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Can the Indian national ambient air quality standard protect against the hazardous constituents of $PM_{2.5}$?

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HIGHLIGHTS

- We assess the risk to health from exposure to $PM_{2.5}$-bound PCBs, metals and PAHs below the Indian NAAQS of 40 μg/m^3.
- The estimated risk levels in urban, peri-urban and rural areas greatly surpass the acceptable risk value.
- People dwelling in rural areas have greater risks of adverse effects than those in urban or peri-urban areas.
- It would require a more stringent standard in India, such as the global AQG of 5 μg/m^3, to meet the acceptable risk level.

GRAPHICAL ABSTRACT

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ABSTRACT

Globally, exposure to ambient fine particulate matter ($PM_{2.5}$) pollution claims ~9 million lives, yearly, and a quarter of this deaths occurs in India. Regulation of $PM_{2.5}$ pollution in India is based on compliance with its National Ambient Air Quality Standard (NAAQS) of 40 μg/m^3, which is eight times the revised global air quality guideline (AQG) of 5 μg/m^3. But, whether the NAAQS provides adequate protection against the hazardous components in $PM_{2.5}$ is still not clear. Here, we examined the risk to health associated with exposure to $PM_{2.5}$–bound polychlorinated biphenyls (PCB), heavy metals and polycyclic aromatic hydrocarbons (PAHs) in an Indian district averaging below the NAAQS. The annual average concentrations of $PM_{2.5}$ mass, Σ_{28}PCB and Σ_{13}PAHs were 34 ± 17 μg/m^3, 21 ± 12 ng/m^3 and 458 ± 246 ng/m^3, respectively. Concentrations of As, Cr, Mn and Ni in $PM_{2.5}$ surpassed the screening levels for residential air. Substantial level of risks to health were associated with exposure to dioxin-like PCBs (Σ_{12}dlPCB), PAHs, As, Cr and Ni. The hazard index or lifetime cancer risk were 240, or 9 cases per 1000 population, respectively. The estimated risks to health through exposure to hazardous components, except Ni, were greatest in rural areas, having a lower average $PM_{2.5}$ concentration, than urban or peri-urban areas, suggesting higher toxicity potential of rural combustion sources. The large disparity between the estimated risk values and the acceptable risk level suggests that it would take a more

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stringent standard, such as the global AQG, to protect vulnerable populations in India from hazardous components in $PM_{2.5}$.

1. Introduction

Globally, exposure to ambient fine particulate matter ($PM_{2.5}$) pollution is a leading cause of deaths and diseases (Cohen et al., 2017). Every year, about nine million people, worldwide, die from various diseases caused by exposure to the pollution (Burnett et al., 2018), with hundreds of millions of lost years of healthy life and a loss of trillions of dollars, yearly (WHO, World Health Organization, 2021). Nearly a quarter of the estimated death toll occurs in India (Burnett et al., 2018), with an upward trend, due to increasing vulnerability and susceptibility of the population to the pollution (Etchie et al., 2019). For example, our study (Etchie et al., 2017) found that ageing alone would increase the $PM_{2.5}$-related deaths in India by 17% in every five years. However, in order to keep the $PM_{2.5}$-related death rate constant, average $PM_{2.5}$ concentrations in India must decline by 20–30% over the next 15 years, merely to offset the death increases resulting from ageing population (MoHFW, 2015f). Thus, only purposeful mitigation measures can significantly reduce the health impact arising from $PM_{2.5}$ pollution exposure in India.

The regulation of $PM_{2.5}$ pollution in India is based primarily on localities complying with the National Ambient Air Quality Standard (NAAQS) for annual $PM_{2.5}$ concentration of 40 $\mu g/m^3$ (CPCB, Central Pollution Control Board Government of India, 2009). This value, which exceeds the World Health Organization's (WHO, World Health Organization, 2021) Interim Target 1 (IT-1) of 35 $\mu g/m^3$, is eight times the revised global Air Quality Guideline (AQG) of 5 $\mu g/m^3$. Yet, the NAAQS remains the cornerstone for identifying non-attaining localities, and for gauging the progress of air quality intervention measures across India (Chowdhury and Dey, 2016; Chowdhury et al., 2019; Purohit et al., 2019). For example, the recently launched National Clean Air Programme (NCAP) aimed for all localities in India to comply with the NAAQS in a reasonable timeframe (NCAP, 2019; Ganguly et al., 2020). However, whether this NAAQS provides adequate level of protection against the hazardous components of $PM_{2.5}$ or not, is still not clear. Namely, the risk to health associated with exposure to the hazardous components of $PM_{2.5}$ below the NAAQS is currently unknown.

Per unit mass of $PM_{2.5}$, the concentrations of hazardous components vary remarkably in time and space, depending on the sources emitting the $PM_{2.5}$. For example, $PM_{2.5}$ from combustion sources were found to contain higher concentrations of hazardous constituents such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), dioxins and furans, heavy metals, and other by-products of incomplete combustion or pyrolysis, compared to $PM_{2.5}$ from non-combustion sources (Ostro et al., 2015). In addition, the risk of mortality from combustion $PM_{2.5}$ was found to exceed five times that from non-combustion $PM_{2.5}$, on a per $\mu g/m^3$ basis (Lelieveld et al., 2015; Silva et al., 2016; Thurston et al., 2016; Etchie et al., 2018a). Therefore, the ideal regulatory standard for $PM_{2.5}$ should proffer acceptable levels of risk to health from all harmful constituents, regardless of the type or source of the $PM_{2.5}$.

Previous studies characterizing $PM_{2.5}$ in India focused primarily on polluted localities where the annual average $PM_{2.5}$ levels exceed the NAAQS value. Thus, it is not clear whether localities complying with the NAAQS can attain acceptable levels of risk to health from individual hazardous components. For example, several studies have investigated concentrations of heavy metals in $PM_{2.5}$ in polluted localities in Agra, Delhi, Kolkata and Lucknow, where the annual $PM_{2.5}$ concentrations averaged between 90 and 313 $\mu g/m^3$ (Kulshrestha et al. 2009, 2014; Pandey et al., 2013; Pant et al., 2015; Das et al., 2015; Sah et al., 2019). The average concentrations of Cd, Cr, Mn, Ni and Pb found in the $PM_{2.5}$ ranged from 1 to 54 ng/m^3, 3–1600 ng/m^3, 70–146 ng/m^3, 40–290 ng/m^3 and 32–610 ng/m^3, respectively. One study (Police et al., 2018) however investigated the concentrations of metals in $PM_{2.5}$ in a locality in Mumbai averaging below the NAAQS. The annual $PM_{2.5}$ concentration in the locality was 30 ± 15 $\mu g/m^3$, and the average (range) concentrations of As, Cr, Mn, Ni and Pb found in the $PM_{2.5}$ was 2 (0.4–5) ng/m^3, 10 (1–89) ng/m^3, 39 (2–201) ng/m^3, 15 (1–136) ng/m^3 and 107 (3–838) ng/m^3, respectively.

Our study (Etchie et al., 2018b) was the first to determine concentrations of PAHs in $PM_{2.5}$ below the NAAQS in India. The annual average concentrations of Σ_{13}PAHs in the $PM_{2.5}$ from urban, peri-urban and rural areas of the district were 543 ± 276 ng/m^3, 239 ± 79 ng/m^3 and 593 ± 164 ng/m^3, respectively. The values fall within the range of PAHs concentrations of <1–2100 ng/m^3 reported for polluted areas in Delhi, Agra, Mumbai, Chennai, Kolkata, Patiala, Raipur and Jamshedpur (Abba et al., 2012; Mohanraj et al., 2011; Rajput et al., 2011; Singh et al. 2011, 2021; Singla et al., 2012; Giri et al., 2013; Dubey et al., 2015; Hazarika and Srivastava, 2017; Kulshrestha et al., 2019; Kumar et al., 2020; Yadav et al., 2020).

So far, no information is available on the concentrations of PCBs in the respirable size fraction ($PM_{2.5}$) in India. However, the available information shows that PCBs concentrations in the gas phase, total suspended particles (TSP) or total air in some localities in India ranged from 0.2 to 72 ng/m^3, 0.03–660 pg/m^3 or 0.025–52 ng/m^3, respectively (Zhang et al., 2008; Pozo et al. 2011; Chakraborty et al., 2013; Goel et al., 2016; Prithiviraj and Chakraborty, 2020; Chakraborty et al., 2021; Nayak et al., 2021; Prithiviraj et al., 2021; Ajay et al., 2022a,b). Although PCBs concentrations are typically higher in gas than particulate phase, PCBs having the greatest potency (the "dioxin-like PCBs) are almost entirely particle-bound. Furthermore, available evidence suggests that PCBs concentrations increase inversely with particle size, with higher PCBs accumulation in $PM_{2.5}$ than TSP or PM_{10} (Degrendele et al., 2014; Zhu et al., 2017, 2018; Yang et al., 2021). Thus, suggesting that TSP-bound PCBs can underrepresent actual particle-bound PCBs exposure in human health risk assessment.

In this study, we examined the risk to health associated with exposure to $PM_{2.5}$-bound PCBs and heavy metals in Nagpur district, averaging below the annual NAAQS value of 40 $\mu g/m^3$. Such assessment can help to reevaluate the efficacy of the regulatory standard in protecting the population against the harmful effects of $PM_{2.5}$. To our knowledge, ours is the first study to elucidate on the relation between harmful $PM_{2.5}$ constituents and the Indian NAAQS, for informed decision-making.

2. Methodology

2.1. Site selection and description

Nagpur district, located at the exact center of India, is regarded as one of the cleanest and greenest district in India (Wanjari, 2012; Borkar et al., 2014). Both ground-level measurements and satellite-derived estimates show that the annual average $PM_{2.5}$ concentrations in the district average below the Indian NAAQS of 40 $\mu g/m^3$. For example, Pal et al. (2018) combined ground-level measurements of $PM_{2.5}$ concentrations and satellite information across India, from the year 1998–2015, and reported an 18-year average concentration of $PM_{2.5}$ of 38 $\mu g/m^3$ for Nagpur district. Similarly, Chowdhury and Dey (2016) calibrated satellite-derived $PM_{2.5}$ estimates across India using coincident ground-level $PM_{2.5}$ measurements and reported an 11-year (2000–2010) average $PM_{2.5}$ concentration of 34 $\mu g/m^3$ for the district. Our field monitoring campaign across nine sites, comprising three each of urban, peri-urban and rural areas of the district, conducted from February 2013 to June 2014, also revealed a district-wide annual

average $PM_{2.5}$ concentration of 34 ± 17 μg/m^3, or PM_{10} concentrations of 103 ± 47 μg/m^3 (Etchie et al., 2017). Further analysis of $PM_{2.5}$ datasets (CPCB, Central Pollution Control Board Government of India, 2009) from the available (urban) monitoring station in Nagpur district (latitude 21.15, longitude 79.05) gave a similar annual average $PM_{2.5}$ concentration of 32 μg/m^3 for the year 2020, but a substantially higher average value of 52 μg/m^3 for the year 2021.

Detailed description of the sampling sites has been documented (Etchie et al., 2017, 2018b). In brief, we sampled nine sites comprising three each of urban, peri-urban and rural areas of the district for approximately 18 months, from February 2013 to June 2014 (Supplemental Materials, Table S1). The urban (Laxminagar, Mankapur and Arti Town Colony), peri-urban (Koradi, Ghogali and Chandkapur) and rural (Suradevi, Satak and Mhasala) areas, all have distinct characteristics within their subgroups. For example, even though Laxminagar, Mankapur and Arti Town Colony are all urban environments, the latter is strictly a residential area, while Laxminagar is a blend of residential and commercial areas. Mankapur is a commercial hub with heavy traffic congestion and dense population. Koradi, Chandkapur, Mhasala and Suradevi are peri-urban and rural areas located close to two large coal-fired thermal power plants. Satak and Ghogali vary remarkably in distance from the plants.

2.2. Determination of concentrations of $PM_{2.5}$-bound PCB congeners and PAHs ($PM_{2.5}$ below the NAAQS)

2.2.1. Sampling method for $PM_{2.5}$-bound PCBs and PAHs

We obtained 24-hr ambient $PM_{2.5}$ samples on pre-heated (400 °C for 5 h) glass microfibers filters (47 mm diameter), using previously calibrated low volume air samplers (LVSs) with a mean airflow rate of 16.67 L/min (Netel Fine Dust Sampler, Model: NPM-FDS-2.5A; and Dutt Fine Dust Air Sampler, Model: DFPM-2.5E). The LVSs were mounted on open roof-tops at heights ranging from 3.7 to 7.6 m (Supplemental Materials Table S1). They were calibrated on the field using a rotameter to ensure a standard air flow rate of 16.67 L/min. No flow rate deviated beyond 10% during the sampling period. After 24 h of sampling, the sample filters were folded in half twice (with sample side inward), wrapped in methanol pre-cleaned aluminum foil using clean forceps, labelled, and placed in a freezer. For comparison, we also collected 24-hr PM_{10} samples using collocated LVSs.

We sampled for seven consecutive days (Monday to Sunday) in each site (Laxminagar, Mankapur, Arti Town Colony, Koradi, Ghogali, Chandkapur, Suradevi, Satak and Mhasala) and season (winter, monsoon, post-monsoon and summer). The post-monsoon sampling was conducted several days before or after Diwali festival. Thus, we did not sample $PM_{2.5}$ during Diwali in any of the sites. We obtained a total of 378 daily (24-hr) $PM_{2.5}$ or PM_{10} sample filters across the nine sites, each for PCBs or PAHs determination.

2.2.2. Sample filters extraction, cleanup and analysis for PCBs

The $PM_{2.5}$ or PM_{10} sample filters obtained over a week, at each location, were combined in a 500 mL Soxhlet extractor, spiked with 1.0 mL of 0.1 μg mL^{-1} of ^{13}C-labelled PCB toxic/LOC/windows defining standard in nonane, and extracted with 300 mL of toluene for 16-h at about 5 cycles per hr. The ^{13}C-labelled PCB toxic/LOC/windows defining standard, purchased from the Cambridge Isotope Laboratories, USA, was used to determine the percent recovery of PCBs for the whole analytical protocol.

We utilized two cleanup steps to remove impurities from the extracts before the instrumental analysis following the EPA Method 1668B (USEPA, United States Environmental Protection Agency, 2008). In the first cleanup step, acid/base back extraction was used to remove color in the extract, while in second cleanup step, neutral, acidic and basic silica gels was used to remove non-polar and polar interferences. The final volume of the cleaned extract in hexane was reduced to 1 mL, and an aliquot of 0.1 μg/mL of ^{13}C-labelled injection internal standard in nonane solution was added (Supplemental Material Table S2). Additional 1 mL of nonane was added to the vial, mixed, and concentrated to the 2 mL level of the nonane. 1 mL of the cleaned extract was transferred to the GC vial, sealed, labelled and analyzed. The leftover was sealed, marked and stored in a freezer.

We determined concentrations of 28 PCB congeners prioritized by WHO in the cleaned extracts by internal standardization method using an optimized gas chromatography quadrapole mass spectrometry (GC-MS) (Clarus 680, PerkinElmer). The GC-MS optimization method follow standard protocol. We used DB-5 column having internal diameter of 30 m × 0.25 mm, with film thickness of 1 mm silicone-coated fused-silica capillary column. The GC column was temperature controlled and interfaced directly to the MS ion source. Carrier gas was helium.

Before the analysis, we calibrated the GC-MS by analyzing six calibration standards containing the target native (unlabelled) PCB congeners, the ^{13}C-labelled toxics/LOC/window defining solution (the recovery standard) and the ^{13}C-labelled injection internal standard solution (Supplemental Material Table S2). The mass spectral of the target PCB congeners were identified using the NIST spectral Library. The PCBs identification and quantification were based on a combination of retention times and relative abundances of selected ions. Retention time qualifier was set at +0.1 min of the library retention time of each PCB congener. The relative retention time and relative response factor of each target native or labelled PCB congener relative to the appropriate internal standard were used for quantification (Supplemental Material, Table S3). The mean recovery of the PCB congeners ranged from 73 to 110%, and the average relative standard deviation for the 28 PCB congeners ranged from 19 ± 5% to 28 ± 3%, indicating good recovery and precision of the analytical protocol (Supplemental Material, Table S4). PCBs concentrations in the blanks were below the detection limit. Therefore, we did not perform blank correction.

2.2.3. Sample filters extraction, cleanup and analysis for PAHs

Detailed description of the method of extraction, cleanup and analysis of the PAHs has been documented (Etchie et al., 2018b). In brief, $PM_{2.5}$ or PM_{10} sample filters obtained over a week, at each location, were combined in a 500 mL Soxhlet extractor, spiked with 1.0 mL of 8.0 μg/mL of deuterated p-terphenyl surrogate standard solution, and extracted with 300 mL of methylene chloride for 16-h at about 5 cycles per hr. The deuterated p-terphenyl surrogate standard solution, purchased from Accustandard Inc. USA, was used to determine the percent recovery of PAHs for the whole analytical protocol. Furthermore, two cleanup steps, acid-base partitioning cleanup and alumina and silica column cleanup, were used to remove impurities from the extracts prior to analysis. The concentrations of thirteen priority PAHs were determined in the cleaned extracts by internal standardization method using the optimized GC-MS (Clarus 680, PerkinElmer). The GC-MS was calibrated by analyzing five calibration standards containing the 13 PAHs mix standards, deuterated internal standards (naphthalene-d_8, acenaphthene-d_{10}, phenanthren-d_{10}, chrysene-d_{12} and perylene-d_{12}) and surrogate standard (p-terphenyl-d_{14}) prior to the analysis. The average recovery of p-terphenyl-d_{14} was 93 ± 29%, and the mean relative standard deviation for the PAHs ranged from 22 ± 7% to 29 ± 3%, indicating good recovery and precision of the analytical procedure (Etchie et al., 2018b). PAHs concentrations in the blanks were below detection limit, so no blank correction was carried out.

2.3. Determination of concentrations of $PM_{2.5}$–bound heavy metals ($PM_{2.5}$ below the NAAQS)

The sampling of $PM_{2.5}$ or PM_{10} for heavy metals determination follow similar protocol as that of the PCB congeners or PAHs, except that in this case polytetrafluoroethylene (PTFE) membrane filters (46.2 mm diameter) were used. A total of 378 daily (24-hr) $PM_{2.5}$ or PM_{10} sample filters were collected for heavy metals determination. The concentrations of fourteen heavy metals (Al, As, Be, Cd, Co, Cr, Cu, Fe, Pb, Mn, Ni,

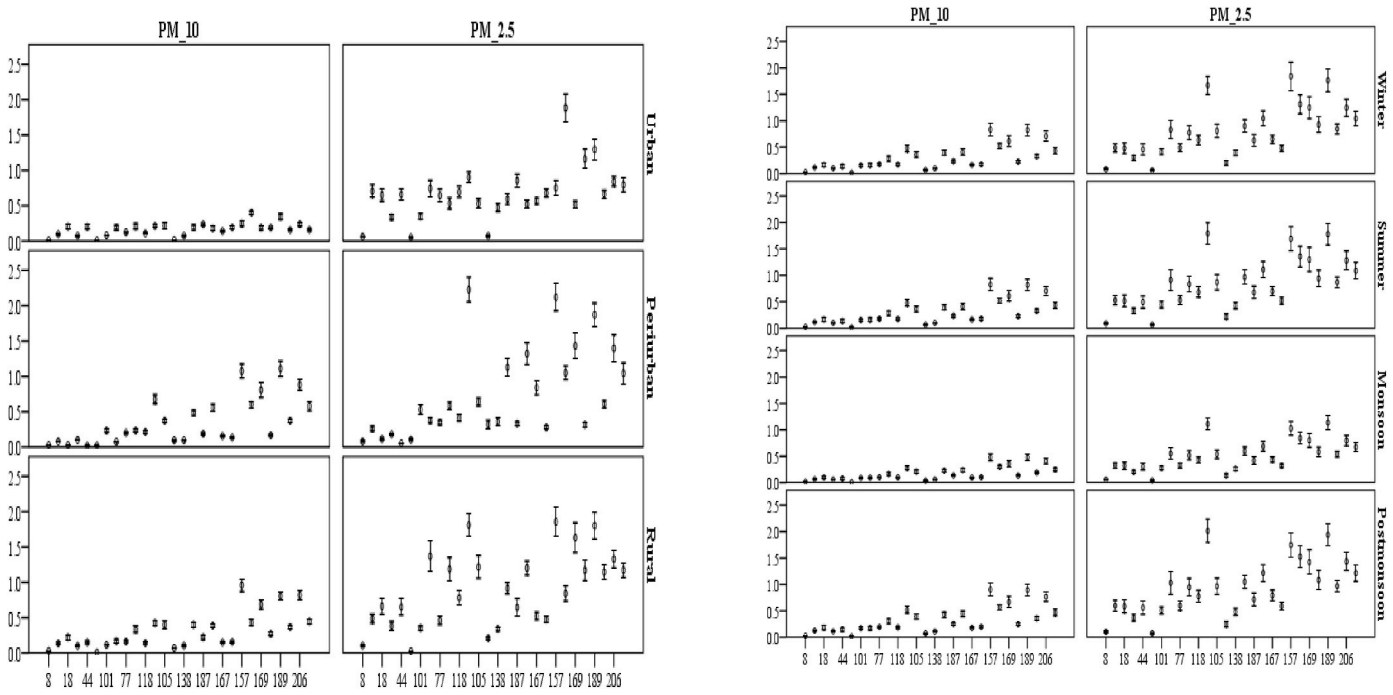

Fig. 1. Average (and 95% confidence interval) concentrations ($ng\ m^{-3}$) of 28 PCB congeners (8, 28, 18, 52, 44, 66, 101, 81, 77, 123, 118, 114, 105, 153, 138, 126, 187, 128, 167, 156, 157, 180, 169, 170, 189, 195, 206 and 209) in $PM_{2.5}$ and PM_{10} across sites and seasons in Nagpur district.

Se, V and Zn) were determined in the individual sample filters using inductively coupled plasma-mass spectrometry (ICP-MS) (PerkinElmer NexION 300X) and ICP-optical emission spectrometry (ICP-OES) (Thermo Fisher iCAP 6300 DUO), after samples digestion following the Method 3050B (US EPA, 1996). Hg concentrations were determined directly in the sample filters by thermal decomposition, amalgamation-atomic absorption spectrophotometry (TDA-AAS) i.e. direct Hg analyzer (DMA-80Milestone Inc.) according to the Method 7473 (USEPA, United States Environmental Protection Agency, 2007).

2.4. Statistical analysis

We assessed the temporal and spatial variability of concentrations of PCB congeners and heavy metals using repeated-measures multivariate analysis of variance (MANOVA, $p = 0.05$) in SPSS 17.0. The multivariate tests utilized were Hotelling's Trace, Wilk's Lambda, Roy's Largest Root and Pillai's Trace. The post hoc tests were Dunnett T3, Bonferroni adjusted comparisons and Least Significant Difference.

2.5. Assessing risk to health from exposure to $PM_{2.5}$–bound constituents ($PM_{2.5}$ below the NAAQS)

We assessed the risk to health of the PCB congeners based on their potential dioxin-like activity relative to the potency of 2,3,7,8-tetrachloro dibenzo-p-dioxin (TCDD) (van den Berg et al., 2006). Thus, concentrations of the dioxin-like PCB congeners were converted to the toxicity equivalent of 2,3,7,8-TCDD (TEQ) using toxicity equivalent factors (TEFs) (van den Berg et al., 2006). Similarly, we calculated the cancer and non-cancer risks from exposure to $PM_{2.5}$-bound PAHs using benzo[a]pyrene (B[a]P) as the indicator PAH. We converted individual PAH concentrations into B[a]P cancer and non-cancer toxicity equivalence (B[a]Peq) using relative potency factors (RPFs), and relative toxicity factors (RTFs) derived from quantitative structure-activity relationships, respectively (Etchie et al., 2018b). We adjusted the RTFs to account for the differential half-lives of PAHs elimination from the body of 35 h and 34 weeks for particle-bound low molecular weight PAHs and high molecular weight PAHs, respectively (Etchie et al., 2019). The time-weighted exposure (EC) to TEQ, B[a]Peq and metals ($\mu g/m^3$) were estimated using Equ. 1 (USEPA, United States Environmental Protection Agency, 2009).

$$EC_n = \frac{CA \times ET \times EF \times ED_n}{AT} \quad 1$$

where:

ECn is time-weighted average exposure concentration (ng/m^3) over a period n.

CA is annual average concentration of dioxin-like PCBs, PAHs or metals in ng/m^3

ET is exposure time (24 h/day) (USEPA, United States Environmental Protection Agency, 2009; USEPA, United States Environmental Protection Agency, 2017a)).

EF is exposure frequency (350 days/year) (USEPA, United States Environmental Protection Agency, 2009; USEPA, United States Environmental Protection Agency, 2017a)).

AT is averaging time = average life expectancy of Indians (L) × 365 days × 24 h/day) (USEPA, United States Environmental Protection Agency, 2009; USEPA, United States Environmental Protection Agency, 2017a). The average life expectancy for Indians is 68.6 years (females = 70.3 years and males = 68.6 years) (IHME, 2017).

EDn is exposure duration over a period n.

We assumed that most people would spend their first 30 years of life within the district. For example, available information for Nagpur district (Census India, 2011) showed that only about 19 percent of the residents younger than 35 years of age migrated from other districts or States in India to Nagpur district. Namely, 81 percent of the inhabitants below 35 years old were born in Nagpur district. Therefore, we considered 30 years exposure duration in estimating the risk of non-cancer effects. For cancer risk assessment, we disaggregated the exposure duration of 30 years into n = 2 years, 14 years and 14 years, for inhalation exposures taking place from 0 to <2 years ($EC_{<2}$), 2 to <16 years ($EC_{2\text{-}16}$), and >16 years ($EC_{>16}$), in order to include age-dependent adjustment factors for early-life vulnerability to cancer of 10, 3 and 1, respectively (USEPA, United States Environmental Protection Agency, 2009; USEPA, United States Environmental Protection

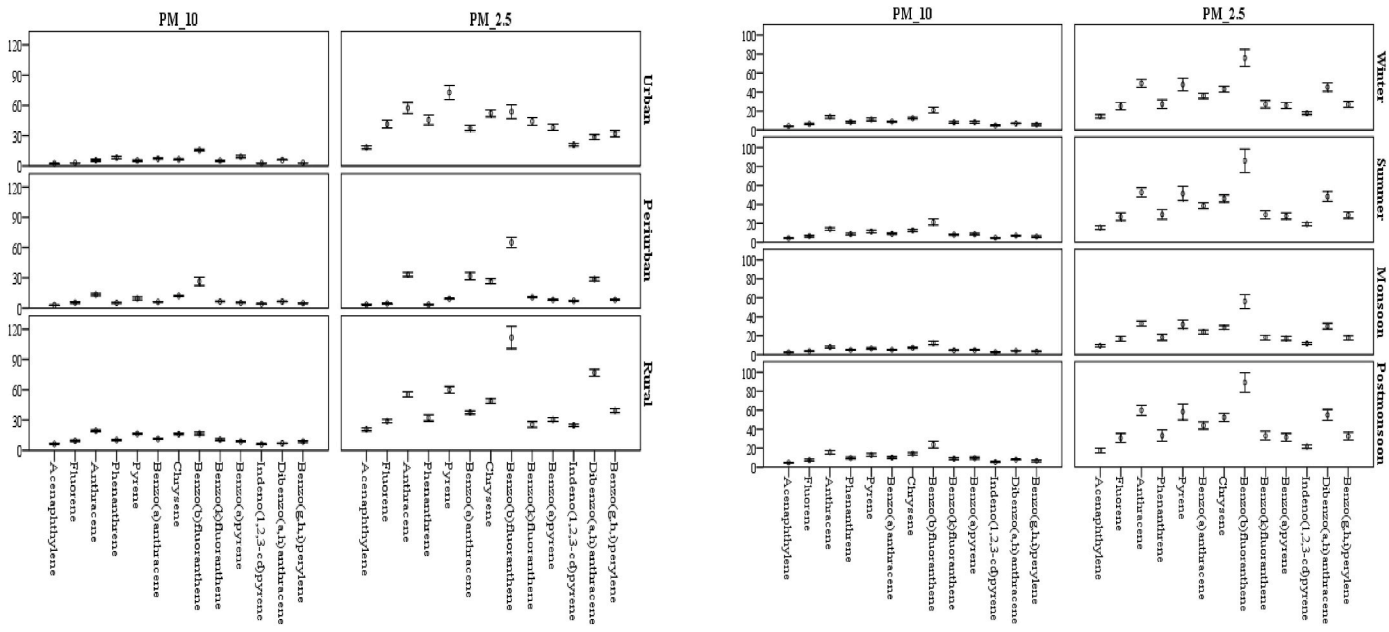

Fig. 2. Average (and 95% confidence interval) concentrations ($ng\ m^{-3}$) of 13 priority PAHs in $PM_{2.5}$ and PM_{10} across sites and seasons in Nagpur district.

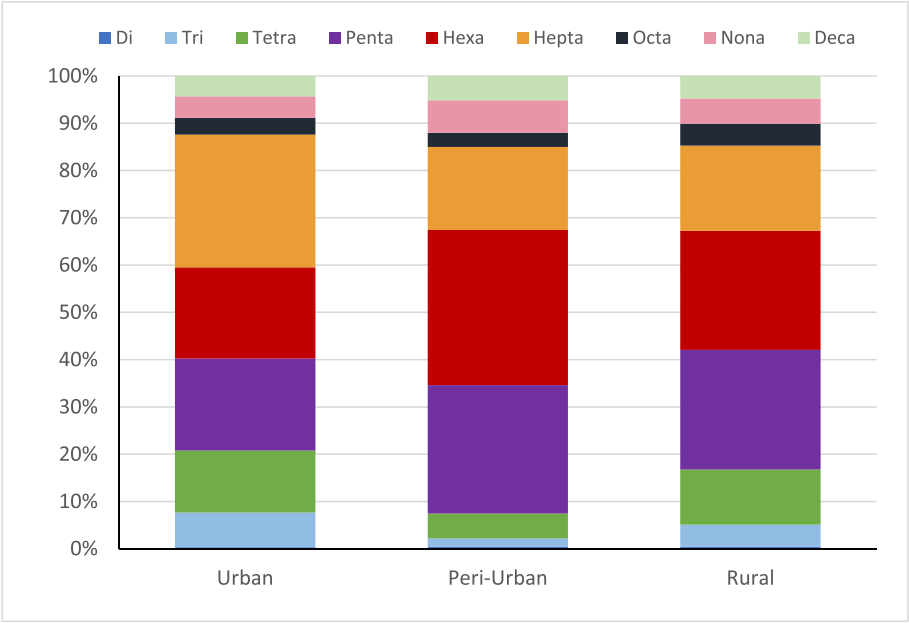

Fig. 3. Percent homolog of $PM_{2.5}$-bound PCB congeners' concentrations in urban, peri-urban and rural areas of Nagpur district.

Agency, 2017a)).

3. Results

3.1. Concentrations of $PM_{2.5}$-bound PCB congeners and PAHs ($PM_{2.5}$ below the NAAQS)

The distribution of PCB congeners and PAHs in $PM_{2.5}$ or PM_{10} across the sites and seasons are shown in Fig. 1 and Fig. 2, respectively. The annual average concentrations of the total measured PCB congeners (Σ_{28} PCBs) in $PM_{2.5}$ and PM_{10} in Nagpur district were 21 ± 12 ng/m^3 and 7.6 ± 4.8 ng/m^3, respectively, while those of the PAHs (Σ_{13} PAHs) were 458 ± 246 ng/m^3 and 112 ± 52 ng/m^3, respectively. We found PCBs and PAHs concentrations to be significantly higher ($p = 0.05$) in $PM_{2.5}$ compared to PM_{10}. This observation corroborates previous studies that reported higher accumulation of PCBs in $PM_{2.5}$ than PM_{10} (Degrendele et al., 2014; Zhu et al., 2017, 2018; Yang et al., 2021). Detailed discussion on the concentrations of the PAHs is available elsewhere (Etchie et al., 2018b).

Individually, PCB concentrations in $PM_{2.5}$ ranged from 18 ± 8 pg/m^3 (for a tetra-PCB, congener 66, in rural areas in monsoon) to 2.8 ± 1.3 ng/m^3 (for a penta-PCB, congener114, in peri-urban areas in post-monsoon). In PM_{10}, the PCB concentrations ranged from 5 ± 3 pg/m^3 (for PCB 66 in rural areas in monsoon) to 1.3 ± 0.7 ng/m^3 (for a hepta-PCB, congener 189, in peri-urban areas in post-monsoon) (see Supplemental Materials, Tables S5 and S6). The penta-, hepta- and hexa-CBs homolog dominated $PM_{2.5}$, accounting for 19–27%, 19–33% and 18–28%, respectively, of the total measured PCBs concentrations in the

Table 1
Comparison of $PM_{2.5}$-bound PCBs concentrations in different localities, worldwide.

S/N	Study locality	Study period	Environment type	$PM_{2.5}$ concentrations (μg/m^3)	PCBs concentrations (ng/m^3)		Reference
					ΣPCBs	Mean (or range)	
1	Nagpur district, India	February 2013–June 2014	Urban Peri-urban Rural	36 ± 16[a] 35 ± 21[a] 31 ± 13[a]	28	19 ± 9 20 ± 11 25 ± 14	This study
2	Santiago, Chile Temuco, Chile	August–October 1998	Urban	NS	47	2.0 (1.2–2.8) 1.4 (0.67–1.8)	Mandalakis and Stephanou (2002)
3	Beijing, China	May 2002–April 2003	Urban	33–185	37	0.079 (0.017–0.17)	Xu et al. (2005)
4	Taiyuan, China	January 2006 & December 2006	Urban	NS	144	0.046 (0.027–0.14)	Fu et al. (2009)
5	Zagreb, Croatia	October 2000–May 2001	Urban	NS	6	5 (1–55) (× 10^{-3})	Dvoršćak et al., 2015
6	Gwangju, South Korea	October 2016–April 2017	Urban	22–35	63	1.4–9.3 (× 10^{-3})	Kim et al. (2019)
7	Wangdu, China	November 2017	Rural	<75–>150	18	0.002–0.1	Sun et al. (2020)
8	Shandong Province, China	April 2017	Urban	79–99	12	0.1–0.2 (× 10^{-3})	Yang et al. (2021)
9	Dalian, China	May 2020–March 2021	Urban	NS	12	0.02–0.4 (× 10^{-3})	Mila et al. (2022)
10	Zouk, Lebanon Mikael, Lebanon	December 2018–October 2019	Urban	NS	12	0.5 ± 0.2 (× 10^{-3}) 0.6 ± 0.1 (× 10^{-3})	Fadel et al. (2022)

[a] Etchie et al., (2017); NS: not stated.

district (Fig. 3). A study conducted during wintertime in a rural area (Wangdu) in Northern China also reported higher proportions (34% and 29%, respectively) of penta- and hexa-CBs, and about 77% of the measured total PCBs (Σ_{18} PCBs) concentrations were attributed to waste incineration in the area (Sun et al., 2020).

The multivariate tests showed a significant variation in PCBs concentrations across sites and seasons (Supplemental Materials, Table S7). PCBs concentrations were significantly highest in $PM_{2.5}$ from rural areas, followed in a declining order by peri-urban and urban. We observed similar higher concentrations of $PM_{2.5}$-bound PAHs (Σ_{13}PAHs) in rural areas compared to urban or peri-urban areas (Etchie et al., 2018b). The results therefore suggests that rural combustion processes such as biomass burning in traditional cook stoves, open burning of agricultural wastes and mixed household refuses, and other combustion activities performed typically in rural areas for religious or traditional rites are significant contributors to ambient PCBs in the district. This is especially true as emission inventory reveals that rural combustion processes alone account for about half of ambient $PM_{2.5}$ concentrations in India (EDGAR, 2015). Also, emission source profiling of airborne PCBs in urban and peri-urban areas in Chennai in India revealed that open burning of dumped wastes and biomass burning contribute about 60% of the total measured PCBs concentrations, whereas vehicular and industrial emissions merely contributed 17% and 11%, respectively (Prithiviraj and Chakraborty, 2020).

By contrast, PCBs concentrations were higher in PM_{10} from peri-urban areas, followed in a declining order by rural and urban areas (peri-urban > rural > urban). The peri-urban areas may have received a higher burden of PCBs from the two coal-fired thermal power plants located within the areas i.e. Koradi and Chandkapur (Etchie et al., 2017. 2018b). Coal-thermal power plants are known to emit fly ash and PM_{10} containing high levels of PCBs (Biterna and Voutsa, 2005; Kakareka and Kukharchyk, 2005; EHE, Environmental Health & Engineering, 2011). Wind-blown dust can re-suspend PM_{10} rich in PCBs from top soils and surfaces contaminated with fly ash.

The post hoc tests showed no significant variations in concentrations of PCBs in $PM_{2.5}$ or PM_{10} in any two seasons, except for comparison that included the monsoon. The concentrations of PCBs were significantly lower in monsoon than in any other season. The low PCBs concentrations in monsoon could be attributed to increased precipitation. Rainfall scavenges both $PM_{2.5}$ and PM_{10} from ambient air (Etchie et al., 2017, 2021). Furthermore, our post-monsoon measurements did not cover the *Diwali* festival. We note however that PCBs concentrations may peak alongside the overall $PM_{2.5}$ mass concentrations during this period. So far, no information is yet available on the concentrations of PCBs in ambient air during *Diwali* festival celebration.

We did not observe a significant difference in PCBs concentrations between winter and summer in the district. A study that compared ambient air concentrations of PCBs in winter and summer in a peri-urban area in Chennai also did not find a significant variation between these two seasons (Prithiviraj and Chakraborty, 2020). Ambient measurements of PCBs concentrations during winter can greatly underestimate actual PCBs exposures during this cold period. People in India spend more time around biomass and waste combustion sources for warming during winter. There is also increased frequency of these combustion activities for heating during this period. In addition, the poor weather conditions in winter – stagnant air (low wind speed), low temperature, no rainfall and high frequency of low-heights temperature inversions – reduces the pollution dispersion, concentrating it within human breathing levels. For example, a study found higher concentrations of dioxin-like PCBs during heating season compared to non-heating season in two cities (Jinan and Baotou) in China (Yin et al., 2020). Therefore, by sampling away from pollution hotspots i.e. from close proximity to cooking or heating sources, dense traffic corridors or coal-fired thermal power plants chimneystacks, in an attempt to obtain a district-wide average levels, we may have significantly underreported actual inhalation concentrations of vulnerable groups who live, school, work, or spend most part of their time during winter in emission hotspots. Bearing in mind that the overall objective of monitoring and guideline is to ensure good health for all, this aspect calls for further debate on where $PM_{2.5}$ samplers should be located to best capture people's exposure for health risk assessment.

We could not compare our PCBs concentrations in $PM_{2.5}$ or PM_{10} in Nagpur district with those reported elsewhere in India. Previous studies that investigated PCBs levels in India have reported concentrations in the gas phase, TSP and total air, but not in the respirable particle fraction ($PM_{2.5}$) or inhalable particle fraction (PM_{10}). Nevertheless, the reported concentrations of PCBs in the gas phase, TSP and total air in Indian localities ranged from 0.2 to 72 ng/m^3, 0.03–660 pg/m^3 and 0.025–52 ng/m^3, respectively (Zhang et al., 2008; Pozo et al. 2011; Chakraborty et al., 2013; Goel et al., 2016; Prithiviraj and Chakraborty, 2020; Chakraborty et al., 2021; Nayak et al., 2021; Prithiviraj et al., 2021; Ajay et al., 2022a,b). Our average concentrations of PCBs in $PM_{2.5}$ and PM_{10} in

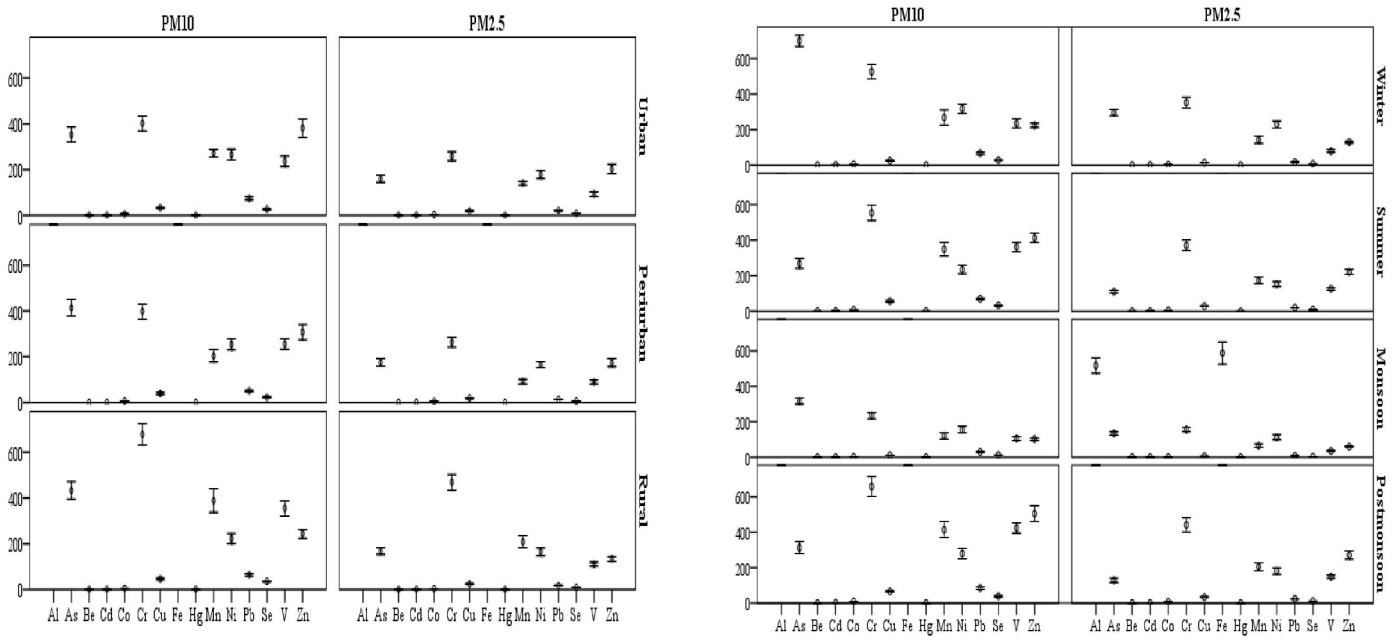

Fig. 4. The average (and 95% confidence interval) concentrations ($ng\,m^{-3}$) of metals in $PM_{2.5}$ and PM_{10} across sites and seasons in Nagpur district. The concentrations of Al and Fe exceeded the scale of the charts, thus not shown in the charts.

Nagpur district of 21 ± 12 ng/m^3 and 7.6 ± 4.8 ng/m^3, respectively, surpassed the range of PCBs concentrations reported for TSP, but fall within the range of values reported for the gas-phase or total air in India.

The global literature on PCBs concentrations in $PM_{2.5}$ is very sparse. However, the levels of PCBs in $PM_{2.5}$ in Nagpur district exceeded values reported elsewhere around the world. For example, the concentrations of PCBs in $PM_{2.5}$ in Nagpur district exceeded the range of $PM_{2.5}$-bound PCBs concentrations of 1.4–9.3 pg/m^3 in Gwangju, South Korea (Kim et al., 2019); 1–55 pg/m^3 in Zagreb, Croatia (Dvoršćak et al., 2015) and 0.3–0.7 pg/m^3 in Zouk and Mikael, Lebanon (Fadel et al., 2022). The concentrations also exceeded the ranged of $PM_{2.5}$-bound PCBs concentrations of 670–2800 pg/m^3 in Santiago and Temuco, Chile (Mandalakis and Stephanou, 2002), and 0.04–1700 pg/m^3 found in some localities in China (Xu et al., 2005; Fu et al., 2009; Zhu et al., 2017; Sun et al., 2020; Yin et al., 2020; Yang et al., 2021; Mila et al., 2022). The sum of PCBs congeners considered in those studies ranged from 6 to 144.

$PM_{2.5}$-bound PCBs are produced primarily from incomplete combustion of fuels or wastes containing chloride (Chen et al., 2009; Pandelova et al., 2009; Atkins et al., 2010; Solorzano-Ochoa et al., 2012; Thacker et al., 2013; Zhou et al., 2015; Ssebugere et al., 2019; Ajay et al., 2022a,b). Therefore, the high levels of PCBs detected in $PM_{2.5}$ in Nagpur district (Table 1) owes to various combustion processes occurring in urban, peri-urban and rural areas. For example, biomass and oil burning for cooking in rural areas, combustion of coal in two thermal power plants located in peri-urban areas, and open incineration of different wastes (agricultural, domestic, municipal, medical, sewage sludge, industrial, hazardous and e-wastes).

The sum of twelve dioxin-like PCBs (Σ_{12}dlPCB) in $PM_{2.5}$ in Nagpur district averaged 11.6 ± 6.8 ng/m^3 or 124 ± 94 pg TEQ/m^3. This value surpassed the levels of Σ_{12}dlPCB recently reported in air (gaseous and TSP) at local street waste burning sites and municipal solid waste dumpsites in India, which ranged from 0.2 to 2.3 pg TEQ/m^3 (Ajay et al., 2022a). The disparity in the results between our study and Ajay et al. (2022) may be attributed to two main reasons. First, PCBs emitted from combustion processes are typically associated with the finer particle sizes such as $PM_{2.5}$ than TSP (Degrendele et al., 2014; Zhu et al., 2017, 2018; Yang et al., 2021). Secondly, the dioxin-like PCBs with the greatest potency e.g. pentaCB 126 and hexaCB 169 with TEFs of 0.1 and 0.03, respectively (van den Berg et al., 2006), are almost entirely particle bond, and accounted for about 99.6% (70.8% and 28.8%, respectively) of our total TEQ.

3.2. *Concentrations of $PM_{2.5}$-bound heavy metals ($PM_{2.5}$ below the NAAQS)*

The distribution of metals in $PM_{2.5}$ or PM_{10} across the sites and seasons are shown in Fig. 4. We determined the concentrations of fifteen ubiquitous heavy metals (Al, As, Be, Cd, Co, Cr, Cu, Fe, Hg, Pb, Mn, Ni, Se, V and Zn) in both $PM_{2.5}$ and PM_{10} in urban, peri-urban and rural areas, covering summer, winter, monsoon and post-monsoon seasons (Supplemental Material, Tables S8 and S9). All metals investigated were detected in both $PM_{2.5}$ and PM_{10}, except Be. The concentrations of Be in $PM_{2.5}$ or PM_{10} in monsoon were below detection limit. In contrast, concentrations of Al and Fe were highest amongst the metals investigated. The concentrations of Al and Fe exceeded the scale and thus could not be shown in Fig. 4.

The multivariate tests showed that the concentrations of metals in $PM_{2.5}$ or PM_{10} varied significantly ($p < 0.05$) across sites and seasons (Supplemental Materials Table S10). Unlike the PCBs, or PAHs (Etchie et al., 2018b), the concentrations of all metals determined, except Be, were significantly higher in PM_{10} than in $PM_{2.5}$. We did not observe a significant difference in concentrations of Be between PM_{10} and $PM_{2.5}$, suggesting that the metal was primarily emitted from combustion sources. The concentrations of some metals such as Al, Be, Cd, Fe, Pb, Ni and Zn were highest in $PM_{2.5}$ or PM_{10} from urban areas compared to the other areas. Similarly, the concentrations of Cr, Cu, Hg, Mn, Se and V were highest in $PM_{2.5}$ or PM_{10} from rural areas than elsewhere. Co concentrations were highest in $PM_{2.5}$ or PM_{10} from peri-urban areas, while As concentrations were highest in $PM_{2.5}$ from peri-urban areas or in PM_{10} from rural areas, than elsewhere. Generally, the concentrations of metals in $PM_{2.5}$ or PM_{10} were significantly highest in post-monsoon followed in a decreasing order by summer, winter and monsoon. Metals concentrations generally follow the PM mass concentrations.

We compare the levels of metals in $PM_{2.5}$ in this study with those reported elsewhere in India. The annual average concentrations of some metals e.g. Cr, Mn and Ni in $PM_{2.5}$ in Nagpur district are within the range of values reported for polluted localities in India, which averages between 3 and 1600 ng/m^3, 70–146 ng/m^3 and 40–290 ng/m^3,

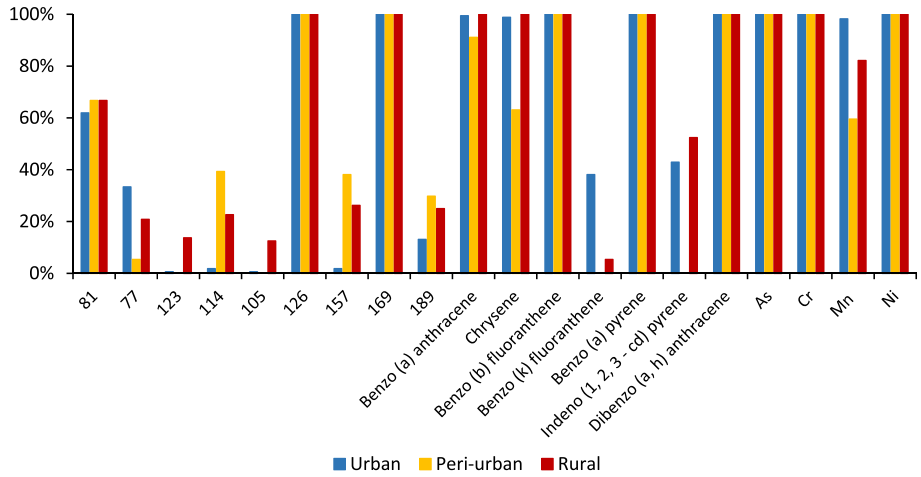

Fig. 5. Toxicity potential of $PM_{2.5}$ across sites in Nagpur district. Calculated as percentage exceedances of individual PCBs, PAHs and metals above the screening levels for residential air (USEPA, 2021).

respectively (Kulshrestha et al. 2009, 2014; Pandey et al., 2013; Pant et al., 2015; Das et al., 2015; Sah et al., 2019). However, the annual average concentrations of Cd and Pb in $PM_{2.5}$ in Nagpur district are lower than the average values reported in those studies, which ranged from 1 to 54 ng/m^3 and 32–610 ng/m^3, respectively. Furthermore, the concentrations of all metals, except Pb, in Nagpur district exceeded the levels reported for another locality in India whose $PM_{2.5}$ mass concentrations averaged below the NAAQS (Police et al., 2018). The concentrations of most $PM_{2.5}$-bound metals in Nagpur district is also greater or comparable to levels recently reported in different localities around the globe (Cheng et al., 2022; Fadel et al., 2022; Kazemiparkouhi et al., 2022; Lin et al., 2022; Liu et al., 2022; Othman et al., 2022; Qiu et al., 2022; Xue et al., 2022; Yan et al., 2022; Yang et al., 2022; Yen et al., 2022).

We compared the concentrations of metals in $PM_{2.5}$ in Nagpur district with their annual average limits specified in the NAAQS. So far, only three metals, As, Ni and Pb, are regulated under the Indian NAAQS, and the allowable limits in residential air are 6 ng/m^3, 20 ng/m^3 and 500 ng/m^3, respectively (CPCB, Central Pollution Control Board Government of India, 2009). The annual average concentrations of As and Ni, but not Pb, in the $PM_{2.5}$ exceeded the limits. Furthermore, the United States, Environmental Protection Agency has provided screening levels for most metals in residential air (USEPA, 2021). The annual average concentrations of four $PM_{2.5}$–bound metals (As, Cr, Mn and Ni) in Nagpur district exceeded the recommended limits, warranting a health risk assessment.

3.3. *Toxicity potential of $PM_{2.5}$ across sites*

We compared the toxicity potential of $PM_{2.5}$ across urban, peri-urban and rural areas in Nagpur district (Fig. 5), by calculating the percentage exceedances of individual PCBs, PAHs and metals above their reference levels for residential air (USEPA, 2021). Of the twenty-eight PCB congeners (or twelve dioxin-like PCB congeners), thirteen PAHs and fifteen metals investigated, only nine dioxin-like PCB congeners (measured in dioxin toxicity equivalent concentration), seven high molecular weight PAHs (measured in benzo(a)pyrene equivalent concentration) and four metals (As, Cr, Mn and Ni) exceeded the reference levels. Seven pollutants (PCB-126, PCB-169, benzo(b)fluoranthene, benzo(a)pyrene, dibenzo(a,h)anthracene, As and Ni) had 100% exceedances across the sites, while thirteen pollutants had variable percentages across the sites. Overall, the percentage exceedances of pollutants were highest in rural areas (70%) compared to urban (60%) and peri-urban (60%) areas. This suggests a high toxicity potential of rural combustion sources, and calls to attention the need to include rural areas in air quality monitoring and mitigation intervention strategies, given that the current actions against $PM_{2.5}$ pollution focus primarily on urban areas (NCAP, 2019; Ganguly et al., 2020).

3.4. *The risk to health from exposure to $PM_{2.5}$–bound constituents ($PM_{2.5}$ below the NAAQS)*

The risks to health associated with exposure to hazardous $PM_{2.5}$ components in Nagpur district is shown in Table 2. We considered the twelve dioxin-like PCB congeners (Σ_{12}dlPCB) with TEFs (van den Berg et al., 2006), thirteen priority PAHs (Σ_{13}PAHs) (Etchie et al., 2018b), and four metals (As, Cr, Ni and Mn) whose annual average concentrations exceeded the USEPA (2021) recommended screening levels for residential air. Dioxin-like PCBs elicit toxic and biological responses by binding to a cytosolic aryl hydrocarbon receptor (AhR) in humans (van den Berg et al., 2006).

The estimated level of exposure to the Σ_{12}dlPCB in Nagpur district (mean upper 95% confidence limit, UCL) of 58 pg TEQ/m^3 surpassed the chronic reference exposure level of 40 pg/m^3 for impairment of respiratory, developmental, hematologic, reproductive, endocrine and alimentary systems (OEHHA, 2008). The chronic reference exposure level is a concentration that is not expected to cause adverse noncancer health effects over long-term exposure. The estimated cancer risk of about 6 cases per 1000 people also exceeded the acceptable risk level of 1 case per million persons.

In our previous study (Etchie et al., 2018b) we calculated the level of exposure to Σ_{13}PAHs in $PM_{2.5}$ in Nagpur district, in benzo[a]pyrene equivalent concentrations (B[a]P_{eq}). After adjusting for the half-lives of PAHs elimination from the body, the estimated level of exposure to the PAHs was 449 ng B[a]P/m^3. The value substantially surpassed the inhalation reference concentrations of 2 ng B[a]P/m^3 and 3 ng B[a]P/m^3 for the impairment of developmental and reproductive systems, respectively (USEPA, United States Environmental Protection Agency, 2017a). Similarly, the estimated cancer risk from the PAHs exposure, which is about 4 cases per 10,000 people, also exceeded the acceptable risk level.

For metals, the level of exposure (mean UCL) to As and Ni in Nagpur district of 77 ng/m^3 and 78 ng/m^3, respectively, is about 5–6 times greater than the chronic reference exposure level of 15 ng/m^3 and 14 ng/m^3, respectively. Long-term exposure to As and Ni beyond these reference levels were found to elicit several adverse health effects including impairment of the developmental, respiratory, cardiovascular, nervous and hematopoietic systems (OEHHA, Office of Environmental Health Hazard Assessment, 2014). Furthermore, assuming the ratio of Cr^{+6} to Cr in $PM_{2.5}$ is 3.5 percent (Yu et al., 2014; Tirez et al., 2011), the

Table 2
The risks to health of $PM_{2.5}$-bound constituents in Nagpur district, with annual $PM_{2.5}$ levels averaging below the Indian NAAQS of 40 μg m^{-3}.

$PM_{2.5}$-bound components	Risk of non-carcinogenic effects		Risk of cancer
	Hazard quotient	Adverse effect	
Σ_{12}dlPCB (TCDDeq)	1.5	Impairment of respiratory, hematologic, alimentary (liver), reproductive and endocrine systems, and developmental impairment (OEHHA, 2008)	~6 excess cancer cases per 1000 population. Estimated based on IUR value of 38 per μg m^{-3} for TCDD (OEHHA, 2011).
As	5.1	Developmental effects in humans; impairment of cardiovascular, nervous and respiratory systems (OEHHA, Office of Environmental Health Hazard Assessment, 2014)	6 excess cancer cases per 10,000 population. Estimated based on IUR value of 3.3×10^{-3} per μ g m^{-3} for As (OEHHA, 2011).
Cr^{+6}[a]	0.05	Lower respiratory effects (USEPA, 2021)	2 excess cancer cases per 1000 population. Estimated based on IUR value of 1.5×10^{-1} per μ g m^{-3} for Cr^{+6} (OEHHA, 2011).
Mn	0.8	Nervous system impairment (OEHHA, Office of Environmental Health Hazard Assessment, 2014)	–
Ni	5.3	Impairment of respiratory and hematologic system; and developmental impairments (OEHHA, Office of Environmental Health Hazard Assessment, 2014)	5 excess cancer cases per 100,000 population. Estimated based on IUR value of 0.26×10^{-3} per μg m^{-3} for Ni (OEHHA, 2011).
Σ_{13}PAHs (B[a]P_{eq})[b]	225	Developmental and reproductive impairments (USEPA, United States Environmental Protection Agency, 2017a)	~4 excess cancer cases per 10,000 population. Estimated based on IUR value of $0.6 \times 10^{-3\ per}$ μ g m^{-3} for B[a]P (USEPA, United States Environmental Protection Agency, 2017a).

[a] Assuming the ratio of Cr^{+6} to total Cr in ambient $PM_{2.5}$ is 3.5% (Yu et al., 2014; Tirez et al., 2011).

[b] Adapted from (Etchie et al., 2018b); acceptable hazard quotient for non-carcinogenic effect = 1; acceptable cancer risk = 1 excess cancer case per 1 million population.

levels of exposure to Cr and Mn, which is 13 ng/m^3 and 69 ng/m^3, respectively, fall below the reference exposure levels of 100 ng/m^3 and 90 ng/m^3, respectively (OEHHA, Office of Environmental Health Hazard Assessment, 2014; USEPA, 2021). In addition, the estimated cancer risk associated with exposure to As, Cr and Ni, but not Mn, exceeded the acceptable risk level.

4. Discussion

Exposure to $PM_{2.5}$ pollution affects human health worldwide (WHO, World Health Organization, 2021). However, the specific $PM_{2.5}$ components responsible for the adverse health effects can vary significantly in time and space, depending on the type of sources producing the $PM_{2.5}$ (Silva et al., 2016; Thurston et al., 2016). In India, where combustion sources predominate (EDGAR, 2015), nearly 98% of the mortality from exposure to ambient $PM_{2.5}$ pollution results from incomplete combustion emissions (Lelieveld et al., 2015). Therefore, stringent regulatory

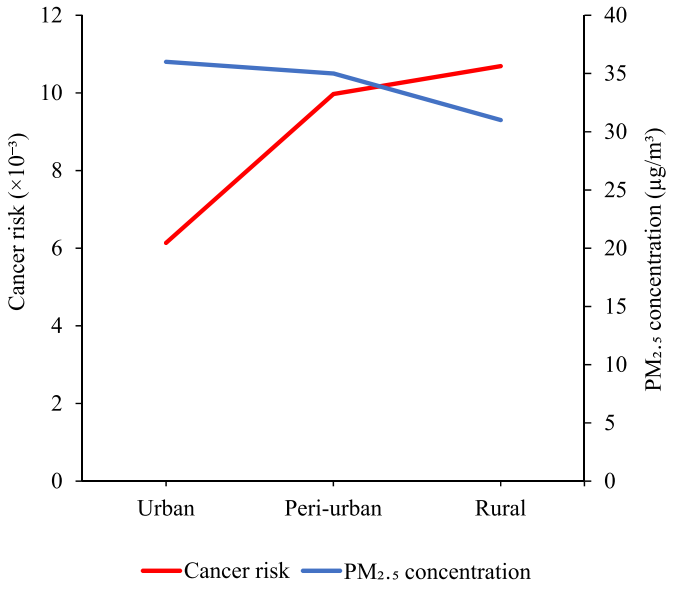

Fig. 6. Comparison of the annual average $PM_{2.5}$ concentrations and the corresponding cancer risks from exposure to the hazardous components (PCBs, PAHs, As, Cr^{+6}, Mn and Ni) across sites in Nagpur district.

standards for $PM_{2.5}$ are required to protect the populations from the harmful effects of $PM_{2.5}$ components.

In this study, we examined whether current Indian NAAQS for annual average $PM_{2.5}$ concentration of 40 μg/m^3 could keep the risk to health from hazardous components of $PM_{2.5}$ within acceptable risk level. Our results revealed high risks to health from long-term exposure to $PM_{2.5}$ components even below the NAAQS. This suggests that the standard is not protecting populations in attainment localities in India from the harmful effects of $PM_{2.5}$ components.

The risk to health from exposure to the $PM_{2.5}$ components were high regardless of the type of environment whether urban, peri-urban or rural. In fact, we found higher concentrations of incomplete combustion by-products such as PCBs and PAHs in rural areas, which had relatively lower average $PM_{2.5}$ mass concentrations of 31 ± 13 μg/m^3, compared to urban or peri-urban areas with average $PM_{2.5}$ mass concentrations of 36 ± 16 μg/m^3 or 35 ± 21 μg/m^3, respectively (Etchie et al., 2017). This suggests a higher toxicity potency of rural combustion sources compared to urban or peri-urban. For example, a comparison of the annual average $PM_{2.5}$ concentrations and the corresponding cancer risks from exposure to hazardous components (PCBs, PAHs As, Cr^{+6}, Mn and Ni) across sites (Fig. 6) revealed that the highest risk of cancer was in rural areas followed in a decreasing order by peri-urban and urban areas. Therefore, our results calls to attention the need to include rural areas in the ambit of the India's NCAP, given that the current focus is only on urban areas (NCAP, 2019; Ganguly et al., 2020). Such inclusion will help to lower the magnitude of the risks to health associated with exposure to rural combustion sources, keeping in mind that the ultimate goal of the NCAP is to ensure good health for all. Furthermore, because the levels of $PM_{2.5}$ in Nagpur district averaged around the WHO recommended interim target-1 of 35 μg/m^3, adopting this interim target value as the revised standard would also not protect populations in attaining localities in India from the harmful effects of $PM_{2.5}$ components.

The WHO has recently revised its AQG from 10 μg/m^3 to 5 μg/m^3, and expanded the number of interim targets from three to four, due to new body of epidemiological evidence linking exposure to $PM_{2.5}$, at much lower levels than previously studied, with serious health effects such as mortality and hospital admissions or emergency room visits (WHO, World Health Organization, 2021). The large disparity between our risk estimates and the acceptable risk level suggests that it would take the adoption of a very stringent $PM_{2.5}$ standard in India, such as the

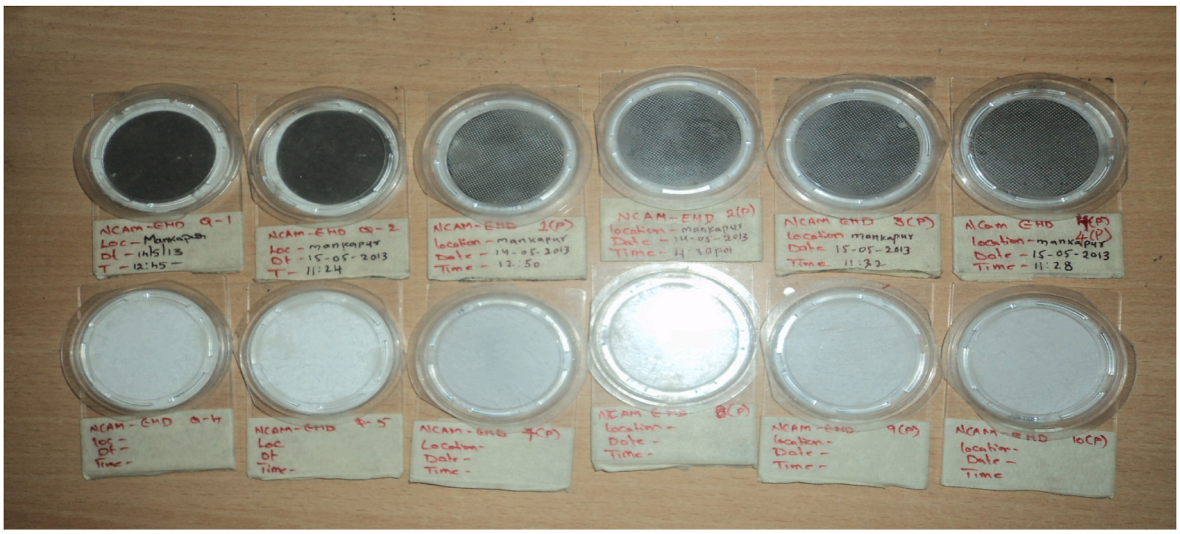

Fig. 7. Top: 24-hr samples of $PM_{2.5}$ (first two from left) and PM_{10} (last four from left) from an urban area in Nagpur district during summer; bottom: blank filters.

revised global AQG of 5 μg/m^3, to meet the acceptable risk level for hazardous $PM_{2.5}$ components. Therefore, we support the adoption of WHO interim targets-1 to 4 of 35 μg/m^3, 25 μg/m^3, 15 μg/m^3 and 10 μg/m^3, respectively, as incremental steps in a progressive reduction of $PM_{2.5}$ concentrations in polluted localities in India, towards attaining the global AQG of 5 μg/m^3 in a realistic period.

It is important to note that our risk estimates are very likely to be an underestimation, rather than an overestimation of the actual risks to health, because our exposure values were derived from ambient $PM_{2.5}$ measurements rather than from individual exposure measurements. Ambient exposure measurements often underreport the level of exposure and risk to health of vulnerable sub-populations who spend most part of their time, or engage in activities that increase their breathing rates, around pollution hotspots and peak periods. For example, our exposure values may greatly underrepresent athletics, schoolchildren or vendors running, cycling or walking along dense traffic corridors or young children playing around their mothers cooking with solid fuels (Cruz et al., 2022; Du et al., 2022; Etchie et al., 2020; Hu and Zhao, 2022; Sharma and Kumar 2022). Also, our exposure values can underrepresent the actual exposure of people residing close to the two coal-fired thermal power plants chimneystacks or other industrial emission hotspots in the district. Notwithstanding, attainment of the revised global AQG through its interim targets in India should protect these vulnerable subpopulations from the hazardous components of $PM_{2.5}$, and is therefore supported.

5. Conclusion

The risk to health associated with exposure to hazardous $PM_{2.5}$ components below the NAAQS of 40 μg $PM_{2.5}$/m^3 (Fig. 7) is high, and surpasses the acceptable risk level. Considering the large disparity between our risk values and the acceptable risk level, it would take the attainment of a more stringent standard such as the recently revised global air quality guideline level of 5 μg/m^3 to protect vulnerable populations from the hazardous components of $PM_{2.5}$.

Credit author statement

1. Tunde Ogbemi Etchie: Methodology, Data Curation, Software, Formal Analysis, Writing – Original Draft.

2. Saravanadevi Sivanesan: Supervision, Validation, Visualization and Writing - Review and Editing.

3. Ayotunde Titilayo Etchie: Data Curation, Validation, Visualization, Software, Formal Analysis and Writing - Review and Editing.

4. Kannan Krishnamurthi: Conceptualization, Project Administration and Funding Acquisition, Resources, Supervision, Visualization and Writing - Review and Editing.

5. Gregory Olufemi Adewuyi:, Supervision, Visualization, Writing - Review and Editing.

6. K.V. George: Visualization, Writing - Review and Editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2022.135047.

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