig. 1 Study area and surface soil sampling locations

Table 1 Total concentration of toxic metals in surface soil samples (mg/kg)

Station	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn
1	3.3	11	69	35	1033	23	25	20
2	4	10	94	46	899	23	35	64
3	3.7	10	59	37	1067	27	30	120
4	3	17	71	45	1046	20	47	54
5	3.5	16	35	32	771	18	32	70
6	3.1	8	62	49	892	19	27	26
7	4.1	16	76	52	924	21	28	65
8	3	19	66	30	944	32	32	50
9	4.5	9	66	57	1026	22	22	160
10	4.3	10	71	60	1019	24	27	70
11	3	14	74	53	970	19	38	35
12	3.1	11	66	54	985	21	32	50
13	4.9	16	53	40	774	19	25	100
14	3	20	78	37	1044	31	49	85
Max	4.9	20	94	60	1067	32	49	160
Min	3	8	35	30	771	18	22	20
Mean	3.61	13.36	67.14	44.79	956.71	22.79	32.07	69.21
SD	0.65	3.95	13.38	9.71	96.02	4.41	7.98	37.72
Earth crust ^a	0.1	20	100	50	950	80	14	75
Shale ^b	0.22	19	39	39	850	68	23	120
Background values ^c	0.45	11	25	37	444	43	23	63

^aAllaway (1995)^bTurekian and Wedepohl (1961) and Eghbal et al. (2019)^cFazeli et al. (2018)**Table 2** Anthropogenic concentration (in mg/kg) and share (percent of total concentration) of toxic metals in surface soil samples

Station	Cd		Mn		Pb		Cu		Co		Ni		Cr		Zn	
	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%
1	2.83	85.76	40.05	3.88	8.22	32.88	2.64	7.54	0.81	7.36	8.16	35.48	26.60	38.55	1.10	5.50
2	3.70	92.50	36.20	4.03	15.10	43.14	3.78	8.22	0.95	9.50	8.51	37.00	38.10	40.53	4.90	7.66
3	3.21	86.76	41.33	3.87	10.21	34.03	2.49	6.73	0.83	8.30	10.19	37.74	22.40	37.97	8.32	6.93
4	2.60	86.67	40.54	3.88	17.94	38.17	3.51	7.80	1.15	6.76	8.50	42.50	27.60	38.87	2.94	5.44
5	3.11	88.86	28.40	3.68	11.11	34.72	2.46	7.69	1.38	8.63	7.73	42.94	14.80	42.29	3.42	4.89
6	2.61	84.19	33.97	3.81	8.94	33.11	3.72	7.59	0.69	8.63	8.31	43.74	25.20	40.65	1.04	4.00
7	3.78	92.20	37.84	4.10	10.63	37.96	4.84	9.31	1.17	7.31	7.33	34.90	31.80	41.84	3.90	6.00
8	2.50	83.33	36.29	3.84	12.93	40.41	2.30	7.67	1.61	8.47	15.11	47.22	25.70	38.94	2.20	4.40
9	4.09	90.89	42.09	4.10	7.82	35.55	4.91	8.61	0.88	9.78	7.93	36.05	28.20	42.73	8.21	5.13
10	3.97	92.33	43.59	4.28	11.75	43.52	5.10	8.50	0.95	9.50	8.39	34.96	29.70	41.83	5.40	7.71
11	2.50	83.33	35.41	3.65	12.50	32.89	4.00	7.55	1.32	9.43	7.52	39.58	27.10	36.62	1.51	4.31
12	2.69	86.77	38.71	3.93	11.00	34.38	4.16	7.70	0.78	7.09	6.93	33.00	25.60	38.79	2.11	4.22
13	4.57	93.27	32.97	4.26	11.54	46.16	3.80	9.50	1.37	8.56	7.22	38.00	23.10	43.58	6.94	6.94
14	2.50	83.33	39.82	3.81	17.96	36.65	2.69	7.27	1.70	8.50	11.74	37.87	30.20	38.72	4.11	4.84
Min	2.50	83.33	28.40	3.65	7.82	32.88	2.30	6.73	0.69	6.76	6.93	33.00	14.80	36.62	1.04	4.00
Max	4.57	93.27	43.59	4.28	17.96	46.16	5.10	9.50	1.70	9.78	15.11	47.22	38.10	43.58	8.32	7.71
Mean	3.19	87.87	37.66	3.94	11.98	37.40	3.60	7.98	1.11	8.42	8.83	38.64	26.86	40.14	4.01	5.57
SD	0.70	3.75	4.10	0.19	3.16	4.37	0.96	0.77	0.32	0.97	2.20	4.06	5.24	2.07	2.47	1.28

Table 3 Bioavailable concentration (in mg/kg) and share (percent of total concentration) of toxic metals in surface soil samples

Station	Cd		Mn		Pb		Cu		Ni		Cr		Zn		Co	
	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%
1	0.06	1.94	14.50	1.40	0.92	3.68	2.33	6.66	0.84	3.65	1.33	1.93	1.36	6.80	0.16	1.46
2	0.09	2.25	12.29	1.37	1.39	3.97	3.31	7.20	0.89	3.87	1.91	2.03	4.62	7.22	0.13	1.30
3	0.07	1.92	16.57	1.55	1.10	3.67	2.48	6.70	1.05	3.89	1.22	2.07	6.73	5.61	0.14	1.40
4	0.05	1.67	13.69	1.31	1.31	2.79	2.91	6.47	0.92	4.60	1.31	1.85	3.39	6.28	0.25	1.44
5	0.06	1.71	11.97	1.55	1.19	3.72	2.11	6.59	0.84	4.67	0.80	2.29	4.46	6.37	0.23	1.44
6	0.06	1.97	12.38	1.39	1.02	3.78	3.18	6.49	0.73	3.84	1.21	1.95	1.51	5.81	0.11	1.31
7	0.09	2.10	14.46	1.56	1.34	4.79	3.87	7.44	0.69	3.29	1.64	2.16	5.13	7.89	0.24	1.49
8	0.05	1.67	12.16	1.29	1.12	3.50	2.10	7.00	1.02	3.19	1.26	1.91	3.14	6.28	0.27	1.42
9	0.10	2.22	17.39	1.69	1.12	5.09	4.20	7.37	0.90	4.09	1.39	2.11	9.50	5.94	0.12	1.32
10	0.09	2.07	16.59	1.63	1.52	5.63	3.95	6.58	1.11	4.63	1.47	2.07	5.28	7.54	0.15	1.50
11	0.06	1.83	12.55	1.29	1.39	3.66	3.11	5.87	0.87	4.58	1.18	1.59	2.11	6.03	0.18	1.29
12	0.06	1.97	12.88	1.31	1.16	3.63	3.51	6.50	0.69	3.29	1.22	1.85	2.94	5.88	0.13	1.21
13	0.12	2.45	12.81	1.66	1.43	5.72	3.41	8.53	0.79	4.16	1.36	2.57	6.72	6.72	0.25	1.57
14	0.06	2.00	13.26	1.27	1.02	2.08	2.35	6.35	1.19	3.84	1.16	1.49	5.31	6.25	0.26	1.32
Min	0.05	1.67	11.97	1.27	0.92	2.08	2.10	5.87	0.69	3.19	0.80	1.49	1.36	5.61	0.11	1.21
Max	0.12	2.45	17.39	1.69	1.52	5.72	4.20	8.53	1.19	4.67	1.91	2.57	9.50	7.89	0.27	1.57
Mean	0.07	1.98	13.82	1.45	1.22	3.98	3.06	6.84	0.90	3.97	1.32	1.99	4.44	6.47	0.19	1.39
SD	0.02	0.23	1.83	0.15	0.18	1.02	0.70	0.64	0.15	0.51	0.25	0.27	2.26	0.68	0.06	0.10

Table 4 Classification ladder for ecological risk index (RI) (Hakanson 1980)

Value	Ecological risk level
RI < 150	Low
150 < RI < 300	Moderate
300 < RI < 600	Considerable
RI > 600	Very high

HClO₄ (Chester and Hughes 1967). After filtration, the final volume was calibrated to 50 mL.

To determine the bioavailable and anthropogenic share of total metal concentrations, single step extraction schemes were considered (Hosseini Alhashemi et al. 2011). For anthropogenic share detection, 2 g of sieved samples was digested by 15 mL of 0.53 N HCl for half an hour and made to a final volume of 50 mL after filtration. To quantify the bioavailable share 10 g of sieved samples was digested for 30 min by a mixture of NaOH (1 N) and acetic acid at pH 5 and refluxed for a whole day. The metal contents (total, bioavailable and anthropogenic) in relevant solutions were analyzed by ICPAES. Duplicate/triplicate samples as well as certified reference material (MESS-1) measurement were performed to check the QC/QA of the procedures. The relative standard deviation of the results was less than 10%.

PAHs Detection

To detect PAHs, soil samples were freeze-dried and sieved to achieve the fraction < 63 µm. PAHs extraction scheme in this study is explained in detail by Liu et al. (2016). Concisely, 2 g of sieved samples was digested by a mixture of acetone and DCM (1:1, v/v) for 18 h using a Soxhlet apparatus at 65 °C. Purification was performed by a self-packet silica–alumina column. The final eluent was concentrated to 1 mL. The PAHs content in soil samples was analyzed by a Varian 3900 GC coupled with a Varian Ion Trap Saturn 2000 MS, with helium as the carrier gas at 1 mL/min flow. Quality assurance and control were checked according to the procedure suggested by Liu et al. (2016); two blanks were analyzed through which target compounds were determined to be under detection limits. Furthermore, a mixture of 16 EPA PAHs as a standard was added to each sample prior to extraction. The average recovery range of added standard was measured to be between 74.5% and 115%. The following 16 PAHs approved by USEPA were considered for analysis in this research: acenaphthene (AC), acenaphthylene (ACE), anthracene (AN), benzo[a]anthracene (BaA), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), benzo[g,h,i]perylene (BP), chrysene (CH), dibenzo[a,h]anthracene (DA), fluorine (FL), fluoranthene (FLU), indeno[1,2,3-cd]pyrene (IP), phenanthrene (PH), naphthalene (NA) and pyrene (PY).

Table 5 Values of toxic response factor (T_r) and risk factors (E_r) of toxic metals and ecological risk index (RI) of surface soil samples

Stations	Cd		Cr		Cu		Ni		Pb		Zn		RI
	Tr	Er	Tr	Er	Tr	Er	Tr	Er	Tr	Er	Tr	Er	
1	7.33	220.00	2.76	5.52	0.95	4.73	0.53	2.67	1.09	5.43	0.32	0.32	238.68
2	8.89	266.67	3.76	7.52	1.24	6.22	0.53	2.67	1.52	7.61	1.02	1.02	291.70
3	8.22	246.67	2.36	4.72	1.00	5.00	0.63	3.14	1.30	6.52	1.90	1.90	267.95
4	6.67	200.00	2.84	5.68	1.22	6.08	0.47	2.33	2.04	10.22	0.86	0.86	225.16
5	7.78	233.33	1.40	2.80	0.86	4.32	0.42	2.09	1.39	6.96	1.11	1.11	250.62
6	6.89	206.67	2.48	4.96	1.32	6.62	0.44	2.21	1.17	5.87	0.41	0.41	226.74
7	9.11	273.33	3.04	6.08	1.41	7.03	0.49	2.44	1.22	6.09	1.03	1.03	296.00
8	6.67	200.00	2.64	5.28	0.81	4.05	0.74	3.72	1.39	6.96	0.79	0.79	220.81
9	10.00	300.00	2.64	5.28	1.54	7.70	0.51	2.56	0.96	4.78	2.54	2.54	322.86
10	9.56	286.67	2.84	5.68	1.62	8.11	0.56	2.79	1.17	5.87	1.11	1.11	310.23
11	6.67	200.00	2.96	5.92	1.43	7.16	0.44	2.21	1.65	8.26	0.56	0.56	224.11
12	6.89	206.67	2.64	5.28	1.46	7.30	0.49	2.44	1.39	6.96	0.79	0.79	229.44
13	10.89	326.67	2.12	4.24	1.08	5.41	0.44	2.21	1.09	5.43	1.59	1.59	345.54
14	6.67	200.00	3.12	6.24	1.00	5.00	0.72	3.60	2.13	10.65	1.35	1.35	226.85
Max	10.89	326.67	3.76	7.52	1.62	8.11	0.74	3.72	2.13	10.65	2.54	2.54	345.54
Min	6.67	200.00	1.40	2.80	0.81	4.05	0.42	2.09	0.96	4.78	0.32	0.32	220.81
Mean	8.02	240.48	2.69	5.37	1.21	6.05	0.53	2.65	1.39	6.97	1.10	1.10	262.62
SD	1.44	43.16	0.54	1.07	0.26	1.31	0.10	0.51	0.35	1.73	0.60	0.60	42.77

Results

The metals considered for evaluation of toxicity in urban soil in this study are cadmium, cobalt, chromium, copper, manganese, nickel, lead and zinc. The concentration of each metal accompanied by comparison with earth crust, shale and background mean values is presented in Table 1. In comparison with background values (mean values of Tehran City circumference), all metals except for Ni showed higher contents. When compared with shale, apart from Co and Zn, other metals' mean values exceeded the reference values. In comparison with the mean earth crust values, however, only Cd and Pb had higher concentrations. Cd rather than other metals showed extremely high values (around 36, 17 and 8 times greater than those of mean earth crust, shale and background values, respectively).

The total metal concentration in soil samples consists of lithogenic (minerals content) and anthropogenic (caused by human impacts) fractions. Anthropogenic concentrations of metals are measured and shown in Table 2. Anthropogenic fractions may be classified into three distinct levels of high (Cd by more than 87%), medium (Cr, Ni and Pb by around 40%) and low (Co, Cu, Zn and Mn by less than 10%). Fossil fuel combustion derived from traffic and heating systems, material usage and abrasion/corrosions, lights, batteries, medical materials and domestic wastes are considered among anthropic sources of metal pollution in urban areas (Wu et al. 2019).

Both lithogenic and anthropogenic metal concentrations may contain bioavailable fractions which are easily uptaken

by biota. Accordingly, the higher the bioavailable fraction of a specific metal, the higher is the expected risk level of that metal. The bioavailable fractions of the total metal concentrations are shown in Table 3. Cu (6.84%) and Zn (6.47%) show the highest bioavailable fractions, while Mn (1.45%) and Co (1.39%) are considered as metals showing minimal values.

Index Analysis

To evaluate the toxicity level of metal pollutants in soil samples, ecological risk index (RI) is used. The formula for RI is as follows:

$$RI = \sum E_r^i, \quad (1)$$

where E_r^i is the relevant risk factor for contaminant (i) and is calculated as:

$$E_r^i = T_r^i \times C_f^i, \quad (2)$$

where T_r^i is the toxic response factor for contaminant (i) and is defined by dividing the metal concentration in soil by the background value. C_f^i is the contamination factor of each contaminant (30 for Cd, 5 for Pb, Cu and Ni, 2 for Cr and 1 for Zn). The higher the value of C_f , the higher is the risk exposed to the ecological environment by the contaminant. The classification of different RI values and relevant risk levels is shown in Table 4.

The values of toxic response factor (T_r), risk factors (E_r) and ecological risk index (RI) of different surface soil samples are calculated and shown in Table 5. According to the

Table 6 Concentration of PAHs in surface soil samples in mg/kg [total concentration (Σ PAHs), total carcinogenics (Σ CPAHs), low molecular weights (Σ 2–3 rings), high molecular weights (Σ 4–6 rings) and the ratio (LMW/HMW) are also included]

Station	AC ^a	ACE	AN	BaA	BaP	BbF	BkF	BP	CH	DA	FLU	FL	IP	NA	PH	PY	Σ PAHs	Σ CPAHs	Σ 2–3 rings	Σ 4–6 rings	LMW/HMW
1	0.0065	0.003	0.007	0.073	0.105	0.09	0.02	0.068	0.14	0.03	0.23	0.009	0.08	0.013	0.17	0.3	1.34	0.55	0.21	1.14	0.18
2	0.018	0.012	0.024	0.18	0.19	0.3	0.087	0.13	0.215	0.027	0.4	0.015	0.15	0.025	0.21	0.29	2.27	1.17	0.30	1.97	0.15
3	0.028	0.009	0.031	0.16	0.27	0.25	0.086	0.145	0.29	0.051	0.45	0.019	0.14	0.036	0.3	0.33	2.60	1.28	0.42	2.17	0.19
4	0.0036	0.0065	0.011	0.072	0.033	0.095	0.041	0.081	0.075	0.017	0.145	0.004	0.075	0.07	0.09	0.13	0.95	0.48	0.19	0.76	0.24
5	0.011	0.008	0.015	0.098	0.084	0.11	0.038	0.074	0.19	0.015	0.32	0.008	0.09	0.055	0.33	0.34	1.79	0.68	0.43	1.36	0.31
6	0.0055	0.0019	0.0099	0.061	0.105	0.095	0.025	0.059	0.087	0.014	0.115	0.006	0.056	0.004	0.106	0.175	0.93	0.45	0.13	0.79	0.17
7	0.014	0.013	0.023	0.155	0.14	0.13	0.046	0.085	0.32	0.034	0.29	0.011	0.165	0.085	0.22	0.51	2.24	1.08	0.37	1.88	0.20
8	0.0014	0.0037	0.0066	0.032	0.064	0.072	0.021	0.042	0.065	0.008	0.11	0.003	0.055	0.009	0.077	0.115	0.68	0.33	0.10	0.58	0.17
9	0.0083	0.018	0.028	0.19	0.22	0.255	0.098	0.17	0.16	0.048	0.34	0.01	0.17	0.014	0.185	0.24	2.15	1.16	0.26	1.89	0.14
10	0.021	0.006	0.026	0.14	0.22	0.2	0.079	0.125	0.23	0.037	0.36	0.021	0.165	0.034	0.28	0.44	2.38	1.11	0.39	2.00	0.19
11	0.0028	0.004	0.0081	0.04	0.05	0.077	0.027	0.051	0.07	0.011	0.085	0.003	0.044	0.009	0.06	0.08	0.62	0.33	0.09	0.54	0.16
12	0.0074	0.0084	0.015	0.075	0.097	0.215	0.048	0.105	0.15	0.025	0.16	0.004	0.098	0.011	0.091	0.14	1.25	0.72	0.14	1.11	0.12
13	0.017	0.024	0.046	0.235	0.26	0.435	0.1	0.245	0.36	0.041	0.43	0.017	0.22	0.045	0.37	0.66	3.51	1.70	0.52	2.99	0.17
14	0.0095	0.0055	0.014	0.059	0.078	0.105	0.029	0.068	0.085	0.016	0.13	0.007	0.068	0.013	0.085	0.155	0.93	0.45	0.13	0.79	0.17
Max	0.028	0.024	0.046	0.235	0.27	0.435	0.1	0.245	0.36	0.051	0.45	0.021	0.22	0.085	0.37	0.66	3.51	1.70	0.52	2.99	0.31
Min	0.0014	0.0019	0.0066	0.032	0.033	0.072	0.02	0.042	0.065	0.008	0.085	0.003	0.044	0.004	0.06	0.08	0.62	0.33	0.09	0.54	0.12
Mean	0.011	0.009	0.019	0.112	0.137	0.174	0.053	0.103	0.174	0.027	0.255	0.010	0.113	0.030	0.184	0.279	1.69	0.82	0.26	1.43	0.18
SD	0.008	0.006	0.011	0.064	0.080	0.107	0.030	0.056	0.098	0.014	0.130	0.006	0.055	0.025	0.104	0.168	0.86	0.42	0.14	0.73	0.05

^aAcenaphthene (AC), acenaphthylene (ACE), anthracene (AN), benzo[a]anthracene (BaA), benzo[a]anthracene (BaP), benzo[a]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), benzo[e]pyrene (BPe), chrysene (CH), dibenzo[a,h]anthracene (DA), fluorine (FL), fluoranthene (FLU), indeno[1,2,3-cd]pyrene (IP), phenanthrene (PH), naphthalene (NA) and pyrene (PY)

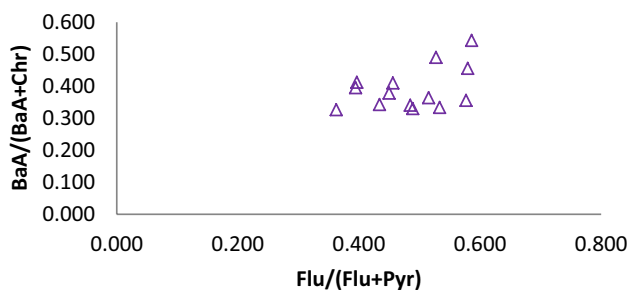


Fig. 2 Cross plot of BaA/(BaA + Chr) versus Flu/(Flu + Pyr) for surface soil samples

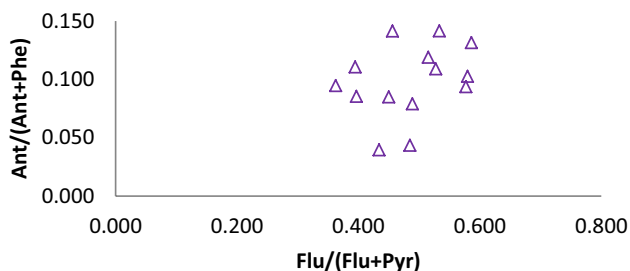


Fig. 3 Cross plot of Ant/(Ant + Phe) versus Flu/(Flu + Pyr) for surface soil samples

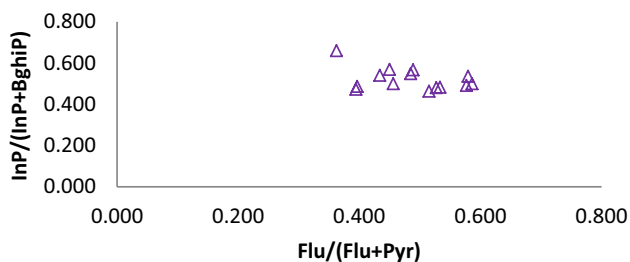


Fig. 4 Cross plot of InP/(InP + BghiP) versus Flu/(Flu + Pyr) for surface soil samples

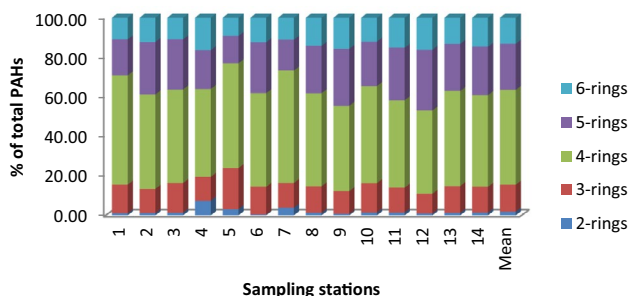


Fig. 5 Distribution pattern of low and high molecular weight (2–6 ring) PAHs in surface soil samples

classification ladder (Hakanson 1980), 3 samples (around 21% of the whole area) are categorized in the considerable risk level, while the other 11 samples remained within the moderate class.

As typical and ubiquitous pollutants in urban areas, PAHs were also considered for analysis in this study. The concentrations of 16 EPA-approved PAHs as well as the contents of carcinogenics (Monaco et al. 2017) including benzo[a]pyrene (carcinogenic), benzo[a]anthracene (probably carcinogenic to humans), benzo[b]fluoranthene, benzo[k]fluoranthene, chrysene, dibenzo[a,h]anthracene, indeno[1,2,3-cd]pyrene and naphthalene (probably carcinogenic to humans) were provided. To track the pollution sources, a couple of supplementary metrics were also calculated including the concentration of low molecular weight (LMW, $\Sigma 2-3$ rings) and high molecular weight (HMW, $\Sigma 4-6$ rings) PAHs and the ratio (LMW/HMW). The results are shown in Table 6.

PAHs in the environment are categorized into two distinct classes of petrogenics and pyrolytics. Petrogenics are those containing two or three rings with relatively lower molecular weights. With higher molecular weights, pyrolytics have four to six rings in their chemical structure (Yang et al. 2016). The major source of petrogenics is considered to be crude oil or petroleum spill/leakage, while detection of pyrolytics is often attributed to biomass and fossil fuel combustion (Katsoyiannis and Breivik 2014).

To track the source of PAHs more specifically, a variety of parameters are suggested by researchers; ratios of fluoranthene (FLU)/[FLU + pyrene (PY)] values lower than 0.4, between 0.4 and 0.5, and higher than 0.5 indicate crude oil/petroleum components, petroleum combustion and coal/biomass combustion, respectively (Franco et al. (2017). Ratio of BaA/(BaA + Chr) as well as InP/(InP + BghiP) values lower than 0.2 refers to petroleum, while higher values are considered as combustion-derived products (Wang et al. 2015). The same rule works for the ratio of Ant/(Ant + Phe); however, the limit here is proved to be 0.1 (Qiao et al. 2006). Furthermore, if the ratio (LMW/HMW) is higher than unit, the source of PAHs is attributed to petroleum products while lower than one values are due to petroleum combustion (Tu et al. 2018).

According to Figs. 2, 3 and 4, it seems that the main source of PAHs in the majority of samples is petroleum combustion. Additionally, low values of LMW/HMW (between 0.12 and 0.31) also confirm the source apportionment of PAHs within the study area (Fig. 5).

To compare the distribution pattern of major inorganic (toxic metals) and organic (PAHs) pollutants in this urban district, the values of risk index (RI) and Σ PAHs concentrations are illustrated in a symbolic way to show the probable similarities (Fig. 6).

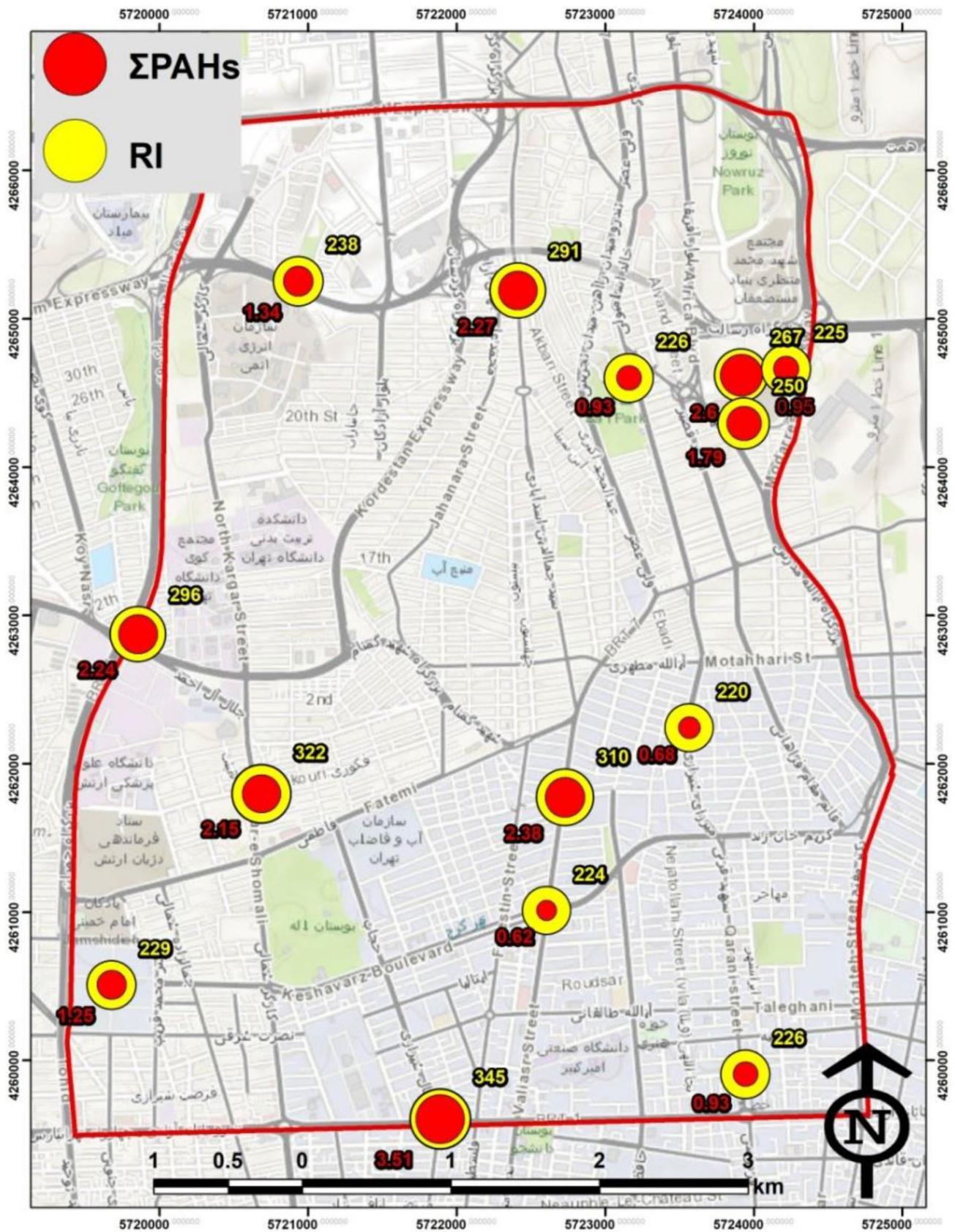


Fig. 6 Evaluating the correlation of ΣPAHs concentration and risk index (RI) values in surface soil samples within the district

As it is seen, all minimal, maximal and intermediate values for both metrics are coincided indicating a kind of similarity in their source and even transport scheme.

Conclusions

In this study, the adverse effects of urbanization on soil quality are investigated. The case study was selected in such a way as to cover an overcrowded district in the megacity of Tehran, where a variety of urban land use is observed. To have a thorough overview of soil pollution, both toxic metals and PAHs were considered for analysis. Furthermore, supplementary information over anthropogenic and bioavailable fractions of total metal concentration as well as source apportionment of PAHs was taken into consideration. Hotspots including some gas stations, construction sites, bus terminal, municipal waste recovery center and hospital were selected as the final 14 stations for composite sampling. Rather than Cd which shows remarkably high concentrations, the total concentration of other metals were not at all or at least slightly higher than the reference values. The descending order of anthropogenic fraction in metals was calculated as follows: Cd (87.87%) > Cr (40.14%) > Ni (38.64%) > Pb (37.40%) > Co (8.42%) > Cu (7.98%) > Zn (5.57%) > Mn (3.94%). Such order places an emphasis on attributing extremely high values of Cd to heavy vehicle traffic as suggested by Dias-Ferreira et al. (2016) in Portugal, Horváth et al. (2015) in Hungary and Qing et al. (2015) in China. Bioavailable concentration of metals in soil was classified as: Cu (6.84%) > Zn (6.47%) > Pb (3.98%) > Ni (3.97%) > Cr (1.99%) > Cd (1.98%) > Mn (1.45%) > Co (1.39%). Relatively considerable mobility of Pb and Ni (around 4%) as well as Cd and Cr (around 2%) may cause subsequent concerns of surface and groundwater pollution. Such potential hazard was confirmed by the results of RI calculation; around 80% of total samples were proved to locate at a considerable level of ecological risk.

In terms of PAHs, the majority of the detected components were those with higher molecular weights, indicating the pyrolytic source. Petroleum combustion due to heavy traffic load as well as gas combustion due to heating systems is considered the main source of such pollution as a result of a variety of metrics including the ratios of Flu/(Flu + Py), BaA/(BaA + Chr), InP/(InP + BghiP), Ant/(Ant + Phe) and LMW/HMW. A kind of synergy is observed in the spatial distribution pattern of PAHs and toxic metals, which may be further studied in detail regarding human health issues in megacities like Tehran.

Compliance with Ethical Standards

Conflict of interest The authors declare that they have no conflict of interest.

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