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Assessment of Clean up Levels Due to Inhalation of Polyaromatic Hydrocarbons in Contaminated Soils

SAEID GITIPOUR*, EHSAN TAHERI, NIMA HEIDARZADEH and SAEID GIVEHCHI
Faculty of Environment, University of Tehran
No 23, Ghods St, Enghelab Ave, Tehran, Iran
E-mail: gitipour@ut.ac.ir

Polyaromatic hydrocarbons (PAHs) are types of hazardous and carcinogenic compounds that their inhalation could have adverse effects on human health. Leakage from oil refinery facilities such as storage tanks, underground oil pipelines and evaporation ponds are the means of contaminants leaking to the environment, particularly to soils and groundwater. In this research, due to the widespread oil's leakages occurring in Tehran oil refinery in Shahre-Ray, Iran, soil samples were collected from different contaminated locations in the south of the refinery. The samples were analyzed for two PAH compounds, namely benzo(a)pyrene and benzo(k)fluoranthene. Physical and hazardous characteristics of the contaminants were evaluated based on geotechnical characteristics of the soils located near to the refinery. More ever the soils' clean up levels at the site were calculated *via* inhalation of these volatile carcinogenic organics. Results of the study indicate that maximum concentrations of the soil samples were 638 ppm and 651 ppm for benzo(a)pyrene and benzo(k)fluoranthene, respectively. Benzo(a) pyrene concentration in the soil was higher than the clean up level of 50 ppm, indicating that the soil should be treated at the site for this compound. Benzo(a)pyrene is chemically complex contaminant. Its' hazardous characteristics could be reduced by destructing of its structure to more simple chains. Thus, phyto-remediation technique was recommended for treatment of this contaminant at the site.

Key Words: Polyaromatic hydrocarbons, Tehran oil refinery, Phyto-remediation, Clean up levels, Inhalation of volatile.

INTRODUCTION

The application of old technologies in some oil refineries has caused hydrocarbons leaking from underground oil transfer pipelines, storage tanks and evaporation ponds. Leakages from Tehran oil refinery in Iran are one of the worst of such incidences in the world which has caused soil contamination in the areas adjacent to the refinery.

The raw oil for the refinery is being transferred from Ahwaz oil wells. The main products of the Tehran oil refinery are liquefied gas, gasoline, lead-free gasoline, light and heavy condensate, kerosene, fuel oil and sulfur[1]. Because of the hydrocarbonic nature of the refinery's products, this study is focused on two polyaromatic hydrocarbons (PAHs) namely; benzo(a)pyrene and benzo(k)fluoranthene. These contaminants are among EPA's priority pollutant list which could have carcinogenic effects on the people living in or near to the refinery site[2].

Fine particles of the contaminated soil can be entered in human body *via* various paths such as direct ingestion and inhalation[3]. In addition, toxic effects to soil organisms such as earthworms when in contact with PAHs contaminated soil have been observed[4]. Chemical effects of the two mentioned PAHs cause dermatosis, irritations and darkening of the skin[5,6]. There have been reports regarding the eye damage and long-term human health difficulties (*i.e.*, skin, lung and mammary cancers) due to contact with these hydrocarbons[7,8].

Based on the above observations, environmental organizations have limited the concentration of these two compounds in the air[9-11]. Also, according to toxicity equivalent factor (TEF) of these compounds (*i.e.*, 1 and 0.1 for benzo(a)pyrene and benzo(k)fluoranthene, respectively), both of the chemicals are classified as probable carcinogenic hydrocarbons[3,12]. Thus, in this research, permissible soil clean up levels for benzo(a)pyrene and benzo(k)fluoranthene around the Tehran oil refinery area have been determined and the results have been compared with the *in situ* concentrations of these contaminants to evaluate the necessity of soil treatment at Tehran oil refinery site.

EXPERIMENTAL

The study area is located at the south of Shahre-Ray city adjacent to TOR. The coordination of the site is 51º 25' 5" eastern longitude and 35º 31' 24" northern latitude. The contaminated underground water resulting from leakages of petroleum hydrocarbons has been pumped and directed to a stream for irrigation of agricultural and farming activities in the refinery area. Fig. 1 presents a photograph of the stream where the samples have been collected.

Fig.1. Contaminated soil along sides of the stream

Soil sampling procedure: Grid sampling method was used to collect soil samples from the stream location adjacent to Tehran oil refinery.

For determination of benzo(a)pyrene and benzo(k)fluoranthene concentrations and to assess site geotechnical characteristics, 12 soil samples (*i.e.*, A1 to A6 and B1 to B6) were collected from 3 and 10 m lateral distances of the stream axis (Fig. 2). In addition, seven soil samples (*i.e.*, C1, C2, C3, A7, A8, B7 and B8) were accumulated from center and around the contaminated stream.

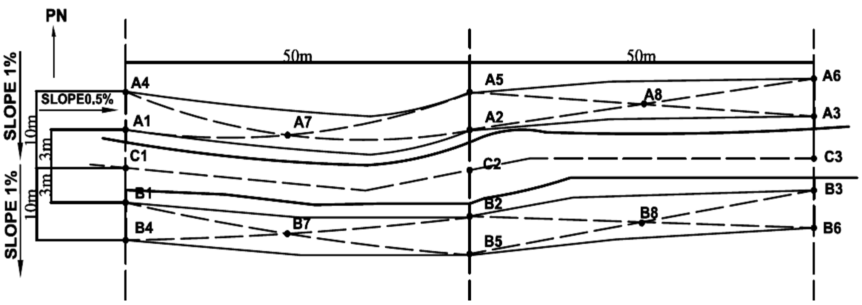


Fig. 2. Soil sampling locations at contaminated area

Gas chromatographic method was applied to analyze the PAHs in the soil samples. The procedure was consisted of three main phases of extraction, condensation and injection. Soxhlet extraction method 3540A (U.S. EPA-SW 846) was used[13] for the analysis of the samples.

RESULTS AND DISCUSSION

Table-1 show the soil samples analysis results.

TABLE-1
PAHs CONCENTRATIONS AT DIFFERENT SECTION OF THE STREAM

AT CENTRAL SECTION

Polyaromatic hydrocarbons	Sample C1 (ppm)	Sample C2 (ppm)	Sample C3 (ppm)
Benzo(a)pyrene	638	572	513
Benzo(k)fluoranthene	651	587	524

AT NORTHERN SECTION

	Sample A1 (ppm)	A2 (ppm)	A3 (ppm)	A4 (ppm)	A5 (ppm)	A6 (ppm)	A7 (ppm)	A8 (ppm)
Benzo(a)pyrene	404	364	331	137	127	108	257	221
Benzo(k)fluoranthene	411	370	337	128	118	101	256	220

AT SOUTHERN SECTION								
	Sample							
	B1 (ppm)	B2 (ppm)	B3 (ppm)	B4 (ppm)	B5 (ppm)	B6 (ppm)	B7 (ppm)	B8 (ppm)
Benzo(a)pyrene	453	418	372	267	247	216	349	306
Benzo(k)fluoranthene	469	422	398	277	253	235	362	311

As shown in Table-1, the soil concentrations are consistent at the stream axis. Nevertheless, it should be noted that the longer the distance from the beginning point of the stream (*i.e.*, sample C1), the lower concentration of the contaminants would be. Also, the concentrations of the soil samples at 3 m lateral distances of the stream were reduced in comparison with the central sample concentrations (Table-1). For all the 3 m lateral samples, the average concentrations of benzo(k)fluoranthene were higher than benzo(a)pyrene $\frac{1}{6}\sum_{i=1}^{i=3}(A_i + B_i) = 401$ ppm and $\frac{1}{6}\sum_{i=1}^{i=3}(A_i + B_i) = 390$ ppm, respectively). Moreover, at southern section of these samples, the average PAHs' concentrations [(414 + 430)/2 = 422 ppm] were *ca.* 15 per cent higher than northern area of the stream [(373 + 366)/2 = 370 ppm] mainly because of the slope of the site to the south (Fig. 3).

For the samples located at lateral distances of 10 m at the northern section of the stream axis (*i.e.*, samples A4, A5 and A6), benzo(a)pyrene with the average concentration of 124 ppm was the prevailing contaminant. For the southern section soils (*i.e.*, samples B4, B5 and B6) however, benzo(k)fluoranthene with an average concentration of 255 ppm was the leading contaminant.

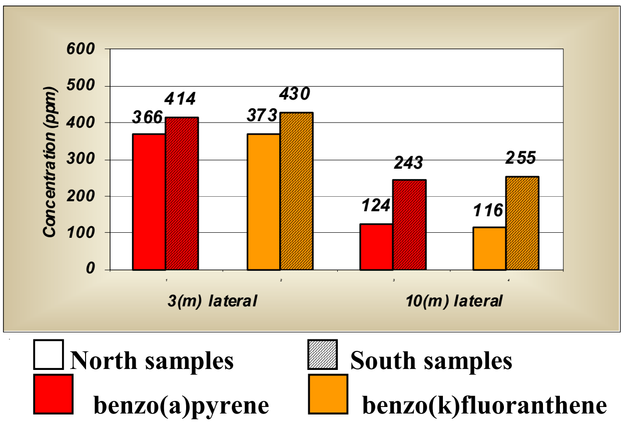


Fig. 3. Concentrations of PAHS Samples in Northern *vs.* Southern Sections of the Stream

For the 10 m lateral soils (*i.e.*, samples A4 through A6 and B4 through B6), the average concentration of southern area samples (*i.e.*, 249 ppm) were 110 per cent higher than the northern soils (*i.e.*, 120 ppm). Mainly because of the downward slope of the site which enhances the contaminants mobility due to advection and mechanical dispersion in this region (Fig. 3).

As shown in the Table-1, it should be noted that the lateral distances from the stream axis and the rates of the pollutions have adverse relationships due to the degree of contaminants' diffusion in the soil.

Assessment of permissible clean up levels for benzo(a)pyrene and benzo(k)fluoranthene in contaminated soil: According to U.S. EPA guidelines for carcinogenic effect of volatile contaminants, the following factors should be considered to evaluate of the risk levels by inhalation[13]: (i) Contaminant's evaporation in the air, which is a function of its physicochemical characteristics and geotechnical properties of the soil at the site. (ii) Unit risk factor (URF) and contaminant exposure parameters.

URF and exposure parameters have been illustrated in Table-2. Tables 3 and 4 present geotechnical properties of the soils and the physical characteristics of the two PAHs contaminants.

TABLE-2
UNIT RISK FACTOR (URF) AND EXPOSURE PARAMETERS FOR BENZO(a)PYRENE AND BENZO(k)FLUORANTHENE

		Benzo(k)fluoranthene	Benzo(a)pyrene
	URF $(\mu g/m^3)^{-1}$	1.1×10^{-4}*	1.1×10^{-3}*
Exposure parameters	AT (years)	70**	70**
	EF (350 d/year)	350**	350**
	ED (year)	30**	30**

*Ref. 15,16; **Ref. 3.

TABLE-3
GEOTECHNICAL CHARACTERISTICS OF THE SOIL AT SOUTH OF TEHRAN OIL REFINERY

θ_a	n	θ_w	ρ_b (g/cm^3)
0.3	0.49	0.19	1.33

TABLE-4
PHYSICAL CHARACTERISTICS OF BENZO(a)PYRENE AND BENZO(k)FLUORANTHENE

	D_j* (cm^2/s)	K_H* (dimless)	D_w* (cm^2/s)	K_{oc}** (cm^3/g)	f_{oc}* (g/g)
Benzo(a)pyrene	4.32×10^{-2}	4.63×10^{-5}	9.00×10^{-6}	549541	0.006
Benzo(k)fluoranthene	2.26×10^{-2}	3.40×10^{-5}	5.56×10^{-6}	549541	0.006

*Ref. 17; **Ref. 18.

For calculation of the clean up levels due to inhalation of two respected PAHs at the site the following equation has been used:

$$\text{Clean-up level (mg/kg)} = \frac{R \times AT(365\ d/year)}{URF \times (1000\ \mu g/mg) \times EF \times ED \times \frac{1}{VF}} \quad (1)$$

where:

- R: Target cancer risk level (it is recommended as 10^{-6})[3].
- AT: Average time: for carcinogenic compound it is considered 70 years
- EF: Exposure frequency: it is recommended 350 d/year.
- ED: Exposure duration: it is assumed 30 years.
- URF: Unit risk factor $(\mu g/m^3)^{-1}$; that is the hazard factor of the contaminants.
- VF: Soil-to-air volatilization factor (m^3/kg); it can be calculated[14] by eqn. 2:

$$VF = \frac{(Q/C)(3.14 D_a T)^{1/2}(10^{-4}\ m^2/cm^2)}{2 \times \rho_b \times D_a} \quad (2)$$

where:

- Q/C: It is the average rate of contaminant flux (g/m^2-s) based on an overall site emission rate of 1 g/s divided by the maximum normalized air concentration in kg/m^3. It is recommended 90.8 (g/m^2-s)/(kg/m^3) for this area[3].
- T: Exposure interval (s). It is considered 9.5×10^8 second for the site[3].
- ρ_b: Dry soil bulk density (g/cm^3).
- D_a: Apparent diffusivity (cm^2/s) calculated by the following equation:

$$D_a = \frac{[(\theta_a^{10/3} \times D_j \times K_H + \theta_w^{10/3} \times D_w)/n^2]}{\rho_b \times K_d + \theta_w \times K_H} \quad (3)$$

where:

- θ_a: Air-filled soil porosity ($n-\theta_w$), dimensionless.
- D_j: Diffusivity in air (cm^2/s)
- K_H: Henry's law constant, dimensionless
- θ_w : Water-filled soil porosity, dimensionless
- D_w : Diffusivity in water (cm^2/s)
- n : Soil porosity, dimensionless
- K_d : Soil-water partition coefficient, (cm^3/g); Calculated by the following equation:

$$K_d = K_{oc} \times f_{oc} \quad (4)$$

where: • K_{oc} : Soil organic carbon-water partition coefficient, (cm^3/g);
• f_{oc} : Organic carbon content of soil (g/g)

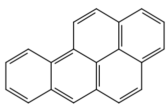
According to Table-5, the soils' clean up level due to inhalation of benzo(a)pyrene at the site is 50 ppm. Analyses of the soil samples indicate that the benzo(a)pyrene's concentrations in and around the stream ranged from 108 to 638 ppm. These values correspond to samples A6 and C1, respectively (Table-1). Thus, the soils at the site are polluted and is essential to treat the site for benzo(a)pyrene.

TABLE-5
VALUES OF THE CLEAN UP LEVELS FOR BENZO(a)PYRENE AND BENZO(k)FLUORANTHENE

	K_d (cm^3/g)	D_a (cm^2/s)	VF (m^3/kg)	Clean up level (ppm)
Benzo(a)pyrene	3297.2 →	6.79×10^{-11} →	2.26×10^{7} →	50
Benzo(k)fluoranthene	3297.2 →	3.40×10^{-11} →	3.20×10^{7}	707

The soil in the contaminated area was consisted of fine grained clay particles and sand with an average to low permeabilities. As a result of these characteristics, physical treatment methods such as soil washing, soil flushing and air sparging by which water, air and reagents would enter into the soil for removing contaminants can not be an efficient approach due to the destruction of soil structure and its inflammation[19,20]. Regarding the efficiency of soil vapour extraction, this method is a function of contaminants' Henry's constants and vapour pressures and because benzo(a)pyrene has a low Henry's constant and vapour pressure value (Table-6), thus the efficacy of this method would be insignificant for decontamination of the site[19,21].

TABLE-6
STRUCTURE AND PHYSICAL PROPERTIES OF BENZO(a)PYRENE

	Benzo(a)pyrene*
Structure	
Chemical formula*	$C_{20}H_{12}$
Henry's constant** (dimensionless)	4.63×10^{-5}
Vapour pressure*** (mm Hg)	5.60×10^{-9}

*Ref. 26, **Ref. 3, ***Ref. 27.

Considering above concerns and due to the complex structure of benzo(a)pyrene, phyto-remediation technique is recommended to destruct the chemical structure of this contaminant. After destruction of the rings, it is expected that the hazardous effects of this hydrocarbon be reduced[22,23]. Phyto-remediation is an *in situ* soil treatment technique by plants[24]. That is an appropriate technique for clean up of polluted soils with organic contaminations[25]. This method also has valuable esthetic aspects which could reduce the adverse effects of the pollution.

Phyto-transformation and rhizosphere bioremediation are two proper phyto-remediation mechanisms[28] for treatment of benzo(a)pyrene. The technique is based on fragmentation of benzo(a)pyrene chemical structure[28,29] (Fig. 4).

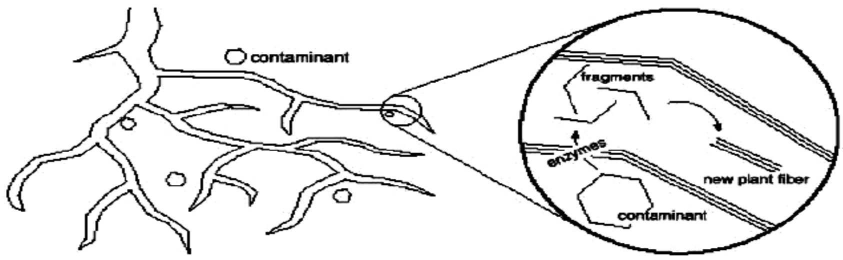


Fig. 4. Phyto-remediation method fragments benzene rings

In case of benzo(k)fluoranthene, the respected soils' clean up level due to inhalation is 707 ppm. That is higher than its maximum observed concentration 651 ppm at center of the stream (*i.e.*, sample C1). Therefore, benzo(k)fluoranthene concentration falls below the permissible level and it could not have any hazardous effect for the site *via* inhalation.

Conclusion

Because Tehran oil refinery storage tanks and underground pipelines have been in service for quite a long time, wearing out of these installations has lead the oil leakage to spread to the surrounding areas, causing an environmental disaster in Shahre-Ray City. Benzo(a)pyrene is one of the most hazardous polyaromatic hydrocarbons with high concentrations in the soils of the area where this research was carried out.

The concentrations of benzo(a)pyrene in contaminated soils ranged from 108 to 638 ppm, exceeding the permissible clean up level of 50 ppm as specified by the U.S. EPA's equations. Thus, the inhalation of this compound in the air at the refinery and its' surrounding areas would have diverse health effects to the refinery employees and the local residences.

The clean up of the pollutants from the contaminated site, after controlling the pollution source, include removal of the contaminated soils from the site and their transport to a hazardous-waste facility for storage and/or treatment. The contaminated soils could be also used as materials in roads and highways constructions, provided suitable grading and compaction efforts[30].

The physical methods such as soil vapour extraction, soil flushing, air sparging and soil washing were not applicable due to physical properties of benzo(a)pyrene and clay texture of the, thus phyto-remediation technique *via* phyto-transformation and rhizosphere bioremediation which are based on the destruction of benzo(a)pyrene structure have been recommended to treat the site.

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