# Investigation of Endocrine disruptor - PAEs and Carcinogenic - PAHs bound to ambient fine particulate matter over Northwest Indo-Gangetic Plain


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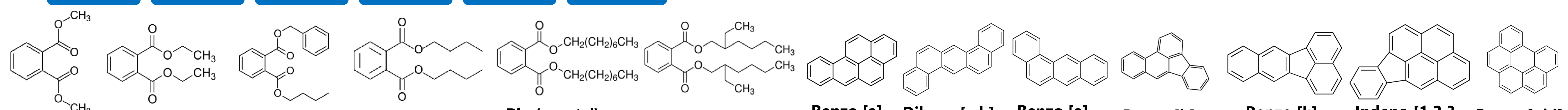
## Introduction

**Phthalic Acid Esters (PAEs)**

Plastics | Polymers | Toys | Rubber | Paints | Medical devices

**Polycyclic Aromatic Hydrocarbons (PAHs)**

Traffic emissions | Coal Combustion | Industrial emissions | Cigarette smoke | Biomass Burning | Volcanic eruption



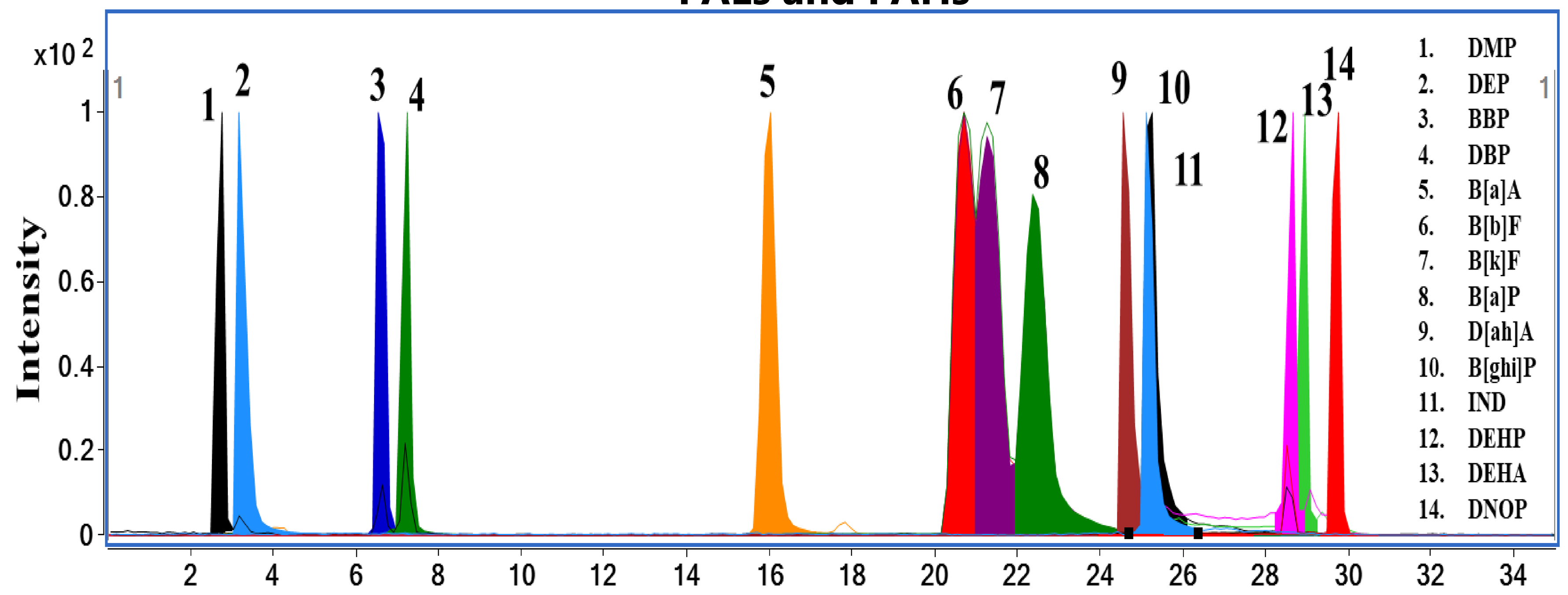
Dimethyl phthalate (DMP) | Diethyl phthalate (DEP) | Benzyl butyl phthalate (BBP) | Dibutyl phthalate (DBP) | Bis-(n-octyl) phthalate (DNOP) | Bis-(2ethyl hexyl) phthalate (DEHP) Group 2B | Benzo [a] pyrene (B[a]P) Group 1 | Dibenz [a,h] anthracene (D[a,h]A) Group 2A | Benzo [a] anthracene B[a]A Group 2B | Benzo [b] fluorenthene (B[b]F) Group 2B | Benzo [k] fluorenthene (B[k]F) Group 2B | Indeno [1,2,3-cd] pyrene (IND) Group 2B | Benzo [ghi] perylene (B[ghi]P) Group 2B

## Materials and Methods

Sample filter in n-hexane → Ultrasonication → Filtration → LC-MS/MS Analysis

- Instrument : Agilent LC-MS/MS QQQ
- Agilent Zorbax RRHD eclipse plus $C_{18}$ column (3.0 x 100 mm, 1.8 μm)
- Mobile Phase: A)100% water, B) 5mM Ammonium Formate in MeOH:ACN (80:20 v/v)
- Ionization Mode: ESI Positive

**Optimization of novel LC-MS/MS Method for simultaneous determination of PAEs and PAHs**




## Results

**Table 1.** Linearity, Intraday analysis, Interday analysis, Recovery, LOD and LOQ of targeted PAEs and PAHs.

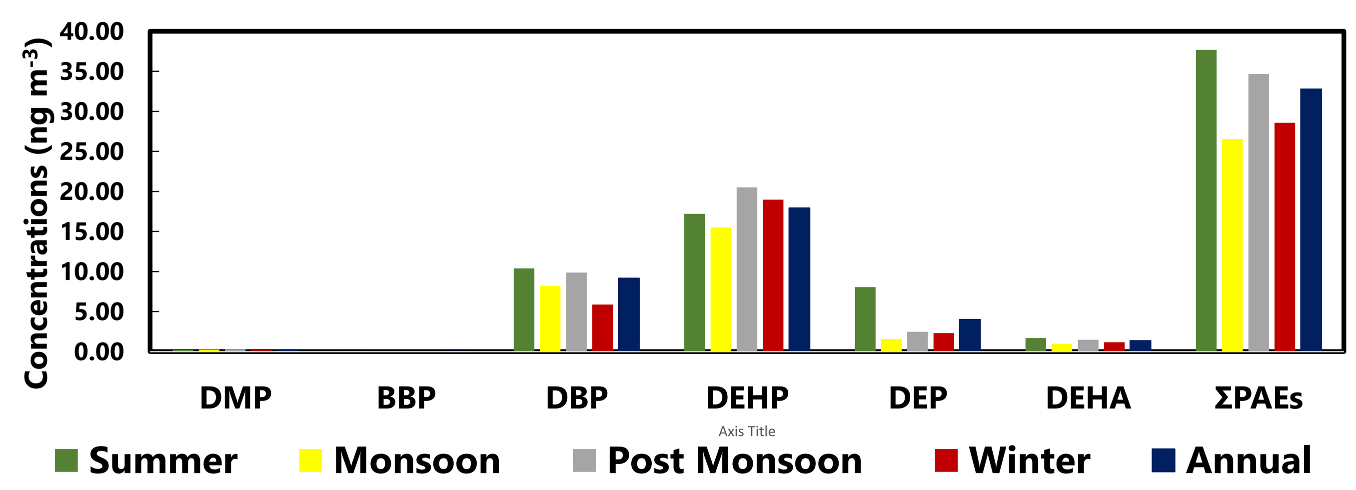
| Compound | Correlation coefficient ($r^2$) | Recovery (%) | LOD (ng $m^{-3}$) | LOQ (ng $m^{-3}$) |
|---|---|---|---|---|
| PAEs | | | | |
| DMP | 0.9903 | 62.00 | 0.15 | 0.51 |
| DEP | 0.9946 | 95.53 | 0.33 | 1.09 |
| BBP | 0.9988 | 100.42 | 0.03 | 0.09 |
| DBP | 0.9980 | 108.10 | 0.33 | 1.10 |
| DEHP | 0.9952 | 103.89 | 1.15 | 3.85 |
| DEHA | 0.9919 | 117.09 | 0.07 | 0.23 |
| DNOP | 0.9964 | 114.33 | 0.13 | 0.42 |
| PAHs | | | | |
| B[a]A | 0.9918 | 90.61 | 0.16 | 0.53 |
| B[b]F | 0.9943 | 117.65 | 0.14 | 0.45 |
| B[k]F | 0.9907 | 92.43 | 0.06 | 0.18 |
| B[a]P | 0.9943 | 103.65 | 0.04 | 0.12 |
| D[ah]A | 0.9901 | 95.73 | 0.18 | 0.59 |
| B[ghi]P | 0.9903 | 106.10 | 0.75 | 2.49 |
| IND | 0.9992 | 99.83 | 1.81 | 6.03 |

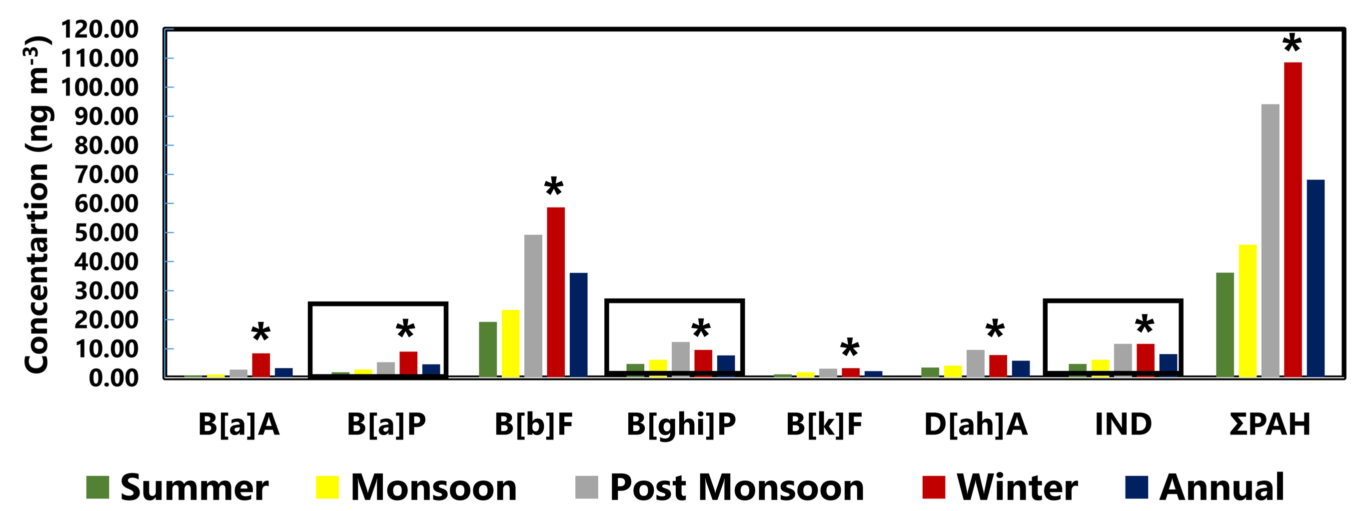
a: standard deviation represents the ambient variability, b: no. of samples, bdl: below detection limit

**Table 2.** Annual mean mass concentrations of PAEs and PAHs bound to $PM_{2.5}$ samples collected at the measurement site

| Compound | Mean ± S.D[a] (ng $m^{-3}$) (n[b]=31) | Range (ng $m^{-3}$) | Frequency of detection (%) |
|---|---|---|---|
| PAEs | | | |
| DMP | 0.23 ± 0.09 | bdl - 0.41 | 83.87 |
| DEP | 4.01 ± 3.88 | 0.45 – 13.42 | 100.00 |
| BBP | 0.05 ± 0.04 | bdl – 0.17 | 87.10 |
| DBP | 9.16 ± 3.76 | 3.09 -17.50 | 100.00 |
| DEHP | 17.94 ± 4.35 | 4.42 - 25.06 | 100.00 |
| DEHA | 1.38 ± 0.71 | 0.32 – 3.11 | 100.00 |
| PAHs | | | |
| B[a]A | 3.31 ± 4.48 | bdl - 18.23 | 93.10 |
| B[b]F | 36.13 ± 31.45 | bdl – 130.86 | 96.55 |
| B[k]F | 2.27 ± 1.95 | bdl – 9.30 | 93.10 |
| B[a]P | 4.66 ± 5.22 | bdl – 24.74 | 96.55 |
| D[ah]A | 5.90 ± 4.71 | bdl – 17.75 | 93.10 |
| B[ghi]P | 7.70 ± 5.01 | bdl – 18.65 | 93.10 |
| IND | 8.18 ± 5.06 | bdl - 19.28 | 93.10 |

a: no of samples, b: relative standard deviation




- Order of mean concentrations of $\sum_6$PAEs :Summer (39.78 ± 13.81 ng $m^{-3}$)>Post Monsoon (32.35 ± 9.11 ng $m^{-3}$)>Winter (29.18 ± 7.69 ng $m^{-3}$)>Monsoon(26.09 ± 10.46 ng $m^{-3}$)
- Higher concentrations of **PAEs** in **summer** is due to the **semi volatile nature of PAEs and weak intermolecular force of attraction of PAEs with their polymer matrix**
- Order of mean concentrations of $\sum_7$PAHs : Winter (108.53 ng $m^{-3}$) > Post Monsoon (94.17 ng $m^{-3}$) > Monsoon (45.84 ng $m^{-3}$) > Summer (36.20 ng $m^{-3}$)
- **Diagnostic ratios (DRs)** revealed that higher concentrations of **PAHs** in **winter** is due to the **coal combustion / biomass burning**
- **B[a]P (Group 1 carcinogen) concentrations at the sampling site exceeded the threshold limit (1 ng m-3) set by NAQQS, India**
- **Health risk assessment:**

$$LADD\ (\mathrm{mg\ kg^{-1}\ day^{-1}}) = \frac{(C \times IR \times EF \times ED)}{(BW \times AT)} \times CF$$

$$ILCR = LADD \times CPF$$

**LADD:** Lifetime average daily dose, **ILCR:** Incremental lifetime cancer risk, **CPF:** Cancer potency factor ; 0.014 mg kg-1 day-1 for DEHP and 3.14 mg kg-1 day-1 for B[a]P , **C:** Concentration of the pollutant (For PAEs, C: Concentration of both gaseous and particulate PAEs and For PAHs, C: toxicity equivalent concentration (TEQ) obtained using all the measured PAHs), **TEQ :** $\sum C_i * TEF_i$ (Toxicity equivalent factor), **IR:** Inhalation rate ($m^3$ $d^{-1}$) ; Children (10 $m^3$ $d^{-1}$) & Adults (20 $m^3$ $d^{-1}$), **EF:** Exposure frequency (days $year^{-1}$); 365 days $year^{-1}$ , **ED:** Exposure duration (years); Children (6 years) & Adults (70 years), **BW:** Body weight (kg); Children (15 Kg) & Adults (70 Kg), **AT:** Average time span (days), **CF:** Conversion factor ($10^{-6}$)

**ILCR for Adults in NWIGP**
DEHP :0.37 x $10^{-6}$
$B[a]P_{equ}$ :**1.40 x $10^{-5}$**

**ILCR for Children in NWIGP**
DEHP :0.88 x $10^{-6}$
$B[a]P_{equ}$ :**3.28 x $10^{-5}$**

## Conclusions

- This is the first ever method developed for the simultaneous determination of PAEs and PAHs bound to particulate matter using LC-ESI-MS/MS
- This study reveals that the health risk due to exposure to PAEs and PAHs bound to $PM_{2.5}$ should be of concern
- In addition to PAEs and PAHs, other hazardous pollutants like heavy metals, and chlorinated compounds are bound to fine particulate matter. Therefore, comprehensive investigations on fine particulate matter is needed to assess the cumulative health risk

## References


1. Durga Prasad Patnana, B.P. Chandra, Pooja Chaudhary, Baerbel Sinha, Vinayak Sinha (2022). Optimized LC-MS/MS method for simultaneous determination of endocrine disruptors and PAHs bound to PM2.5: Sources and health risk in Indo-Gangetic Plain. Atmospheric Environment 290, https://doi.org/10.1016/j.atmosenv.2022.119363


Sharing is encouraged

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