



Potential Application of Synchronous Fluorescence Spectroscopy to Identification of PAHs in Airborne PM_{2.5}

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Received: 24.07.2021, Revised: 14.01.2022, Accepted: 14.01.2022

ABSTRACT

A simple and rapid method for the highly sensitive determination of polycyclic aromatic hydrocarbons (PAHs) from airborne fine particulate matter (PM_{2.5}) in an urban environment of Delhi was developed. The target compounds were 10 of the 16 United States Environmental Protection Agency (US-EPA) priority PAHs: fluoranthene, pyrene, chrysene, benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo[a]pyrene, dibenzo(ah)anthracene, benzo(ghi)perylene, indeno(1,2,3-cd)pyrene. For collecting the samples, the following two locations in Delhi (India) were chosen: ITO and Okhla Industrial Area. Two sets of samples at these locations were collected for the purpose of investigation. The fine particulate matter samples were collected on glass fiber filter papers for 24h, from which the PAHs were extracted using dichloromethane (DCM) and hexane using ultrasonication method. Comparison of the characteristic emission spectra of PAHs with standard spectra indicated the degree of condensation of aromatic compounds present in the investigated mixtures. However, this identification could be more effective with the use of the respective values of $\Delta\lambda$ parameter for each particular component of the mixture. It has been found that the concentration of the PAHs is maximum during the winter season and minimum during the summer and monsoon seasons at both the locations.

Keywords: Air pollution, Polycyclic aromatics, Particulate matter, Urban environment, Delhi.

INTRODUCTION

Polycyclic Aromatic Hydrocarbons (PAHs) are the group of ubiquitous persistent and toxic chemicals, composed of multiple aromatic fused rings, which are considered as a carcinogenic (Xue et al., 2010; He et al., 2014), teratogenic, and mutagenic organic compounds (Boeuf et al., 2016; Hazarika et al., 2019). Long-range atmospheric transport of PAHs and its environmental stubbornness led to their widespread distribution across the world. Under favourable meteorological conditions, PAHs can be transported to long distances before being deposited through precipitation on to soil, water, and vegetation (Crimmins et al., 2004; Ding et al., 2007; Friedman et al., 2013). In general, PAHs can be categorized into two broad categories - low molecular weight and high molecular weight compounds. The low molecular weight PAHs primarily exist in vapour phase and consist of two or three aromatic fused rings, whereas the high molecular weight PAHs consist of more than four aromatic fused rings, mainly associated with airborne fine particulate. Some of the PAHs with low vapour pressure can exist in both vapor phase and particulate phase. Many PAHs, particularly those with intermediate molecular weights and vapour pressures, can exist in either the gas or particle phase (or both) depending on environmental conditions.

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The phase distribution affects transport, deposition, re-emission, and biological effects. Under the specific metrological conditions, PAHs associated airborne particulates undergo dry deposition (Esen et al., 2010; Hanedar et al., 2014; Shahpoury et al., 2018). PAHs with 2-ring include Naphthalene(Naph); 3-ring include Acenaphthylene (Acy), Acenaphthene(Ace), Fluorene (Flu), Phenanthrene (Phen), and Anthracene (Anth); 4-ring include Fluoranthene (Flan), Pyrene (Pyr), Benzo[a]anthracene B(a)A, and Chrysene (Chy); 5-ring include Benzo(b)fluoranthene B(b)F, Benzo(k)fluoranthene B(k)F, and Benzo(a)pyrene B(a)P; 6 ring include Dibenzo(ah)anthracene Db(ah)A, and Benzo(ghi)perylene B(ghi)P, Indeno(123-cd)pyrene IND. The high molecular weight PAHs tend to adsorb onto the small inhalable particulate matter present into the atmosphere (Sisovic et al., 2008). $PM_{2.5}$ ($< 2.5\mu m$ in aerodynamic diameter), is the most significant pollutant of ambient air. Particulate PAHs, especially those of high molecular weight, are mainly found in fine particulate matter ($PM_{2.5}$) in the urban atmosphere. About 95% of total PAHs have a size of less than $3\mu m$ (Venkataraman et al., 1994), which lies in the range of aerodynamic diameter, which enhances its long-range transportability. In general, sources of PAHs can be broadly classified into two main groups: natural processes and anthropogenic activities where natural sources involve forest-prairie fires, volcanic eruptions, and exudates from the tree, whereas the anthropogenic sources include coal-, oil-, and gas-burning facilities, waste incineration and industrial activities, such as oil refining, coke and asphalt production, aluminum production, steel and iron industries, etc. (Sharma et al., 2008; Wang et al., 2013; Jamhari et al., 2014).

Among all the emission sources, the largest source of emission of PAHs in the atmosphere is vehicular emission [Wu et al., 2017; Lin et al., 2019; Hao et al., 2019; Yang et al., 2019; Kumar et al., 2020; Wang et al., 2021). However, PAH data in urban air are still scarce, and most of the studies show large spatial and temporal uncertainties because of the complex sampling and analytical procedures required. In fact, the analysis of PAHs in aerosol samples faces many problems because of the very low PAH concentrations in ambient air as well as the presence of other organic compounds that can interfere with the PAH determination (Liu et al., 2007). The most frequently used techniques in standard procedures rely on gas chromatography (GC) provided with FID as detector or preferably with gas chromatography-mass spectroscopy (GC-MS), high-performance liquid chromatography [HPLC]-UV/vis or HPLC-FLD) (Poster et al., 2006; Krupadam et al., 2010). Nevertheless, these measurements tend to be laborious, relatively expensive, and time consuming, because they require a great pretreatment of the samples in order to increase the sensitivity and selectivity of the PAH analysis. Therefore, there is still a great interest in developing more sensitive and selective methods to analyze PAHs in aerosol samples for routine analysis involved in environmental control and health protection.

Fluorescence spectroscopy is an extremely sensitive analytical technique for the study of PAHs, which can be detected at sub-ppb levels because of their luminescent properties in the UV–vis range. However, the application of the conventional fluorescence spectroscopy has been limited by its lack of selectivity because of the broad excitation and emission spectra of PAHs that complicate a multi-component analysis in environmental samples. In this regard, synchronous fluorescence spectroscopy has been applied to optimize the spectral resolution of PAHs. The synchronous fluorescence technique introduced by Lloyd (Lloyd et al., 1971) has been used to characterize complex mixtures (Lloyd et al., 1974; Apicella et al., 2004) providing fingerprints of complex samples, such as crude oils of different origins (Gargiulo et al., 2015) and extracts and pyrolysis tars of coals (Li et al., 1994; Gargiulo et al., 2016). A methodology for the application of synchronous fluorescence has been further developed and applied to a synthetic mixture of PAHs (Vo-Dinh et al., 1978). The synchronous

luminescence technique is now frequently being used in the investigations of aromatic components of mixtures of various origins [Matuszewska et al., 2000; Matuszewska et al., 2002; Sharma et al., 2007). For air quality purposes, the synchronous fluorescence technique has been mainly used to identify PAHs in aerosol samples (Sharma et al., 2013). Thus, synchronous fluorescence methods with high sensitivity, selectivity and simplicity compared to other conventional spectroscopic techniques could serve as a simple analytical tool for identification of PAHs in environmentally complex samples.

The aim of the presented work is to develop an analytical method for the determination of PAHs in the airborne fine ($PM_{2.5}$) particulate matter by synchronous fluorescence spectrometry technique, which are of great interest because of their mutagenic and carcinogenic properties. Such study is expected to provide very useful information about the environmental levels of these harmful substances in Delhi, India.

MATERIALS AND METHODS

Delhi ($28^{\circ}39'N$ and $77^{\circ}13'E$) is situated at the bank of river Yamuna, having a geographical area of 1483 km^2 and its altitude is at 216 m above the mean sea level. The city is bounded by diverse climatic zones, i.e., the Himalayas from north, central plains from south, the Thar Desert in the west and the Indo-Gangetic plain (IGP) from east, which is the main reason of its semi-arid climate. Delhi has become a nucleus of trade, commerce and industry in the northern region of India. Government office complexes are a major source of employment and the city is also home to important agricultural and educational institutions. Steady increase in industrial units has been witnessed in the city despite the introduction of planning restrictions on large industries. The Delhi metropolitan region has a population of more than 17.1 million with an annual average growth rate of 1.92 % (Delhi Statistical Handbook 2016). The overall population density is $11,297 \text{ km}^{-2}$. Up till March 2015, the total number of registered vehicles in Delhi were more than 9.7 million (Statistical abstract of Delhi 2016). Temperatures ranges between $7 \pm 3^{\circ}C$ in winter and $45 \pm 3^{\circ}C$ in summer (Kumar et al., 2017). This area is under the influence of monsoon winds (ranging from NE to NW in winter and from SE to SW in the summer), with average yearly rainfall of approximately 73 cm (Sharma et al., 2016). Delhi has three distinct seasons: winter, summer and monsoon. The winter season is from November to February, summer months are from March to June and monsoon months are from July to October. During October and March, the weather conditions are stable. The days are sunny and only a few showers are occasionally observed. Two sampling sites (ITO and Okhla Industrial Area) were selected based on different anthropogenic activities, such as vehicular traffic density, industrial, commercial and other local activities in Delhi, India (Fig. 1).

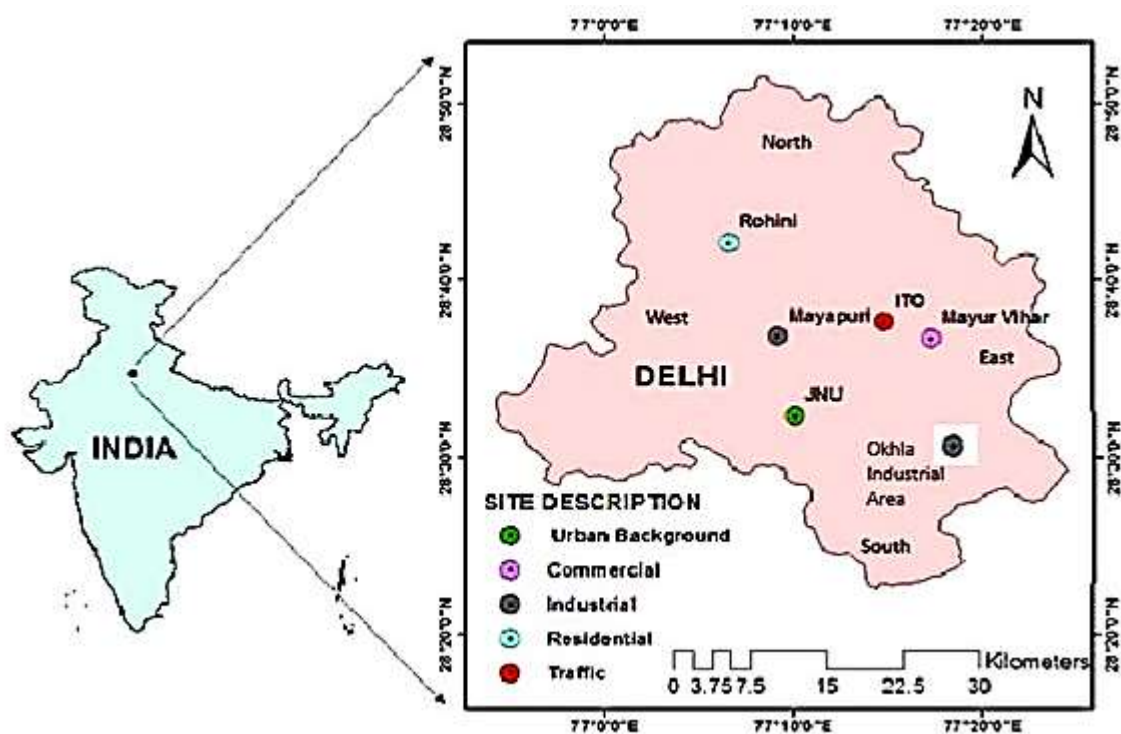


Fig.1. Map of sampling Locations in Delhi, India

The ITO site, which is located in the central part of Delhi, is densely populated with residential houses and commercial establishments. Moreover, it has heavy vehicular traffic, fueled by gasoline, diesel, and compressed natural gas (CNG). During peak hours traffic jams are frequent in this location. The average vehicular speed is almost $20\text{--}25\text{ kmh}^{-1}$ at this location. This area receives maximum impact from local anthropogenic sources (commercial and residential). The Okhla site, located in South-East Delhi, is an industrial-cum-residential area. Most of the industries in Delhi, mainly readymade and leather garment factories, pharmaceutical manufacturing units, plastic and packing industries, printing presses, machinery manufacturers and others are in this area. Increasing industrial productivity combined with rapid urbanization means that there is a greater demand for energy in Delhi that can be supplied and hence the industry cannot generate at full capacity. Delhi has two major thermal power plants which are not sufficient to cater to the total power needs of the city. Generator sets are thus used in commercial, residential and industrial areas as backup power. All these activities have led to increased fuel demand and accrued into deteriorating air quality. Cooking, generator sets, various internal combustion engines, burning of organic wastes landfill, sewage treatment plants and slums are some of the prominent sources of PAHs in Delhi.

The samples for particulate matter were collected by Fine Particulate Sampler APM 550 (Envirotech Instruments Pvt. Ltd., New Delhi). The Fine Particulate Sampler was kept at the rooftop $\sim 14\text{m}$ above the ground. Collection for $\text{PM}_{2.5}$ was performed in winter (09/01/2017), summer (15/05/2017) and monsoon (21/08/2017). The ambient air is drawn in a laminar flow at the rate of 16.5 L/min . The airborne particles were collected for 24h on glass-fiber filter papers (size: $8\text{ cm} \times 10\text{ cm}$). The filter papers were kept in a vacuum desiccator for 24h to remove any moisture content before mounting them on the Fine Particulate sampler. After the sampling, the filter papers were again kept in a desiccator for 24h to de-moisturize them again. The filter papers were wrapped separately in aluminum foils and stored in a fridge at

~4°C prior to analysis. It is pertinent to mention here that only the particulate PAHs associated with PM_{2.5} may be trapped on the glass fiber filter. Since in the present study no collection media (sorbent) was used down-stream of the filter to collect the gaseous component of PAHs, the measured values of PAHs would have in all probability a low bias. The USEPA TO-13A Method (Method TO-13A 1999) was followed during sample collection and the analysis of PAH compounds.

The PAHs were extracted from the SPM collected on the filter paper using appropriate solvents (50:50, DCM + hexane). The solution was ultrasonicated (Misonix ultrasonic Processor-XL) for 30min at 20 Hz in a water bath (10 -15°C). The extracts were then centrifuged for 30 min and filtered with Whatman-1 filter. The filtered extract was concentrated on a rotavapour (Buchi Rotary Evaporator) until its volume was reduced to about 1–2ml. The temperature of the water bath was kept below 40°C to rule out any possibility of breakdown of the PAH species. The reduced volume was dissolved in HPLC grade n-hexane. The experimental procedure for measurement of PAHs is already described in our earlier work (Sharma et al., 2013).

The corrected fluorescence spectra were measured on a Cary Eclipse computer controlled spectrofluorimeter (Instrument Serial Number-EL-01035456, Varian India Pvt. Ltd.) with a Xenon lamp. A standard 1cm² fluorescence quartz cell was used to hold the sample. A Xenon lamp with exceptionally long lifetime, pulsed at 80 Hz with pulse width at half peak height ~2μs and peak power equivalent to 75 kW was used. The detector was a high performance R928 photomultiplier. A separate 928 PMT was used as the reference signal. To ensure the best signal-to-noise performance, it is necessary to select a slow scanning speed. The synchronous fluorescence spectra of n-hexane solutions were recorded at a rate of 600 nm/min. The corrected synchronous spectra were recorded in an excitation scale.

The polycyclic aromatic hydrocarbons viz., fluoranthene (Flan), benz(a)anthracene (BaA), benzo(a)pyrene (BaP), benzo(k)fluoranthene (BkF), pyrene (Pyr) and benz(ghi)perylene (BghiP) used in the present study were purchased from Sigma–Aldrich and used as standards. The solvents methanol, hexane, n-hexane, dichloromethane and acetone were procured from Merck. The chemicals were used without further purification.

The experiments were carried out in winter, summer and monsoon seasons, the meteorological parameters for which are given in Table 1.

Table 1: Measurements for particle mass concentrations (PM_{2.5}) and meteorological parameters in the sampling time. The data for temperature, relative humidity and wind speed given in table 1 were taken from Indian Meteorological Department (IMD), New Delhi.

Month	Temperature (°C)			Relative humidity (%) ^a			Wind Speed (km/h)		PM _{2.5} (μg/m ³)
	Mean	Maximum	Minimum	Average	Maximum	Minimum	Relative Wind Speed ^a	Max Wind Speed	ITO/ Okhla
09/01/2017 (winter)	14	19	08	81	100	56	5	13	320/275
15/05/2017 (summer)	36	44	28	23	45	9	9	18	397/345
21/08/2017 (monsoon)	32	36	28	66	84	54	7	17	180/171

RESULTS AND DISCUSSION

The selection of the experimental conditions is very important for achieving the identification of the different PAHs in the PM_{2.5} mixture. The solvent is one of the factors which influences the

most the fluorescence signal. Several workers (Vo-Dinh et al., 1978; Gargiulo et al., 2016) have reported that the synchronous fluorescence spectroscopy allows narrowing of spectral bands, simplification of emission spectra and contraction of the spectral range. This method increases the analysis sensitivity, essentially by avoiding different perturbing effects (Rayleigh and Raman scatter). If the synchronous technique is used, the resulting spectrum consists of a series of exceptionally well-resolved peaks. Each corresponds unequivocally to one component in the mixture and can be correlated perfectly with its synchronous signal in each individual spectrum. The first correlation between the structure of a PAH compound and its fluorescence spectrum is reflected by the dependence of the energy of the 0–0 band with the ring size of the compound. The spectrum of a higher ring number linear cyclic compound occurs generally at a longer wavelength than that of a lower ring number compound. Non-linear PAHs also follow, to a certain extent, this basic rule. With conventional spectrometry, because of severe spectral overlap, this simple rule cannot be efficiently applied, especially when many constituents in a mixture have to be analyzed. With the synchronous fluorescence technique, however, the effect of limiting each individual spectrum to a definite spectral band provides the most useful feature to locate the presence of specific compounds in a mixture. The synchronous technique can achieve some sort of spectral confinement or spectral separation into individual components without requiring any actual physical separation process. The solution n-hexane was chosen because it has a good extractive capacity for organic compounds from many matrices (Lopez de Alda et al., 1995) and it does not show important interferences when the extracts are studied by spectrofluorimetry (Eiroa et al., 2000), although it is possible to use more polar solvents which improve the fluorescence efficiency of some molecules. It offers many advantages over alternative solvents. For instance, it is commercially available in the grade of purity necessary and is essentially free of interfering Raman bands (Lopez de Alda Villaizan et al., 1994).

Table 2: Wavelength intervals ($\Delta\lambda$) selected for each PAH and maximum excitation wavelength (λ_{exc}) used for their identification

PAHs*	Present Work		Work from other authors (Reference: Matuszewska et al., 2000; Patra et al., 2001; Matuszewska et al., 2002; Lage-Yusty et al., 2005)	
	Optimized wavelength intervals $\Delta\lambda$ (nm)	Excitation wavelength λ_{exc} (nm)	Optimized wavelength intervals $\Delta\lambda$ (nm)	Excitation wavelength λ_{exc} (nm)
Flan	155	289	155	289
Pyr	50	334	50	334
Chy	115	269	115	269
B(a)A	95	290	95	290
B(b)F	160	302	160	302
B(k)F	25	402	25	402
B(a)P	15	387	15	387
Db(ah)A	95	299	95	299
B(ghi)P	115	302	115	301
IND	190	315	190	316

The use of optimized $\Delta\lambda$ value does not require an ‘a priori’ knowledge of the components in a mixture. Exceptions to the general rule requiring matching of the 0-0 bands are those situations where the compounds exhibit no overlapping or weak emission and/absorption bands. Optimized synchronous parameters for selected PAHs in the synchronous excitation wavelength range 250–600nm were found by changing $\Delta\lambda$ in the range 5-205 nm in an interval of 10 nm.

Any $\Delta\lambda$ values higher than 205 nm present Raman bands in the solvent and cannot be utilized. The $\Delta\lambda$ which gave highest synchronous fluorescence intensity for a particular species was chosen as optimized $\Delta\lambda$ for that species and the corresponding peak as the optimized peak (λ_{SFS}^{Max}). Synchronous optimized parameter ($\Delta\lambda$ and λ_{exc}) of different selected PAHs are given in Table 2 and the synchronous fluorescence spectra are shown in Figs. 2 - 21.

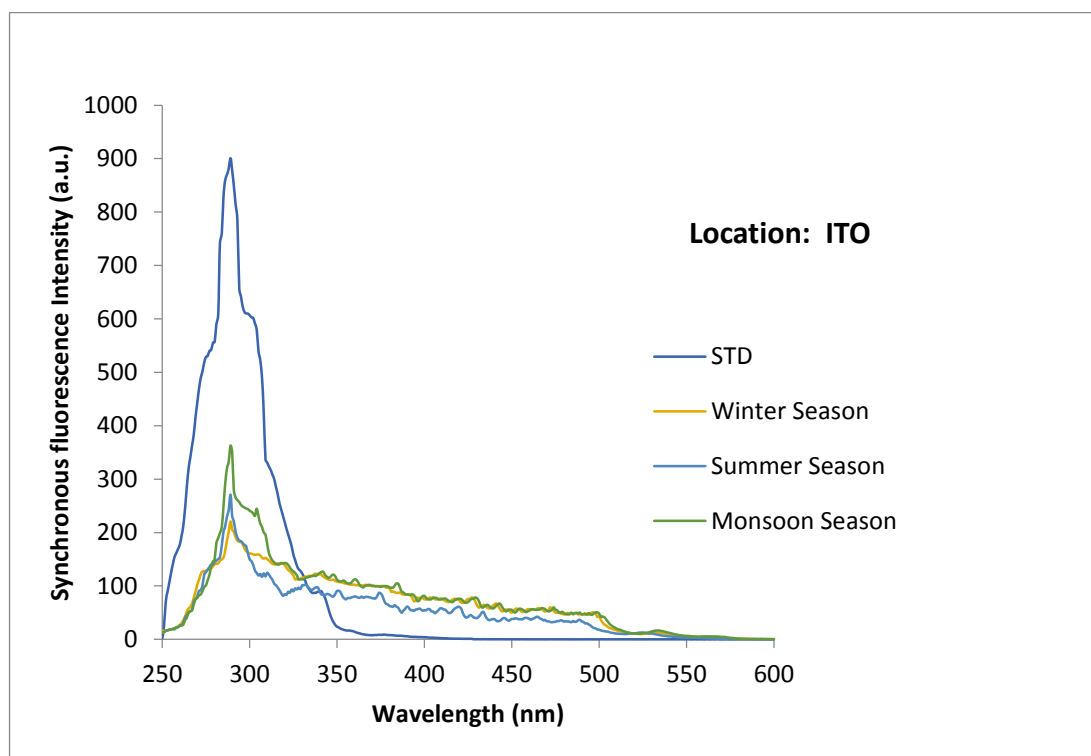


Fig.2. Synchronous fluorescence spectra of fluoranthene in n-hexane at $\Delta\lambda = 115$ nm. In the above figure, STD refers to the standard compound, fluoranthene.

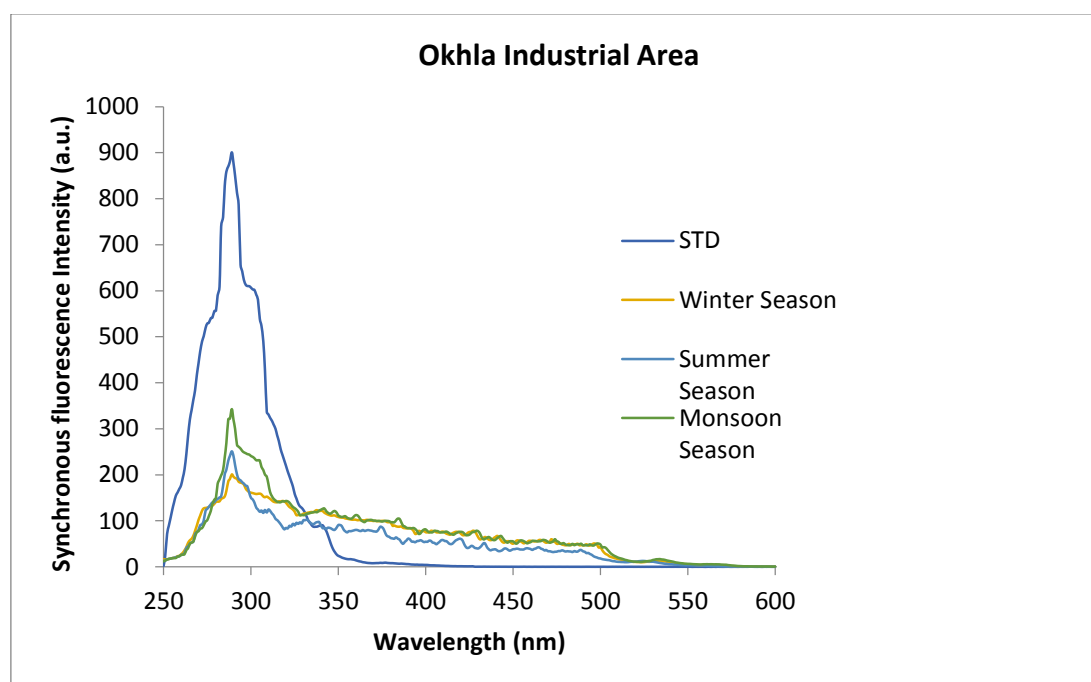


Fig.3. Synchronous fluorescence spectra of fluoranthene in n-hexane at $\Delta\lambda = 115$ nm.

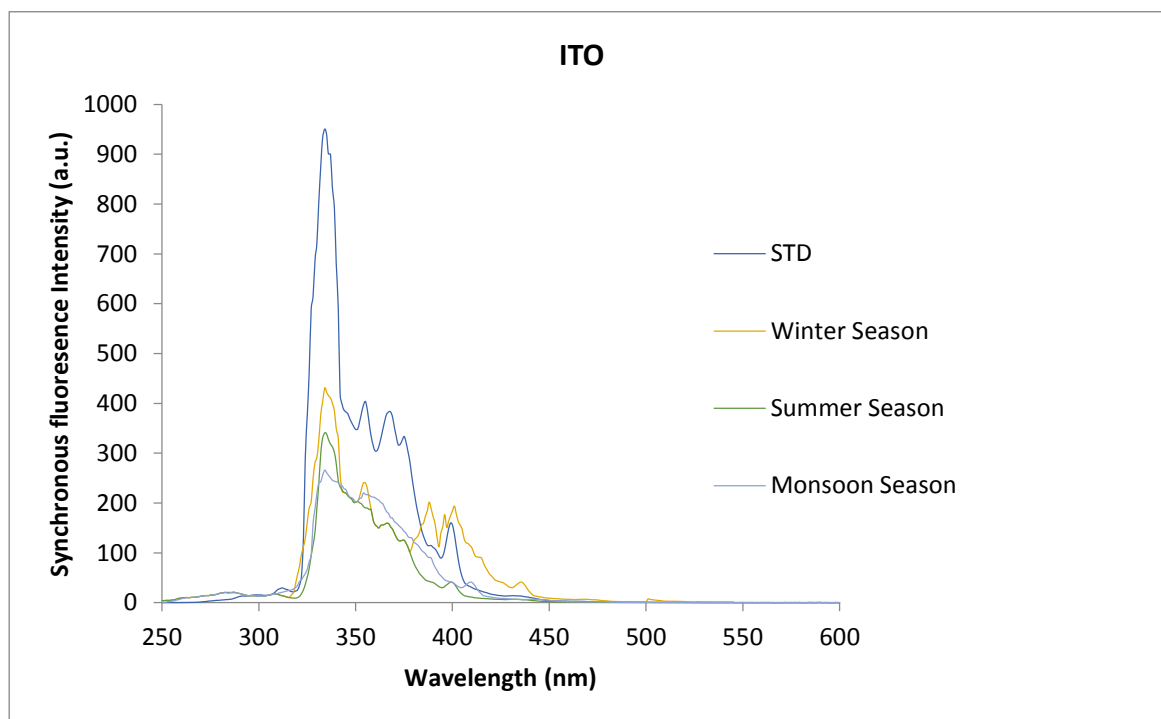


Fig. 4. Synchronous fluorescence spectra of pyrene in n-hexane at $\Delta\lambda = 50\text{nm}$.

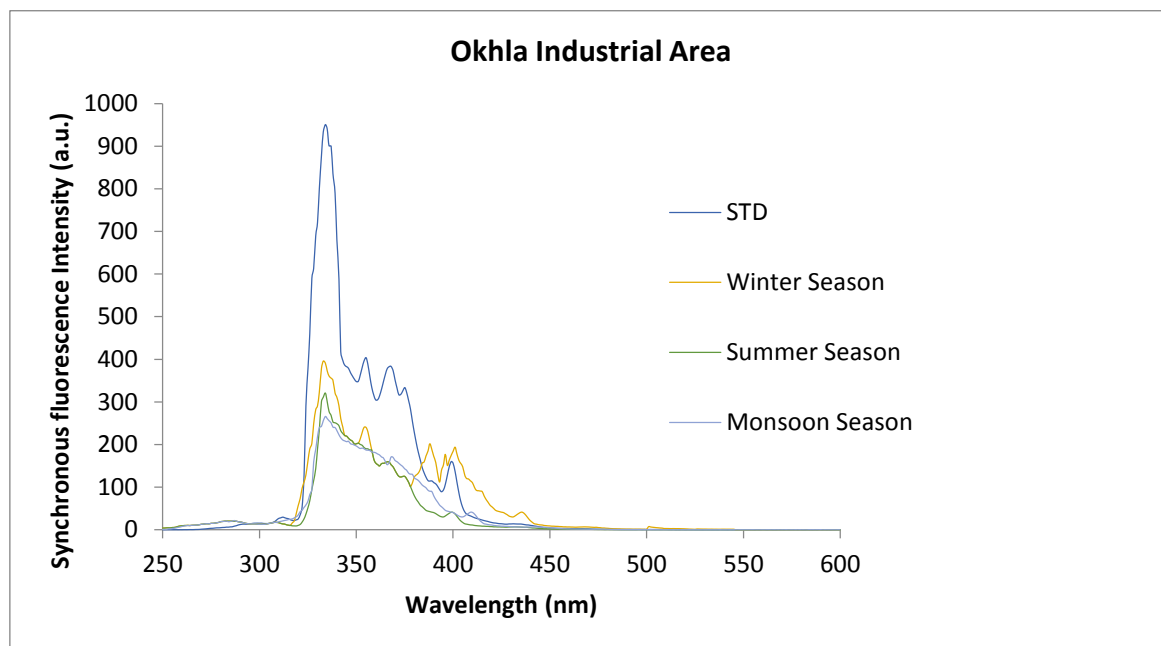


Fig. 5. Synchronous fluorescence spectra of pyrene in n-hexane at $\Delta\lambda = 50\text{nm}$.

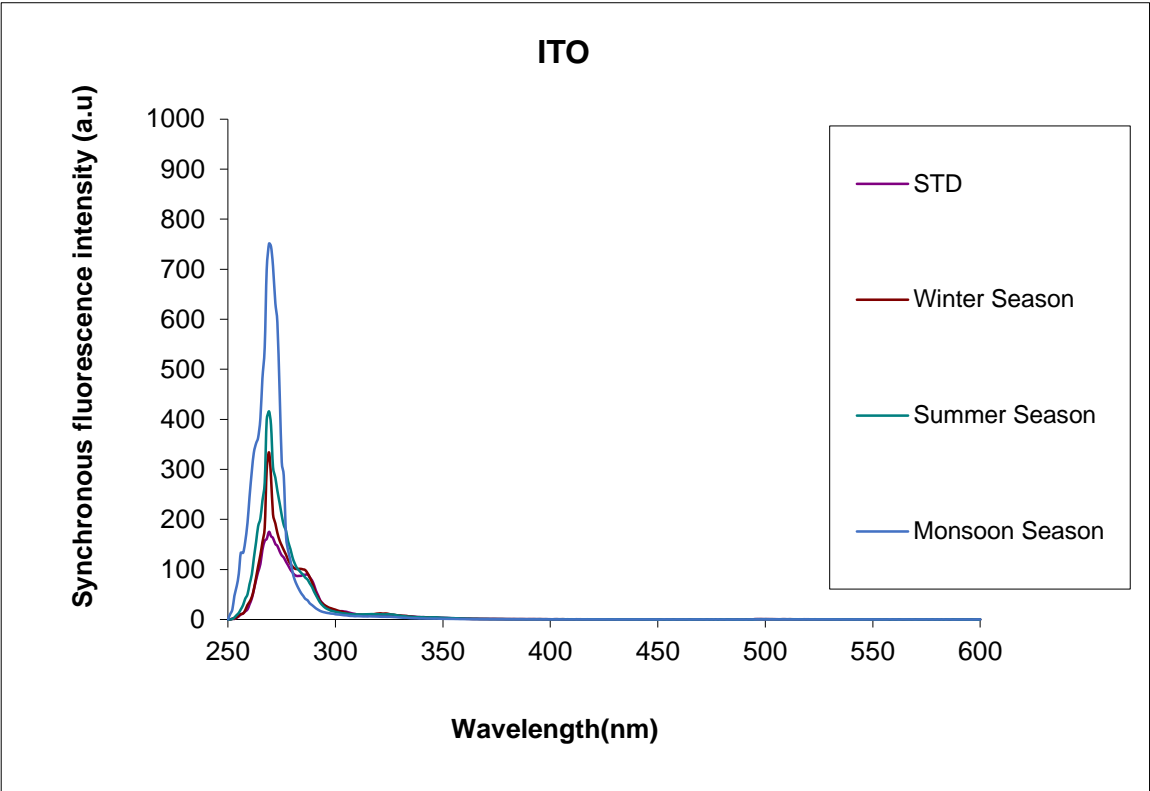


Fig. 6. Synchronous fluorescence spectra of chrysene in n-hexane at $\Delta\lambda = 115\text{nm}$.

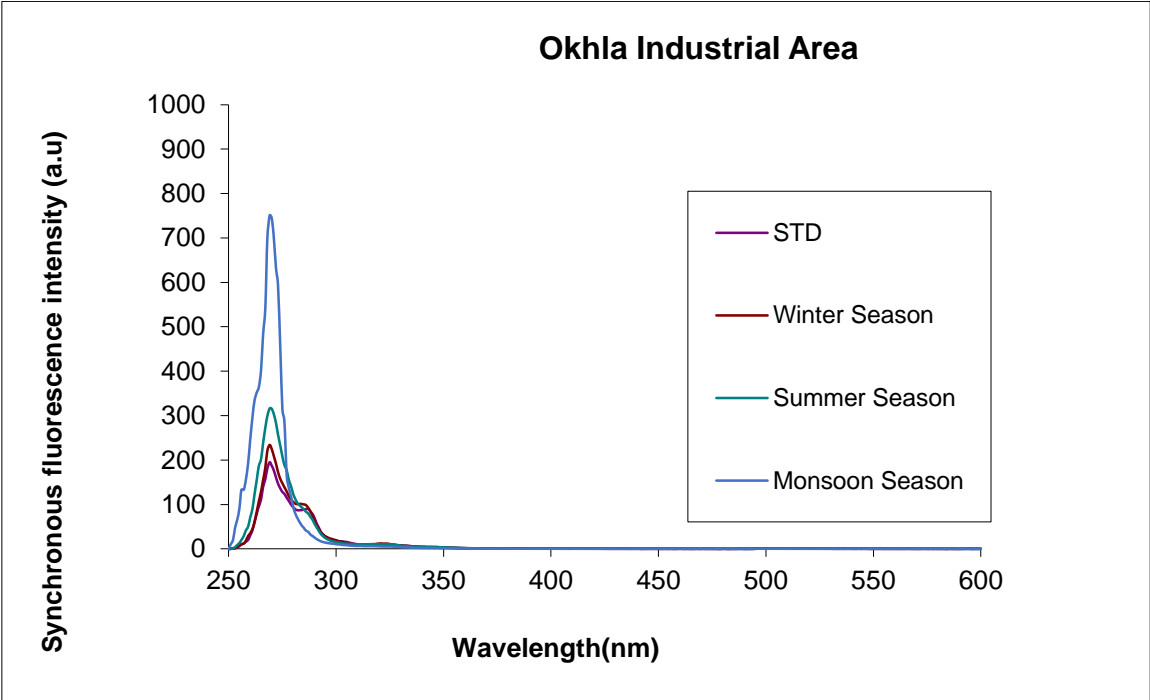


Fig. 7. Synchronous fluorescence spectra of chrysene in n-hexane at $\Delta\lambda = 115\text{nm}$.

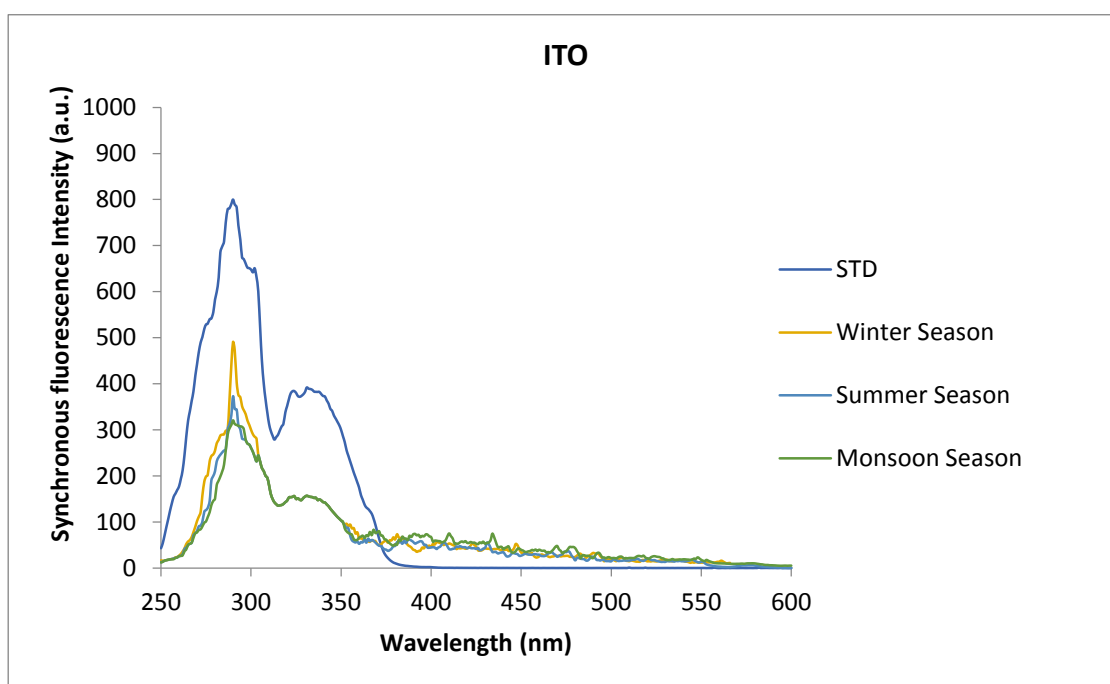


Fig. 8. Synchronous fluorescence spectra of benz(a)anthracene in n-hexane at $\Delta\lambda = 95\text{nm}$.

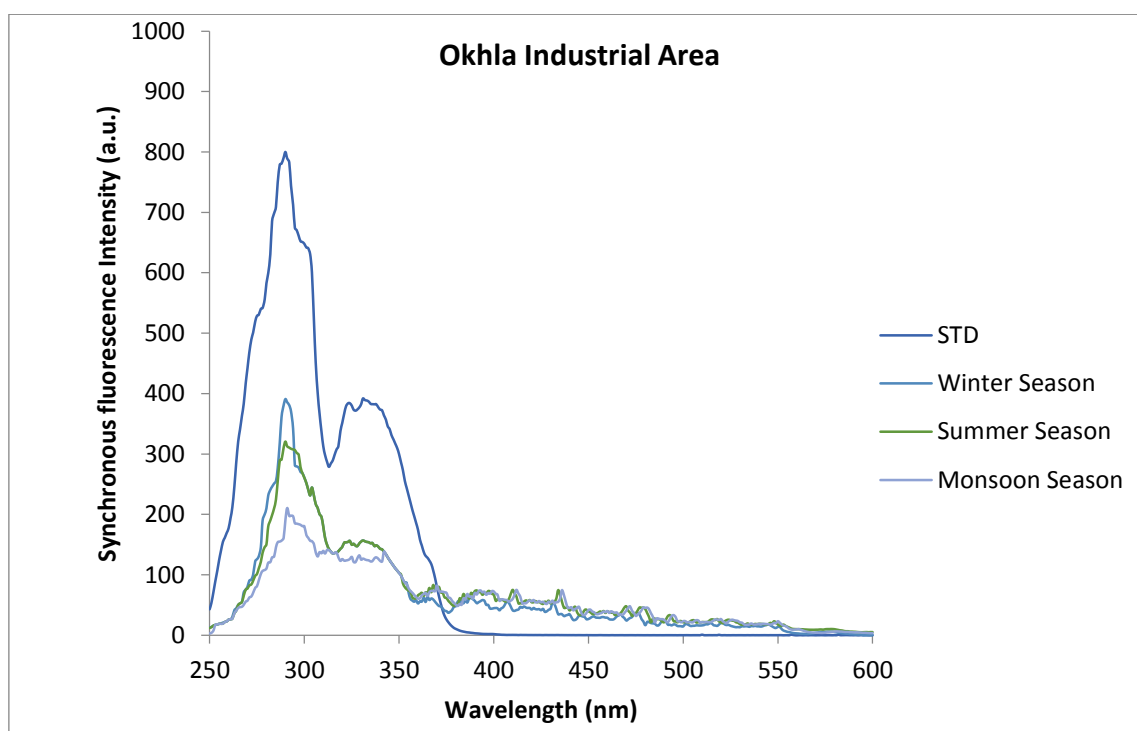


Fig.9. Synchronous fluorescence spectra of benz(a)anthracene in n-hexane at $\Delta\lambda = 95\text{nm}$.

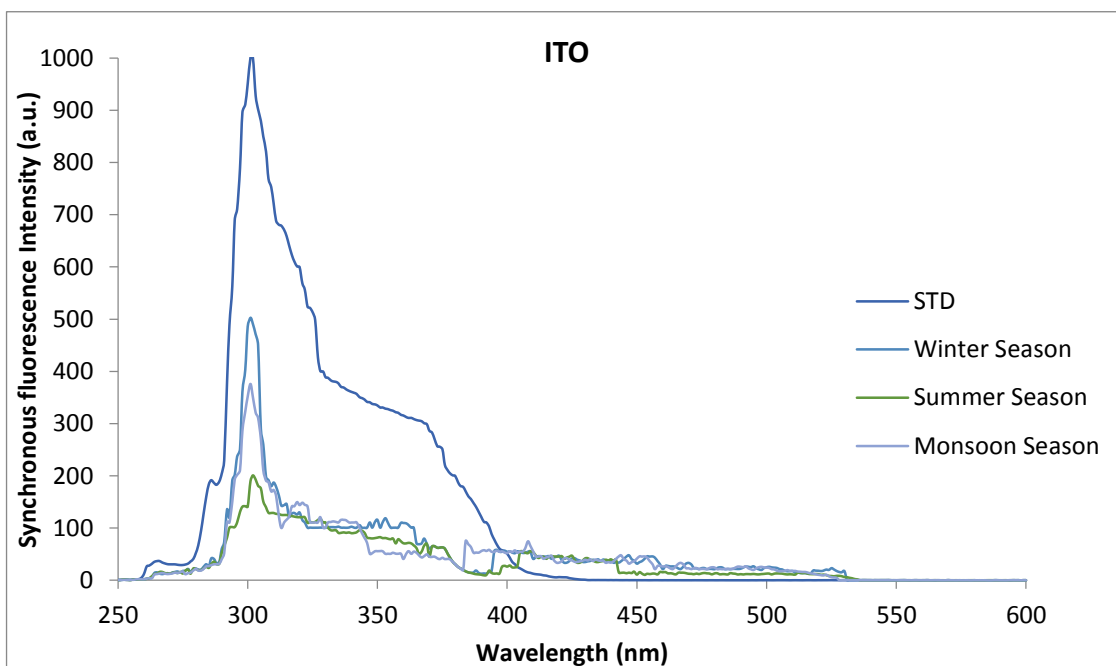


Fig.10. Synchronous fluorescence spectra of benzo(b)fluoranthene in n-hexane at $\Delta\lambda = 160\text{nm}$.

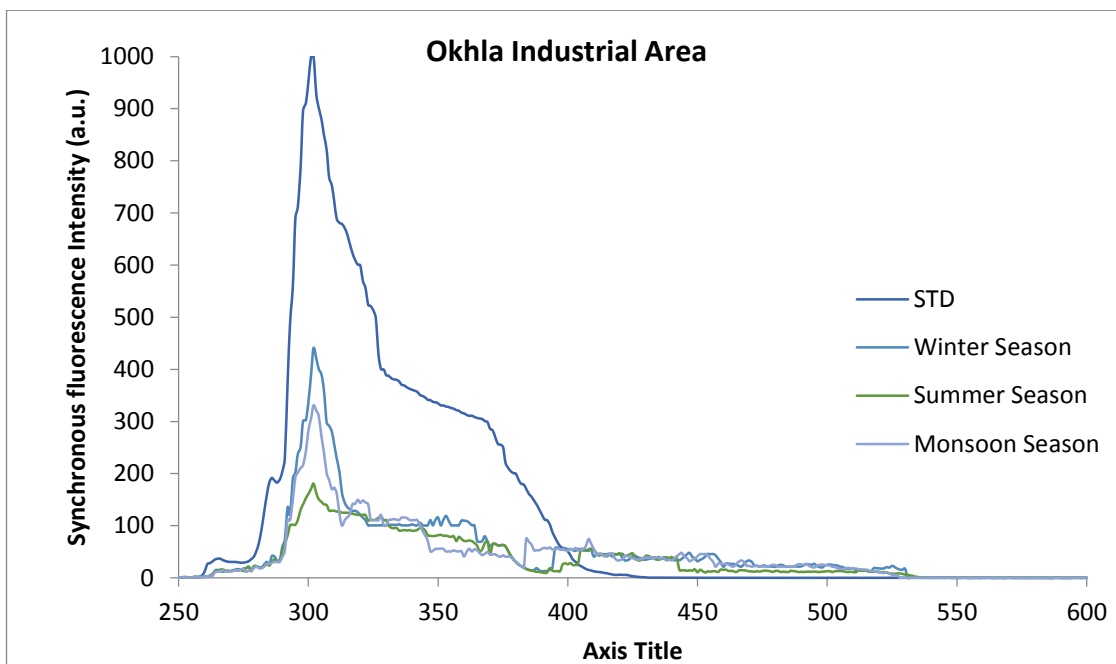


Fig.11. Synchronous fluorescence spectra of benzo(b)fluoranthene in n-hexane at $\Delta\lambda = 160\text{nm}$.

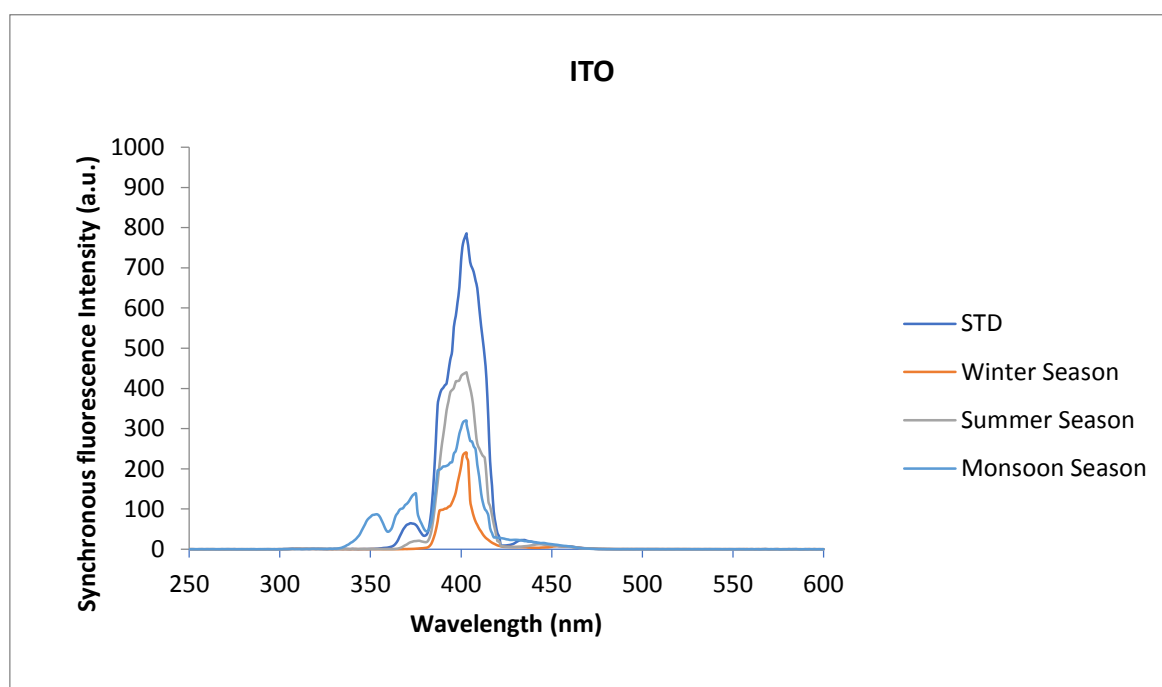


Fig.12. Synchronous fluorescence spectra of benzo(k)fluoranthene in n-hexane at $\Delta\lambda = 25\text{nm}$.

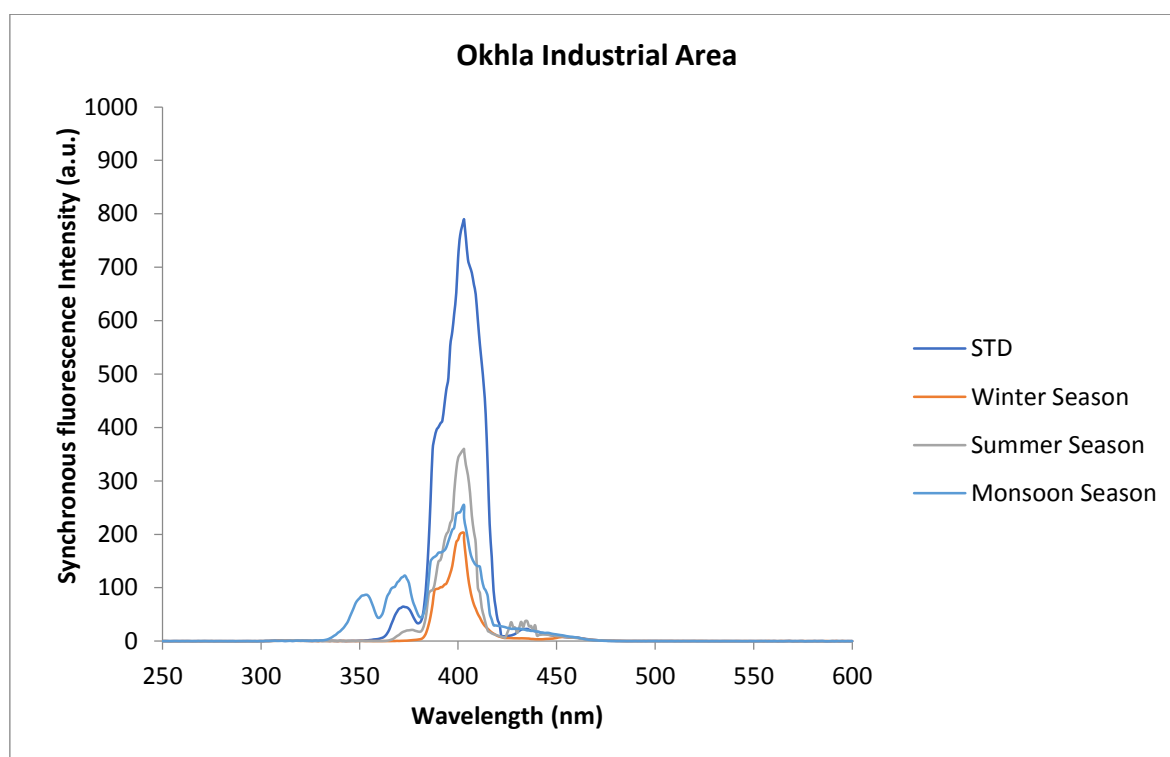


Fig.13. Synchronous fluorescence spectra of benzo(k)fluoranthene in n-hexane at $\Delta\lambda = 25\text{nm}$.

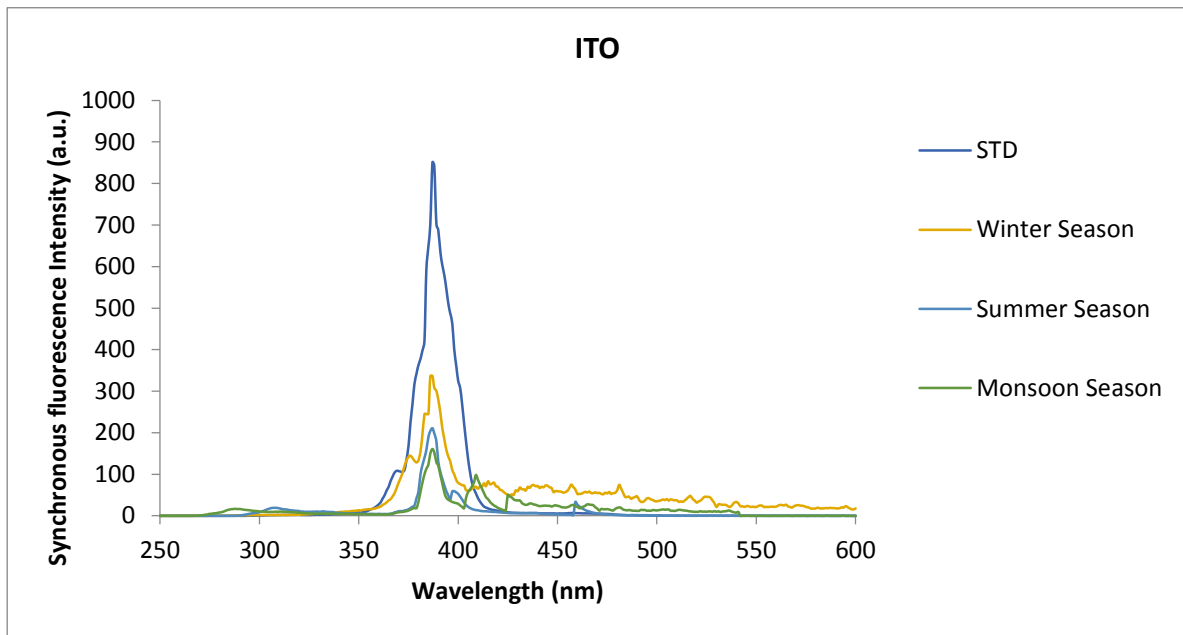


Fig.14. Synchronous fluorescence spectra of benzo(a)pyrene in n-hexane at $\Delta\lambda = 15\text{nm}$.

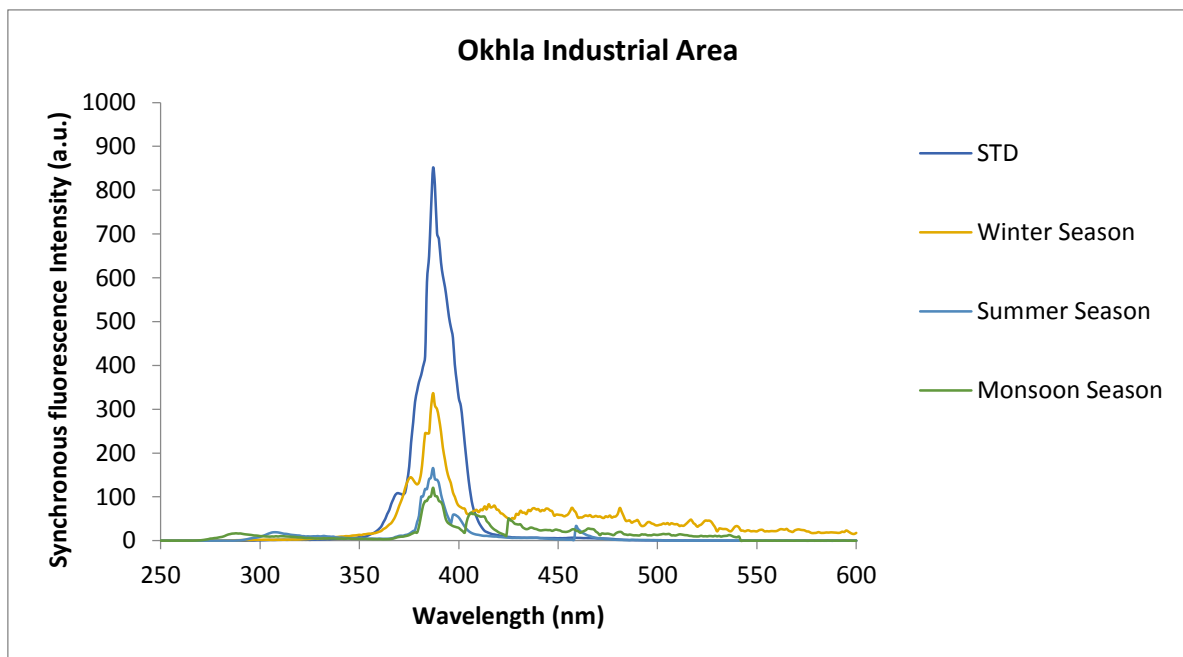


Fig.15. Synchronous fluorescence spectra of benzo(a)pyrene in n-hexane at $\Delta\lambda = 15\text{nm}$.

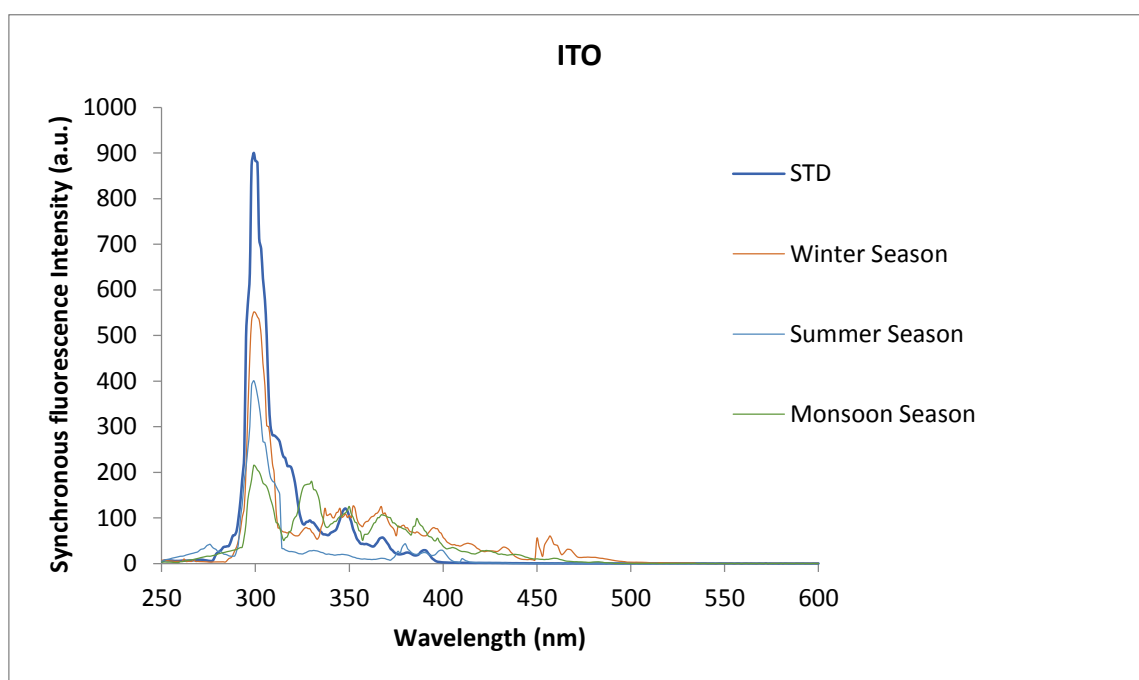


Fig.16. Synchronous fluorescence spectra of dibenzo(ah)anthracene in n-hexane at $\Delta\lambda = 95\text{nm}$.

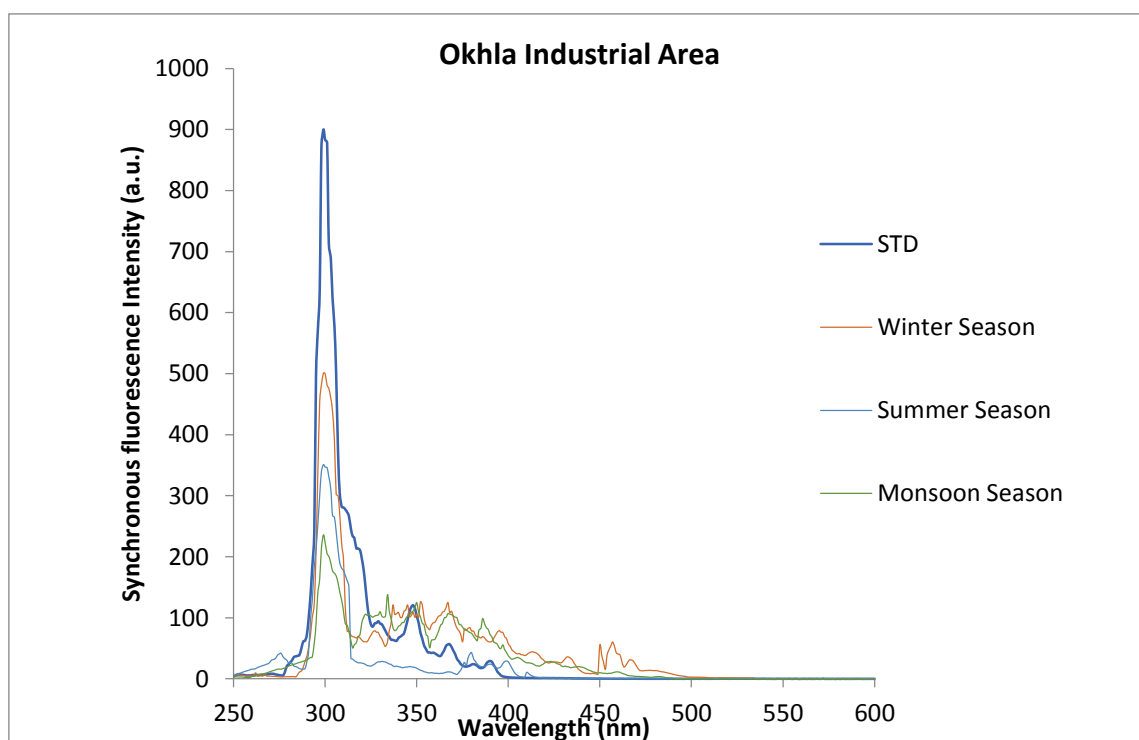


Fig. 17. Synchronous fluorescence spectra of dibenzo(ah)anthracene in n-hexane at $\Delta\lambda = 95\text{nm}$.

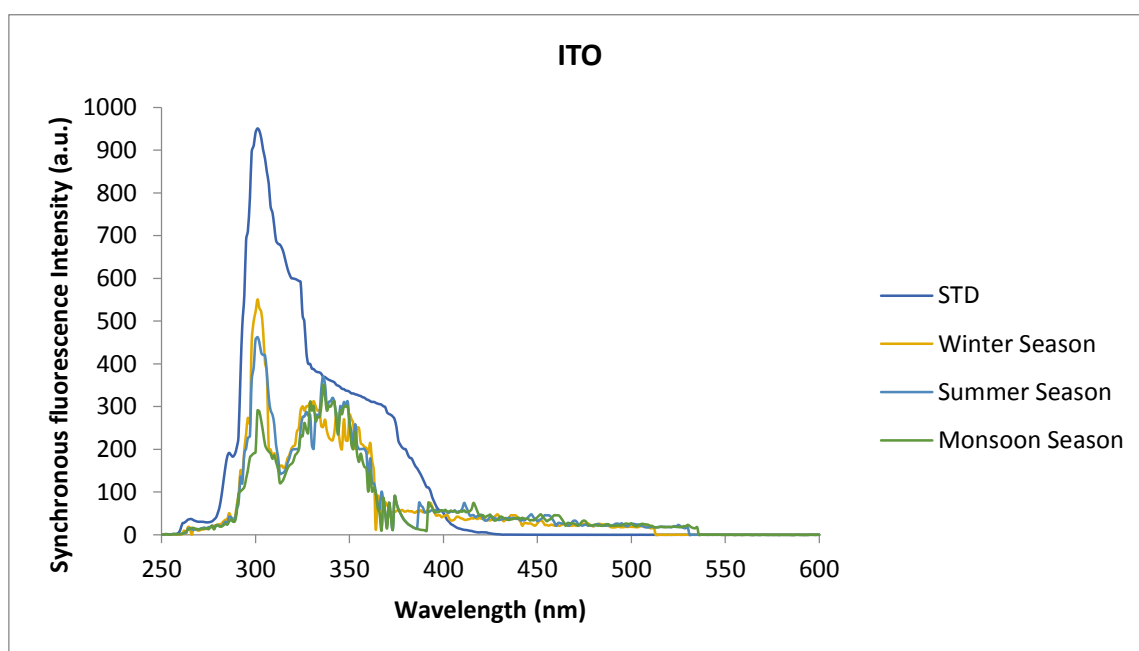


Fig.18. Synchronous fluorescence spectra of benzo[ghi]perylene in n-hexane at $\Delta\lambda = 115\text{nm}$.

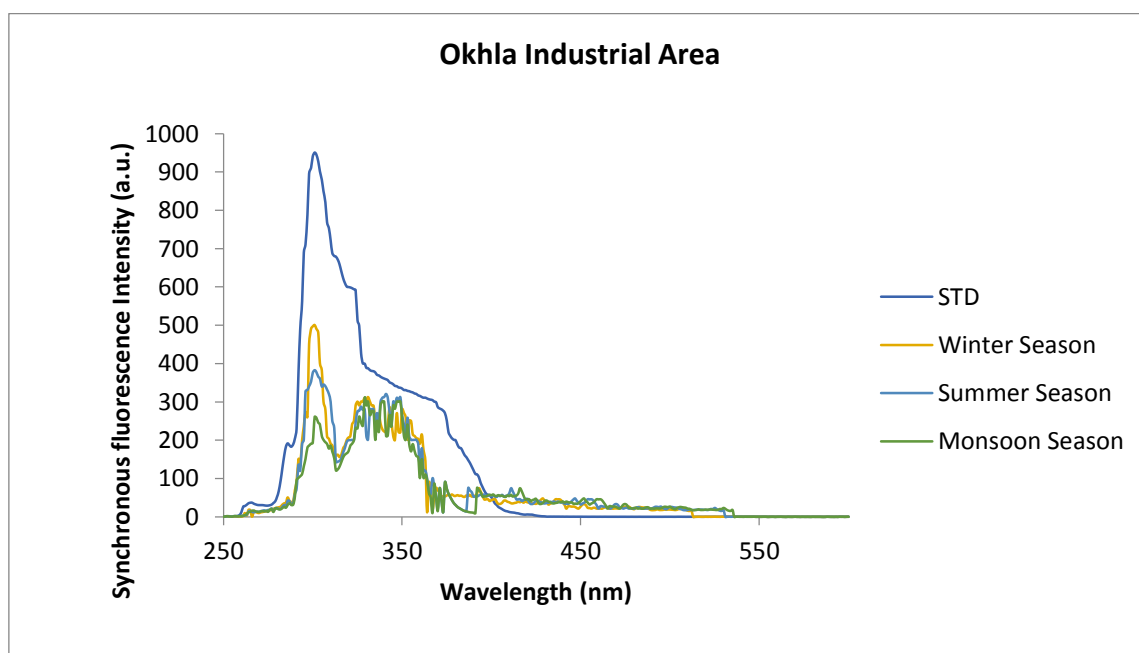


Fig.19. Synchronous fluorescence spectra of benzo[ghi]perylene in n-hexane at $\Delta\lambda = 115\text{nm}$.

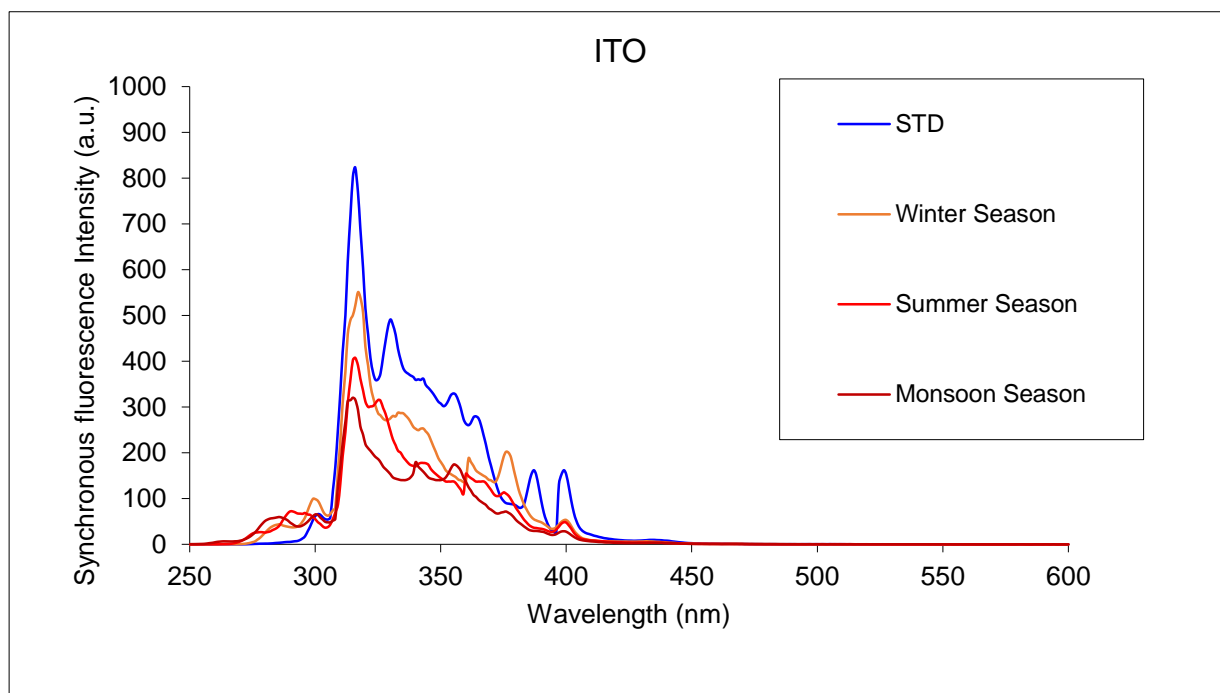


Fig. 20. Synchronous fluorescence spectra of Indeno (1,2,3-cd) pyrene in n-hexane at $\Delta\lambda = 190$ nm.

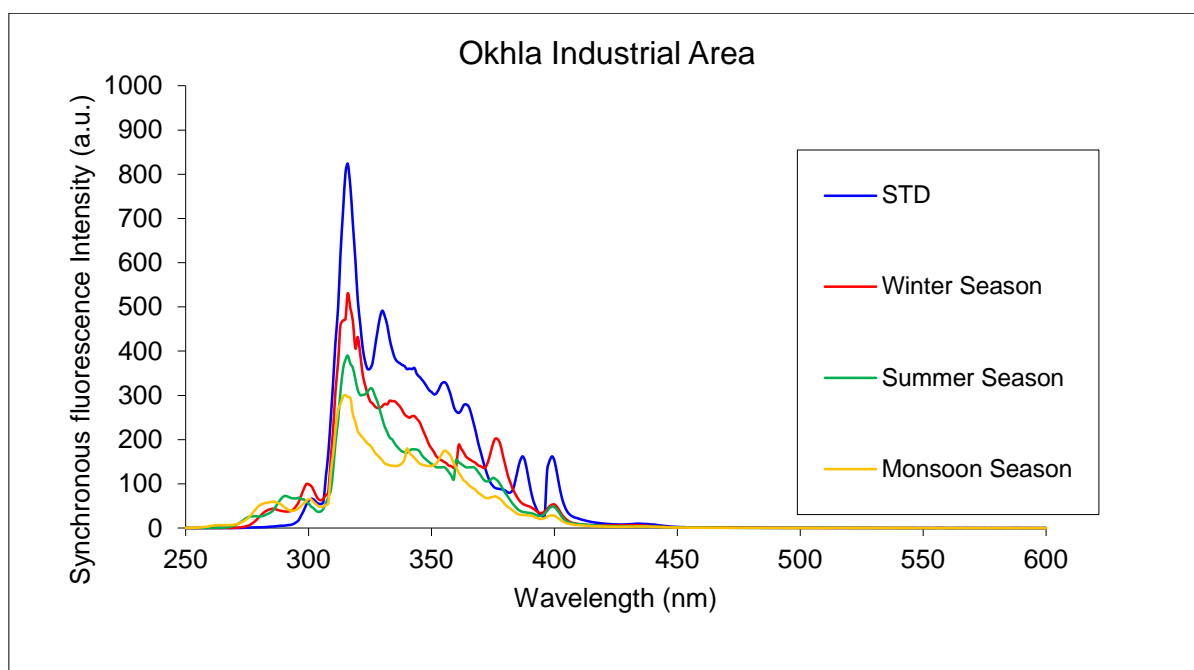


Fig. 21. Synchronous fluorescence spectra of Indeno (1,2,3-cd) pyrene in n-hexane at $\Delta\lambda = 190$ nm.

In these figures, the intensity of the emission peaks is given in an arbitrary scale of 0 - 1000. The optimized $\Delta\lambda$ values as well as maximum excitation wavelength (λ_{exc}) of each compound were used as the individual identification peak for each fluorophore in their unknown mixture. In each of the above figures, we have generally plotted four different spectra, the fluorescence of the standard compound (STD) and those of the samples collected during the winter, summer and monsoon seasons. In some cases, however, the emission during the monsoon seasons could be detected poor amount of concentration of the samples collected from the environment. Since the intensity of an emission peak of a PAH is directly

related to its concentration, the above results demonstrate that the concentration of the PAHs is maximum during the winter season and minimum during the summer and monsoon seasons. In summer, high wind speeds and high temperatures along with enhanced photodecomposition of PAHs, lead to increased dispersion and decrease in the concentration of PAHs, whereas in winter low wind speeds, inversion conditions and low temperatures make the atmosphere stable. Under calm and stable conditions, the pollutant dispersion is the least leading to accumulation and more gas-to-particle conversion of PAHs, which in turn lead to higher concentration of PAHs (Sharma et al. 2007). The higher concentrations during winter season could be due to the contribution from other sources such as domestic heating, traffic congestion, increased fossil fuel usage for space heating causes the enhanced particulate PAH concentrations in the winter season (Liu et al., 2014). In the monsoon season, the concentrations of PAHs are less because they are scavenged away by precipitation as compared to that found in the summer season. They tend to react with other gases, leading to reduced concentrations in comparison to concentrations observed in winter. Most of the total individual PAH concentrations at ITO sampling site were higher than at the Okhla. It may be mentioned that a major fraction of PAHs concentration in the atmosphere of Delhi originated from vehicular emissions with predominance of emissions from automobile exhaust running on diesel and gasoline in winter and summer seasons but in winter season especially, biomass burning is a one of the major source of PAHs emissions, which is already described in our earlier work (Sharma et al., 2007).

CONCLUSION

It is seen that the synchronous fluorescence spectroscopy technique can be applied successfully for the qualitative analysis of PAHs from the airborne fine particulate matter samples, which were extracted by DCM + hexane. The special advantage of SFS technique is the possibility of analysis of complex environmental PAHs mixtures without the need of multistage sample fractionation. The identification of 10 PAHs (most of them belonging to the EPA list) was achieved in the working mixture of airborne fine particulate matter in n-hexane. It has been found that the concentration of the PAHs is maximum during the winter season and minimum during the summer and monsoon seasons at two locations. In conclusion constant-wavelength synchronous fluorescence spectrometry proved to be inexpensive, sensitive, easy operation and rapidity, when applied to the identification of PAHs. The study provides highly useful information about the air pollution of urban areas which is currently a matter of concern for the environmentalist throughout the world.

GRANT SUPPORT DETAILS

The present research did not receive any financial support.

CONFLICT OF INTEREST

The authors declare that there is not any conflict of interests regarding the publication of this manuscript.

LIFE SCIENCE REPORTING

No life science threat was practiced in this research.

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