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Evaluation of Remediation Methods for Soils Contaminated with Benzo[a]Pyrene

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ABSTRACT: Leakage of petroleum compounds around the Tehran Oil Refinery (TOR) for the past 30 years has caused oil pollutants to spread in a large area around this refinery, Therefore, remediation of the soil in this area is on the priority necessity. In the present paper, in order to obtain a better site perception, gas chromatography analysis and permeability tests were conducted on soil samples. Measurement shows the present concentrations of Benzo[a]Pyrene between 108 to 638 ppm that is 800 to 5000 times higher than the clean up level (120 ppb).Due to clayey texture and low permeability of the soils that ranges between 5.5×10^{-6} to 7.3×10^{-6} (cm/s), the low volatility of Benzo[a]Pyrene with Henry's constant equal to 4.63×10^{-5} (dimless) and also a vapor pressure of 5.6×10^{-9} (mm Hg), physical methods such as soil flushing and soil vapor extraction were more costly and not suitable to treat TOR contaminations. Consequently, the phyto-remediation method via phyto-transformation and rhizosphere-bioremediation which are based on fragmentation of contaminants was found to be more compatible with geotechnical characteristics of the area in the south of (TOR), and was selected as the most appropriate method.

Key words: Benzo[a]Pyrene, ingestion, flushing, vapor extraction, phyto-remediation, soil, oil, refinery

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INTRODUCTION

As Tehran oil refinery (TOR), its storage tanks, and its oil transfer pipelines have all been in service for over 30 years, oil leakage to the surrounding soil has been occurred. This refinery receives its oil from Ahwaz oil wells, and its products include liquid gas, ordinary gasoline, light and heavy naphtha, kerosene, gas oil, furnace oil, mineral oil, and sulphur (khosravi, 1998).

Poly-aromatic hydrocarbons (PAHs) are a large sub-group of petroleum compounds, some of which are hazardous and may cause cancer (Irwin, *et al.,* 1997b; Wcisło, 1998). These compounds might be inhaled, ingested accidentally, or absorbed through the skin, posing a danger to the individual thus affected (U.S. EPA, 1996a; ATSDR, 1992). As Benzo[a]Pyrene is one the most carcinogenic compounds and has high concentration in the respected area; this study investigates ways of soil remediation for soils contaminated with Benzo[a]Pyrene. Chemical effects of this compound cause dermatosis, irritations and darkening of the skin (ATSDR, 1995; NJDHSS, 1998). There have been also reports about the eye damage and long-term human health problems (i.e.: Skin, lung and mammary cancers) due to contacting with this compound (Irwin, *et al.,* 1997a; Davis, *et al.,* 1993). Also based on Toxicity Equivalent Factor (TEF) of PAHs, U.S.EPA has recommended Toxicity Equivalent Factor (TEF) of 1 for Benzo[a]Pyrene (U.S. EPA, 1996a). It is also classified as probable carcinogenic compound (U.S. EPA, 1996a; IARC 1987).

As the leakage of petroleum compounds into surrounding soil is a widespread eco-environmental complication throughout the world, many methods have been innovated for its solution. The effectiveness of these methods depends on the geotechnical characteristics of the area and the physical characteristics of the contaminants (Okoh and Anthony, 2006, Henstock, 2007; Rister-Roberts, 1998; Nathanil, *et al.*, 2001). This paper first explains each of these remediation techniques, and then introduces an optimum solution which is proportional to the physical and chemical properties of Benzo[a]Pyrene, and in which geotechnical features of the mentioned area have been taken in to account. In soil flushing method, water is sprayed on the contaminated soil, separating the contaminants from it and entering them into the submerged part of the soil. Once the contaminants have reached this part, extracting them would be easier. After the contaminants have been extracted, remediation operations are conducted at the ground level (Rister-Roberts, 1998; U.S. EPA, 1996b). Soil vapor extraction method was devised for extracting volatile organic compounds (VOC), such as BTEX and PAHs, from soil in an unsaturated zone (Hensen, 1998; U.S. EPA, 1996c). An air stream is sent through the contaminated soil, absorbing the volatile contaminants, and carrying them with it out of the soils (Rister-Roberts, 1998; Anderson, 1994). Phyto-remediation is used for on-site removal of contaminants from the soil, and is most applicable for places with low-depth contaminations, or with organic and metal contaminations (U.S. EPA, 1999; Aprill and Sims, 1990). According to the type and depth of pollutants that are amenable to one of five applications: phyto-transformation, rhizosphere bioremediation, phyto-stabilization, phyto-extraction, or rhizo-filtration (Schnoor, 1997). The phyto-transformation and phyto-sphere-bioremediation are appropriate for PAHs compounds, as they fragment the molecular structure of these contaminants (Schnoor, 1997; Hedge and Fletcher, 1996).

MATERIALS & METHODS

The contaminated area under investigation lies to the south of Shahar-e-ray in south of the TOR, at a geographic longitude of 51°25'5" east, and latitude of 35°31'24" north. The contaminated underground water has been pumped and conveyed in to the stream near the refinery. Fig. 1 shows the stream which is used for irrigation of agricultural land causing soil contamination in the area. To determine the concentration of Benzo[a]Pyrene and also the geotechnical properties of the soil, 12 samples were taken at crosswise distances of 3 and 10 meters from the axis of the stream, and at 50 meters intervals along the length of the stream. Also, four samples were taken from the center of the network, and also in order to determine the maximum concentration of the pollutant three samples from the stream (Fig. 1). The gas chromatographic (GC) method was applied for analyzing the PAHs concentrations in the soil samples (U.S. EPA, 2002). Permeability coefficient (k) was determined in the laboratory by falling head method (ASTM, 2006). Results from the analyses show that there are 12 PAHs compounds in the area (Fig. 2). More than 50% of the contamination is due to the following four compounds: Benzo[a] Pyrene, Benzo [k] Fluoranthene, Benzo[a]Anthracene, and Chrysene, all of which are carcinogens. Benzo[a]Pyrene has the highest concentration and based on TEF, it is the most hazardous one among four pollutants (Table 1). All these compounds have a complex structure with 4 or 5 rings and have low volatility (Table 1).

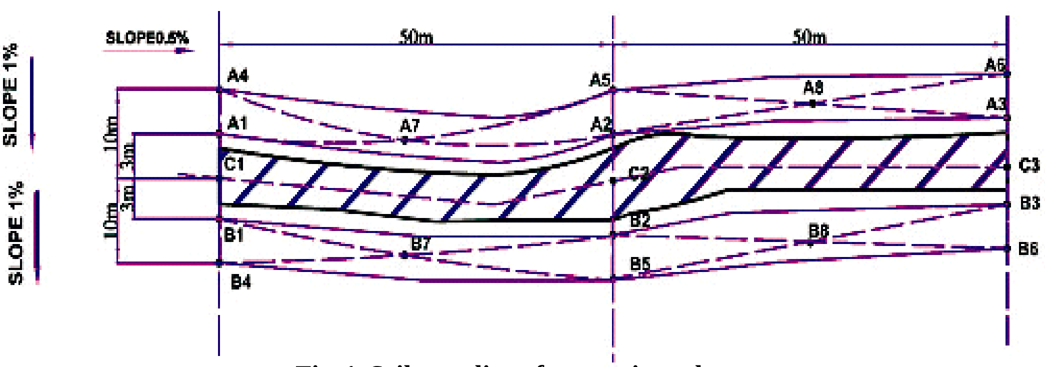


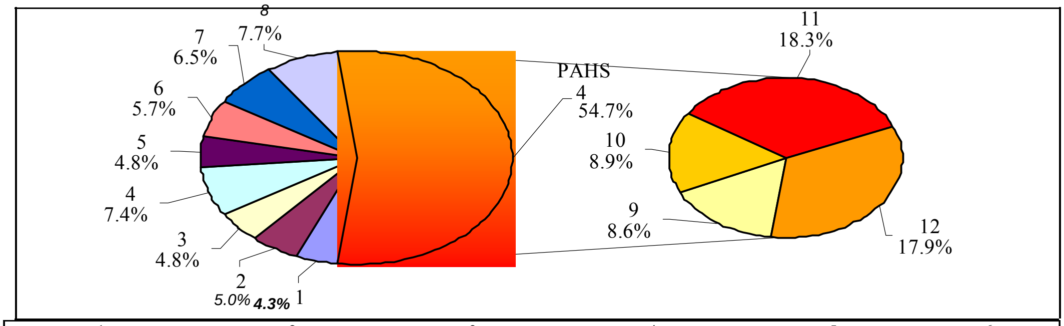
Fig. 1. Soil sampling of contaminated zone

Figure 3 shows permeability coefficient of the soil samples at the stream sides. Permeability ranges from 5.5×10^{-6} to 7.3×10^{-6} cm/sec. Thus, the permeability of soil is relatively low (Das, 1993). A child playing in contaminated soil, a gardener planting trees in the contaminated area, or a worker digging wells in the contaminated soil, might all accidentally ingest polluted soil (Dawoud and Purucker, 1996; Lagoy, 1987; Carman, *et al.*, 1995).

- According to the U.S. EPA regulations, the clean-up level for accidental ingestion of carcinogenic compounds is calculated from the following formula (U.S. EPA, 1996a): Where the terms are defined as follows:

Clean-up Leveel(mg/kg)=

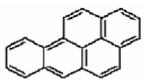
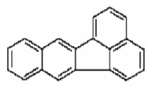
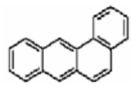
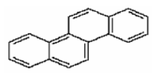
$$\frac{R \times W \times AT(365day/year)}{CSF \times (10^{-6}\,kg/mg) \times IR \times EF \times ED}$$



1	2	3	4	5	6
Naphtalene	Acenaphthylene	Acenaphtene	Fluorene	Phenanthrene	Anthracene
7	8	9	10	11	12
Fluoranthene	Pyrene	Benzo[A] Anthracene	Chrysene	Benzo[K] Fluoranthene	Benzo[A] Pyrene

Fig. 2. Percentage chart for PAHs found in the south of TOR

Table 1. Structures, TEF and volatility factors of four respected contaminants

PAH$_S$	**Benzo [A] Pyrene**	**Benzo [K] Fluoranthene**	**Benzo [A] Anthracene**	**Chrysene**
Structure [(a)]				
TEF [(b)]	1	0.1	0.1	0.01
Henry's Constant [(b)] *(dimless)*	4.63×10^{-5}	3.4×10^{-5}	1.37×10^{-4}	3.88×10^{-3}
Vapor Pressure [(c)] *(mm Hg)*	5.6×10^{-9}	9.6×10^{-11}	2.2×10^{-8}	6.3×10^{-7}

[(a)] *(ATSDR, 1995)*, [(b)] *(U.S. EPA, 1996a)*, [(c)] *(U.S. EPA, 1982)*

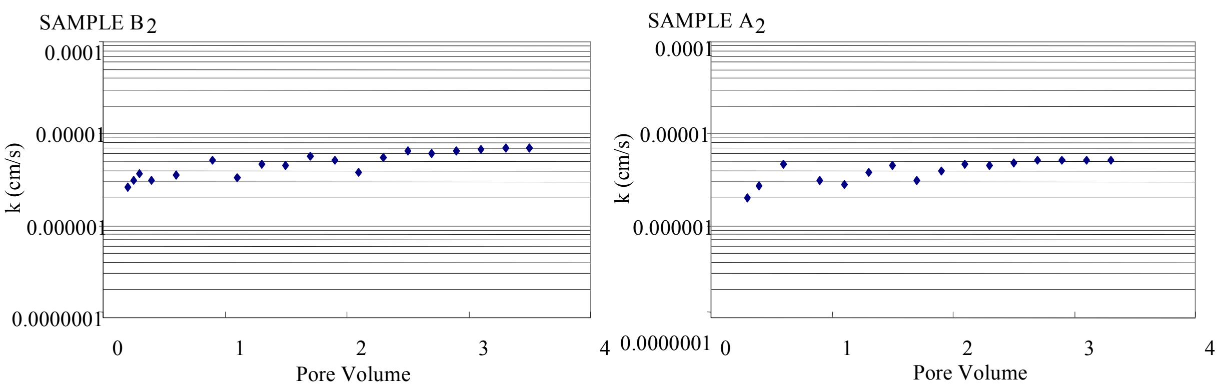


Fig. 3. Soil permeability at the stream sides

- **R:** target excess individual cancer risk (usually specified as 10^{-6}) (U.S. EPA, 1996a).
- **W:** average weight 70 kg, average weight of a person during the contamination period (U.S. EPA, 1996a).
- **AT:** average time, the length of time during which the contaminant can adversely affect a human. It is consider 70 years for carcinogenic compounds (U.S. EPA, 1996a).
- **EF:** exposure frequency, the frequency of coming into contact with the contaminant by a person, which is expressed by the number of days in a year the person, encounters the compound. As the area around (TOR) is residential, it is considered 350 days per year (U.S. EPA, 1996a).
- **ED:** exposure duration, It expresses the number of years the person has been in contact with the contaminant, As the area under investigation is residential, it is considered 30 years (U.S. EPA, 1996a).
- **IR:** contact rate, the amount of contaminant ingested in mg in one day. This number ranges from 50 to 200 mg/day for different ages. As the presence of children in the studied area is certain, it is considered 200 mg/day (U.S. EPA, 1996a; Dawoud and Purucker, 1996).
- **CSF:** cancer slope factor, the carcinogenic potential a chemical compound has for causing cancer as a result of digestion. The more the CSF, the greater the probability of cancer. CSF is obtained as 7.3 $(mg/kg\text{-}day)^{-1}$ for Benzo[a]Pyrene (U.S. EPA, 1996a; IRIS, 2005).

Substitution of the above mentioned value in the clean-up level formulae results in:

Clean-up level for Benzo[a]Pyrene=

$$\frac{(10^{-6})(70)(70)(365)}{(7.3)(10^{-6})(200)(350)(30)} = 0.12\ mg/kg = 120\ ppb$$

Therefore, the clean-up level for Benzo[a]Pyrene is obtained as 120 ppb. Concentration of this compound in the area varies between 108 ppm and 638 ppm, the greatest concentration being for Sample C1 (638 ppm), and the least concentration for Sample A6 at a distance 10 meters from the stream axis is about 108 ppm. The concentration in the area was found to be 800 to 5000 times more than the allowable concentration (120 ppb). This drastic results shows the soil to be highly contaminated, and makes remediation of the area an absolute necessity.

RESULTS & DISCUSSION

According to the results obtained from the analysis of soil samples, and also the calculated clean-up level for accidental ingestion of Benzo[a]Pyrene, the concentration of this carcinogen compound in the area is much higher than the allowable level.

As mentioned before, different methods can be used for remediation of Benzo[a]Pyrene contaminated soils at south of TOR. Each method was separately explained, but ultimately, the Phyto-remediation method via Phyto-transformation and rhizosphere bioremediation is recommended as the best method, because of the geotechnical characteristics of the area, and the chemical and physical properties of Benzo[a]Pyrene. Other methods such as soil flushing and soil vapor extraction are not suitable for the following reasons:

- The soil in the contaminated area is fine grained and contains clay. As a result, physical methods like soil flushing in which water is entered into soil for removing contaminants, cannot be used because they would result in destruction of soil structure, adhesion of soil particles, and soil inflammation (Rister-roberts, 1998, Das, 1993).
- Soil permeability in the contaminated area is relatively low (5.5×10^{-6} to 7.3×10^{-6} cm/sec), and therefore, pumping water and vapor in soil flushing and soil vapor extraction methods would be very costly. (Popovicova and Brusseau, 1998).
- The efficiency of soil vapor Extraction method is a function of Henry's constant and water vapor pressure, so that lower values of Henry's constant and vapor pressure cause decrease in efficiency (Rister-Roberts, 1998; Farhan, 2001). The area studied in this paper is mostly contaminated with Benzo[a]Pyrene and this contaminant has a complex structure with 5 rings and also has a Henry's constant equal to 4.63×10^{-5} (dimless), and a vapor pressure of 5.6×10^{-9} (mm Hg), both of which

are very low (Table 1). Therefore, this method would need more cost and energy.

- Regard petroleum compounds have penetrated the soil texture, surface active agents instead of water should be considered in soil flushing method (Jafvert, 1996). Thus Possibility of secondary changes in soil texture, change of soil acidity as a result of using acid and alkaline flushing agents and possibility soil contamination through flushing agents would be occurred (Jafvert, 1996; U.S. EPA, 1995).

Considering the above reasons and also the fact that phyto-remediation method is much less expensive and it is compatible with clay soils, this method has a further advantage of creating green space in the area, which would reduce the psychological problems associated with pollution as well as remediate the soils (U.S. EPA, 1999; Hedge and Fletcher, 1996). Benzo[a]Pyrene has a complex chemical structure including five benzene rings (Table 1). After destruction of the rings, it is expected that the hazardous effects of this contaminant will be reduced (ToxProbe Inc, 2001; MOE, 1997).

CONCLUSION

Applicable methods to clean-up sites polluted with hydro-carbonic compounds such as soil flushing, soil vapor extraction and phyto-remediation were evaluated. And based on clay texture and relatively low permeability of the soils around TOR, low volatility of Benzo[a]Pyrene the most carcinogenic PAHs in the site and also considering esthetical and psychological aspects, phyto-remediation method via Phyto-transformation and rhizosphere bioremediation is recommended as the best method. Grasses with fibrous roots such as rye, fescue and Bermuda for contaminants up to 1 meter deep and phreatophyte trees such as poplar, willow, cottonwood and aspen for pollutants up to 3 meters deep are suitable for Benzo[a]Pyrene and also compatible with climatology conditions of TOR adjacent areas.

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