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Distribution and migration of polychlorinated biphenyls in topsoil of a ridge-valley hilly megacity: terrain effects from a case study of Chongqing, SW, China

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Abstract

This study combines source identification and health risk assessment of polychlorinated biphenyls (PCBs) with an analysis of their terrain-driven migration in urban environments. We examined the distribution, sources, and health risks of 18 PCB congeners in surface soils from Chongqing, a mountainous metropolis characterized by a parallel ridge–valley configuration. Concentrations of ∑18PCBs, quantified by GC-MS at 47 sites, ranged from 5.56 to 15.75 ng/g. Principal component analysis–multiple linear regression (PCA-MLR) resolved five sources: industrial combustion (45.5%), pigment/coatings legacy (30.2%), traffic emissions (12.7%), electrical equipment leakage (5.9%), and urban thermal treatment (5.8%). The spatial patterns support the hypothesis that the ridge–valley configuration modulates and redistributes anthropogenic source signals, thereby shaping PCB fate—an effect that has so far received little attention in parallel ridge–valley settings. We propose that this ridge–valley modulation operates through two pathways: (1) orographic confinement, whereby mountain barriers limit atmospheric dilution and retain industrial emissions within convergent valleys; and (2) fluvial sequestration, whereby terrain-modified air drainage along river corridors accumulates traffic- and combustion-derived emissions. Distance-from-source gradients alone cannot establish this modulation, and the mechanisms therefore remain inferential pending in-situ meteorological observation. Health risk assessment following U.S. EPA protocols indicates acceptable carcinogenic risk at the population level, whereas children experience higher exposure through soil-handling behaviors and should be prioritized in monitoring. Beyond hotspot mapping, the framework proposed here embeds terrain into source-oriented risk assessment and thus offers a transferable approach for supporting targeted interventions in complex-terrain cities. We acknowledge that sampling was confined to a single winter campaign and that the terrain-driven mechanisms are inferred from spatial patterns without in-situ meteorological observations; these limitations are discussed below.

1. Introduction

Polychlorinated biphenyls (PCBs), listed as persistent organic pollutants (POPs) under the Stockholm Convention (United Nations, 2001), comprise 209 organochlorine congeners renowned for their environmental persistence and toxicity. Because of their thermal stability and dielectric properties, these compounds were manufactured on an industrial scale (Gao et al., 2005; Niu, 2022; Megson et al., 2023); their chemical inertness renders them resistant to degradation (Strémy et al., 2019; Shariatifar et al., 2022; Neyestani et al., 2024), and IARC (2016) classifies them as carcinogens. Their lipophilic nature drives bioaccumulation in biological tissues and biomagnification along food chains, posing a global threat to ecosystem integrity and human health (Liu et al., 2020; Capozzi et al., 2023; Wu, 2023).

The distribution and fate of PCBs in the environment are far from uniform and are strongly governed by geomorphic and terrain processes. In coastal regions, accumulation is driven by wastewater discharge, mangrove sedimentation and tidal deposition (Davis et al., 2007; Souza et al., 2008). In inland areas, the urban fractionation effect, driven by heat islands and nocturnal temperature inversions, produces complex vertical distribution patterns (Harner et al., 2004; Zhang et al., 2008), whereas high-altitude

systems exhibit altitude-dependent partitioning controlled by monsoon transport and glacial dynamics (Gai et al., 2014; Guo et al., 2025; Zhang et al., 2025). Although PCB congeners are known to undergo terrain-related fractionation in mountain soils (Zheng et al., 2014), how terrain governs legacy PCBs in urban environments remains a major unresolved uncertainty (Castro-Jiménez et al., 2017; Muñoz-Arnanz et al., 2018; Rajan et al., 2021; Melymuk et al., 2022).

Research on these terrain–contaminant relationships nonetheless remains limited, particularly in parallel ridge–valley urban systems where three mountain belts alternate with river valleys. In such settings, the transport and transformation of PCBs are expected to deviate markedly from the patterns reported for flat terrain. Specifically, the urban fractionation effect (Lu et al., 2015; Wu et al., 2011) has yet to be adequately validated in complex mountainous settings dominated by steep slopes and thermal inversions. Chongqing, with its parallel ridge–valley topography and intense anthropogenic activity (Liao et al., 2025; Liu et al., 2016), offers an ideal natural laboratory in which to close this gap. Although recent work from our group examined PAHs within the same ridge–valley framework (Liao et al., 2025), PCBs differ substantially in physicochemical behavior (semi-volatile, particle-partitioning, dioxin-like toxicity) and in source profiles, which warrants a dedicated investigation. By coupling congener-resolved source apportionment with a terrain-based interpretation of PCB burdens, this work moves beyond conventional distance-to-source assessments in parallel ridge–valley cities. Accordingly, this study is designed to (1) quantify the spatial patterns, toxicity gradients and source contributions of PCBs; (2) mechanistically resolve the key terrain-contaminant interactions, including ridge confinement and thermal stagnation; and (3) assess the human health risks associated with PCB exposure in this complex urban environment. Together, these findings are expected to inform terrain-mediated regulatory strategies and targeted risk reduction in complex-terrain cities worldwide.

2. Materials and methods

2.1 Sample Collection and Preparation

A total of 47 composite topsoil samples were systematically collected from the main urban area of Chongqing, China (Fig. 1), in December 2023. At each sampling site, five sub-samples were collected from a depth of 15–30 cm and homogenized to form a single composite sample with a minimum weight of 500 g. Samples were immediately wrapped in tin foil, placed in sealed bags, and stored in a portable refrigerator at 4°C for transport to the laboratory. In the lab, samples were air-dried, manually purified to remove stones and plant debris, ground, and sieved through a 100-mesh sieve. The processed samples were stored at 4°C until analysis.

2.2 Extraction, Cleanup, and GC-MS Analysis

Quantitative analysis of 18 target polychlorinated biphenyl (PCB) congeners was performed using gas chromatography–mass spectrometry (GC-MS; Fuli S900). The analyzed congeners included tri-CB (PCB 28), tetra-CBs (PCB 52, 77, 81), penta-CBs (PCB 101, 105, 114, 118, 123, 126), hexa-CBs (PCB 138, 153,

156, 157, 167, 169), and hepta-CBs (PCB 180, 189). The analytical procedures followed established methods (Zhu et al., 2022) and the Chinese National Standard (HJ 922–2017). For extraction, a 10 g aliquot of each prepared soil sample was spiked with 10 μL of 2,2',4,4',5,5'-Hexabromobiphenyl (PBB-153, 50 μg/L) as a surrogate standard. The sample was then mixed with 2 g of anhydrous sodium sulfate (to remove moisture) and 1 g of copper powder (for sulfur removal). A 30 mL solvent mixture of acetone and *n*-hexane (1:1, v/v) was added, and the mixture was subjected to ultrasonic extraction for 15 min, followed by centrifugation at 4000 rpm for 5 min. The supernatant was collected, and the extraction process was repeated twice. The combined extracts were concentrated to approximately 2 mL using a termovap sample concentrator.

The concentrated extract was purified using a magnesium silicate solid-phase extraction column, eluted with a mixture of dichloromethane and *n*-hexane. The eluent was concentrated to 0.5 mL, and 20 μL of an internal standard (decachlorobiphenyl, 200 μg/L) was added. The final volume was adjusted to 1.0 mL with *n*-hexane/acetone and transferred to a 1.5 mL vial for GC-MS analysis. The entire pretreatment process was conducted in strict accordance with Chinese National Standard HJ 743–2015.

2.3 Quality Assurance and Quality Control (QA/QC)

Stringent QA/QC protocols were implemented to ensure data accuracy and precision. Qualification was performed using the internal standard method. Procedural blanks, consisting of 10 g of pre-heated quartz sand, were processed with every batch of 20 samples to monitor background contamination; all blanks were below the method detection limits. A laboratory control sample (spiked quartz sand) and replicate analyses (one duplicate per 15 samples) were performed to assess precision and accuracy. The relative percentage difference between duplicates was consistently ≤ 15%. Surrogate recovery (PBB-153) was evaluated for each sample to monitor procedural performance; recovery rates fell within the acceptable range defined by standard protocols (HJ 743–2015), confirming the robustness of the extraction and analysis methodology.

2.4 Statistical analysis and source identification

Statistical analyses were carried out using SPSS 26 (SPSS Inc., Chicago, IL, USA) and Canoco 5.0 for RDA. PCA was conducted on the soil samples containing PCBs using SPSS, with varimax rotation and factors having eigenvalues > 1 retained. PCA-MLR was applied to investigate the proportional contributions of identified sources to soil PCBs. Redundancy Analysis (RDA) was used to examine statistical relationships between PCB concentrations and environmental/socioeconomic variables. To enhance visualization of source-specific contributions, the analytical data were processed using an established model (Zhou et al., 2024) defined by Eq. (2 − 1), in which xi represents the environmental load intensity of a pollution source factor at sampling site i, ci denotes the measured concentration of a specific PCB congener at location i, and FLi signifies the factor loading coefficient derived from component analysis. Negative factor loadings (FLi < 0) were uniformly assigned a value of 0 to eliminate interference. All concentration distribution maps were generated using the Inverse Distance Weighting (IDW) interpolation method.

$$x_i = \sum c_i \times \mathrm{FL}_i \quad (2-1)$$

Concentration values modified via Eq. (2 − 1) were subsequently visualized for Chongqing using spatial statistical methods. This standardized processing of area-wide sampling data enables the generation of spatial differentiation maps illustrating source-specific contribution intensities, a methodology particularly suitable for regional soil pollution surveys, thereby effectively revealing spatial heterogeneity patterns in PCB pollution sources. We acknowledge that receptor models such as positive matrix factorization (PMF) could provide cross-validation of the PCA-MLR results; given the sample-size constraints of this field survey, PCA-MLR was applied here, and its inherent limitations should be considered when interpreting the proportional source contributions.

2.5 Deterministic human health risk assessment

The 2005 WHO toxicity equivalency factor (TEF) values, which were reaffirmed in the 2022 WHO re-evaluation, are used for the 12 dioxin-like PCBs measured in this study (van den Berg et al., 2006; Wittsiepe et al., 2007; DeVito et al., 2024). TEFs are essential for assessing the potential human health risks of dioxin-like mixtures. 2,3,7,8-Tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD), assigned a TEF of 1, serves as the reference compound for determining the relative toxicity of other dioxin-like PCBs. The toxicity equivalence (TEQ) of each dioxin-like PCB is calculated by multiplying its concentration by its respective TEF. The sum of these individual TEQs represents the sample's total dioxin-like toxicity. The corresponding equations are as follows:

$$\mathrm{TEQ} = \sum_{i=1}^{N} \mathrm{TEF}_i \times C_i \quad (2\text{–}2)$$

In this equation, TEF_i denotes the toxicity equivalent factor for a specific PCB congener, while C_i represents the concentration of the corresponding PCB congener. In assessing the potential risks of PCBs in surface soils of Chongqing to human health, this study employs the health risk assessment methodology recommended by the U.S. EPA(U.S. EPA, 2014 ,2015). Comprehensive parameter specifications are provided in Table S1. Note that a deterministic exposure–risk assessment based on U.S. EPA default exposure parameters was adopted here, rather than a Monte Carlo-based probabilistic simulation.

The evaluation considers the carcinogenic and non-carcinogenic risks associated with exposure to PCBs through various pathways, including ingestion, inhalation, and dermal contact for both adults and children(Man et al., 2011; Lingli et al., 2014; U.S. EPA, 2014 ,2015; Yao et al., 2018). The corresponding equations are as follows:

$$\mathrm{CDI}_{\mathrm{ing}} = \frac{C \times \mathrm{ED} \times \mathrm{CF} \times \mathrm{IR} \times \mathrm{EF}}{\mathrm{AT} \times \mathrm{BW}} \quad (2\text{–}3)$$

$$\mathrm{CDI}_{\mathrm{derm}} = \frac{C \times \mathrm{ABS} \times \mathrm{AF} \times \mathrm{CF} \times \mathrm{ED} \times \mathrm{EF} \times \mathrm{SA}}{\mathrm{AT} \times \mathrm{BW}} \quad (2\text{–}4)$$

$$\mathrm{CDI}_{\mathrm{inh}} = \frac{C \times \mathrm{IR} \times \mathrm{EF} \times \mathrm{ED}}{\mathrm{PEF} \times \mathrm{AT} \times \mathrm{BW}} \quad (2\text{–}5)$$

$$R_i = \mathrm{CDI}_i \times \mathrm{SF}_i \quad (2\text{–}6)$$

$$R_T = \sum R_i \quad (2\text{–}7)$$

$$\mathrm{HQ}_i = \frac{\mathrm{CDI}_i}{\mathrm{RfD}} \quad (2\text{–}8)$$

$$\mathrm{HI} = \sum \mathrm{HQ}_i \quad (2\text{–}9)$$

Comprehensive parameter specifications are provided in Table S2.

3. Results and discussion

3.1 Concentration Levels, Composition, and Global Comparison

All 18 target polychlorinated biphenyl (PCB) congeners were detected in the 47 surface soil samples collected from Chongqing's main urban area (Fig. 2). The total concentration (∑18PCBs) ranged from 5.56 to 15.75 ng/g (dry weight), with a mean value of 7.37 ng/g. The detection rates for individual congeners were high, ranging from 62% (PCB 52) to 100% for the majority of compounds, indicating ubiquitous occurrence across the study area.

The homologue-specific concentrations of polychlorinated biphenyls (PCBs) measured in this study are presented in Fig. 3. This compositional pattern is consistent with historical Aroclor mixtures commonly used in industrial applications (e.g., Aroclor 1254/1260) (Ba et al., 2009; Hao, 2022; Wei, 2023; Ulanova et al., 2024). Spatially, low-chlorinated PCBs (≤ 4 Cl atoms) showed a dispersed spatial distribution, consistent with their higher volatility and greater potential for atmospheric transport. In contrast, high-chlorinated PCBs (> 4 Cl atoms) showed more spatially clustered patterns, reflecting stronger particle affinity and preferential deposition near source areas.

Compared with soils from heavily industrialized regions and historic PCB production sites globally, the PCB levels in Chongqing are relatively low (Table 1). The mean concentration of 7.37 ng/g is comparable to background areas of Mongolia (7.4 ng/g; Mamontova et al., 2013), about one-third of the mean for London urban soils (22 ng/g; Vane et al., 2014), and close to the mean of Ulsan industrial soils (5.10 ng/g; range 0.03–143 ng/g; Cho et al., 2024). This is expected given the absence of major PCB manufacturing facilities in Chongqing (Gao et al., 2014). However, concentrations are slightly higher than remote mountain soils such as the Gyirong Valley in the Himalayas (~ 0.15 ng/g; Guo et al., 2025) and agricultural soils near Anseong, South Korea (0.11–0.22 ng/g; Kim et al., 2016). This suggests that while the presence of PCBs is ubiquitous, the contamination intensity in Chongqing's urban topsoil is moderate, likely reflecting the city's later industrial development and the absence of major primary PCB manufacturing facilities.

Table 1
Research on Polychlorinated Biphenyls Worldwide

Locations	Area type	Number of PCBs	Types of PCBs	Source apportionment method	∑PCBs range (ng/g)	Mean (ng/g)	Reference
Chongqing, China	urban soils	18	12 dioxin-like PCBs and 6 other PCBs	PCA-MLR	5.56–15.75	7.37	This study
The Gyirong Valley in the Himalayas	natural zones	31	12 dioxin-like PCBs and 19 other PCBs	PMF	0.04–0.38	0.15	(Guo et al., 2025)
Ulsan, South Korea	urban soils	19	12 dioxin-like PCBs and 7 other PCBs	PCA	0.03–143	5.10	(Cho et al., 2024)
Industrial bays, South Korea	coastal sediments	18	12 dioxin-like PCBs and 6 other PCBs	PCA	—	—	(Son et al., 2024)
South China	soil and aquatic	27	12 dioxin-like PCBs and 15 other PCBs		—	—	(Shi et al., 2022)
Taizhou, China	urban soils	19	12 dioxin-like PCBs and 7 other PCBs	PCA	1,321 ± 132	1,321	(Liu et al., 2020)
The Liaohe River, China	sediments	24	1 dioxin-like	PCA-MLR	—	—	(Zhong et al., 2020)

Locations	Area type	Number of PCBs	Types of PCBs	Source apportionment method	∑PCBs range (ng/g)	Mean (ng/g)	Reference
			PCBs and 23 other PCBs				
Lanzhou, China	urban soils	18	12 dioxin-like PCBs and 6 other PCBs		—	—	(Ding et al., 2018)
Anseong, South Korea	agricultural soil	29	12 dioxin-like PCBs and 17 other PCBs		0.11–0.22	0.15	(Kim et al., 2016)
London, UK	urban soils	7	1 dioxin-like PCBs and 6 other PCBs	point source identification	1–750	22	(Vane et al., 2014)
Mongolia	natural zones	37	7 dioxin-like PCBs and 30 other PCBs	cluster-method	0.53–114	7.4	(Mamontova et al., 2013)
Glasgow, Scotland	urban soils	19	1 dioxin-like PCBs and 18 other PCBs	PCA	—	—	(Cachada et al., 2009)

3.2 Spatial Distribution and Terrain-Driven Fate Mechanisms

The spatial distribution of ∑18PCBs showed clear spatial heterogeneity across the metropolitan area (Fig. 2). Elevated concentrations were mainly clustered in the northern and central districts, which

coincide with heavy industrial centers in the central region and emerging manufacturing bases in the northeast, indicating that these activities are major anthropogenic sources. Low-concentration areas occurred mainly in the southwestern and southeastern sectors, which are dominated by agricultural landscapes. This contrast indicates a direct association between land use and PCB contamination. In addition to source proximity, the complex mountainous topography may modulate PCB transport through a proposed ridge–valley effect. Three observations are consistent with this interpretation. (1) Ridge confinement: high-concentration plumes from northern industrial sources appear restricted within particular valleys rather than dispersing uniformly, as would be expected over flat terrain. (2) Atmospheric segregation: terrain-induced disruption of airflow may retain heavier congeners in basin areas while allowing lighter, more volatile congeners to disperse more readily, which would help account for the clustered distribution of high-chlorinated PCBs. (3) Anomalous deposition: isolated low-concentration points in the northwestern and eastern zones, despite their proximity to urban centers, suggest that local micro-topography and wind patterns modify simple distance-from-source relationships. These patterns indicate that conventional dispersion models based on flat geography may underestimate PCB hotspots in mountainous cities such as Chongqing. The proposed mechanisms, however, remain inferred from spatial patterns and require meteorological validation.

3.3 Source identification of PCBs in the topsoil of Chongqing

3.3.1 PCA-MLR analysis

Principal Component Analysis (PCA) was used to identify the main sources of PCB contamination in the surface soils of Chongqing. The analysis was run in SPSS, which autoscaled (standardized) the congener concentration data. Factors with eigenvalues above 1 were retained, and varimax rotation was applied to simplify the factor structure through orthogonal transformation. The suitability of the data for PCA was supported by a Kaiser–Meyer–Olkin (KMO) measure of 0.689 and a significant Bartlett's test of sphericity ($p < 0.001$). Five principal factors were extracted, together accounting for 76.47% of the total variance in the 18 congeners and capturing most of the systematic variation. The factors were interpreted from their congener loading patterns and established chemical markers. (1) Factor 1 (Industrial Combustion): loaded mainly with PCB52, PCB105, and PCB169. This profile indicates high-temperature industrial thermal processes, such as paint manufacturing and steel smelting (Ishikawa et al., 2007; Odabasi et al., 2009). The prominence of this factor is consistent with evidence that unintentionally produced PCBs from industrial processes are a major source of PCBs in soils (Song et al., 2018; Mao et al., 2021), suggesting that current industrial activity, in addition to historical legacy, remains a major driver. (2) Factor 2 (Traffic Emissions): characterized by high loadings of PCB180 and PCB123, this factor represents combustion emissions from diesel engines, including those used in maritime shipping and heavy vehicles (Nunes et al., 2017; Kang et al., 2020). This identifies transport infrastructure as a significant diffuse source, with implications for urban air quality near major traffic corridors. (3) Factor 3 (Urban Thermal Treatment): defined by high loadings of the dioxin-like congeners PCB114 and PCB81, which are recognized combustion tracers (Frame et al., 1996; Ba et al., 2009; Ulanova et al., 2024). The association of PCB114

with Aroclor 1254 further points to urban thermal industries or waste incineration. The high toxicity of these dioxin-like congeners supports continued monitoring and emission control at waste incineration facilities and other thermal plants. (4) Factor 4 (Pigment and Coatings Legacy): high loadings of PCB138 and PCB167, linked to Chinese 2# PCB, a historical byproduct of pigment and coating manufacturing (Frame et al., 1996; Ren et al., 2007; Hao, 2022; Wei, 2023). This indicates historical releases from paints and construction materials, and the renovation or demolition of older buildings may remobilize these PCBs as a secondary exposure source. (5) Factor 5 (Electrical Equipment Leakage): high loadings of PCB77 and PCB28. PCB28 is a major constituent of Chinese 1# PCB, historically used in electrical equipment, indicating leakage from capacitors and transformers (Ren et al., 2007; Odabasi et al., 2009; Hao, 2022; Wei, 2023). Although this factor contributes the least, it confirms the long-term persistence of PCBs from obsolete equipment and the need for proper identification and disposal of old electrical infrastructure.

The factor scores were used as inputs to Multiple Linear Regression (MLR) on the absolute principal component scores to quantify the contribution of each source to the total PCB burden. The MLR model showed a high coefficient of determination ($R^2 = 0.972$), strong significance ($F = 291.06$, $p < 0.0001$), and no detectable multicollinearity (Variance Inflation Factor, VIF = 1). The resulting source apportionment (Fig. 4) shows that the largest contributions to soil PCBs came from industrial combustion (45.5%) and pigment/coatings legacy (30.2%), followed by traffic emissions (12.7%), electrical equipment leakage (5.9%), and urban thermal treatment (5.8%). The combined industrial combustion and coatings legacy contribution (75.7%) supports prioritizing regulatory and emission-control measures in these sectors. The spatial distribution of the factor scores, interpolated using Eq. (2 − 1), is shown in Fig. 7a–e, with the topography of the study area in Fig. 7f, and these maps provide spatial evidence for the source assignments. The presence of multiple source pathways indicates that a holistic management strategy is needed, one that addresses both point sources and diffuse urban emissions from traffic and construction materials. This source profile can support predictive models of contamination under different urban development and policy scenarios.

3.3.2 Moran’s I spatial autocorrelation analysis

(1) Spatial Autocorrelation Analysis

Global Moran's I spatial autocorrelation was used to assess the clustering patterns of the identified PCB source factors (Fig. 5). All principal components except Factor 1 (PC1) showed statistically significant spatial clustering ($p < 0.05$). The lack of significant autocorrelation for PC1 indicates a more spatially random distribution. Because PC1 combines congeners with contrasting mobility (the relatively volatile PCB52 together with the less volatile PCB169), its spatial pattern cannot be attributed to volatility alone, and the observed randomness may reflect a combination of widespread atmospheric deposition and spatially dispersed industrial processes. The significant positive autocorrelation of the remaining factors (PC2–PC5) indicates strong spatial clustering, consistent with fixed-location anthropogenic sources. This contrast between a spatially random factor and clustered factors supports the PCA-derived source

apportionment and helps distinguish widely dispersed, atmospherically influenced contamination from emissions associated with persistent point sources.

(2) Redundancy Analysis of Environmental and Socioeconomic Drivers

To quantify the influence of environmental and socioeconomic variables on PCB congener distribution, Detrended Correspondence Analysis (DCA) was first conducted. The gradient length was 0.7 (< 3 standard deviations), confirming a linear response model and supporting the use of Redundancy Analysis (RDA). The RDA ordination (Fig. 6 and Fig. S1) combined PCB congener data with drivers, including socioeconomic indicators from the Chongqing Statistical Yearbook 2023. Most PCB congeners showed significant negative correlations with the total output value of primary industry (TPI). This inverse relationship implies that the dominant PCB emission sources are spatially separated from agricultural and rural areas and concentrated in urban and industrial centers dominated by secondary and tertiary industries. No significant relationship was found between PCB distribution and relative altitude elevation (RAE), indicating that broad altitudinal gradients do not systematically control PCB dispersal across the city and that any terrain effects operate at a finer scale, such as valley confinement and micro-topography, rather than as a simple elevation gradient. Taken together, these results depict a contamination profile dominated by spatially diffuse urban-industrial sources, with terrain modulating rather than overriding their spatial redistribution. This conclusion is consistent with the spatial autocorrelation analysis. The combination of spatial statistics (Moran's I) and constrained ordination (RDA) provides a framework for examining the drivers of contaminant distribution in heterogeneous landscapes.

3.4 Terrain-driven fractionation of PCB congeners

Terrain-related fractionation may influence the spatial distribution of PCB congeners in Chongqing. Lighter tri-chlorinated biphenyls, transported through volatilization, accumulate in the northern and southern peripheries, where orographic barriers enhance deposition (Fig. 3a). Mid-chlorinated (tetra- to hexa-) congeners form centralized plumes co-located with industrial sources in central and northeastern regions (Fig. 3b–d). Heavier hepta-chlorinated congeners cluster linearly along major waterways, consistent with transport-related emissions (Fig. 3e). All homologs except tri-PCBs show fragmented distributions constrained by terrain, indicating widespread orographic blocking. The main hotspots correspond to these hydro-geomorphological features (Figs. 3f, 7f). This pattern is consistent with broader evidence that congener fractionation in mountain soils reflects both source characteristics and terrain-related redistribution (Zheng et al., 2014). Although congener-specific properties cause minor gradient variations, topography appears to be an important secondary factor controlling transport and deposition in topographic depressions, alongside the primary distribution of anthropogenic sources.

3.5 Health risk assessment of PCBs in soil

Relative to the Chinese national standard (GB 36600 – 2018), PCB Toxic Equivalency (TEQ) concentrations in Chongqing surface soils exceed the Class I and II risk screening values (0.01 and 0.04 ng TEQ/g, respectively) but remain below the corresponding risk intervention values (0.1 and 0.4 ng

TEQ/g, respectively). Elevated TEQ values are localized in historically industrialized zones (Fig. 8), supporting continued monitoring. The hazard quotients (HQ) are consistently higher for children than adults across all exposure pathways (ingestion > dermal contact > inhalation), confirming children's greater vulnerability. The aggregate Hazard Index (HI) for both groups remains below 1 (U.S. EPA IRIS guidelines), indicating negligible non-carcinogenic risk under current conditions (Tables S3, S4).

PCB toxicity is congener-specific, with coplanar dioxin-like PCBs (e.g., PCB-126, -169) showing the highest carcinogenic potency due to their structural analogy to PCDD/Fs. Exposure analysis shows three patterns: (1) ingestion is the dominant exposure pathway; (2) a pronounced disparity exists between pediatric and adult carcinogenic risk from ingestion; and (3) children's hand-to-mouth behaviors significantly amplify their ingestion risks.

4. Conclusions

Surface soil in Chongqing contains ∑18PCB concentrations of 5.56–15.75 ng/g (mean: 7.37 ng/g), lower than those reported for many other metropolitan regions. The parallel ridge-valley topography likely acts as a secondary factor that modulates PCB dispersion in addition to anthropogenic influences, through two proposed mechanisms: (1) orographic confinement, in which mountain barriers obstruct prevailing winds and retain industrial and electrical-source PCBs within convergent valleys by limiting atmospheric dilution; and (2) fluvial sequestration, in which terrain-altered microcirculation in river corridors accumulates transport and combustion emissions.

This dual terrain forcing may contribute to spatially segregated, block-like contamination clusters. The elevated TEQ values near industrial zones may therefore be partly associated with this terrain-related accumulation, driven mainly by high-potency congeners such as PCB-126. Although the aggregate carcinogenic and non-carcinogenic risks for the general population remain below acceptable thresholds, children show greater vulnerability associated with soil-handling behaviors. This supports prioritized monitoring and soil protection in recreational areas, particularly at localized hotspots above screening values. Overall, this study presents complex topography as a plausible secondary control on urban PCB fate that operates alongside the primary anthropogenic source patterns. The framework offers a transferable approach in which ridge-valley configuration can help identify pollution hotspots and support targeted intervention in cities with complex terrain.

Limitations. This study has several limitations. First, soil sampling was conducted during a single campaign in December 2023 (winter), when atmospheric inversions are most frequent and dispersion conditions are poorest, so the measured concentrations may represent seasonal maxima rather than annual averages. Second, the 47 sampling sites, although spatially distributed, were not designed as paired ridge-valley transects, which limits direct statistical isolation of terrain effects from source proximity. Third, ambient wind field and inversion data were not measured at each site, so the proposed ridge-valley mechanisms are inferred from spatial patterns rather than directly observed. Fourth, soil organic carbon (SOC) content was not measured. Because SOC is a well-established control on PCB retention in soils, its omission means that part of the observed spatial variation cannot be separated from

differences in organic carbon, and this variable should be included in future work. Fifth, source apportionment relied solely on PCA-MLR without PMF cross-validation. Sixth, the health risk assessment used U.S. EPA default exposure parameters rather than locally derived values for Chongqing residents. Future studies should include seasonal sampling, paired ridge-valley transects, SOC measurement, and in-situ meteorological observations to further test and quantify the proposed terrain effects.

Declarations

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.

Author Contribution

K.W. conceived and designed the study, designed the sampling campaign, led the field investigation and data interpretation, and wrote the first draft of the manuscript. H.W. carried out the soil pretreatment and GC-MS analysis, performed the statistical and source-apportionment analyses, and prepared figures 1–8.R.W. developed the source-apportionment methodology and revised the manuscript.J.D. and P.H. contributed to the field investigation, resources and formal analysis. X.W. supervised the project, acquired the funding and revised the manuscript. All authors reviewed and approved the final manuscript.

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Data Availability

The raw data generated in this study are available from the corresponding author upon reasonable request

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