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Polycyclic aromatic hydrocarbons in indoor and outdoor sites of hissar city

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ABSTRACT Air pollution is one of the serious environmental problem now-a-days, particularly in urban

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areas of all over the world. Pollution of air is broadly due to particulate matter dispersed in it or gaseous pollutant like CO, NOx, polycyclic aromatic hydrocarbons (PAHs), completely miscible with it in various proportions. PAHs are one of the carcinogenic compound observed in environment due to automobile exaust and other sources. In this work PAHs samplings were done by collection of particulate matter (PM) with the help of cascade impactor. Cascade impactor collect the respirable PM. The effect of these particulate matters were also observed on the basis of size of PM. For this purpose three sampling sites were selected at various petrol pump of Hissar city. Both indoor and outddor sampling were done for this . PAHs analysis were done with the help of high pressure liquid chromatography.

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Introduction

Air pollution is one of the serious environmental problem now-a-days, particularly in urban areas of all over the world. Pollution of air is broadly due to particulate matter dispersed in it or gaseous pollutant completely miscible with it in various proportions. Another source of air pollution is the emission from the different types of automobiles. The engines of these automobiles which are not being capable of achieving complete combustion of fuels, they release large amount of CO, NOx, polycyclic aromatic hydrocarbons, particulate matter etc. Thus contribute to air pollution. Polycyclic aromatic hydrocarbons (also called PAH, PAHs) are a group of over 100 different chemicals that are formed during the incomplete burning of coal, oil and gas, garbage, or other organic substances like tobacco or charbroiled meat. Indoor air is also polluted by PAHs, which comes from not only outdoor but also indoor emission sources such as smoking, cooking, heating conditioning, etc. Usually people spent 80% of time in indoor environments, so the quality of indoor air has an impact on person well being. Findings indicate that PAHs concentration in indoor air always exceeds that in outdoor air with certain combustion sources (Yongjain et al 2001). About 500 PAHs have been detected in air but most measurements have been made on BaP (Benzo (a) pyrene). According to Hartwell more than 200 compounds are tested as possible carcinogen. Among these 25% have been tumergenic and about 30% of these were PAHs. Lamb et al. (1993) reported that BaP is a definite carcinogen with LD 50 of 24 µg. Sixteen PAHs were classified as priorities pollutant and most of them were carcinogenic according to the United State Environment protection Agency (USEPA) (WHO 1996). PAH concentrations in the atmosphere are $0.1 - 10 \text{ ng/m}^3$, therefore, large volumes of air must be sampled and sensitive analytic techniques used to quantify the association of PAHs with size-segregated aerosols.

The general strategy used for this to collect particle deposits of aerodynamic diameters with cascade impactor and then to chemically analyze the deposits. Due to the increase of air pollution and its harmful effects on living organism it is require to assessments of gaseous and particulate air pollutants. In this paper assessment of the gaseous as well as particulate pollutant concentration in indoor and outdoor environments were done near petrol pumps sites. Comparison of indoor and outdoor site pollution was also done by quantification of polycyclic aromatic hydrocarbons in indoor and outdoor environments. Quantification of PAHs was done after extraction and purification by high Performance Liquid Chromatography (HPLC) with UV detector.

Material and Methods

Study Area

Hissar city of state Haryana was selected for this study it lays between 28^0 53' 45'' and 29^0 49' 15'' N latitude and $75^013'15''$ and $76^018'15''$ E longitude. Hissar town is located at 29^0 05'N latitude and 74^0 45' E longitude. The climate of Hissar is characterized by its dryness and extremes of temperature. Inversion is a common phenomenon in winter.

Ambient air sampling sites and sampling process:

Samples were taken from three petrol pump sites for quantification and identification of PAHs in outdoor and indoor environment at Hissar city.

The petrol pump sites were situated near the bus stand, auto market, and Blue- bird (Haryana). Samples were collected from October to January at 30 days intervals for eight hours. Sampling were done near the petrol pump machines and from the office room of petrol pump. The height of sampler inlet was 1.5 m above the ground.

Atmospheric particulate matter and PAHs mass size distribution were measured with micro-orifice uniform deposit impactor (MOUDITM). MOUDITM was ten-stage cascade impactor which operates with a flow rate of 30 L/minutes and the size (d× h) of cascade impactor was 80×60 mm (3.1×14.2 "). MOUDI contains 10 different particle cut size diameter from 0.056 – 18 (µm). For sampling, MOUDITM was operated for eight hours at the petrol pump sites before the filter strips were replaced. At each stage of cascade impactor, jets of particle-laden air impinge upon an impaction plate. Particle larger than the cut size of that stage cross the air streamline and gets collected upon the impaction plate.

Teflon filters were used for collecting of particulate matter or as a substrate. For the mass size, distributions determination on the impactor, the substrates were weighted before and after the run. **Extraction and Purification of PAHs**

Ultrasonic extraction methods with dichloromethane were used in this work. The PAHs containing filters were weighed. The filter containing samples were ultrasonically extracted in aluminums foil covered conical flask (4 portions of 20 ml of dichloromethane, 20 minute each). Combine extract was concentrated up to 10 ml in rotator evaporator (T< 40^{0} C) and centrifuged at ambient temperature to exclude solids. Solutions were transferred to test tubes and evaporated under gentle high purity nitrogen flow after addition of Toluene (100µl). The PAHs rich fraction was eluted with hexane, further evaporated under nitrogen flow up to 2 ml. The extract was kept in dark condition and wrapped with black paper. It was then used for cleanup process. The clean up procedure was carried out using chromatographic column with the help of dichloromethane and 0.15g deactivated Fluorescence with 2% v/w. The filtrate was concentrated to 2-3ml and used for HPLC analysis with UV detectors.

Analysis of PAHs

HPLC provides the necessary sensitivity in combination with high specificity so it was used for PAHs analysis. Before analysis PAHs, extracts prepared by using dichloromethane were exchanged into Acetonitrile. The PAH standard were purchased from (Sigma Aldrich) USA. The following PAH analytical Standard were used: Anthracene , Benzo(e) Acephenanthrylene , Benzo(e)Pyrene , Fluoranthene , Napthalene , Phenanthrene , Benzo(e) perylene Pyrene ,Benzo(k) Fluoranthene. Calibration curves of thesestandard PAH were prepared and linearity was found in all cases. After extraction a portion of the extract (2 µL) was injected on to a reversed phase HPLC column and the PAH eluted using a water / Acetonitrile gradient. The concentration of PAH was calculated by comparing the peak area of sample chromatogram with that of peak area of standard chromatogram (Muller et al. 1998).

Peak area of chromatogram X =

Peak area of chromatogram of standard

× Concentration of standards of PAHs

PAH concentration was calculated in the following manner

Х =

Where X =Conc. Of PAHs in ng/ml

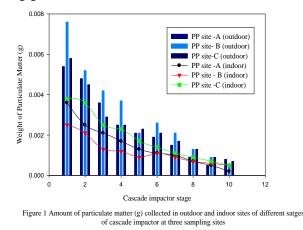
Y =Dry weight of particulate matter of the sample

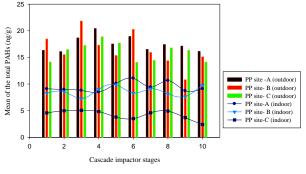
C = Final Conc. of PAHs in ng/g.

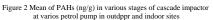
Results and Discussion

The present study was conducted for identification and characterization of PAHs associated with respirable suspended particulate matter in outdoor and indoor environment of the petrol pump Hissar. From the analysis it was observed that concentration of particulate matter (PM) was higher in case of petrol pump site -B as compared to other two sampling sites in outdoor (Figure-1) due to the higher load of traffic in that area and the site was near the bus stand area. In case of indoor site it was observed to be highest at petrol pump -C due to various indoor pollutants. Concentration of PM was observed to be higher in case of outdoor as compared to indoor in case of all sampling sites (Figure - 1).

Higher concentration of PAHs was observed to be higher in outdoor atmosphere as compared to indoor (Figure 2). The high concentration of PAHs in outdoor atmosphere was due to the spillage of petrol and diesel near the machines but in the indoor, there were no spillage of petrol and diesel and no source of smoking. The highest amount of total PAHs and individual PAHs was due to their maximum congested area and more sale of diesel and lack of any type of vegetation. The total mean concentration of PAHs in ambient atmosphere (outdoor) of petrol pump B was observed to be 165.18 ng /g. At that site Benzo Perylene contributes the maximum with mean concentration of 21.23ng/g and minimum concentration was contributed by Anthracene with mean concentration of 16.85ng/g.







The total mean concentration of PAHs in petrol pump A (outdoor) was 209.9 ng/g among which Anthracene contribute the maximum with mean concentration of 23.34ng/g while Benzo pervlene contributed the minimum of 16.14ng/g. The maximum deposition of total PAHs at petrol pump site A (outdoor) occurred at place in the 4th stage of cascade impactor in which particulate matter were in the range of 1.8µm in cut size and minimum deposition of the total PAHs were take place in the 10th stage of cascade impactor in which particulate matter were in the range of 0.056µm in cut size. Total deposition of PAHs in various stage of impactor is given in Figure-2. It was observed that the petrol pump B Indoor and Outdoor contributes less PAHs pollution than petrol pump A Indoor and Outdoor due to less congested area and lesser sale than petrol pump A. The total mean concentration of PAHs in petrol pump C (Outdoor) was 116.30ng/g which was lower than the other two petrol pump sites. Among which Phenanthrene contributes 121.73ng/g. Fluoranthene contributes minimum concentration with mean concentration 15.04ng/g. The high concentration of PAHs in outdoor atmosphere was due to the spillage of petrol and diesel near the machines but in the indoor, there was no spillage of petrol and diesel and no source of smoking. The highest amount of total PAHs and individual PAHs was due to their maximum congested area and more sale of diesel and lack of any type of

vegetation. The maximum attachment of total PAHs with particulate matter were observed in 4th stage of cascade impactor with 1.8um in cut size. The minimum attachment of PAHs with particulate matter takes place in 10th stage of impactor which was 0.056 um in cut size (Figure – 2). The health risk is primarily from deposition of the particle smaller than 0.5um in the alveoli where they cause damage to the respiratory organs. In our study we observe that individual PAHs and total PAHs are associated with particulate matter 0.56um to 3.2um, these PAHs are deposited as far as bronchioles and causes the cancer in this region.

In the atmosphere PAHs will distribute between particulate and vapors phase that predominantly depends on the physical characteristics of compounds themselves and environmental situation such as temperature and humidity. From Figure 3, it was observed that Benzo (k) fluoranthene (19.9ng/g) was observed to be maximum in outdoor region and the concentration of Phenenanthrene was maximum in Indoor region. The concentration of Fluoranthene 16.37ng/g in outdoor region and the concentration of Fluoranthene 8.18 ng/g were reported to be the minimum. It was due to the molecular weight of PAHs. High molecular weight PAH (252-278) like Benzo(a) anthracene, Benzo (k) fluoranthene, Benzo(e) pyrene, Benzo perylene are found attached with particulate matter and the PAHs having the molecular weight between (202-252) like Fluoranthene, Pyrene are found in both gaseous and particulate phase according to the temperature variation. The molecular weight less than 202are like Naphthalene, Phenanthrene, Anthracene always found in gaseous phase.

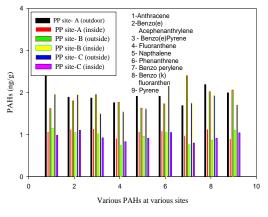


Figure 3 Mean concentration of various PAHs at different petrol pump site at indoor and outdoor

During all the three sampling at all the sites it was observed that the third sampling conducting during December 2005 have the higher amount of total PAHs than the first and second sampling conducting on October and November 2005. It was due to the variation in temperature and humidity since the third sampling was done during the December month the high concentration of total PAHs in air could be due to low temperature and inversion. In the study of (Yong et al. 2001) it was observed that the indoor atmospheric concentration of PAH is higher in autumn and winter season than the summer season. In our study we also observed that PAH concentration in winter season is higher than summer season. The observation from (Naumova et al. 2001) study observed that indoor PAH concentration, but in our study it was observed that total PAH concentration, in outdoor were exceed than indoor PAH concentration, it may due to the lack of PAH sources.

Conclusion:

In the present study at all petrol pump sites in outdoor and indoor air it was observed that petrol pump site A have higher concentration of PAH as compared to all the other sites. The PAHs concentration was observed to be lowest at the petrol pump site C in the outside and inside air than the other two petrol pump. It was observed that individual PAH and total

PAHs were reported at the 3rd or 4th stage of cascade impactor, the associated particulate matter fallen in the range of 0.56-3.2um in cut size. Benzo(k)fluoranthene was observed to be maximum in case of outdoor sites and Fluoranthene was minimum in case of indoor sites at all petrol pumps. PAHs concentration was observe highest during December due to inversion process. It was concluded that PAHs distribution also depends upon local environment conditions and their molecular weight.

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