Highly Volatile POPs in Urban Air across Asia and Africa: Dominance of Volatile Methylsiloxanes

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Abstract

Highly volatile persistent organic pollutants (HV-POPs) are characterized by high volatility, environmental persistence, bioaccumulative potential, toxicity, and ability to long-range transport, posing environmental and health concerns. However, research on HV-POPs remains limited, particularly in rapidly urbanizing regions, constraining understanding of their sources, environmental fate and risks. This study investigated 52 HV-POPs, including Stockholm Convention-listed POPs like hexachlorobutadiene (HCBD) and hexa-/penta-chlorobenzene (HCB/PeCB), and non-listed HV-POPs such as volatile methylsiloxanes (VMS) and chlorinated nitrobenzenes (CNBs), using active air samplers in six major cities across Asia and Africa. The median total concentrations of HV-POPs were highest in Guangzhou (351 ng/m^3), followed by Kuala Lumpur (167 ng/m^3), Accra (82.4 ng/m^3), Dhaka (73.3 ng/m^3), Nairobi (44.9 ng/m^3), and Islamabad (33.5 ng/m^3). VMS dominated at all sites, accounting for 84 ± 18% of total HV-POPs, up to 2–5 orders of magnitude higher than other compounds. Source analysis showed VMS emissions in Guangzhou were mainly from industrial activities, while in the other cities from usage of personal care products. Inhalation risk assessments indicated negligible non-carcinogenic and carcinogenic risks at all sites. This study provides the first multi-regional HV-POP dataset in urban air, supporting chemical risk assessment efforts and broader international regulatory initiatives.

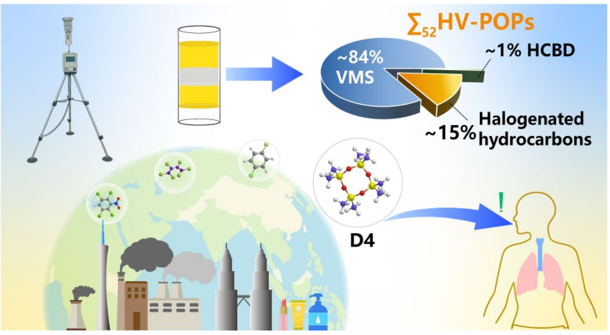
Keywords

Highly volatile Persistent Organic Pollutants (HV-POPs), Volatile Methylsiloxanes (VMS), Hexachlorobutadiene, Urban Atmosphere, Risk Assessment, Active Air Sampling, Asia, Africa

Synopsis

Global monitoring of highly volatile persistent organic pollutants (HV-POPs) in urban atmosphere revealed the dominance of volatile methylsiloxanes (VMS).

TOC



Introduction

Persistent organic pollutants (POPs) have attracted global attention due to their persistence, toxicity, bioaccumulative potential, and ability to undergo long-range transport.[1] Among them, highly volatile POPs (HV-POPs) are POP-like chemicals with high vapor pressures and environmental stability that remain poorly characterized.[2] Representative HV-POPs include both regulated and non-regulated, such as hexachlorobutadiene (HCBD), hexachlorocyclohexanes (α-, β-, and γ-HCH), volatile methylsiloxanes (VMSs), halogenated hydrocarbons (HHCs), and chlorinated nitrobenzenes (CNBs).The high volatility of HV-POPs facilitates frequent air–surface exchange and widespread atmospheric occurrence, such that some of them have been detected in air,[3] water,[4] and soil,[5] and even in remote regions such as the poles,[3, 6] where they may persist and accumulate in biota.[7] These properties and behaviors underscore the global environmental significance of HV-POPs, and present major challenges for accurate monitoring and comprehensive risk assessment.

HCBD, listed under the Stockholm Convention in 2015, is nephrotoxic, highly persistent (atmospheric half-life up to 14 months) and bioaccumulative.[3, 8, 9] Despite production bans, it continues releasing unintentionally from organochlorine industry and thermal processes,[10] with atmospheric concentrations in proximity to emission sources often exceeding occupational exposure limits.[11] It has been widely detected in air,[12-14] water,[15] soils,[8] sewage sludge,[4] and even polar regions.[3, 6, 16] VMSs, widely-used in personal care products (PCPs) and industrial applications, are high-production-volume chemicals[17-19] with annual global output exceeding 7 million tonnes[20] and are currently under regulatory evaluation in the European Union.[21, 22] The major VMS congeners, octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5), and dodecamethylcyclohexasiloxane (D6) show considerable high environmental persistence (air: 6-21 days; water, soil and sediment: 3-3000 days) and notable bioaccumulation potential (vPvB).[23] Their high volatility leads to widespread atmospheric occurrence,[19, 24-26] and elevated exposure has been linked to hepatic, endocrine, and neurotoxic effects.[27, 28] HHCs and CNBs, used in dye, pesticide, and chemical manufacturing, pose environmental and health concerns due to their persistence and neurotoxicity.[29, 30, 31] CNBs are particularly long-lived; for example, tetrachloronitrobenzene has an atmospheric half-life of up to 6.1 years.[32]

Globally, there has been an apparent monitoring data gap of many HV-POPs in the atmosphere, largely owing to limitations in sampling and analytical techniques. In particular, the use of the widely-used polyurethane foam (PUF) as a sampling absorbent may lead to underestimations of the concentrations of HV-POPs, due to breakthrough effects, especially in warm climates or highly contaminated sites.[3, 33] Data gaps are especially pronounced in developing countries, where industrialization often occurs rapidly but with less concerns on chemical pollution and environmental quality. Here, we conducted active air sampling using PUF/XAD/PUF cartridge in six megacities across Asia and Africa during 2022–2023, aiming to: (1) characterize the concentrations, composition, and spatial distribution of 52 HV-POPs in urban atmosphere, including Stockholm Convention-listed POPs (e.g., HCBD, HCHs and pentachlorobenzene (PeCB)) and non-listed POPs (e.g., VMS, HHCs, and CNBs); (2) identify key emission sources and influencing factors of HV-POPs in these urban areas; and (3) assess their potential inhalation health risks. This study provides a global cross-sectional dataset on HV-POPs in urban air, addressing key monitoring gaps under the Stockholm Convention's Global Monitoring Plan (GMP) and supporting evidence-based global chemical management.

Materials and Methods

Sampling Campaign

During 2022-2023, active air sampling campaigns were conducted in six megacities across Asia and Africa: Guangzhou (China), Accra (Ghana), Dhaka (Bangladesh), Kuala Lumpur (Malaysia), Islamabad (Pakistan), and Nairobi (Kenya). All six countries are participants in the United Nations Environment Programme-Global Environment Facility (UNEP-GEF) Global Monitoring Plan (GMP) projects and are signatories to the Stockholm Convention. Sampling was conducted at urban sites characterized by intense, mixed-source atmospheric pollution, representing diverse urban air pollution scenarios. Detailed site descriptions are available in Table S1.

The four Asian megacities represent a range of urban pollution sources and climatic conditions. Guangzhou is a manufacturing hub with high industrial emissions under a subtropical monsoon climate.[34] Dhaka, one of the world's most densely populated cities, is affected by both local emissions and regional pollutant transport.[35] Kuala Lumpur is influenced by motor vehicle exhaust and seasonal biomass burning,[36] while Islamabad is impacted by domestic heating and agricultural combustion.[37] In contrast, the two African cities are dominated by emissions from e-waste activities. Accra is a known hotspot for informal e-waste and solid waste burning as well as emissions from vehicle exhaust,[38] and Nairobi, a high-altitude city, is affected by open burning and unregulated waste recycling in informal settlements.[39]

In this study, we deployed high-volume active air samplers (100 L/min, TH-150H, Tianhong Instruments, Wuhan, China) equipped with Whatman quartz fiber filters (QFFs; 203 × 254 mm; GE Healthcare Bio-Sciences, Pittsburgh, PA) to collect particle-phase compounds and PUF/XAD/PUF sandwich cartridges to collect gas-phase compounds. The cartridge consisted of two polyurethane foam plugs (PUFs; 65 mm diameter, 35 mm height, 0.03 g/cm^3 density) and approximately 10 g polystyrene adsorbent resin (XAD). Although particle-phase samples were collected, this study focuses exclusively on the analysis of gas-phase HV-POPs. A total of 78 air samples were collected, including 29 from Guangzhou, 9 from Dhaka and 10 each from the remaining four cities. Before sampling, PUF plugs and XAD resin were precleaned with acetone and dichloromethane. Detailed sampling protocol and sampling volume calibration, site information, and training materials are provided in Text S1, Table S2 and Figure S1.

Sample Pretreatment and Analysis

The sample pretreatment and analytical methods employed in this study were adapted and optimized from previously established protocols by our research group in earlier work.[34, 40] Detailed procedures are described in Text S2. Each PUF/XAD/PUF sandwich was spiked with ^{13}C-labeled hexachlorobutadiene (^{13}C-HCBD), 1,4-dichlorobenzene-[D4], ^{13}C-labeled decamethylcyclopentasiloxane (^{13}C-D5), and ^{13}C-labeled hexachlorobenzene (^{13}C-HCB) as recovery surrogates, and extracted for 24 h in a Soxhlet apparatus using dichloromethane (DCM)/acetone (ACE) (1:1, v/v). The extracts were concentrated via rotary evaporation, purified by using a multilayer neutral silica gel column, and further concentrated under gentle nitrogen blowdown. Hexamethylbenzene was added as an internal standard before instrumental analysis. Samples were analyzed using an Agilent 7890B gas chromatograph coupled with a 7000A triple-quadrupole mass spectrometer (GC–MS/MS) equipped with a DB-5MS UI column (60 m × 0.25 mm × 0.25 μm) operating in a multiple reaction monitoring (MRM) mode. Information on the 52 target compounds, including physicochemical properties, is detailed in Table S3. The instrumental analysis, precursor/product ions and retention times are provided in Text S3 and Figure S2.

Quality Assurance and Quality Control

Quality assurance and quality control (QA/QC) measures included the analysis of field blanks, procedural blanks, and surrogate spiked recoveries. Detailed QA/QC protocols are provided in Text S4. Only four cVMSs were detected in field blanks, while no target analytes were found in procedural blanks. The method detection limit (MDLs) and the instrument detection limit (IDLs) for all analytes ranged from 0.02–631 pg/m^3 and 0.00–0.92 ng, respectively (Table S5). The average recoveries for ^{13}C-HCBD, 1,4-dichlorobenzene-[D4], ^{13}C-D5, and ^{13}C-HCB were 74 ± 19%, 79 ± 20%, 65 ± 17%, and 72 ± 20%, respectively. All reported concentration data were corrected based on surrogate recoveries and blank subtraction. A breakthrough test indicated that losses to the bottom PUF were minimal, with an average rate of 5% ± 6%, confirming the effectiveness of the cartridge in capturing gas-phase HV-POPs (Table S6).[41] To strictly control VMS contamination, we have implemented several measures, with details in Text S4. To better evaluate the stability of the experimental results, duplicate analyses of three representative samples under identical conditions showed high consistency (slope=1.1, r^2=0.98), as shown in Figure S3. Solvent blank spiking, matrix spike recoveries for both PUF and XAD phases, and routine procedural blanks further validated the reliability of the method.

Health Risk Assessment

Inhalation dose, carcinogenic and non-carcinogenic risks for each sampling city were calculated using pollutant concentrations obtained from this study and country-specific exposure parameters.[42-50] Details of the calculation methods and selected exposure parameters for each country are provided in Text S5 and Table S19.The average daily inhalation dose (ADD_{inh}) was calculated as:

$$ADD_{inh}=\frac{CA \times IR \times ET \times EF \times ED}{BW \times AT} \tag{1}$$

where ADD_{inh} represents the daily inhalation dose (mg/(kg·d)); CA is the concentration of target compound (mg/m^3); IR is the inhalation rate (m^3/h); ET is the daily exposure time (h/day), EF is the exposure frequency (days/year); ED is the sum of the exposure durations for all events (years); BW is the body weight (kg) and AT is the averaging time for exposure (days), calculated as ED multiplied by 365 days.

Carcinogenic risk (Risk) through inhalation is calculated as:

$$Risk=EC_{inh} \times IUR \tag{2}$$

$$EC_{inh}=(CA \times ET \times EF \times ED)/AT \tag{3}$$

where EC_{inh} is the inhalation exposure concentration (mg/m^3) and IUR is the inhalation unit risk (μg/m^3)$^{-1}$.

Non-carcinogenic risks were evaluated using the hazard quotient (HQ_{inh}) and hazard index (HI), calculated as:

$$HQ_{inh}=\frac{EC_{inh}}{Rfc \times 1000\ \mu g/mg} \tag{4}$$

$$HI=\sum HQ_{inh} \tag{5}$$

where HQ_{inh} represents the non-carcinogenic hazard quotient, Rfc is the reference concentration (mg/m^3), and HI is the hazard index. Other parameters are the same as above.

Statistical Analysis

All data analyses were performed using R software (version 4.1.0). To assess the normality of data while considering the small sample size (N=79), we examined both original and log-transformed concentration data across different sampling sites using the Shapiro-Wilk test.[51] As not all data conformed to a normal distribution, we employed non-parametric tests (Kruskal-Wallis test) to evaluate significant differences between groups. All samples were assumed to be independent in our analysis. Spearman's correlation was used to explore relationships between variables. A p-value < 0.05 was considered statistically significant. Further details on data distribution characteristics, sample independence assessment, and Spearman's correlation analysis are provided in Text S6.

Results and Discussion

General Profile of HV-POPs

The gaseous and particulate phase concentrations of 52 HV-POPs measured in 78 urban air samples from six cities are summarized in Table S7 and Table S8. Total concentrations ranged from 1.52×10^4 to 1.17×10^6 pg/m^3 (gas phase: 1.30×10^4-1.17 $\times 10^6$ pg/m^3 (Figure 1), particle phase: 746-1.80×10^4 pg/m^3). The gaseous phase accounted for 96 ± 4% of the total concentration, indicating that HV-POPs were overwhelmingly present in the gas phase; therefore, only gaseous concentrations are further discussed. Median gaseous concentrations were highest in Guangzhou (3.51×10^5 pg/m^3, 1.65×10^5-1.17×10^6 pg/m^3), followed by Kuala Lumpur (1.67×10^5 pg/m^3, 1.28×10^5-2.57×10^5 pg/m^3), Accra (8.24×10^4 pg/m^3, 2.54×10^4-4.44×10^5 pg/m^3), Dhaka (7.33×10^4 pg/m^3, 1.30×10^4-1.39×10^5 pg/m^3), Nairobi (4.49×10^4 pg/m^3, 3.25 $\times 10^4$-2.61×10^5 pg/m^3), and Islamabad (3.35×10^4 pg/m^3, 2.47×10^4-1.15×10^5 pg/m^3), indicating significant regional variability.

Based on structural characteristics, the 52 HV-POPs were categorized into five groups: HCBD, $\sum_{23}$HHCs, $\sum_7$VMS, $\sum_{17}$CNBs, and $\sum_4$HCHs. To avoid misclassification, HCBD was considered separately from $\sum_{23}$HHCs because it is listed as a restricted POP under the Stockholm Convention, whereas the other halogenated hydrocarbons remain unregulated. The median concentration of HCBD was 187 pg/m^3 (33.7-1.57×10^4 pg/m^3), while the concentrations of other HV-POPs were ranked as follows: $\sum_7$VMS (1.26×10^5 pg/m^3, 1.07×10^4-1.16×10^6 pg/m^3) ≫ $\sum_{23}$HHCs (9.20×10^3 pg/m^3, 1.29 $\times 10^3$-6.79×10^4 pg/m^3) > $\sum_{17}$CNBs (147 pg/m^3, 40.6-657 pg/m^3) > $\sum_4$HCHs (10.4 pg/m^3, 0.747-107 pg/m^3). $\sum_7$VMS accounted for 84 ± 18% of the total HV-POPs concentrations, and together with $\sum_{23}$HHCs, they contributed approximately 99 ± 1%, highlighting their dominance in the urban atmosphere. Detection rates of individual HV-POPs across all samples ranged from 13 to 100%, with 46-49 compounds detected in over 50% of samples, and 26-38 compounds present in all samples.

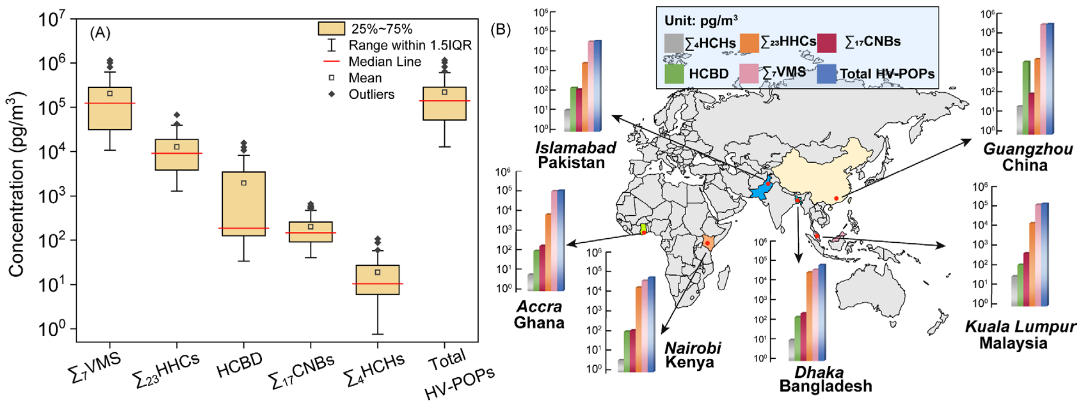


Figure 1. (A) Composition and gaseous concentration (pg/m^3) of total HV-POPs in 78 urban air samples. (B) Spatial profiles of HV-POPs ($\sum_7$VMS, $\sum_{23}$HHCs, HCBD, $\sum_{17}$CNBs and $\sum_4$HCHs) at six sampling sites across Asia and Africa. The figure (B) was modified on the base map of China sourced form "MAP WORLD" (https://www.tianditu.gov.cn/).

Comparison of HV-POPs and other air pollutants in Guangzhou

To better understand the importance of HV-POPs relative to other POPs, we compared HV-POPs concentrations with other air pollutants' data from the same sampling site in Guangzhou (Figure 2 and Text S7).[34, 52] HV-POPs were higher than all other analyzed POPs, accounting for approximately 50% of the total measured compounds. Other notable POP groups, in descending order of median concentration, included short-chain chlorinated paraffins (SCCPs: 168 ng/m^3, 39.3-589 ng/m^3), medium-chain chlorinated paraffins (MCCPs: 109 ng/m^3, 2.65-497 ng/m^3), polycyclic aromatic hydrocarbons (PAHs: 23.6 ng/m^3, 12.0-50.4 ng/m^3) and organophosphate flame retardants (OPFRs: 1.64 ng/m^3, 0.638-14.4 ng/m^3). In contrast, legacy POPs, such as polychlorinated biphenyls (PCBs), polychlorinated naphthalenes (PCNs), organochlorine pesticides (OCPs), polybrominated diphenyl ethers (PBDEs) and novel brominated flame retardants (NBFRs) showed much lower concentrations (3.13×10^{-3} ng/m^3-1.32 ng/m^3), predominantly at the pg/m^3 to ng/m^3 level. Notably, the mean HV-POPs concentration was more than twice that of SCCPs and MCCPs, highlighting their dominance in urban air.

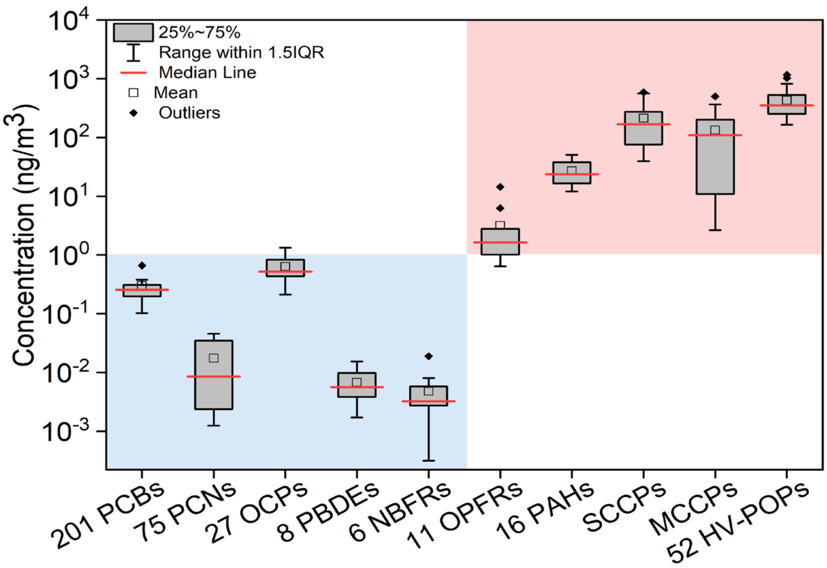


Figure 2. Comparison of the concentrations (ng/m^3) of various pollutants in the gas phase at the same sampling site in Guangzhou. Pollutants include: 201 polychlorinated biphenyls (PCBs), 75 polychlorinated naphthalenes (PCNs), 27 organochlorine pesticides (OCPs), 8 polybrominated diphenyl ethers (PBDEs), 6 novel brominated flame retardants (NBFRs), 11 organophosphate flame retardants (OPFRs), 16 polycyclic aromatic hydrocarbons (PAHs), short-chain chlorinated paraffins (SCCPs), medium-chain chlorinated paraffins (MCCPs), and 52 HV-POPs.

Stockholm Convention-listed HV-POPs

Hexachlorobutadiene

Figure 3 shows the concentrations of HCBD across cities (p < 0.05), with median concentrations as follows: Guangzhou (3,540 pg/m^3, 2,590-15,700 pg/m^3) ≫ Dhaka (192 pg/m^3, 33.7-231 pg/m^3) > Islamabad (184 pg/m^3,105-236 pg/m^3) > Kuala Lumpur (124 pg/m^3, 88.06-198 pg/m^3) > Nairobi (120 pg/m^3, 79.9-146 pg/m^3) > Accra (112 pg/m^3, 55.5-171 pg/m^3). HCBD concentrations in Guangzhou were approximately 30-40 times higher than those in other cities, suggesting significant unintentional emissions from local sources. Current sources of HCBD in the atmosphere include its production as a commercial chemical and unintentional emissions from industrial activities such as chemical production, metal smelting, waste incineration and landfills.[53, 54] Among the studied countries, only China has enforced a complete ban (production, use, and trade) on HCBD since 2023, while other countries have yet not announced specific regulatory measures or policies.[55] This suggests that unintentional emissions are likely the dominant atmospheric source of HCBD in China, posing significant challenges for effective control under current regulations.

Moreover, chlorinated chemical manufacturing remains the primary unintentional HCBD source.[7] High concentrations of HCBD have been detected near chlor-alkali production facilities. For example, in 2015, HCBD concentrations of 1170 μg/m^3 and 5530 μg/m^3 were measured near a tetrachloroethylene production facility in China.[56] Similarly, in 2018, concentrations of 0.21 μg/m^3 were detected near a chlor-alkali plant in Catalonia, Spain.[14] Guangzhou is one of China's seven major petrochemical industrial bases, with 698 petrochemical enterprises producing approximately 240,000 tons of chemical reagents and 930,000 tons of coatings annually (as of 2022).[57] Consequently, intensive petrochemical industries likely contribute to the elevated HCBD concentrations found in the air samples. Furthermore, the ratio between maximum to minimum HCBD concentrations in each city ranged from 1.8 to 6.9, indicating relatively low variability across the cities.

A comparison of HCBD concentrations obtained in this study with other active and passive air sampling (PAS) studies is presented in Table S13. Atmospheric HCBD concentrations in all six cities exceeded those reported from the Arctic,[3] where active sampling using PUFs was conducted (<0.37–21 pg/m^3), indicating that urban areas exhibit significantly elevated HCBD levels relative to remote areas far from industrial emissions. In contrast, HCBD concentrations in Guangzhou in this study were significantly lower than those previously reported in other Chinese cities (<0.05–9.55 μg/m^3),[13] likely due to the differences in sampling and analytical methods.

Previous studies on atmospheric HCBD primarily employed active sampling methods such as Summa canister, Tenax-TA adsorbent tubes, and activated charcoal (Table S13).[12, 16, 58] Summa canisters, however, are susceptible to storage conditions, pre-cleaning procedures, and internal gas concentrations, resulting in relatively high detection limit (typically ~2 μg/m^3),[59] considerably higher than the detection limit achieved with PUF/XAD/PUF cartridges in this study (17.9 pg/m^3). Thus, the sampling method used here offers improved sensitivity and accuracy for quantifying trace-level HCBD concentrations.

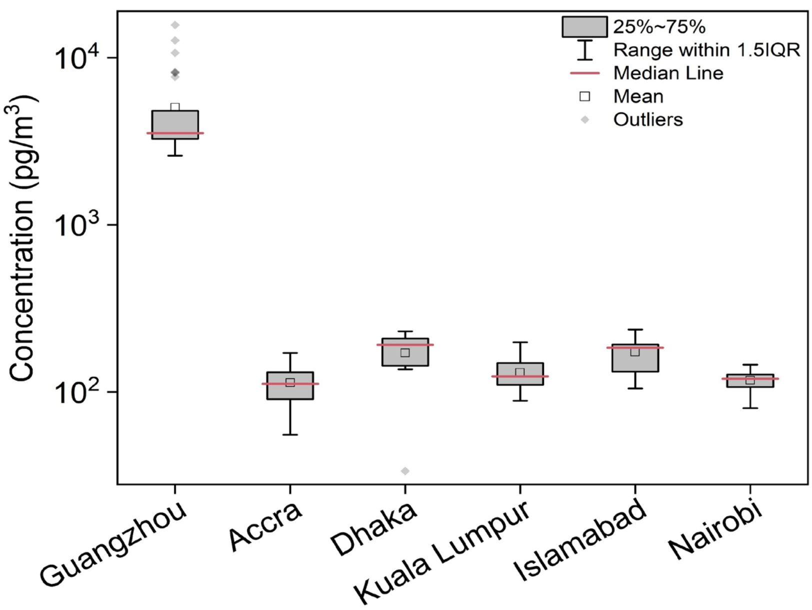


Figure 3. Box plot of HCBD concentrations (pg/m^3) in urban air across six cities.

Hexachlorobenzene and Pentachlorobenzene

Concentrations of hexachlorobenzene (HCB) and pentachlorobenzene (PeCB) measured via active air sampling and passive air sampling are summarized in Tables S14 and S15. Among the six cities, median concentrations of PeCB were highest in Dhaka (99.2 pg/m^3, 37.7-442 pg/m^3), followed by Guangzhou (90.4 pg/m^3, 29.1-216 pg/m^3), Kuala Lumpur (54.8 pg/m^3, 36.0-123 pg/m^3), Nairobi (43.8 pg/m^3, 22.5-56.4 pg/m^3), Accra (36.5 pg/m^3, 14.1-83.5 pg/m^3), and Islamabad (31.7 pg/m^3, 17.7-44.8 pg/m^3) (p < 0.05). These concentrations are broadly consistent with global active sampling datasets, where typical urban PeCB concentrations range 20 to 80 pg/m^3, similar to levels reported in Beijing (75.8 ± 66.5 pg/m^3), Yantai (39.8 ± 29.5 pg/m^3), and Kuwait (24.6 ± 24.1 pg/m^3).[60, 61] For passive air sampling, urban and agricultural sites in the Latin American and Caribbean Group (GRULAC) region exhibited higher PeCB levels (39 to 146 pg/m^3).[62] PeCB concentrations in Ghana appear to show an upward trend, as earlier studies reported lower concentrations, including 15 pg/m^3 at a background site, 9 pg/m^3 at an urban site, and 10 pg/m^3 at a suburban site.[38]

The median concentrations of HCB among the six cities were ranked as follows: Guangzhou (121 pg/m^3, 34.6-268 pg/m^3) > Kuala Lumpur (85.6 pg/m^3, 54.0-141 pg/m^3) > Dhaka (62.7 pg/m^3, 30.1-259 pg/m^3) > Islamabad (42.4 pg/m^3, 31.1-63.4 pg/m^3) > Nairobi (41.5 pg/m^3, 30.6-53.2 pg/m^3) > Accra (38.1 pg/m^3, 17.0-107 pg/m^3)

(p < 0.05). In Guangzhou, HCB concentrations was 2-3 times higher than levels measured at the same sampling site in 2018 (8.65–132 pg/m^3).[34] Globally, HCB concentrations in the Asian and African cities (17.0–268 pg/m^3) were slightly higher than those in Europe (15.8–74.7 pg/m^3).[63]

PeCB and HCB were detected in all samples and showed a significant positive correlation (r = 0.709–1, p < 0.01), suggesting potential shared industrial sources or emission pathways. Similarly, Spearman's correlation analysis (Table S10) revealed a strong correlation between HCBD and ten other chlorinated benzenes, excluding HCB, in Guangzhou (r = 0.471–0.780, p < 0.01). These findings support the hypothesis that HCBD and chlorinated benzenes (CBs) likely originate from similar industrial activities, particularly as unintentional byproducts of chemical production. However, regulatory frameworks for HCBD vary across regions, which may influence emission profiles and control measures.

Regional correlations between HCBD and HCB (Figure 4) provide additional insights into potential emission sources. HCBD has never been intentionally produced in China, but is known to be generated as a byproduct of industrial processes, particularly the production of trichloroethylene and perchloroethylene, making it a useful indicator of unintentional emissions.[53]While all the studied countries have banned the use of HCB, regulatory measures for HCBD remain inconsistent, contributing to regional differences in its occurrence and distribution. However, existing bans do not necessarily eliminate emissions. While the production and use of HCB have ceased in past decades, it is crucial not to ignore its unintentional release as a byproduct of incomplete combustion or chlorinated chemical manufacturing process.[64] Moreover, a comprehensive evaluation of existing bans necessitates considering their enforcement mechanisms, the impact of legacy contamination, and potential gaps in emission inventories or trade monitoring. Although comprehensive national emission estimates are not yet available for all studied compounds, integrating governmental or independently derived emission data into future work will be of high value. Given these complexities, exploring the relationship between HCBD and HCB may provide valuable insights into the potential sources. Significant positive Spearman correlations between HCBD and HCB were observed in Kuala Lumpur (r = 0.806, p < 0.01) and Islamabad (r = 0.636, p < 0.05), suggesting shared sources or similar environmental behaviors in these cities. In contrast, no significant correlation was observed in Guangzhou, possibly due to more complex industrial inputs or seasonal variability related to monsoonal influence in the Pearl River Delta region. Weaker correlations were also observed in Accra, Dhaka, and Nairobi, where incomplete HCBD bans remain in effect, and more diverse source contributions may lead to varied atmospheric distributions. These findings highlight HCBD's potential as a marker of unintentional emissions, especially in regions with diverse industrial sources and inconsistent regulatory controls.

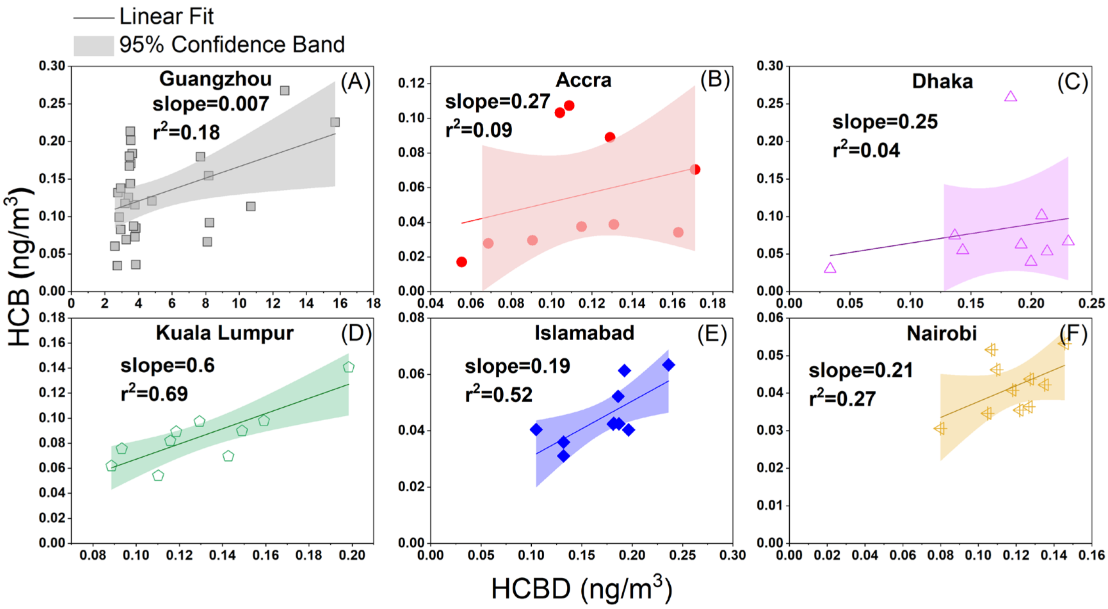


Figure 4. Correlations between HCBD and HCB concentrations in six cities: (A) Guangzhou, (B) Accra, (C) Dhaka, (D) Kuala Lumpur, (E) Islamabad, and (F) Nairobi.

Hexachlorocyclohexanes

Additional data on hexachlorocyclohexane (HCHs) measured by active and passive air sampling were presented in Table S16.The detection rates of the four HCH isomers in all samples ranged from 68 to 95%. Total HCH concentrations ($\sum_4$HCHs) were ranged from 0.747 to 107 pg/m^3 with a median concentration of 10.4 pg/m^3, following the order: Kuala Lumpur (32.8 pg/m^3, 24.7-42.5 pg/m^3) > Guangzhou (19.2 pg/m^3, 1.94-107 pg/m^3) > Islamabad (12.0 pg/m^3, 8.89-16.9 pg/m^3) > Dhaka (9.88 pg/m^3, 5.09-24.3 pg/m^3) > Accra (6.98 pg/m^3, 2.42-10.3 pg/m^3) > Nairobi (4.32 pg/m^3, 0.747-7.38 pg/m^3) (p < 0.05). In Nairobi, the γ-HCH concentration in the urban atmosphere was found to be nearly 67 times lower than that measured in an industrial area in 2017.[39]

Moreover, δ-HCH concentrations reported in this study are at a moderate level compared to rural area in Ghana, whereas α-HCH, β-HCH, and γ-HCH concentrations were significantly lower than those recorded in background and suburban area of Ghana in 2008.[38]

α-HCH was the dominant isomer (56 ± 21%) in Guangzhou, whereas γ-HCH predominated in Kuala Lumpur (72 ± 14%), Accra (47 ± 19%), Dhaka (51 ± 10%), and Nairobi (55 ± 24%). In Islamabad, the proportions of α-HCH, β-HCH, and γ-HCH were approximately equal. Variations in HCH isomer composition reflect source differences, which can be evaluated using the α-/γ-HCH ratio, a commonly used diagnostic indicator for source identification. A ratio of α-/γ-HCH closer to 1 typically indicates the recent or ongoing use of lindane. In contrast, a higher ratio—often exceeding 7—can suggest the influence of long-range atmospheric transport (LRAT), since α-HCH is more volatile and has greater LRAT capacity,[65] while γ-HCH degrades faster in the atmosphere and can photochemically convert to α-HCH.[66] The α-/γ-HCH ratio in five cities ranged from 0.1 to 2, indicating the potential ongoing use of lindane, while the much higher ratio observed in Guangzhou (1.0–22) indicates a stronger influence of LRAT. Compared to monitoring data from the same sampling site in Guangzhou in 2018 (51 ± 20 pg/m^3, α-/γ-HCH ratio: 0.3–3.5),[67] $\sum_4$HCHs concentrations have declined, with a notable increase in the α-/γ-HCH ratio. This provides further evidence that, following the ban on HCHs, atmospheric HCH inputs in Guangzhou are now primarily driven by long-range transport.

Non-listed HV-POPs

Volatile Methylsiloxanes

In this study, $\sum_7$VMS refers to three linear volatile methylsiloxanes (lVMS: L3, L4, L5) and four cyclic volatile methylsiloxanes (cVMS: D3, D4, D5, D6). All seven VMS compounds were detected in 99% samples, indicating their ubiquitous presence in the urban atmosphere. $\sum_7$VMS concentrations ranged from 10.7 to 1,160 ng/m^3, with a median of 126 ng/m^3 (Figure 5), cyclic VMS dominated, accounting for over 98% of $\sum_7$VMS concentration on average. In comparison, $\sum_3$lVMS concentrations ranged from 0.241 to 8.95 ng/m^3 (median:1.13 ng/m^3), with L4 as the dominant congener (60%), followed by L5 (30%). Among all cities, Guangzhou had the highest $\sum_7$VMS concentration (341 ng/m^3, 145-1160 ng/m^3), which was 2 to 9 times higher than other cities (p < 0.05).

D5 was the dominant congener in Kuala Lumpur (51%), Dhaka (46%), and Islamabad (41%), while D6 predominated in Accra (38%). Nairobi showed a more balanced composition, with similar proportion of D4, D5 and D6. Uniquely, D4 was the dominant congener in Guangzhou (70%), significantly higher than that in other cities. This pattern contrasts sharply with previous studies conducted in Chicago, New York, and southern Saitama, Japan, where D5 was consistently dominated (>50%).[68-70] Moreover, the average D5/D4 ratio in Guangzhou was 0.33, while the average ratios for other five cities were all greater than 1.2. Given that all sampling sites were urban sites, and D5 has a shorter half-live than D4, these inter-city differences in VMS composition reflect variations in emission sources. Major urban sources of VMS include silicone polymer manufacturing and the use of personal care products (PCPs) like shampoos, moisturizers, and body washes.[68, 71] D5 is the dominant congener used in PCPs, accounting for approximately 25% of its total global production.[72, 73] In contrast, less than 5% of D4 production is used in PCPs.[73] However, elevated concentrations and proportions of D4 have been detected in air samples near siloxane manufacturing facilities,[71] indicating its substantial use or production in industrial processes. These findings imply that a D4-dominated VMS profile may be characteristic of areas influenced by industrial sources, rather than consumer product use.

China is the world's largest producer of silicon and the second-largest cosmetic consumer market, with an annual organosilicon output reaching 6 million tons by 2022.[74, 75] Guangzhou is a major hub for silicone manufacturing, contributing 55% of China's total cosmetics production.[76] Within a 10.5 km radius of the sampling site in Guangzhou, there is a cosmetics industrial cluster with 1,288 manufacturing enterprises.[77] Therefore, the dominance of D4 in Guangzhou strongly suggests that local industrial production activities, rather than PCP usage, are the primary VMS source. In contrast, D5 dominated in Kuala Lumpur and Dhaka, consistent with previous studies,[19, 69] indicating PCPs usage is the main source. Spearman correlation analysis among VMS congeners in Guangzhou (r = 0.483–0.870, p < 0.01) (Table S9) further supports this, indicating similar industrial sources and atmospheric behaviors.

Table S12 summarizes VMS concentrations reported in previous studies using both active and passive air sampling. Compared with other regions, VMS levels in Guangzhou were relatively high, second only to those reported in New York, where $\sum_4$cVMS ranged from 18.8 to 2,010 ng/m^3.[70] Additionally, when compared with the SIP-PAS sampling data (2017) from urban sites in the Global Atmospheric Passive Sampling (GAPS) network, Guangzhou's VMS concentrations were in the upper concentration observed in the GAPS dataset.[24, 25] When compared with studies using active air samplers equipped with PUF/XAD/PUF cartridges, $\sum_7$VMS concentrations at a semi-urban site in Toronto (122 ± 71.0 ng/m^3) were comparable to those in Accra and Kuala Lumpur in this study.[78] By contrast, atmospheric VMS concentrations measured near point sources (e.g., siloxane production facilities, oil refineries, wastewater treatment plants) can be 1–6 orders of magnitude higher than those reported at all urban sites in this study,[71, 79-81] further highlighting Guangzhou's elevated VMS levels, likely driven by the high density of silicone-related industries and strong industrial emissions.

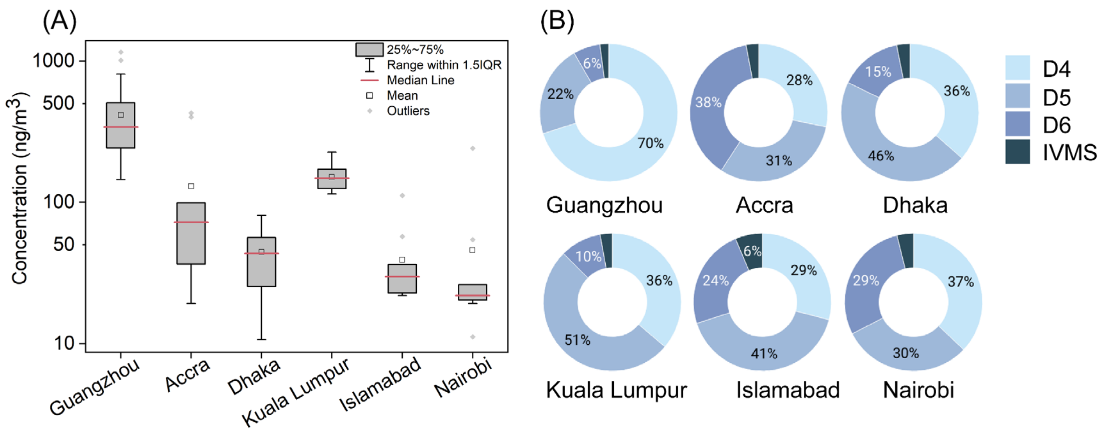


Figure 5. Atmospheric concentrations (ng/m^3) (A) and compositions (B) of $\sum_7$VMS in six cities.

Halogenated hydrocarbons

In this study, 23 halogenated hydrocarbons (HHCs) were grouped as $\sum_{23}$HHCs, including 11 chlorinated benzenes ($\sum_{11}$CBs), three chlorotoluenes, dichloronaphthalene, hexachlorocyclopentadiene, hexachloroethane, bromobenzene, pentabromobenzene, 1-bromo-2-nitrobenzene, 1,3,5-tribromobenzene, and two bromochlorobenzenes. Dhaka had the highest $\sum_{23}$HHCs median concentration (32.0 ng/m^3, 2.18-67.9 ng/m^3), followed by Nairobi (22.0 ng/m^3, 11.6-26.7 ng/m^3), Kuala Lumpur (16.7 ng/m^3, 9.84-28.4 ng/m^3), Accra (6.22 ng/m^3, 4.51-14.6 ng/m^3), Guangzhou (6.60 ng/m^3, 1.29-19.1 ng/m^3), and Islamabad (3.23 ng/m^3, 1.61-4.76 ng/m^3) ($p < 0.05$). Among these compounds, $\sum_{11}$CBs accounted for 34–99% of the total $\sum_{23}$HHCs, with concentrations ranging from 0.9 to 66.6 ng/m^3 (median: 5.08 ng/m^3) across six cities. Relatively high median concentrations of $\sum_{11}$CBs were found in Dhaka (31.4 ng/m^3, 1.92-66.6 ng/m^3), Nairobi (21.3 ng/m^3, 10.8-25.9 ng/m^3) and Kuala Lumpur (16.3 ng/m^3, 9.49-27.9 ng/m^3).

1,4-Dichlorobenzene (1,4-DCB) was the dominant congener among $\sum_{23}$HHCs, contributing 67 ± 28% to the total, with concentrations ranging from 0.616 to 61.9 ng/m^3 (median:4.17 ng/m^3). The textile industry is a major component of Bangladesh's economy, accounting for about 82% of the country's total export earnings as of 2018.[82] CBs are extensively used as solvents and auxiliaries in the textile and dyeing industries.[83] The elevated levels of $\sum_{11}$CBs and 1,4-DCB concentrations in Dhaka are likely attributable to its role as one of the world's largest garment production hubs, which hosts a highly concentrated textile industry that makes extensive use of dyes and auxiliary chemicals. Moreover, Spearman correlation analysis (Table S11) showed significant positive correlations among the 11 CBs across all cities ($r = 0.384–1$, $p < 0.05$), suggesting that these CBs may have similar sources.

Chlorinated Nitrobenzenes

Concentrations of 17 chlorinated nitrobenzenes ($\sum_{17}$CNBs), including isomers containing one to four chlorine atoms, were measured (Figure 6), ranging from 40.6 to 657 pg/m^3 (median:147 pg/m^3). The highest median concentration was observed in Kuala Lumpur (528 pg/m^3, 364-657 pg/m^3), followed by Dhaka (252 pg/m^3, 129-430 pg/m^3) and Accra (190 pg/m^3, 57.1-540 pg/m^3) ($p < 0.05$). Lower concentrations were observed in Nairobi (127 pg/m^3, 45.6-257 pg/m^3), Islamabad (123 pg/m^3, 48.0-270 pg/m^3), and Guangzhou (117 pg/m^3, 40.6-283 pg/m^3). The elevated CNB levels in Kuala Lumpur are likely associated with emissions from its chemical, pharmaceutical, electronics, and petrochemical industries, which release chlorinated byproducts during manufacturing.[36] In Dhaka, extensive use of dyes and auxiliaries in the textile industry, along with high population density and traffic emissions, likely contribute to its elevated CNBs concentrations.[35, 84]

Moreover, nitrobenzenes substituted with one to three chlorine atoms were widely detected in all samples (detection frequency: 41-100%), whereas 2,3,4,5-tetrachloronitrobenzene was detected in only 3% of the samples. In all cities, the composition of $\sum_{17}$CNBs was dominated by mono-, di-, and trichlorinated nitrobenzenes, indicating their prevalence in the urban atmosphere. Dichloronitrobenzenes were the dominant congeners (51 ± 22%), followed by monochloronitrobenzenes (27 ± 16%), trichloronitrobenzenes (20 ± 12%), and tetrachloronitrobenzenes (2 ± 5%). Chlorinated nitrobenzenes primarily originate from anthropogenic activities, serving as intermediates in the production of dyes, pesticides, pharmaceuticals, and other organic chemical products, with negligible contributions from natural sources.[84, 85] Lower-chlorinated CNBs are more likely to form than their higher-chlorinated counterparts, due to the nature of unintentional emissions, which are largely driven by radical reactions in industrial or combustion processes. This pattern aligns with the findings of this study, where lower chlorinated nitrobenzenes were more prevalent in the air, whereas highly chlorinated derivatives were far less abundant, reflecting differences in their formation dynamics and emission characteristics. Such patterns are analogous to those of atmospheric PCB distributions, where lighter congeners (e.g., PCB-11) are mainly associated with unintentional emissions than heavier ones (e.g., PCB-138/153).[86]

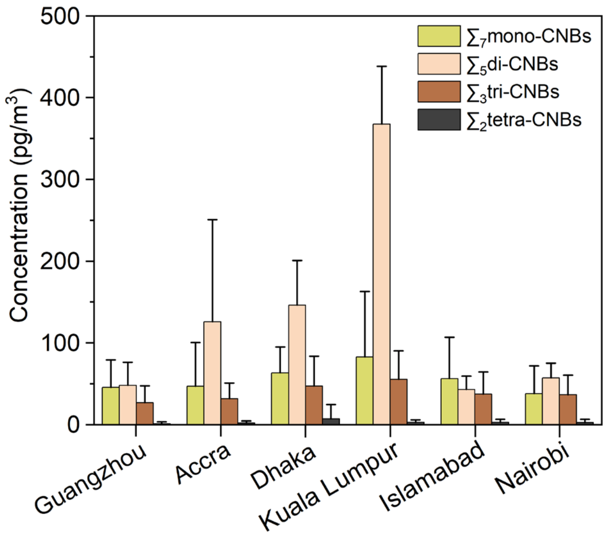


Figure 6. Averaged gaseous concentrations of chloronitrobenzene isomers categorized by degree of chlorination across six cities (pg/m^3). Green bars represent seven monochloronitrobenzenes, pink bars represent five dichloronitrobenzenes, brown bars

represent three trichloronitrobenzenes, and dark gray bars represent two tetrachloronitrobenzenes.

Influencing factors

To identify meteorological and socioeconomic factors influencing gaseous concentrations of HV-POPs, we conducted Spearman's correlation analysis between chemical concentrations and environmental and socioeconomic variables. Although Spearman's correlation doesn't account for collinearity among variables, it was selected for its robustness to non-normality and small sample sizes, providing initial insight into potential influencing factors. Relevant data were obtained from The World Bank (https://data.worldbank.org.cn/) and the Guangzhou Statistical Bureau (https://tjj.gz.gov.cn/datav/admin/home/www_nj/).[57] Full results are presented in Table S17 and S18. In Guangzhou, gaseous concentrations of several target compounds exhibited significant correlations with ambient temperature. Specifically, HCB, four HCH isomers, as well as D4 and D6, showed positive correlations with temperature (r = 0.374–0.759, p < 0.05), which is consistent with nationwide observations that higher temperatures enhance pollutant volatilization from local sources.[87] In contrast, HCBD and most halogenated hydrocarbons displayed strong negative correlations with temperature (r = -0.384– -0.780, p < 0.05), likely due to enhanced atmospheric degradation or increased dispersion under warmer conditions, resulting in lower atmospheric concentrations. In the other five cities, fewer significant correlations were observed (<5 compounds), which may reflect weaker temperature-driven processes or variations in local environmental conditions. Across all six cities, relative humidity and wind speed exhibited weak or non-significant correlations with chemical concentrations (<6 compounds), suggesting that these meteorological factors have limited influence on the distribution of HV-POPs.

Correlation results between HV-POPs concentrations and socioeconomic indicators, including per capita GDP, total population, and national merchandise trade volume, are summarized in Table S18. A significant positive correlation was found between $\sum_7$VMS and both total population (r = 0.545, p < 0.05) and merchandise trade volume (r = 0.784, p < 0.05), suggesting that VMS concentrations are associated with PCP usage and trade-related economic activity. Moreover, $\sum_{23}$HHCs and $\sum_{17}$CNBs showed strong positive correlations with per capita GDP (r = 0.604–0.658, $p < 0.01$), suggesting industrial activities and consumer behavior associated with higher income levels may contribute to increased emissions of these pollutants.

Chemical Risk Assessment

Daily inhalation dose (ADD_{inh}) of HV-POPs for adults (18–60 years old) in outdoor environments was estimated using country-specific exposure parameters, including inhalation rate, exposure time, exposure durations, and body weight. The average ADD_{inh} of total HV-POPs across all cities followed the order: Guangzhou (2×10^4 pg/(kg·d)) > Kuala Lumpur (8×10^3 pg/(kg·d)) > Accra (6×10^3 pg/(kg·d)) > Dhaka (4×10^3 pg/(kg·d)) > Nairobi (3×10^3 pg/(kg·d)) > Islamabad (2×10^3 pg/(kg·d)), with detailed results in Table S21. Guangzhou had the highest ADD_{inh} for both $\sum_7$VMS and HCBD, with values 1 to 2 orders of magnitude higher than other cities. According to the Scientific Committee on Consumer Safety of the European Commission, the maximum total daily exposure to D4 and D5 across all cities were 4×10^4 and 1×10^4 pg/(kg·d), respectively. These exposure levels are far below the chronic reference dose (cRfD) of 1.5×10^8 pg/(kg·d),[88] suggesting that, despite the abundance of D4 and D5 in the environment, current respiratory exposure levels are unlikely to pose significant health risk. While not intended to quantify total personal exposure, this assessment provides a preliminary perspective on ambient VMS levels and their potential regulatory implications.

Non-carcinogenic risk results are presented in Table S22. The total hazard index (HIs) for non-carcinogenic risks across cities ranged from 9×10^{-7} to 7×10^{-5}, indicating negligible non-carcinogenic risks, as the HIs for 1,4-DCB, 1,2,4-TCB, HCCPD, hexachloroethane, bromobenzene, and D5 were all below 0.01, further supporting that inhalation exposure to these compounds at current concentrations poses minimal non-carcinogenic health concerns.

Carcinogenic risk assessments were conducted for five compounds with available inhalation unit risk (IUR) values, including HCB, HCBD, α-HCH, β-HCH and γ-HCH (Table S23). Total carcinogenic risks across all cities were below 10^{-6}, ranging from 2×10^{-9} to 1×10^{-7}. Guangzhou exhibited the highest total carcinogenic risk (1×10^{-7}), mainly contributed by HCBD (55%) and HCB (29%), while Accra showed the lowest total carcinogenic risk (2×10^{-9}). In contrast, the remaining five cities exhibited carcinogenic risks primarily driven by HCB, indicating that inhalation exposure to these HV-POPs currently poses negligible carcinogenic risk. Compared with air samples collected from the same site in Guangzhou in 2020, the estimated carcinogenic risks for HCB, α-HCH, and β-HCH have decreased from potential levels (0.07×10^{-6}-2.11×10^{-6}) to negligible risks (6×10^{-11}-3×10^{-8}), reflecting the effectiveness of HCHs ban in China.[67] Notably, only 10 compounds (representing 19% of the target analytes) had available IUR values for quantitative risk assessment. As such, the cumulative health risks from HV-POPs may be underestimated, particularly given that the majority of measured compounds lack toxicity reference values. Additionally, the risk assessment was based on annual mean concentrations, which may not capture short-term peak exposures near emission sources.

Limitations and Environmental Implications

Despite increasing attention of HV-POPs, major challenges remain in fully understanding their environmental behavior, exposure pathways, and health risks.[89] These challenges include the absence of dedicated and harmonized analytical protocols across laboratories,[90] which limits comparability across the results of scattered case studies, and the lack of long-term and seasonally resolved monitoring data, particularly in developing regions.[91, 92] In this study, short and inconsistent sampling durations across sites may forfeit information on potential seasonal variability and introduced uncertainty in spatial comparisons. The current absence of reliable source profiles from relevant industrial emissions, as well as lack of information on HV-POPs in products, also hinders a sound source diagnostic and apportionment of HV-POPs in the atmosphere.

VMS, a representative class of HV-POPs, exemplify these knowledge gaps. Their potential health impacts remain difficult to quantify due to the lack of inhalation unit risk (IUR) data. It was suggested that oxidation products of VMS (e.g., silanols and formates) may enhance secondary organic aerosol (SOA) formation from personal care product emissions.[93] SOA can elevate fine particle mass and oxidative potential, exacerbating air pollution and posing health risks such as cardiorespiratory diseases.[94, 95] However, model-based evaluations indicate that the contribution of siloxanes to ambient SOA is relatively small,[96, 97] and field-based evidence supporting this pathway remains limited. Noteworthily, there might be distinct regional variation in VMS congener profiles in various PCP formulations on the global market, this will add more uncertainty to source diagnostics.

The observed elevated VMS concentrations in urban air underscore their environmental relevance as a major component of HV-POPs. The widespread presence highlights the necessity of including VMS in atmospheric chemicals monitoring programs, and calls for regulatory awareness and assessment. For HCBD, the high gas-phase concentrations align with its expected partitioning behavior, and brings forth the limitations of particle-phase-only sampling strategies.[10] These results emphasize the need for gas-phase-inclusive methods, such as the use of XAD sorbent, to avoid underestimation of exposure and to improve the accuracy of health risk assessment.

The detection of CNBs across multiple cities provides the first regional evidence of their occurrence in ambient air. The frequent detection of low-chlorinated congeners, combined with the limited availability of toxicological data, suggests the need for further investigation into their potential health effects. Given their persistence and volatility,[32] CNBs may represent an overlooked component of inhalation exposure in urban environments, particularly in regions where industrial or combustion-related activities are widespread.

HV-POPs are prevalent in the gas phase due to their high volatility, however, their partitioning into particles or other environmental media under cold, humid, or highly polluted environments may not be absent in a comprehensive and careful risk assessment. Addressing these broader knowledge gaps surrounding HV-POPs requires coordinated efforts to develop standardized sampling and analytical protocols, and to implement long-term monitoring.[90, 92] Our active sampling dataset, across Asia and Africa, provides direct observational evidence for the evaluation of HV-POPs under the global chemicals management framework, which faces growing pressure to prioritize chemicals posing the greatest global risks.[22]

Supporting Information

Detailed sampling information, instrumental method, detection limits, HV-POPs concentration summaries, comparison with literature, and additional results.

Acknowledgments

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