# POLYCYCLIC AROMATIC HYDROCARBON CONTAMINATION LEVELS IN COLLECTED SAMPLES FROM VICINITY OF A HIGHWAY

**[*]S.V. Samimi, R. Akbari Rad, F. Ghanizadeh**

Environmental and Energy Division, Research Institute of Petroleum Industry, Tehran, Iran

## ABSTRACT

Tehran as the biggest city of Iran with a population of more than 10 millions has potentially high pollutant exposures of gas oil and gasoline combustion from vehicles that are commuting in the highways every day. The vehicle exhausts contain polycyclic aromatic hydrocarbons, which are produced by incomplete combustion and can be directly deposited in the environment. In the present study, the presence of polycyclic aromatic hydrocarbons contamination in the collected samples of a western highway in Tehran was investigated. The studied location was a busy highway in Tehran. High performance liquid chromatography equipped with florescence detector was used for determination of polycyclic aromatic hydrocarbons concentrations in the studied samples. Total concentration of the ten studied polycyclic aromatic hydrocarbons compounds ranged from 11107 to 24342 ng/g dry weight in the dust samples and increased from 164 to 2886 ng/g dry weight in the soil samples taken from 300 m and middle of the highway, respectively. Also the average of $\sum$ PAHs was 1759 ng/L in the water samples of pools in parks near the highway. The obtained results indicated that polycyclic aromatic hydrocarbons contamination levels were very high in the vicinity of the highway.

**Key words:** Polycyclic aromatic hydrocarbons, dust, vehicle exhausts, highway

## INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) were ranked as the ninth most threatening compounds to human health in 2001 (King *et al*., 2002). The carcinogenicity and mutagenicity of several compounds in this category is proved (Simko, 2002). Several epidemiological studies on PAHs especially among workers exposed to these compounds in a number of countries are carried out (Grimmer *et al*., 1998). High molecular weight PAHs, i.e. PAHs with four or more condensed aromatic rings, are considered to be more dangerous than two and three rings PAHs in view of their higher genotoxic potentials (Yang and Silverman, 1988). These compounds are ubiquitous in the environment; formed naturally by forest fires, volcanoes, plants, fungi and bacteria, or anthropogenically through the combustion of fossil fuels (Hoffman *et al*., 1985; Dickhut *et al*., 2000).

It is conceivable that faster deposition of exhaust aerosol droplets occurs close to the highway; while further spreading mediated by their adsorbed form on the dust particles that are distributed with wind (Tuhackova *et al*., 2001), affects other media (e.g. air, water, soil and plants). Therefore significant exposure risk for human population is strongly expected (Hassanien and Abdel-Latif, 2008).

Acute myocardial infarction associated with increased traffic near homes close to a major roadway (Tonne *et al*., 2007). Also 85% increase in prevalence of coronary heart disease is seen among residents living within 30 Km distance from roads (Hoffman *et al*., 2006). The residences within 75 m of a major road were associated with increased risk of lifetime asthma, current asthma, and wheeze (McConnell *et al*., 2006). It is also reported that children growing up within 500 m of a freeway had deficits in lung growth between ages 10 and 18 years (Gauderman *et al*., 2004).

Tehran with a population of more than 10 million has been facing air pollution for a long time. This huge city occupies ~2300 km$^2$ at an elevation of 1200 m above mean sea level. It is bordered on

[*]Coressponding author: *samimisv@ripi.ir*
 Tel: +98 21 5590 1021, Fax: +98 21 6615 3397

the north, northwest, east and southeast by high to medium height (4000-1000 m) mountain ranges (Halek *et al*., 2006).

As thousands of Iranians live near major highways and concerning that concentrations of the hazardous air pollutants increase near highways, determination of PAH contamination levels, as one class of hazardous air pollutants is a very vital subject. The objective of this study was to evaluate the concentration of these contaminants in the dust, soil and water samples collected from the vicinity of a western highway in Tehran that its daily traffic is very high. Analytical procedure includes extraction by ultrasonication, cleanup by column chromatography and determination by HPLC with florescence detector.

## MATERIALS AND METHODS

*Sampling location*

For evaluating the PAH contamination levels, the dust, soil and water samples were taken form the nearest locations to Kashani highway leading to Noor square in Tehran. The sampling locations are shown in Fig. 1 and all samples were collected during summer (Fig. 1).

The dust samples were collected from five sites over highway and transferred in hexane washed aluminum foil sheets. Dust samples 1, 2, and 3 were collected from the guardrails of Kashani highway leading to Noor square, dust 4 was from a bus station that located in front of the fuel station and dust 5 was collected from the verge surface of the highway.

For studying the role of the dusts on the contamination of soil and water resources in the vicinity of highway, three soil and two water samples were collected as pretest. Sampling of soils 1 and 2 were respectively performed in the proximity of the trees that located between the guardrails in the middle and verge of the highway. Soil sample 3 was taken from the most distant site about 300 m from the highway. The collected soil samples homogenised through a sieve (250 µm mesh).

Water samples were collected in the pre-cleaned glass bottles from pools in the two parks near the highway. One was located in the proximity of Noor square and the other in the intersection of Abazar Street and Kashani highway. All of the taken samples were stored at 4ºC prior to extraction.
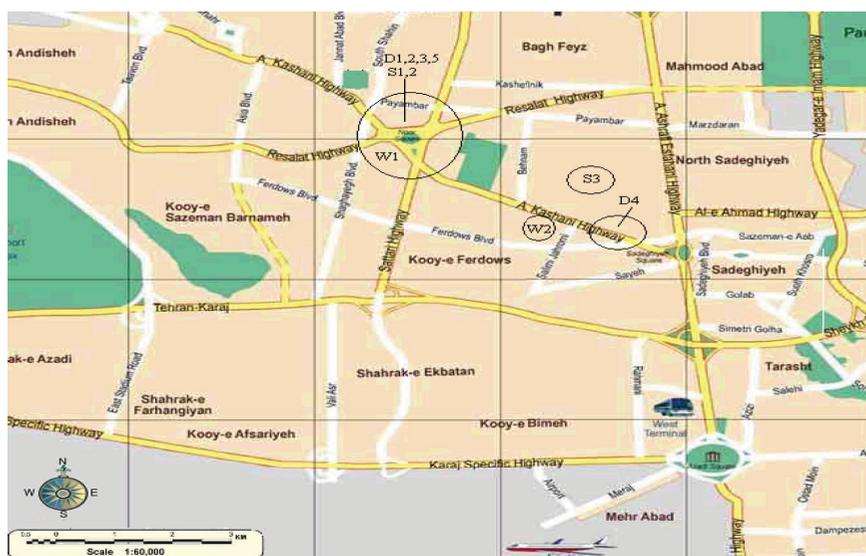


Fig. 1: Sampling locations map of Kashani highway in Tehran (D: Dust, S: Soil, W: Water)

*Chemicals*

EPA 610 PAH reference standard mixture was purchased from Macherey-Nagel and diluted in acetonitril to desired concentrations. The ten studied PAHs were; naphthalene (naph), phenanthrene (phen), anthracene (ant), fluoranthene (flt), pyrene (py), benzo(a)anthracene (baa), chrysene (chry), benzo(k)florantene (bkf), benzo(α)pyrene (bαp), and benzo(ghi)perylene (bghip) and

also individual PAH standards (Aldrich) stock solutions were prepared by dissolving the pure standard compounds in acetonitril. HPLC grade dichloromethane, hexane, acetontril, cyclohexane and anhydrous sodium sulfate were purchased from Merk company. 0.5 μm Millex-SR filters were supplied from Millipore company. Silica gel (100-200 mesh) and alumina (70–230 mesh) were from Aldrich company (Jiries *et al*., 2003).

*Extraction*
An ultrasonic water bath was used in the extraction procedure of the dust and soil samples. The dust samples were air-dried and soil samples were dried in an oven at 60ºC for overnight before extraction. 200 mg of each dust sample and 1-2 g of each soil sample were sonicated for 30 min with 20 mL of dichloromethane in 50 mL Erlenmeyer flasks (twice). The dichloromethane extracts were mixed and then filtered over 0.5 μm filters (Xiaohong *et al*., 2005).
1 L of each water sample was transferred into a 2-L separatory funnel, and then 60 mL of dichloromethane was added. The separatory funnel was shaken vigorously for about two minutes with periodic venting to release vapor pressure. The organic layer was allowed to separate for 10 min and was collected into 250 mL Erlenmeyer flasks. This process was repeated with the aqueous layer (twice). The three portions of dichloromethane extracts were mixed and passed through a funnel containing anhydrous sodium sulfate. The sample extracts were concentrated to dryness by a rotary evaporator in 35 ºC and residue was dissolved in cyclohexane before column chromatography (US EPA method 550).

*Cleanup procedure*
For cleanup procedure a column chromatography method was developed and used. Obtained recovery of the developed column was 95-99% for PAHs standard solution. The chromatographic column (30 cm×1 cm i.d.) was packed with 10 g of silica gel and then 4 g Alumina (activated at 130 ºC and deactivated by 3% (w/w) distilled water). About 1-2 cm of anhydrous sodium sulfate was placed at the top of column to adsorb any water in the sample extracts. The column was pre-

eluted with hexane, and prior to exposure of the sodium sulfate layer to air, concentrated extract in cyclohexane was transferred onto the column and allowed to sink below sodium sulfate layer. The aliphatic fraction was eluted with 20 mL hexane and discarded, and then the aromatic fraction was eluted with a 40 mL mixture of dichloromethane-hexane (50:50 v/v). After evaporation of aromatic fraction to dryness by a rotary evaporator in 35ºC, the residue was redissolved in dichloromethane and transferred into a 4 mL glass vial, then allowed to dryness under a gentle gas stream of purified nitrogen. For PAHs analysis before injection to the HPLC system the residue was dissolved in 1 to 2 mL of acetonitril and filtered using a 0.5 μm syringe filter. The mentioned procedures were performed for all of the sample extracts (Hodgeson, 1990).

*PAHs analysis*
The determination of PAH contents in the samples was carried out with Waters high performance liquid chromatography (HPLC) system equipped with 410 binary pumps, 470 scanning fluorescence detector, Reodyne 7725i injection loop(20 μL) and a PAH C18 column (250×4.6 mm, particle size-5 μm). The following program was developed in the laboratory for separations at a constant flowrate of 1 mL/min:
1- Isocratic elution with a 65:35 (v/v) mixture of acetonitrile and water for 14.5 min.
2- Gradient elution by increasing acetonitrile proportion to 100% within 5 min.
3- Isocratic elution with pure acetonitre for 15.5 min.
The excitation and emission wavelengths of the detector were programmed versus time according to Table 1. Selection of wavelengths was based on specific excitation and emission wavelengths of PAHs.

Table 1: The wavelength vs. time program of the florescence detector

| Time (min) / Wavelength | 0-8 | 8-11.5 | 11.5-17 | 17-22 | 22-30 |
|---|---|---|---|---|---|
| Excitation (nm) | 280 | 260 | 340 | 280 | 383 |
| Emission (nm) | 389 | 420 | 425 | 389 | 405 |

The individual PAH compounds were identified by comparison of retention times with the retention times of reference standard solutions.

Quantifications were based on the peak areas against the five-point external standard calibration curves for each studied PAH.

The limit of detection (S/N=3) and relative standard deviation (RSD%) of three replicates for each studied PAH in the mid point concentrations of the calibration curves (50 ng/g) are demonstrated in Table 2. The instrument was calibrated daily with calibration standards. Quality control procedures for method validation include analyses of method blanks (solvents), spiked blanks (solvents spiked with PAH standards) and spiked matrices. A spiked sample was prepared by adding a standard solution of analytes in acetonitrile at a level of 50 ng/g to uncontaminated dust, soil and distilled water samples. The average recoveries for the studied PAH compounds in the spiked dust and soil samples were 68–87%, and in the spiked water sample were 78-89%.

Table 2: Limits of detection (LOD) in ng/g and relative standard deviation (RSD %) of three replicates for PAHs standard solution (50 ng/g)

| Compound | LOD | RSD (%) |
|----------|-----|---------|
| naph | 0.64 | 8.08 |
| phen | 0.19 | 0.35 |
| ant | 0.01 | 0.48 |
| flt | 0.05 | 2.4 |
| py | 0.02 | 0.78 |
| baa | 0.004 | 7.64 |
| chry | 0.04 | 12.95 |
| bkf | 0.005 | 2.27 |
| bαp | 0.003 | 3.06 |
| bghip | 0.01 | 1.17 |

## RESULTS

Sixteen PAHs are introduced as priority pollutants by the United State Environmental Protection Agency (USEPA) and some of them are considered as human carcinogens by International Agency for Research on Cancer (IARC, 1983) such as benzo(a)anthracene (baa), chrysene (chry), benzo(k)florantene (bkf), benzo(α)pyrene (bαp), (IARC, 1983). The mean concentration of the ten studied PAH compounds in ng/g dw (dry weight) are shown in Table 3 (all samples were analyzed in triplicates).

## DISCUSSION

As there were no previous published data on the PAH contamination of the settled dust in the vicinity of a highway (on surface of guardrail, soil and water) in Iran, the major aim of the present study was to evaluate concentration and source of PAHs in a highway located in the west of Tehran as a basic study for future characterization the level of the PAH contaminants related to traffic in different regions of Tehran.

Halek *et al.*, (2006) have demonstrated air pollution in Tehran atmosphere is higher than the US national ambient air quality standard (NAAQS) for particulate matters smaller than 10 μm (PM 10) and reported the atmospheric level of ∑PAHs for different sites in Tehran in the range of 44.1 ng/m$^3$ to 130 ng/m$^3$ and according to their results the western station was more contaminated than other stations.

In the present study, the ∑PAHs levels ranged from 11107 to 24342 ng/g dw in the dust samples. Dust 3 contained the lowest amount of ∑PAHs, among the other guardrail dusts which is a result of different sampling locations. Dust 1 and 2 were taken from the middle guardrails which

Table 3: The mean concentration of the studied PAHs in ng/g dw of dust and soil samples and also in ng/L of water samples collected from the vicinity of the highway

| PAHs Sample | naph | phen | ant | flt | py | baa | chry | bkf | bαp | bghip | PAHs |
|-------------|------|------|-----|-----|-----|-----|------|-----|-----|-------|------|
| Dust 1 | 3589 | 3304 | 204 | 1958 | 2162 | 161 | 910 | 94.4 | 70.8 | 727 | 13179 |
| Dust 2 | 7102 | 1674 | 181 | 1402 | 2081 | 97.6 | 136 | 67.8 | 72.4 | 465 | 13278 |
| Dust 3 | 6931 | 2084 | 45.3 | 951 | 680 | 37.3 | 193 | 23.0 | 23.4 | 139 | 11107 |
| Dust 4 | 14836 | 3999 | 150 | 1495 | 2345 | 87.5 | 828 | 79.6 | 48.3 | 465 | 24342 |
| Dust 5 | 8482 | 2252 | 75.1 | 525 | 976 | 153 | 560 | 29.3 | 51.4 | 289 | 13393 |
| Soil 1 | 1365 | 672 | 81.5 | 224 | 234 | 9.0 | 28.4 | 13.9 | 30.8 | 227 | 2886 |
| Soil 2 | 515 | 215 | 6.50 | 32.6 | 19.6 | 1.50 | 7.0 | 1.70 | 4.10 | 9.0 | 812 |
| Soil 3 | 55.3 | 66.6 | 2.0 | 13.3 | 13.3 | 0.70 | 10.2 | 0.15 | 0.32 | 1.97 | 164 |
| Water 1 | 733 | 714 | 25.3 | 209 | 120 | 6.60 | 24.8 | 9.80 | 10.8 | 73.4 | 1927 |
| Water 2 | 580 | 612 | 19.3 | 176 | 95.1 | 10.3 | 17.7 | 11.1 | 9.70 | 59.6 | 1591 |

were in contact with the vehicle emissions from two sides, while dust 3 was taken from the verge guardrail that was in contact with only one side. Dust 4 was the most contaminated sample because it was taken from a bus station which was located in front of the fuel station in the highway. Dust 5 from the verge surface of the highway was also contaminated because of direct contact with deposited particles from the vehicle exhaust. Few references exist for PAHs contamination of guardrails for example Oda *et al*., (2001) have reported 15000 ng/g dw (total of pyrene, fluoranthene and phenanthrene) PAH level of guardrail dusts in a roadway tunnel in Japan. Comparing to values observed on guardrails dusts in a tunnel in Japan the overall levels of PAHs in this study in the highway was high.

The levels of the dust PAHs were higher than soil samples; it may be due to emitted particles from exhaust, directly settled on guardrails and surface of highway whereas adsorbed dust PAHs on the soil surface can be washed by runoff water.

The ∑PAHs level of soil 1 (2886 ng/g dw) was approximately three times higher than soil 2 (812 ng/g dw) because soil 1 was taken from the middle of the highway and soil 2 was from the highway verge. Soil 3 had the lowest amount of ∑PAHs (164 ng/g dw) that was taken from the most distance site, i.e. 300 m from the highway and can be regarded as an unaffected location by vehicle exhausts. Also the ∑PAHs level of soil 1 was about eighteen times higher than soil 3. These results indicated that the contamination levels of the soil samples by settled dust are dependant on their distance from source of pollution.

These results are in accordance with reported values for PAH contamination levels of soil ∑PAHs near north-east of France highways i.e. 1292 ng/g dw (Ducoulombier and Rychen, 2003) and 3095 ng/g near Prague, Czech Republic (Tuhackova *et al*., 2001).

Regarding obtained results for water samples of pools 1759 ng/L (average of ∑PAHs for two water samples), contamination of the surface of water in the parks in the highway vicinity by settled dusts of vehicle exhausts was very low in comparison with guardrail dusts.

The PAH depositions depends on the gas particle partition in the ambient air. The gasoline engine exhausts and several diesel exhausts were characterized by high percentages of naphthalene (Pengchai *et al*., 2002). Naphthalene and phenanthrene are compounds mostly found in air (Ducoulombier and Rychen, 2003); the presence of these compounds were from incomplete combustion of fuels by vehicles, which leads to their emission and further adsorption on the suspending particles in the air and settled in the surface of the guardrails, soil and water in the highways vicinity.

As shown in Table 3, the most abundant PAHs species were naphthalene and phenanthrene (low molecular weight PAHs) approximately 70-80% of the ∑PAHs in the investigated samples. These results are in accordance with the reported results of the particle matter distribution of PAHs in Tehran (Haleks *et al*., 2006) and confirmed that their source is incomplete combustion of fuels by vehicles.

Finally, the obtained results indicated that vicinity of highway was very contaminated and the concentrations of the PAHs were varied among sampling location. Therefore, living in highway vicinity will increase the health hazard of people and vehicle drivers that are commuting in the highways. As a consequence, measurement of PAH concentrations is important in establishing basic information for future monitoring and assessment of PAHs accumulation in the surrounding areas of highways.

## REFERENCES

Dickhut, R. M., Canuel, E. A., Gustafson, K. E., Liu, K., Arzyus, K. M., Walker, S. E., Edgecombe, G., Gaylor, M. O., MacDonlad, E. H., (2000). Automotive sources of carcinogenic polycylic aromatic hydrocarbons associated with particulate matter in the Chesapeake Bay Region. Environ. Sci. Techno., **34**: 4635-4640.

Ducoulombier, C. C. and Rychen, G., (2003). Assessment of soil and grass polycyclic aromatic hydrocarbon (PAH) contamination levels in agricultural fields located near a motorway and an airport. J. Agronomic, **23**: 345-348.

Gauderman, W. J., Avol, E., Gilliland, F., (2004). The effect of air pollution on lung development from 10 to 18 years

of age. N. Engl. Med., **351**: 1057-1067.

Grimmer, G., Brume, H., Dettbarn, G., Naujack, K. W., Mohr, U., Hartung, R.W., (1988). Urinary and faecal excretion of chrysene and chrysene metabolites by rats after oral, intraperitoneal, intratracheal or ntrapulmonary application. Arch. Toxicol., **62**: 401-405.

Halek, F., Nabi, G. H., Ganjidoust, H., Keyanpour, M., Mirmohammadi, M., (2006). Particulate polycyclic aromatic hydrocarbons in urban air of Tehran. Iran. J. Environ. Health Sci. Eng., **3** (3): 247-254.

Hassanien, M. A., Abdel-Latif, N. M., (2008). Polycyclic aromatic hydrocarbons in road dust over Greater Cario, Egypt. J. Hazard. Mat., **151**: 247-254

Hoffman, E. J., Latimer, J. S., Hunt, C. D., Mills, G. L., Quinn, J. G., (1985). Stormwater runoff from highways. Water, Air and Soil Pollu., **25**: 349-364.

Hodgeson, J. W., (1990). Determination of polycyclic aromatic hydrocarbons in drinking water by liquid-liquid extraction and hplc with coupled ultraviolet and fluorescence detection**.,** Environ. Monitoring system Lab., Cincinnati, Ohio, 45268.

Hoffman, B., Moebus, S., Stang, A., Beck, E. M., Dragano, N., Möhlenkamp, S., Schmermund, A., Memmesheimer, M., Mann, K., Erbel, R., Jöckel, K. H., (2006). Residence close to high traffic and prevalence of coronary heart disease. Europ. Heart J., **27** (22): 2696-2702.

IARC (International Agency for Research on Cancer), (1983). IARC monographs on the evaluation of the carcinogenic risk of chemicals to human. Polynuclear aromatic compounds, Part I chemical environmental and experimental data. World health organization, Geneva, Switzerland.

Jiries, A. G., Hussein, H. H., Lintelmann, J., (2003). Polycyclic aromatic hydrocarbon in rain and street runoff in Amman, Jordan. J. Environ. Sci., **15** (6): 848-853**.**

King, S., Meyer, J. S., Andrews, A. R. J., (2002). Polycylic aromatic hydrocarbons in soil using hollow fiber

membrane solvent microextraction. J. Chromatogr. A, **982**: 201-208.

McConnell, R., Berhane, K., Yao, L., Jerrett, M., Lurmann, F., Gilliland, F., Künzli, N., Gauderman, J., Avol, E. D., Thomas, D., Peters, J., (2006). Traffic, susceptibility, and childhood asthma. Environ. Health Perspect., **114** (5): 766–772.

Oda, J., Nomura, S., Yasuhara, A., Shibamoto, T., (2001). Mobile sources of atmospheric polycyclic aromatic hydrocarbons in a roadway tunnel. Atmos. Environ., **35** (28): 4819-4827

Pengchai, P., Nakajima, F., Furumai, H., (2002). PAH profiles of vehicle exhaust, Tires and road materials and their contribution to PAHs in road dusts. J. Environ. Sci., **15** (6): 433-442

Simko, P., (2002). Determination of polycyclic aromatic hydrocarbons in smocked meat products and smoke flavouring food additives. J. Chromatogr. B, **770**: 3-18.

Tonne, C., Melly, S., Mittleman, M., Coull, B., Goldberg, R., Schwartz1, J., (2007). A case–control analysis of exposure to traffic and acute myocardial infarction. Environ. Health Perspect., **115** (1): 53–57.

Tuhackova, J., Cajthaml, T., Novak, K., Novotny, C., Mertelik, J., Sasek, V., (2001). Hydrocarbon deposition and soil microflora as affected by highway traffic. J. Environ. Pollut., **113**: 255-26.

US EPA, (1990). Method 550, Determination of polycyclic aromatic hydrocarbons in drinking water by liquid extraction and HPLC with coupled ultraviolet and fluorescence detection.

Xiaohong, L., Xinhui, B., Bixian, M., Guoying, S., Jiamo F., (2005). Separation of PAHs in aerosol by thin layer chromatography for compound-specific stable carbon isotope analysis. Talanta, **66**: 487–494.

Yang, S. K., Silverman, B. D., (1988). Polycyclic aromatic hydrocarbon carcinogenesis: Structure activity relation ships. CRC Press, Boca Raton, FL.