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The Relationship between Polycyclic Aromatic Hydrocarbons and Heavy Metals

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Abstract

Background: Heavy metals and PAH_s in flue gas have received considerable attention in recent years due to their mutagenic or carcinogenic properties. PAH_s are products of incomplete combustion of carbonaceous compounds at high temperatures. Heavy metals are released into the ambient air from the same sources as those earlier mentioned for PAH_s. The present study was carried out to investigate the influence of the quantity of heavy metals on PAH_s formation in ambient air.

Methods: In this study, air particulates were collected on glass fiber filters using a high- volume air sampler. Each filter was exactly cut into equal pieces. One piece was digested with HNO_3 as well as H_2O_2 and used for determination of heavy metals. Another piece was extracted using Soxhlet method. The latter was used for the determination of PAH_s. The concentrations of heavy metals (Cr, Cd, Cu, Pb, and Zn) were measured using Perkin- Elmer atomic absorption spectrometer. The concentration of PAH_s was measured by a PU4400 gas chromatograph equipped with FID detector. The concentrations of PAH_s and heavy metals were determined in different seasons.

Results: The results showed that the concentration of PAH_s was minimum in the weekend and holidays, but maximum in winter. The relationship between ambient air concentrations of PAH_s and heavy metals was investigated and an excellent agreement was found. The general trend of variations in concentration of heavy metals were found very similar to PAH_s, therefore it could be concluded that the source of pollution was the same for both of pollutants.

Conclusion: The general trend of variations in concentration of heavy metals was found very similar to PAH_s, therefore it could be concluded that the source of pollution was the same for both of pollutants.

Key words: *Heavy metals, PAH_s, air pollution, Iran*

Introduction

Polycyclic Aromatic Hydrocarbons (PAHs) produced by combustion sources are ubiquitous in the urban air (1- 3). Polycyclie aromatic hydrocarbons are organic compounds that consist of two or more connected benzene rings. Some researchers have shown that PAHs can be highly carcinogenic and mutagenic (4, 5). The toxicity of heavy metals are due to their "d electrons". These d electrons cause strong chemical reactions in the human body, and their catalysis and strong chemical reactions are the main causes of their serious toxicity. Cr, Pb, Cd, Zn and Hg are the toxic heavy metals that are under control of the laws. Among these so-called five poisons Hg is the most toxic followed by Cd. Hg is vaporized during the high temperature incineration process and coal com-

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bustion, two-thirds of Hg will escape in the flu gas (6-10). Heavy metals will unavoidably be released with flue gas into the atmosphere. As reported in our previous study (10), the presence of heavy metals (Cr, Cd, Pb and Zn) in waste increases the quantity of PAHs in the solid as well as in the gaseous phase. However, the effect of heavy metals on total PAHs formation during the combustion process is still unclear. Hence, this study was carried out to investigate the correlation of the quantity of heavy metals on PAHs formation.

Major sources identified include: vehicular traffic, use of fuel for residential heating, industrial process, and waste incineration (1, 2). PAHs have been linked to adverse health effect in human population (4, 10) and consequently environmental monitoring of these compounds is essential. Measurements of PAHs in ambient urban air were made in the UK as early as the 1950s (6, 7). An investigation in China indicated that the presence of three to four-ring alkylated PAHs might be linked to the high incidence of lung cancer (8, 9). Investigations showed that the health risk associated with PAHs was affected by certain factors such as size of particulate and presence of heavy metals and carbon (10). In another research to investigate the influence of the quantity of heavy metals on PAH formation in fly ash, the obtained results indicated that carbon and heavy metals encouraged not only the adsorption of PAH_s but also catalyzed PAHs formation. Heavy metals such as Ni, Mn, Pb, Cr, etc, are usually released into the atmosphere from the same source as those earlier mentioned for PAHs. It is frequently desirable to measure and control the concentrations of these substances because of their toxicity (10-12)

The main objectives of this study were to determine the concentrations of PAH_s and heavy metals in different samples and find out the relationship between these two pollutants in the city of Isfahan.

Materials and Methods

Sampling of the ambient air of Isfahan city in Iran was carried out using high-volume air sampler at roof-top level (5 m). The particulates were collected on a Whatman 10-cm GF/A filter. Each filter was divided in two equal pieces. One piece was digested in nitric acid and oxygen peroxide, and used for determination of heavy metals (Cu- Pb- Cd- Zn and Cr) by Perkin-Elmer Atomic Adsorption model 2380.

Some of the GF filter samples, which were considered for collection of suspended particulate matter in ambient air, were used for determination of heavy metals as well.

The other piece of filter was extracted with dichloromethane (DCM) and using Soxhelt method for determination of PAHs. The concentration of PAHs was determined by a PU400 Philips model gas chromatograph with FID detector and capillary column (BPX-5).

Several representative station and suitable samples (three stations in Isfahan city, in three seasons and seven days of a week in month), 201 samples in each station were taken out and analyzed average value was used to estimate the concentration of heavy metals. They were later analyzed with GC/FID detector. Multiple analysis and recovery efficiency analysis were carried out to identify the precision and accuracy of our analytical procedure. The standard deviation of the PAHs analysis is about 1-7% and the recovery efficiency of PAHs is about 92-100%.

HPLC-GC conditions were as follows:

The temperature of detector site was set at 280°C and temperature of injection site was 250°C. The temperature of column was 90°C (5 min) and increased 10°C/ min up to 150°C and then increased 5°C/min till 320°C and was kept in this temperature for 10 min. Then, the relationship between the atmospheric concentrations PAHs and heavy metals was studied using Pearson's Correlation Coefficient.

The efficiency of PAHs extraction from suspended particulate was determined using standard sample, SRM-1648.
Table 1 revealed that Soxhelt method was capable to extract PAHs in the collected samples and presented the results quantitative with more than 90% efficiency.

Table 1: PAHs extraction efficiency using Soxhlet method

Extraction	Extraction efficiency
Phenanthrene (PhA)	92 ± 7
Anthracene (AnT)	100 ± 4
Fluoranthene (FluA)	100 ± 3
Pyrene(Pyr)	100 ± 1
Banzo(a)anthracene(BaA)	98 ± 1
Chrysene(Chr)	100 ± 3
Benzo(b)fluoranthene(BbF)	99± 3
Benzo(a)pyrene(BaP)	98 ± 2

Results

Determination of heavy metals such as Cd, Zn, Cr, Cu and Pb in different samples with regards to their effects on air pollution and linked with adverse health effect on human was surveyed. Fig.1 and table 2 show the trend of variations of heavy metals and PAHs concentrations in different samples during the days of the week. Table 3 and 4 show the results of PAHs & heavy metals concentration in ambient air of Isfahan in different seasons.

Table 2: Average variations of PAHs and heavy metals concentrations during the days of the week (ng/m^3)

Days	Cu	Cr	Cd	Zn	Pb	PAHs
Sat	361	38	8	670	910	28.5
Sun	359	36	7.5	598	815	26.3
Mon	401	36.5	7.5	603	822	26.8
Tue	297	22	6	582	711	21.6
Wed	357	37	7.7	609	891	47.7
Thu	326	29	7	897	765	22.2
Fri	210	18	4	317	496	12.5

Table 3: Heavy metals concentrations in ambient air of Isfahan in different seasons (ng/m^3)

Heavy metals	Winter	Spring	Summer	Avg.	Min	Max
Cu	1750	180	380	770	20	2250
Cr	120	80	32	80	10	160
Cd	15	10	20	16	5	50
Zn	890	360	450	560	40	860
Pb	780	490	560	620	20	1600

Table 4: PAHs concentrations in ambient air of Isfahan in different seasons (ng/m^3)

PAHs	Winter	Spring	Summer
PhA	2.2	1.3	1.5
AnT	2.7	1.7	1.4
FluA	3.4	2.2	2.0
Pyr	3.9	3.0	2.9
BaA	3.7	2.8	2.4
Ch	4.0	3.0	2.5
BbF	3.3	2.0	2.7
BaP	3.4	2.1	2.8

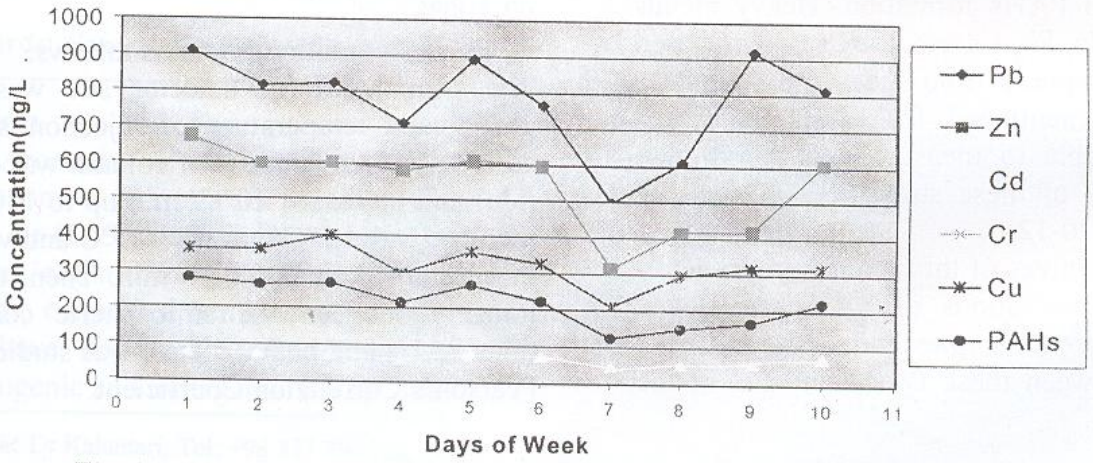

Fig. 1: Variations of PAHs & heavy metals concentration during the days of the week.

The results also demonstrated that the concentration of PAHs was minimum in weekends and holidays while was maximum in winter.

Discussion

The results showed that the trend of variations in concentration of heavy metals in days of the week was maximum in every Tuesday and minimum in weekend days weekly.

The general trend of variations in concentration of heavy metals was found very similar to PAH_s. Therefore it could be concluded that the source of pollution was the same for both of pollutants. Results revealed that the concentration of heavy metals in ambient air of Isfahan (the second largest city in Iran) was very high. Regarding to health adverse effect of these elements, especially on children, the control procedure must be considered.

As reported earlier (13), the presence of heavy metals (Cr, Cd, Pb,Cu and Zn) in waste increases the quantity of PAHs in the solid as well as in the gaseous phase. However, the effect of heavy metals on total PAHs formation during the incineration process is still unclear.

The results of statistic analysis showed very close correlation between heavy metals concentrations and PAHs. The correlation coefficient of around 0.9 between these two compounds revealed the aforementioned description.

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