

Wet deposition of hydrocarbons in the city of Tehran-Iran

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Received: 3 August 2009 / Accepted: 15 September 2009 / Published online: 11 November 2009
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Abstract Air pollution in the city of Tehran has been a major problem for the past three decades. The direct effects of hydrocarbon contaminants in the air are particularly important such as their carcinogenic, mutagenic, and teratogenic effects which can be transported to other environments via dry and wet deposition. In the present study, rainwater samples were collected and analyzed for 16 polycyclic aromatic hydrocarbons (PAHs), benzene, toluene, ethyl benzene, and xylene (BTEX) as well as fuel fingerprints in two ranges of gasoline (C5–C11) and diesel fuel (C12–C20) using a gas chromatograph equipped with a flame ionization detector (GC/FID). Mean concentrations of Σ 16 PAHs varied between 372 and 527 $\mu\text{g/L}$ and for BTEX was between 87 and 188 $\mu\text{g/L}$ with maximum of 36 $\mu\text{g/L}$ for toluene. Both gasoline range hydrocarbons (GRH) and diesel range hydrocarbons (DRH) were also present in the collected rainwater at concentrations of 190 and 950 $\mu\text{g/L}$, respectively. Hydrocarbon transports from air to soil were determined in this wet deposition. Average hydrocarbon transportation for Σ PAHs, BTEX, GRH, and DRH was 2,747, 627, 1,152, and 5,733 $\mu\text{g/m}^2$, respectively.

Keywords Wet deposition · Rainwater · Hydrocarbon · PAHs · BTEX · Air pollution · Tehran · Iran

Introduction

The World Health Organization states that 2.4 million people die annually from causes directly attributable to air pollution (WHO 2008). The hydrocarbon pollutants are especially important in the formation of secondary pollutants such as “photochemical smog” in the atmosphere. The direct effects of hydrocarbon contaminants in the air are particularly important such as their carcinogenic, mutagenic, and teratogenic effects (Maskaoui and Hu 2009; Yang et al. 2008; Zrafi-Nouira et al. 2008). The aromatic hydrocarbons such as benzene, toluene, ethyl benzene, xylene (BTEX), and the polycyclic aromatic hydrocarbons (PAHs) are of extreme importance among the hydrocarbon contaminants due to their dangerous consequences (Futoma et al. 1981). PAHs are composed of two or more fused aromatic rings of carbon and hydrogen atoms. The US Environmental Protection Agency (USEPA) has listed 16 PAHs as priority pollutants (USEPA 1993), and they have been classified into probable or possible human carcinogens by the International Agency for Research on Cancer (2008). Carcinogenicity of polycyclic aromatic hydrocarbons was reported by Sundberg and co-authors in 1998 and exposure to polycyclic aromatic hydrocarbons and their carcinogenic potencies from vehicle engine investigated by Tsai et al. (2004). The effects of PAHs upon the cytochrome P450 monooxygenase system were also widely investigated (Zhang et al. 2006; Roos et al. 2002; Achazi et al. 1998).

The main source of PAHs in the environment is incomplete combustion of modern biomass such as wood and fossil fuels including petroleum and coal. In the cities, traffic has been known to be the greatest PAH sources (Tsai et al. 2004). Menichini et al. (1999) carried out a study in a medium traffic area in Rome to investigate polycyclic aromatic hydrocarbons.

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The air pollution in the city of Tehran, Iran is mainly due to the fact that the city is surrounded by the Alborz Mountains and is also climatically very prone to the inversion phenomena. There are over one million automobiles, thousands of factories, and over ten million people living in the city of Tehran. The air pollutants in Tehran include hydrocarbons, halogenated compounds, heavy metals, NO_x, SO_x, and many others.

Several reports have been published on Tehran air quality (Kakooei et al. 2009; Hosseinpour et al. 2005; Yokoyama and Takahashi 2003; Shirazi and Harding 2001; Asl-Soleimani et al. 2001; Sohrabpour et al. 1999), but a few articles have an approach to hydrocarbon pollution, Halek et al. (2008) evaluated PAHs in the gas phase in Iranian urban atmosphere. Jafari and Ebrahimi (2007) determined the concentration of benzene in Tehran air and estimated the cancer risk assessment of benzene. Pardakhti et al. (2004) investigated quantity of polycyclic aromatic hydrocarbons in the ambient air of the city of Tehran, and Esmaili-Sari (1997) reported the amount of PAHs compounds in Tehran air via wet deposition.

The current study is focused on the determination of hydrocarbon via wet deposition in city of Tehran. Polycyclic aromatic hydrocarbons, benzene, toluene, ethyl benzene and xylene, as well as fuel fingerprints containing gasoline range hydrocarbons (GRH) and diesel range hydrocarbons (DRH), are investigated.

Methods and materials

Sampling

The samples were taken in the central part of Tehran, the capital city of Iran, during the first hour of rainfall in containers with a 500-mm diameter. Collected rainwater samples were immediately sent to the laboratory for hydrocarbon analysis.

Chemical and standards

TCL polynuclear aromatic hydrocarbon mix standards were obtained from Supelco (Bellefonte, PA, USA). Gasoline range and diesel range standards were made from commercial fuels in the environmental laboratory, Faculty of Environment, University of Tehran. BTEX standards, anhydrous granular sodium sulfate, extraction solvents including hexane (Chromatographic grade), and dichloromethane (Chromatographic grade) were all purchased from Merck (Darmstadt, Germany).

Chemical analysis

One liter of each sample was extracted three times by dichloromethane using a separatory funnel following USEPA

method 3510 (USEPA 1991). The extract was then cleaned up by a chromatographic column and dehydrated using 10 g anhydrous granulated sodium sulfate (heated for 8 h at 500°C) and concentrated to 1 mL by a rotary evaporator.

A UNICAM 610 Gas Chromatograph (Unicam, Cambridge, UK) equipped with a flame ionization detector (GC/FID) was employed to analyze the final extract. A DB-5 column with 30 m length, 0.33 mm ID, and 1 μm film thickness was used and the carrier gas was helium. The GC settings were as follows: injector temperature=250°C, detector temperature=340°C, oven initial temperature=45°C, initial time=3 min, ramp=20°C/min, final temperature=310°C, final time=3 min. The injection volume was 1 μL (USEPA 1991).

Quality assurance and quality control

Quality assurance and quality control (QA/QC) was detailed and comprehensive according to method 8000B (USEPA 1991). Instrument blanks were performed after instrument calibration, and laboratory/extraction blanks were analyzed for each batch. No hydrocarbon residue was observed in blank samples ($n=3$). At least four calibration standard concentrations were used for each GC run, and correlation coefficients for calibration curves was higher than 0.98 for all target compounds. Samples were analyzed in triplicate. Percent relative standard deviation (RSD) was calculated using the following equations:

$$\overline{CF} = \frac{\sum_{i=1}^n CF_i}{n} \quad (1)$$

$$SD = \sqrt{\frac{\sum_{i=1}^n (CF_i - \overline{CF})^2}{n - 1}} \quad (2)$$

$$RSD = \frac{SD}{\overline{CF}} \times 100 \quad (3)$$

where n is the number of calibration standards, SD refers to standard deviation and \overline{CF} is mean external standard calibration. Average RSD in this study was 4.33%. Detection limit (signal/noise=3) and average percent recovery for all hydrocarbons is summarized in Table 1.

Data analysis

Statistical analysis of the results was performed using SPSS 16.0 (SPSS Inc., Chicago, IL, USA). Records were compared by ANOVA tests at the level of $p < 0.05$, and the homogeneity of variance was also performed.

Table 1 Detection limit ($\mu\text{g/L}$) and average recovery (%) for each hydrocarbon group

No	Hydrocarbon	Detection limit ($\mu\text{g/L}$)	Average recovery (%)
1	PAHs	5	85.1
2	BTEX	10	78.3
3	GRH	30	82.1
4	DRH	30	94.8

Results and discussion

PAHs

The concentration of 16 polycyclic aromatic hydrocarbons, all on the USEPA priority pollutant list, was reported in Table 2.

Average $\sum\text{PAHs}$ of $452 \mu\text{g/L}$ show an unsafe amount. Figure 1 illustrates normal P–P Plot of expected and observed values of PAHs in Tehran rainwater; it demonstrated that expected and observed values of PAHs followed the regression line tightly and were distributed randomly and normally. In one study performed by World Meteorological Organization in 1993, the average concentrations of PAHs in the rain water (wet deposition) were reported between 0.6 and $231 \mu\text{g/L}$ (Esmaili-Sari 1997). The comparison of these results with the 1993 study clearly indicates that the concentration of carcinogenic PAHs doubled since 1993. Among all, Fluoranthene at $76 \mu\text{g/L}$ had the highest concentration of PAHs found. Figure 2 presents PAHs as the benzene ring numbers. Among all, three-ring PAHs (acenaphthylene, acenaphthene, fluorine,

phenanthrene, anthracene) at $190 \mu\text{g/L}$ was the highest concentration in Tehran rainwater samples. Average five-ring PAHs (benz(a)anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo(a)pyrene) as the most hazardous PAHs were detected at $111 \mu\text{g/L}$. Hollander et al. (1986) reported the concentrations of 11 PAH in rainwater at four locations in the Netherlands in 1983. Kishida et al. (2008) determined PAHs in the air at $1.3 \mu\text{g/m}^3$ in a bus terminal in Hanoi, Vietnam. Delhomme et al. (2008) determined $\sum 16$ PAHs in France at maximum $1,596 \text{ ng/L}$ in Strasbourg. Poster and Baker (1996) measured concentrations of PAHs in atmospheric and precipitation samples collected at a rural site adjacent to the Chesapeake Bay during late summer 1992 and determined phenanthrene at 3.6 ng/L . These results demonstrate that Tehran air pollution by PAHs is of higher value than other published reports.

BTEX

Benzene, toluene, ethyl benzene, and xylene were measured for the first time in Tehran's rainwater. Among BTEX,

Table 2 Polycyclic aromatic hydrocarbons amount ($\mu\text{g/L}$)

No	Name	Abbreviation	Formula	Mean	SD
1	Naphthalene	NPH	C_{10}H_8	27	5.51
2	Acenaphthylene	ACY	C_{12}H_8	17	6.08
3	Acenaphthene	ACE	$\text{C}_{12}\text{H}_{10}$	22	9.61
4	Fluorine	FL	$\text{C}_{13}\text{H}_{10}$	37	4.00
5	Phenanthrene	PHE	$\text{C}_{14}\text{H}_{10}$	59	36.86
6	Anthracene	ANT	$\text{C}_{14}\text{H}_{10}$	54	16.77
7	Fluoranthene	FLT	$\text{C}_{16}\text{H}_{10}$	76	28.54
8	Pyrene	PYR	$\text{C}_{16}\text{H}_{10}$	18	15.95
9	Benz(a)anthracene	BaA	$\text{C}_{18}\text{H}_{12}$	19	20.66
10	Chrysene	CHR	$\text{C}_{18}\text{H}_{12}$	12	10.21
11	Benzo[b]fluoranthene	BbF	$\text{C}_{20}\text{H}_{12}$	17	4.04
12	Benzo[k]fluoranthene	BkF	$\text{C}_{20}\text{H}_{12}$	15	4.51
13	Benzo(a)pyrene	BaP	$\text{C}_{20}\text{H}_{12}$	49	15.10
14	Indeno(1,2,3-cd)pyrene	IP	$\text{C}_{22}\text{H}_{12}$	15	12.86
15	Dibenzo(ah)anthracene	DBA	$\text{C}_{22}\text{H}_{14}$	10	2.02
16	Benzo(ghi)perylene	BghiP	$\text{C}_{22}\text{H}_{12}$	16	5.69

SD standard deviation

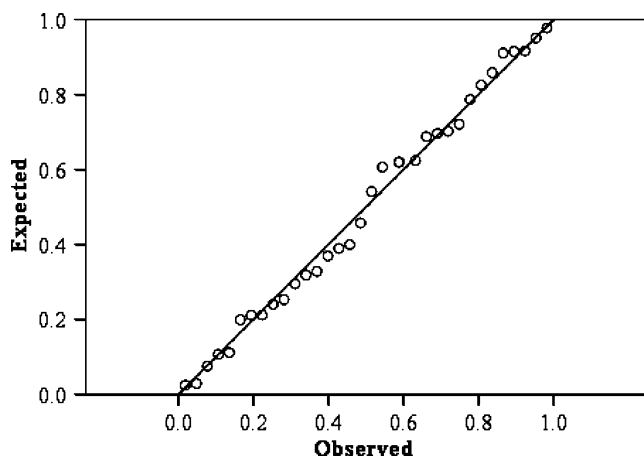


Fig. 1 Normal P–P plot of expected and observed values of PAHs in Tehran rainwater

toluene had the highest concentration of 37 $\mu\text{g/L}$, and xylene was 21 $\mu\text{g/L}$ which includes all three isomers (Σ ortho, meta, and para isomers). The concentrations of BTEX are presented in Table 3. Compared to other reports, Okochi et al. (2004) determined toluene concentration of 14.4 $\mu\text{g/L}$ in rainwater in Yokohama, Japan. The fate of volatile organic compounds (VOCs), which are emitted into the troposphere from various anthropogenic and biogenic sources, remains to be elucidated. In general, air pollutants in the lower troposphere are dispersed by horizontal advection and upward diffusion and removed by deposition process (wet and dry deposition) and chemical transformation, depending on their physicochemical properties. Because of the toxicity of these volatile aromatic compounds (Do Rego and Pereira Netto 2007; An 2004), they should be controlled and monitored regularly in air and water environments.

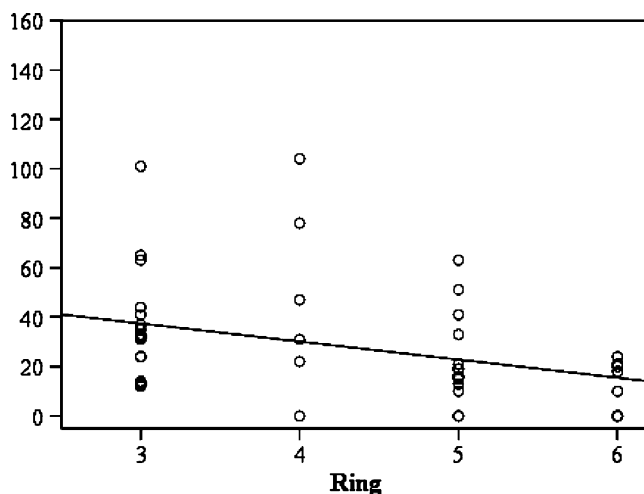


Fig. 2 Relationship between three-, four-, five- and six-ring PAHs in Tehran rainwater

Table 3 BTEX amount ($\mu\text{g/L}$)

No	Name	Formula	Mean	SD
1	Benzene	C_6H_6	25	8.50
2	Toluene	C_7H_8	37	12.66
3	Ethylbenzene	C_8H_{10}	16	14.64
4	xylene	C_8H_{10}	21	5.03

SD standard deviation

GRH and DRH

Unburned hydrocarbon emission contamination has been a serious hazard concern in the city. Employing old and low quality vehicles, substandard engines and poor gas station operation are the main cause of high amount of unburned fuels in Tehran Air. Gasoline and diesel range hydrocarbons were investigated in the Tehran rainwater samples for fuel fingerprints. GRH with the carbon range of C5–C11 and DRH with C12–C20 range (Verschuere 2001) were measured at 190 ± 18 and 950 ± 187 $\mu\text{g/L}$, respectively. Total fuel (Σ GRH and DRH) were between 945 and 1,330 $\mu\text{g/L}$ with an average of 1,140 $\mu\text{g/L}$. Significant positive correlations were observed between GRH and BTEX in all samples; it highly indicated that they can be from the same sources. Nevertheless, the lack of statistically significant correlation between GRH and Σ PAHs ($p < 0.05$) suggests that these hydrocarbons entered Tehran air from different sources. It is estimated that hydrocarbon fuels can enter Tehran soil ecosystems via wet and dry deposition, as well as during refueling of automobiles in the gas stations, industrial runoff, and from leakage underground fuel tanks.

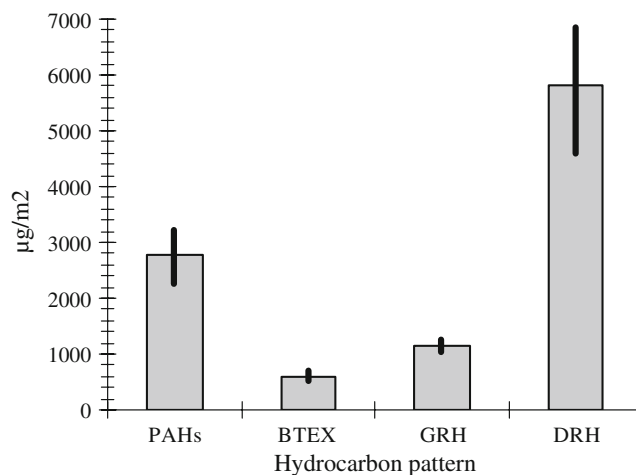


Fig. 3 Hydrocarbon transport from air to soil in city of Tehran via this wet deposition

Pollutant transport evaluation

Pollutant transport (T_P) is a key issue in hydrocarbon monitoring in the environment. Pollutant transports ($\mu\text{g}/\text{m}^2$) were calculated using Eq. 4:

$$T_P = \sum_{i=1}^{i=n} C_P \times V_R \quad (4)$$

where n is rain times, C_P is mean concentration ($\mu\text{g}/\text{L}$) of target pollutant, and V_R donates volume of each rainwater (L/m^2). Pollution transport for each hydrocarbon group is presented in Fig. 3. Olivella (2006) reports wet deposition fluxes of the total PAHs range from 2.5 to 41 $\mu\text{g}/\text{m}^2/\text{month}$, in north Italy. Average ΣPAHs transport in Tehran shows 2,747 $\mu\text{g}/\text{m}^2$. Clearly, these are an alarming amount of hydrocarbon pollutants that eventually end up in the soil ecosystems, surface waters, and the ground waters, causing severe environmental health hazards.

Conclusions

Growing population, increased vehicular emissions, and cheap fuel prices are the major contributors to Tehran hydrocarbon air pollution. Our study demonstrated that the concentrations of hydrocarbons are extremely high in Tehran rainwater samples. Mean concentrations of $\Sigma 16$ PAHs was between 372 and 527 $\mu\text{g}/\text{L}$, BTEX was between 87 and 188 $\mu\text{g}/\text{L}$, and total fuel was between 945 and 1,330 $\mu\text{g}/\text{L}$. Contaminated rainwater can be the major source of hydrocarbon pollution in Tehran soil and groundwater. As a conclusion, action must be taken for changing pollution status in Tehran and should focus on minimizing hydrocarbon pollution in the city.

Acknowledgements Authors would like to Acknowledge Dr. Gh. Nabi bidhendi for his support and also Dr. Shahid Kabir and Dr. Shannon Frances for their valuable comments.

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