

## The Evaluation of Contaminated Soil by Petroleum Mulch in Combating Desertification

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### Abstract

The most usual type of petroleum mulch, which has been successfully used to combat desertification in large area in Iran for more than thirty years, is produced by heavy residue petroleum cuts. The petroleum mulch consists of a wide range of different heavy hydrocarbons such as Polycyclic Aromatic Hydrocarbons (PAHs). PAHs are present at low level in petroleum mulch, where there is contact with water and soil and the potential for transferring of compounds into environment. Some of PAHs, especially benzo (a) pyrene (BaP) have been recommended for determining and comparing with standard criteria on causing cancer. Although Iran has a long domestic experience in sand dune fixation by using petroleum products but so far there is no proper research in probable effects of using petroleum mulch on environment either in Iran or any other involved countries. In this study it was assumed that rainfall and temperature would affect mulch disintegration process, then considering these parameters, different climatic zones in three provinces -Khuzestan, Kerman and Sistan - were selected and samples were prepared from several sites of any provinces, both in mulch-sprayed sites and non-sprayed sites (observation). In order to estimate the content of PAHs, several soil samples were taken in different depths from the above-mentioned sites. Quartering Procedure selected the soil samples beneath mulch layer and the PAHs analysis was performed by solvent extraction and HPLC method with UV fluorescence detection and results were compared to standard criteria. The results indicated that the content of PAHs and mostly BaP in petroleum mulch and soil samples beneath mulch layer are less than the permitted limit in national standards. This component, in the depth of 5 cm, decreased to 1/40 of the initial even after years. Then, it shows very low penetration. Therefore, the petroleum mulch and contaminated soils can be considered as safe materials.

*Keywords:* Petroleum mulch; Polycyclic aromatic hydrocarbon; Contaminated soil; Desertification; Sand dune fixation

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### 1. Introduction

Moving sand dune fixation in Iran initiated in 1965. Sand dunes are kinds of features in arid climatic zone. These are formed as a result of vegetation degradation by natural factors or human activities and erosive winds operation that moves soil particles from their own place to other place. This phenomena damages infrastructures such as residential areas, rangelands, farmlands and causes health problem, poverty and immigration, and so on as

well. In the FRWO Reports (2004) and Asphalt Institute (1973) reported that petroleum mulches by spraying have been widely used for moving sand dune fixation. In this method, a thin layer of the petroleum mulch is sprayed on the soil surface for temporary fixation.

The consumed mulches in Iran are mostly petroleum based produced by Tehran and Abadan Oil Refineries. Petroleum mulch is colloidal mixture of a wide range of heavy hydrocarbon compounds, which classified into four fractions named: saturates naphthene and polar aromatics and asphaltenes. It seems that two middle fractions, naphthene and polar aromatics, contain PAHs. The saturated fraction of mulch has no PAHs and does not easily react

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with the air (oxygen) under severe conditions, but it can be affected and consumed by the soil micro-organisms and bacteria and gradually its colloidal structure of mulch will be decayed and dispersed. Also, by passing of time, the other fractions will be released into the soil. Although the PAH<sub>s</sub> are chemically stable under severe environmental condition and very low soluble in water but soil particles adhere them from the mulch and these attached components would be later transferred by wind and water as suspension. The main source of PAH<sub>s</sub> is distillation residues of crude oil (petroleum) and coal tar (Bqrseh and Dekker, 1983; Lee and Novotny, 1981). But the amount of PAH<sub>s</sub> in heavy fractions of coal tar is much higher than heavy petroleum mulch (table 1) therefore consumption of coal tar based bitumen (or mulch) has been banned.

Rhoda and Wang (1992) has shown PAHs are a group of over 100 different organic compounds composed of two or more benzene rings fused together. They can also found in substances such as crude oil, coal tar, creosote and roofing tar. They are found throughout the environment in the air, water, and soil, as well. These components are considered contaminant and toxic and can cause harmful effects on skin, body fluids, and ability to fight disease. For environmental resources some of PAH<sub>s</sub> have been recommended to determine by EPA<sup>1</sup>. The common PAH<sub>s</sub> are Acenaphthylene (Acy), Acenaphthene (Ace), Fluorine (Flu), phenanthrene (Phe), Anthracene (Ant), Fluoranthene (FLT), Pyrene (Pyr), Benzo (a) anthracene (BaA), Chrysene (Cry), Benzo (b)- and Benzo (k)- Fluoranthene (BKF) and Benzo (a) Pyrene (BaP), Dibenzo (ah) anthracen (DahA), Benzo (g,h,i) Perylene (BghiP), Indeno (1, 2, 3-c, d) Pyrene. According to the WHO<sup>2</sup>, at least the amount of six later components should be tested. Due to high potential virtue on causing cancer, the BaP is the most hazardous component which it remains nearly 99% in soil and the left will be airborne into the environment. It should be measured before using the petroleum mulch. In nature, nearly all types of soils are somehow contaminated with PAH<sub>s</sub>. Bqrseth and Dekker (1983) and EFRA and Environmental Agency (2002) recommended for determining Some of PAH<sub>s</sub> especially BaP and comparing with standard criteria on causing cancer.

Researchers have undertaken many studies of contamination effects of crude oils, coal tar

and their products such as bitumen for road construction, as well. Reinhold (2004) demonstrate that contamination of coal tar products are more than crude oil ones, higher than permitted limits, then using it is not allowed. The Results of tests of this project which has just done for comparison, shows that the contamination of coal tar is almost 350 times more than crude oils products. Bowen and Brandt (2000) have shown the bitumen has a long history of use as a waterproofing agent and is traditionally regarded as a safe product but it does however contain low levels of potentially hazardous materials.

Sprayed mulch film is subjected to sunlight, rainfall, micro-organism. So, after sometime is disintegrated that leads to deterioration of its colloidal structure and probable contamination. It has been proved that some kinds of PAH<sub>s</sub> especially BaP cause cancer in human being, then in this study the changes of PAH<sub>s</sub> before and after treatment was measured. PAH<sub>s</sub> is not soluble in water but it could be transferred by the wind in accompanied with soil particles.

In this study we assumed that even using petroleum mulch on the soil surface can cause soil and water contamination more than permitted limit due to leaching, penetration, and dispersion of the compounds into the depth of soil by rain and other meteorological agents. Then we are going to confirm or deny the assumption in the study.

## 2. Materials and methods

### 2.1. Materials

In this study it was assumed that the rainfall and temperature would affect mulch disintegration process and would cause contamination, then considering these parameters, different climatic zones in three provinces were selected as followed:

a- Sistan province - Zabol city:

Sharifabad Lillam - Zahedan Kohneh - Jungle Niatac- Arg Chehl Dokhtar.

b- Khuzestan province:

Om Aldebes - Gamboieh - Khasraj - Alboeid - Karkkeh River

c- Kerman Province - Bam City (Narmanshir):

Poosht rig - Aliabad - Doholi dunes

The annual average rainfall for abovementioned zones is 60, 230 and 60 mm respectively

The soil samples were prepared from different depths (0-15, 30-50, 75-100 cm) from several sites of any provinces, both in mulch-sprayed and non-sprayed sites (observation), and then, studying the change of PAHs in soil profile.

1- EPA: Environmental Protection Agency

2- WHO: World Health Organization

## 2.2. Methods

2.2.1. The following requirements (criteria) were considered for comparison of contamination in mulch sprayed and non-mulch sprayed parcels (observation).

- The observation parcel is referred to sites without mulching
- The observation should not be in the wind direction from the mulching area
- The observation should be at least 1.5 km far from the mulching area

Note 1: Petroleum mulch is sprayed on the soil surface as a thin film which adheres the sand particles. The chemical fractions from this layer gradually penetrate into the deeper layers of soil because of differences in physical absorptions.

2.2.2. The international standards from NIOSH<sup>1</sup>, OSHH<sup>2</sup>, ACGIH<sup>3</sup> and EPA have presented quality criteria of PAH<sub>s</sub> content for the air and water but not for the soil.

Wcislo (1998) in his paper have named some European Countries such as Netherland, Denmark, Finland and the United Kingdom and so Kosteck and Calabrese (1989) have developed soil quality criteria for selected PAHs or their sum. So, in this paper we used contaminated soil quality criteria from pioneer countries (national standards).

It seems, because of specific complexities and properties of the different soils and environmental factors, there is not enough consensus between scientists to establish (acceptable) limit value as a requirement(criteria) for the PAH<sub>s</sub> content in (remedied or contaminated) soil used for housing, kindergartens as following:

-DHI (The Danish Environmental Protection Agency (2001) has posed the requirements to total determination of PAH<sub>s</sub> in soil, which is seen in table 1.

- NHDES (New Hampshire Department of Environmental Services) (2004) has Presented the permitted limit for PAH<sub>s</sub> in remedied soil, which is use for housing and other applications, which is seen in table 2. The table shows that the maximum permitted content of PAH<sub>s</sub> is 700 mg/kg of remedied soil.

2.2.3. A variety of soil samples beneath mulch layer (there is no mulch in it) and non- mulch sprayed parcels (observation) from three pilots

projects (province) were selected (Quartering Method) and tested.

2.2.4. There are many applicable tests to determine the PAH<sub>s</sub> of mulch and soil. In this study, the PAH<sub>s</sub> analysis was performed by solvent extraction and HPLC method with UV Fluorescence Detection. This method is the same as DIN method (DIN 38414- 21).

Table 1. The Danish EPA requirement for the acceptable content of PAH<sub>s</sub> in soil

PAH compound	Soil quality criteria	Detection threshold value
Requirement to sum of PAH <sub>s</sub> : Flu, BaP, DahA Indeno(1,2,3)pyrene	1.5 mg/kg dry matter	1.5 mg/kg dry matter
Requirement to individual PAH <sub>s</sub> : BaP Dibenzo(a,h) anthracene(DahA)	0.1 mg/kg dry matter 0.1 mg/kg dry matter	0.1 mg/kg dry matter 0.1 mg/kg dry matter

Table 2. The maximum acceptance limit of PAH<sub>s</sub> in remedied soil Presented by NHDES

Chemical name	S-1 (mg/kg)
Benzo (a) anthracene	1.2
Benzo (a) pyrene	07
Benzo (b) fluoranthene	1.2
Benzo (k) fluoranthene	12
Chrysene	120
Dibenzo (a, h) anthracene	0.7
Indeno (1,2,3) pyrene	1.2

## 3. Results

### 3.1. Thickness of the mulch layer

Thickness of mulch layer should be about 1mm. Our observations from the mulching areas in different years showed that the maximum consolidation thickness (depth) doesn't exceed 5 cm.

### 3.2. Determining PAH<sub>s</sub> in mulch

The contents of PAH<sub>s</sub> in medium and heavy crude oils and the petroleum mulches produced from them are seen in Table 3, and so, the contents of some PAH<sub>s</sub> in heavy fraction of coal tar are shown in Table 4. As shown in tables, The content of BaP in petroleum mulch is approximately 2 up to maximum 2.5 mg/kg while in coal tar is approximately 787 mg/kg, i.e. a factor of nearly 400 times greater than the content of BaP in petroleum mulch. Therefore, clearly show that the PAHs of petroleum products is very low in comparison with another hydrocarbon sources.

1- National Institute of Occupational Safety & Health

2- Occupational Safety and Health Organization

3- American Conference of Governmental Industry Hygienists

Table 3. The PAHs concentration in the crude oils, relevant mulch (ppm)

PAH components	Maron medium	Gachsaran	Malch	Mulch
	crude oil	Heavy crude oil	(Tehran)	(Abadan)
Naphthalene (Nap)	49	77	-	-
Acenaphthylene (Acy)	58	50	-	-
Acenaphthene (Ace)	481	532	-	-
Fluorine (Flu)	15	23	-	-
Phenanthrene (Phe)	14	38	-	-
Anthracene (Ant)	11	19	-	-
Fluoranthene (FLT)	66	106	16	7.4
Pyrene (Pyr)	89	232	43	31.7
Benzo (b) Fluoranthene (BbF)	11	33	-	-
Benzo (a) pyrene (BaP)	10	11	2.1	2

Table 4. The PAHs concentration in coal tar creosote

PAH	Phenanthrene (Phe) %Wt	Anthracene (Ant) %Wt	Benzo (a) pyrene(BaP) ppm
Coal tar creosote	10.4	1.9	787

### 3.3. Determining PAHs in contaminated soil

A description of samples is given in Table 5. The results of determining PAHs in contaminated soils for three zones (provinces) are shown in Tables 6, 7 and 8.

The PAHs tests from soil samples in different depth have been shown that the rate of PAHs component's penetration is different regarding to climatic parameters and the amount of this penetration is very low and even lower than permitted criteria.

Table 5. Description of the samples

Code	Description	Code	Description
A	Zahedan	S	The observation soil sample
Z	Kerman	a	The soil sample in depth of 0-15 cm
K	The soil sample under mulch layer	b	The soil sample in depth of 30-50 cm
L	The observation soil sample	c	The soil sample in depth of 75-100 cm

Table 6. PAHs concentration in the soil sample (mg/kg)(Ahwaz – Dasht Azadegan)

Pilot and geographic coordinates	Date of mulching	Sample code	Phen	FLT	Pyr	Bap	BghiP	Nap	Ant	BKF	PAHs
Albagi N313427 E483627	1971	01ALa	0.450	0.400	0.348	0.002	0.016	0.450	0.500	0.048	2.214
		02ALb	108.640	18.800	19.153	1.150	1.990	0.729	43.992	1.857	196.311
		03ALc	39.310	11.230	5.610	0.039	0.870	-	5.610	0.081	62.75
Gamboeyh W312230 L483141	1977	04ALa	106.411	17.811	13.768	0.110	0.140	<1	8.766	0.120	147.126
		05ALb	101.445	19.531	14.866	0.140	0.150	<1	8.760	0.180	145.072
		06ALc	33.433	4.167	4.260	0.26	0.320	<1	0.644	0.200	43.284
Khasraj N313613 E482637	1977	07ALa	96.730	13.750	15.810	0.399	0.443	0.510	82.790	0.626	211.058
		08ALb	103.911	17.878	25.042	0.623	0.848	1.113	60.049	0.935	210.399
		09ALc	87.550	24.624	10.944	0.027	0.071	1.368	2.736	1.109	128.429
		10ASa	82.960	17.598	12.570	0.100	0.143	62.85	15.080	0.198	191.499
OM Aldabes	-	11ASb	56.530	11.906	5.950	0.101	0.142	-	5.653	0.127	80.409
		12ASc	7.713	2.571	1.287	0.488	0.720	1.285	0.514	0.059	14.637

Pilot and geographic coordinates	Date of Mulching	Sample code	Phen	FLT	Pyr	Bap	BghiP	Nap	Ant	BKF	PAHs
Niatac N310703.6 E61370.4	1977	01ZLa	99.050	24.761	15.471	0.351	0.314	117.630	9.280	0.501	258.078
		02ZLb	81.963	21.240	15.172	0.210	0.230	148.741	0.715	0.445	268.714
		03ZLc	734.230	160.381	85.548	0.241	0.454	0.7	117.615	0.755	1099.216
Mohammad Shah karam N305442.6 E614435.3	2002	04ZLa	98.555	46.510	14.268	0.047	0.125	N.D	2.390	0.650	162.537
		05ZLb	83.432	21.611	21.451	0.068	0.165	N.D	18.254	0.511	
		06ZLc	88.676	23.330	9.332	0.051	0.191	2.338	0.930	0.154	145.491
Dahmardeh village N310326.7 E613641.2	observation Sample	07ZSa	35.110	7.020	22.802	0.042	0.122	1.754	10	0.956	74.806
		08ZSb	51.612	13.760	1.035	0.058	0.113	1.720	8.601	0.116	77.015
Lilam- Sharif Abad -	2002	09Z Mulch layer	1885.381	2130	1648.991	48.414	679.48	2224.39	56.960	8.542	8682.158
Lilam- Sharif Abad -	2002 observation Sample	10Z	13.161	1.081	6.646	0.124	1.595	.543	2.161	.501	25.812

Lilam-Sharif Abad	2002 observation Sample	11Z	178.120	60.450	67.177	0459	.331	.233	.537	.924	308.231
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Table 7. PAHs Concentration in the soil sample (mg/kg) (Sistan-Baluchestan province-zabol city)

Table 8. PAHs concentration in the soil sample (mg/kg) (Kerman Province – Bam City (Narmanshir))

Pilot and geographic coordinates	Sample code	Phen	FLT	Pyr	BaP	BghiP	Nap	Ant	BKF	PAHs
Doholi dune	01Kla	8.915	1.109	4.960	0.083	0.139	0.557	0.278	0.111	16.143
	02Klb	0.625	338.011	99.521	3.427	5.723	N.D	N.D	N.D	447.307
	03Klc	41.070	12.080	21.740	0.626	2.367	84.552	N.D	N.D	162.435
Sopattern soil	04KSa	156.415	38.564	29.500	0.0725	0.372	56.722	6.818	0.316	288.7795
	05KSb	31.711	3.723	3.715	0.102	0.042	9.500	0.267	0.031	49.091
Malakabad	06KSc	3.610	4.055	4.086	0.065	0.072	2.681	0.223	0.032	14.824
Malakabad shirabad	07KLa	78.082	11.220	7.446	0.034	0.500	1.531	1.991	0.042	100.315
	08Klb	47.406	5.400	5.838	0.023	0.090	1.455	0.907	0.032	60.696
	09Klc	57.000	6.515	6.928	0.024	0.340	1.183	1.211	0.051	73.069

#### 4. Discussions and Conclusion

By comparison of BaP in surface mulched layer and soil samples taken from lower layers, clears low penetration of PAHs. For example the content of BaP in the depth of 5 cm is very low, decreasing to minimum of 1/40 of the initial value. This ratio is approximately true for all of soil samples from different pilots in all provinces. Furthermore, BaP concentration in soil samples for the depth of 1m beneath the mulch layer of different pilots varied from minimum 0.02 to max 0.26  $\mu\text{g/kg}$ , which in comparison to initial amount in mulch is very low. This subject shows that petroleum mulch could not pollute soil even to the depth of 1m.

The content of PAHs of soil samples in the top of dune (10Z) and the interval spaces dunes (11Z) (table 7) in unfixed sand dune area that located neighboring mulched zone showed higher quantity of PAHs in the late one regarding to wind factor and runoff. Samples in the side of dune is higher than their content in soil sample in the top of dune.

In all areas, the tests showed that PAHs content of soil samples taken from observation site were lower in comparison with mulched soil sample. But anyway the PAHs contents in mulch-sprayed site were lower than permitted limit.

Comparison of mulch penetration in similar soils types in three climatic zones showed that, mulch penetration rate was higher in Ahwaz sites rather than two other provinces due to higher rainfall and soil type. So, this zone was considered exposed to more contamination and studied more precisely in the view point of PAHs.

Results of BaP concentration of soil samples in similar layers (soil depth) of provinces show that the BaP concentration in Ahwaz Pilot (oilfield region) is higher than two provinces of Kerman and Sistan.

The content of BaP in petroleum mulch is maximum 2.1mg/kg, which clearly is under the permitted limit (50 mg/kg) which Reinhold (2004) classifies substances as carcinogenic, according to the German Hazardous Substances Regulation (GHSR).

Sun, rain, and micro-organisms individually or in association cause disintegration and destabilization of the colloidal structure of sprayed mulch. Fortunately, after sand dune stabilization and biological rehabilitation, they will repair the soil.

Mulch constituents selectively show different effects in view point of decomposition, composition and dissolving by the abovementioned factors. As well this will gradually cause the separation of constituents and change in colloidal structure of mulch, resulting in soil remediation.

All numerous contaminated soil and observation samples, which have been tested, showed that the sum of some PAHs and specialty BaP contents are lower than Danish APA and NHDES guidelines. Therefore the petroleum mulch and contaminated soils regarded as safe materials.

The PAHs content of each area (geography) depends on area's history (biology, hydrology, industry establishments and etc.). Based on the obtained results, the PAHs content in some observation soil samples taken from Ahwaz provinces (oilfield region) showed higher than the mulched area in Sistan provinces.

So, by experience, very low rainfall or humidity could not shift the absorbed PAHs from the soil surface toward lower layers.

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