



A 15-year atmospheric record of intentionally produced persistent organic pollutants in Spain: Spatial gradients, thermodynamic fractionation, and temporal trends.

Adrián de la Torre^{a,*}, Juan Muñoz-Arnanz^b, Irene Navarro^a, Pere Colomer-Vidal^b, Covadonga Alonso^a, José L. Roscales^b, Ángeles Jiménez^c, Ana García^c, Begoña Jiménez^{b,1}, María Ángeles Martínez^{a,1}

^a Unit of POPs and Emerging Pollutants in Environment, Department of Environment, CIEMAT, Av. Complutense, 40, Madrid 28040, Spain

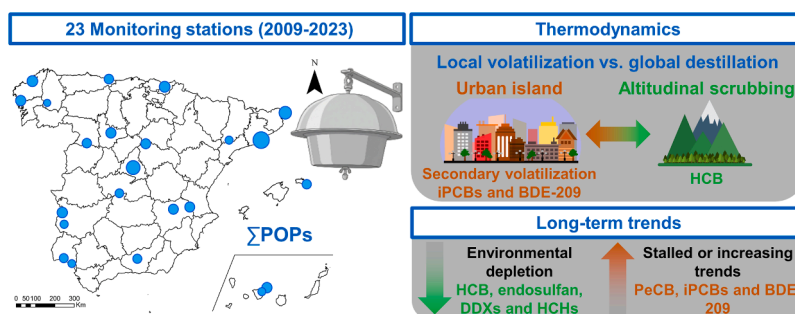
^b Department of Instrumental Analysis and Environmental Chemistry, Institute of Organic Chemistry, IQOG-CSIC, Calle Juan de la Cierva, 3, Madrid 28006, Spain

^c Subdirector General for Pollution Prevention, Ministry for the Ecological Transition and the Demographic Challenge (MITECO), Spain

HIGHLIGHTS

- 15-year atmospheric monitoring evaluates the Stockholm Convention effectiveness.
- Urban heat islands drive the secondary outgassing of legacy POPs and iPCBs.
- Thermodynamic fractionation highlights HCB global distillation and LRAT.
- Early-banned pesticides and lighter PBDEs undergo rapid atmospheric washout.
- PeCB and BDE-209 atmospheric levels remain stagnant or surge in specific hotspots.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

POPs
Air monitoring
Passive Air Sampling
Long-term temporal trends
Stockholm Convention effectiveness evaluation

ABSTRACT

This study presents a comprehensive 15-year (2009–2023) assessment of persistent organic pollutants (POPs) in the Spanish atmosphere to evaluate the Stockholm Convention's effectiveness. Polyurethane foam passive samplers were deployed across 23 sites to monitor legacy pesticides and industrial chemicals. Results reveal a concentration hierarchy dominated by hexachlorobenzene (HCB), which accounted for a median of 41% of the Σ POP concentrations and displayed a remote-enriched spatial pattern characteristic of global distillation. In contrast, legacy pesticides and indicator polychlorinated biphenyls (iPCBs) were influenced by temperature-dependent secondary volatilization from historically contaminated soils, as indicated by Clausius-Clapeyron analyses. These compounds frequently exhibited an unexpected urban enrichment likely associated with heat island effects, while polybrominated diphenyl ethers (PBDEs) displayed a pronounced urban gradient (a 35-fold increase from remote baselines) driven by the late-regulated BDE-209. Long-term temporal analyses underscore a sharp regulatory dichotomy. Early-banned compounds, such as endosulfan, HCB and dichlorodiphenyltrichloroethane (DDT), and lighter PBDEs, are experiencing rapid environmental depletion, with significant annual

* Corresponding author.

E-mail address: adrian.delatorre@ciemat.es (A. de la Torre).

¹ These authors share last authorship

declines of up to −33%. Conversely, pentachlorobenzene (PeCB), iPCBs, and BDE-209 show stalled or locally increasing trends (up to +20%), sustained by unintentional combustion, active consumer goods, and regulatory lag times. Altitudinal profiling across Tenerife sites highlights this divergence: coastal areas reflect local secondary emissions, whereas high-altitude observations confirm the progressive clearance of the global free troposphere. Overall, these findings provide new insights into the spatial and temporal dynamics of atmospheric POPs, reaffirming the role of long-term monitoring in guiding international abatement strategies.

1. Introduction

Persistent Organic Pollutants (POPs) are a group of chemicals characterized by their environmental persistence, ability to biomagnify in food webs, toxicity, and capacity for long-range atmospheric transport (LRAT). Recognizing their global threat to human health and ecosystems, the Stockholm Convention (SC) was adopted in 2001 as a legally binding treaty to eliminate or restrict the production, use, and release of POPs worldwide [1]. Since its ratification by Spain in 2004, the country has actively engaged in fulfilling its obligations under the Convention, including the development and execution of a National Implementation Plan (NIP). Given the crucial importance of long-term monitoring in tracking POPs, the Plan identified air monitoring as a priority, in line with the scientific requirements set out in Article 16 of the Convention. To address this issue, Spain established the Spanish Monitoring Programme on POPs (SMP-POPs in 2008 [2–5]. This network, developed through collaborative efforts between the Centre for Energy, Environmental and Technological Research (CIEMAT) and the Spanish National Research Council (CSIC), employs passive air samplers equipped with polyurethane foam (PUF-PAS) disks to monitor POP concentrations in diverse geographic locations across the country. The SMP-POPs adheres to the Global Monitoring Plan (GMP) guidelines of the SC and has proven effective in supporting large-scale assessments of POP transport, sources, and temporal trends. Previous studies based on early SMP-POPs data explored the initial variability of some POPs [2,4,5]. However, continuous long-term datasets are essential to robustly evaluate regulatory effectiveness, identify ongoing secondary sources, and understand the atmospheric behavior of these compounds.

To address these gaps, the present study provides a comprehensive 15-year assessment (2009–2023) of intentionally produced POPs across the SMP-POPs. Based on 59 sampling campaigns and a robust dataset of 1197 samples, target analytes encompass indicator polychlorinated biphenyls (iPCBs), polybrominated diphenyl ethers (PBDEs), hexachlorocyclohexanes (HCHs), hexachlorobenzene (HCB), pentachlorobenzene (PeCB), endosulfan, and dichlorodiphenyltrichloroethane (DDT) along with its metabolites, dichlorodiphenyldichloroethylene (DDE) and dichlorodiphenyldichloroethane (DDD). The overarching objective of this work is to improve the scientific understanding of the physico-chemical processes governing regional air pollution through an extended time series. Specifically, the study aims to: (i) characterize pollutant profiles and spatial variability to differentiate between contemporary emissions and legacy reservoirs; (ii) elucidate the thermodynamic drivers governing their atmospheric behavior, such as global distillation and temperature-dependent secondary volatilization from soils and urban areas; and (iii) evaluate long-term temporal trends to critically assess the environmental atmospheric removal of legacy POPs versus the stagnation and localized surges of modern tracers. By providing critical insights into the current status and dynamics of intentionally produced POPs in ambient air, this research aligns with the long-term goals of the European Monitoring and Evaluation Programme (EMEP) and aids in the implementation of key European Union directives, including the Ambient Air Quality Directive (2008/50/EC) and the National Emission Ceilings Directive (2016/2284/EU). Furthermore, the in-depth analysis of this comprehensive 15-year dataset strengthens large-scale assessments, reinforcing the indispensable role of national networks in supporting coordinated regional and international environmental policy, decision-making, and the

ongoing evaluation of the Stockholm Convention.

2. Materials and Methods

2.1. Sample collection

Samples were collected from 23 locations across mainland Spain and its archipelagos (the Balearic and Canary Islands) (Table S1 and Fig. S1). Sites were classified by population density according to [6] guidelines, resulting in four remote (<2000 inhabitants within a 10 km radius), ten rural (2000–20,000), four suburban (20,000–200,000), and five urban (>200,000) stations. With a total land area of 500,000 km², the network maintains a spatial resolution of approximately 20,000 km² per site. This density significantly exceeds the recommended threshold for Level 2 sites (50,000 km² per site) established in the EMEP monitoring strategy for 2020–2029. Consequently, the SMP-POPs is a robust program capable of accurately reflecting POPs atmospheric residence times and effectively capturing spatial gradients, deposition, and volatilization phenomena. Notably, our network includes two distinct monitoring stations on Tenerife Island representing an altitudinal gradient: the high-altitude remote background station of Izaña (2390 m a.s.l.) and the urban coastal station of Santa Cruz de Tenerife (28 m a.s.l.).

Passive air samplers utilizing PUF disks (14 cm diameter; 1.2 cm thickness, and 0.03 g/cm³ density; TechnoSpec, Spain) were employed. The principles of this methodology are thoroughly documented [7,8]. Prior to deployment, PUFs were conditioned via two-stage Soxhlet extraction with acetone followed by the specific solvent used for target analyte extraction. Clean PUFs were wrapped in aluminum foil and stored at −20 °C in polyethylene bags. At each site, four PUF-PAS were deployed for three-month periods to ensure seasonal coverage. This set was fractionated to cover the concurrent analysis of iPCBs (PCB–28, −52, −101, −138, −153 and −180; Table S2), PBDEs (BDE–17, −28, −47, −66, −77, −85, −99, −100, −119, −138, −153, −154, −156, −183, −184, −191, −196, −197, −206, −207, and −209), and organochlorine pesticides, including DDTs (*p,p'*- and *o,p'*-DDT), DDEs (*p,p'*- and *o,p'*-DDE), DDD (*p,p'*-DDD and *o,p'*-DDD), HCB, HCHs (α -, β - and γ -HCH), PeCB, and endosulfan (α - and β -endosulfan). Additionally, field blanks were handled and analyzed identically to the samples at each site and field campaign, placing them in the passive sampler housing for approximately 1 min during deployment and retrieval to account for artifact contamination during handling and transport.

2.2. Chemical analysis

Since the inception of the SMP-POPs, sample analysis has been shared equally between CIEMAT and CSIC. Procedures, instrumentation, and QA/QC measures were previously validated [2,3,5] and are provided in Text S1 (Supplementary Material). Briefly, samples were spiked with ¹³C-labeled surrogate standards prior to Soxhlet extraction (Table S3). The resulting extracts were purified and fractionated using solid-liquid adsorption chromatography via manual glass columns or automated systems (Power PrepTM, FMS, Inc., USA; or DEXTech+, LCTech GmbH, Germany). Analysis was performed by gas chromatography coupled to either low-resolution tandem mass spectrometry (GC-MS/MS) or high-resolution mass spectrometry (GC-HRMS), with quantification based primarily on the isotopic dilution method.

2.3. Data analysis

POP air concentrations were calculated by dividing the total analyte mass by the number of PUFs, sampling duration, and the effective sampling rate (m^3/day). A constant sampling rate of $4 \text{ m}^3/\text{day}$ was applied for iPCBs, PBDEs, HCHs, DDTs, DDEs, DDDs, and endosulfan, while site- and season-specific air volumes for PeCB and HCB were estimated using the Harner's Template [9,10]. Limits of quantification (LOQs) were defined at a signal to noise ratio (S/N) of 10:1 (Table S3). To account for the non-normal distribution of environmental data, values below the LOQ were substituted by $\text{LOQ}/\sqrt{2}$, an approach that minimizes bias in statistical estimates. Extreme outliers, defined as values exceeding $3 \times$ the interquartile range, were identified and excluded independently for each analyte and sampling site.

Statistical analyses were conducted using R software (v 4.5.2). The specific R packages used, along with a comprehensive description of the outlier detection protocol and the stepwise temporal trend workflow, are detailed in Text S2. Given the characteristic heteroscedasticity and non-normal distribution of atmospheric POP concentrations (confirmed via Kolmogorov-Smirnov tests, $p < 0.05$), non-parametric methods were prioritized. Spatial variability across locations and urbanization categories (Remote, Rural, Suburban, and Urban) was evaluated using Kruskal-Wallis H tests followed by Dunn-Bonferroni post-hoc comparisons, while Spearman's rank correlation (r_s) was used to explore inter-compound associations. Processes governing atmospheric levels were investigated via a dual approach. First, atmospheric partial pressures were derived from the measured air concentrations utilizing the ideal gas law (Eq. S1). These values then served as the input for the Clausius-Clapeyron (CC) equation (Eq. S2) to differentiate between local secondary sources and LRAT or deposition-dominated regimes. All temperature-dependent thermodynamic calculations were performed using site-specific temperature records corresponding to each individual sampling campaign to ensure the inclusion of local microclimatic conditions, such as urban heat island effects, at each monitoring station. Second, temporal trends were identified using annual median $\log_{10}$ -transformed concentrations following GMP protocols [6]. The normality of these distributions was first assessed via the Shapiro-Wilk

test to determine the appropriate statistical approach. When data met normality criteria, trend significance ($p < 0.05$) was assessed using Pearson correlation, with the magnitude of change (Annual Percentage Change (APC, %) and environmental half-lives ($t_{1/2}$)) quantified via Linear Regression. For datasets failing the normality test, non-parametric Mann-Kendall tests and Theil-Sen estimators were alternatively employed. To ensure robustness, a power analysis was performed following the Arctic Monitoring and Assessment Programme (AMAP) and the OSPAR Commission (OSPAR) guidelines [11,12]. While a target power of 0.80 was prioritized, trends with a power between 0.50 and 0.80 were also considered informative and are explicitly discussed in the results.

3. Results and Discussion

Descriptive statistics for the sum of indicator PCBs (ΣiPCBs), PBDEs (ΣPBDEs), HCHs (ΣHCHs), HCB, DDTs and their metabolites (ΣDDXs), and endosulfan isomers ($\Sigma\text{endosulfan}$), as well as individual HCB and PeCB, are summarized in Table S4. As illustrated in Fig. 1, a consistent hierarchy of median concentrations was observed across the dataset: $\text{HCB} (41.8 \text{ pg/m}^3) > \Sigma\text{iPCBs} (13.8 \text{ pg/m}^3) \approx \Sigma\text{DDXs} (11.9 \text{ pg/m}^3)$. These three families were followed by the next homogeneous statistical tier with lower, yet comparable levels: $\text{PeCB} (12.8 \text{ pg/m}^3) \approx \Sigma\text{HCHs} (12.1 \text{ pg/m}^3)$. Finally, the lowest concentrations were recorded for $\Sigma\text{PBDEs} (2.3 \text{ pg/m}^3)$ and $\Sigma\text{endosulfan} (1.6 \text{ pg/m}^3)$. This pattern indicates that POP contamination in Spain is dominated by legacy organochlorine compounds with high environmental persistence, particularly HCB, iPCBs and DDXs. Beyond central tendencies, the morphology of the raincloud plots provides further insight into atmospheric behavior. Compounds like HCB or PeCB exhibit compact, unimodal distributions. In contrast, ΣiPCBs , ΣPBDEs , and ΣDDXs display broader dispersion and multi-modal profiles. This high internal variability suggests that their concentrations are not governed by a uniform background level, but are heavily influenced by site-specific characteristics and distinct emission sources. Consequently, this concentration profile defines the overall atmospheric footprint across the network (Fig. 2), where HCB overwhelmingly dominates the relative

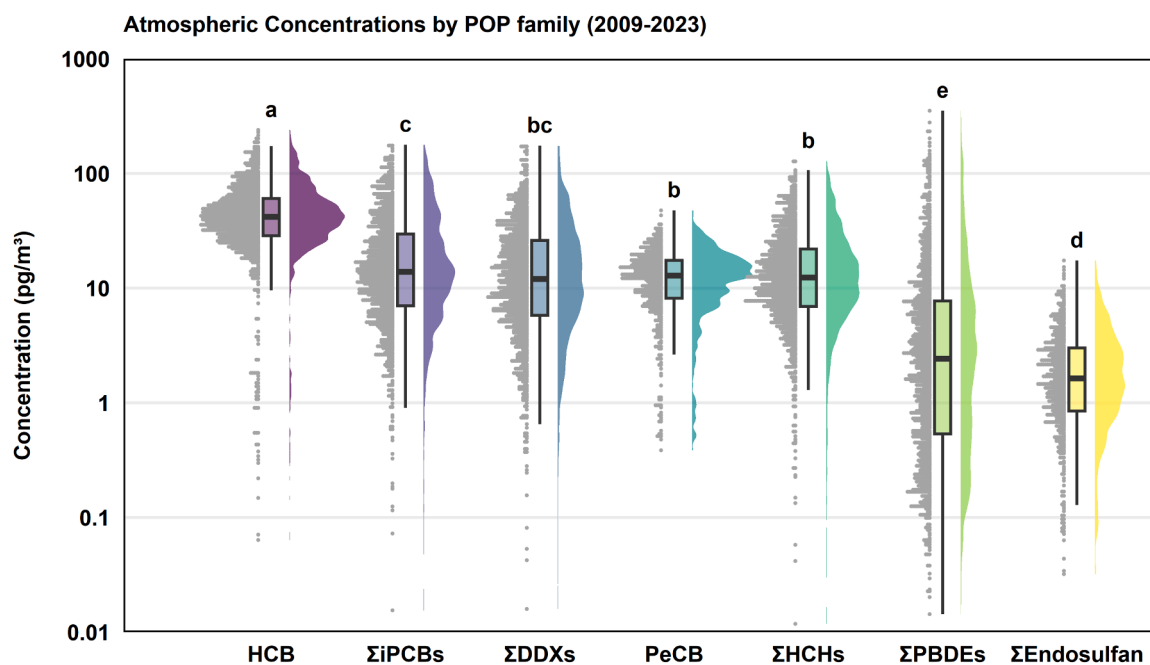


Fig. 1. Atmospheric concentrations (pg/m^3) of POP families (2009–2023). Raincloud plots display individual observations (left jittered points), boxplots (median and interquartile range), and kernel density distributions (right). Different letters above the plots indicate statistically significant differences between groups ($p < 0.05$). The y-axis is shown on $\log_{10}$ scale.

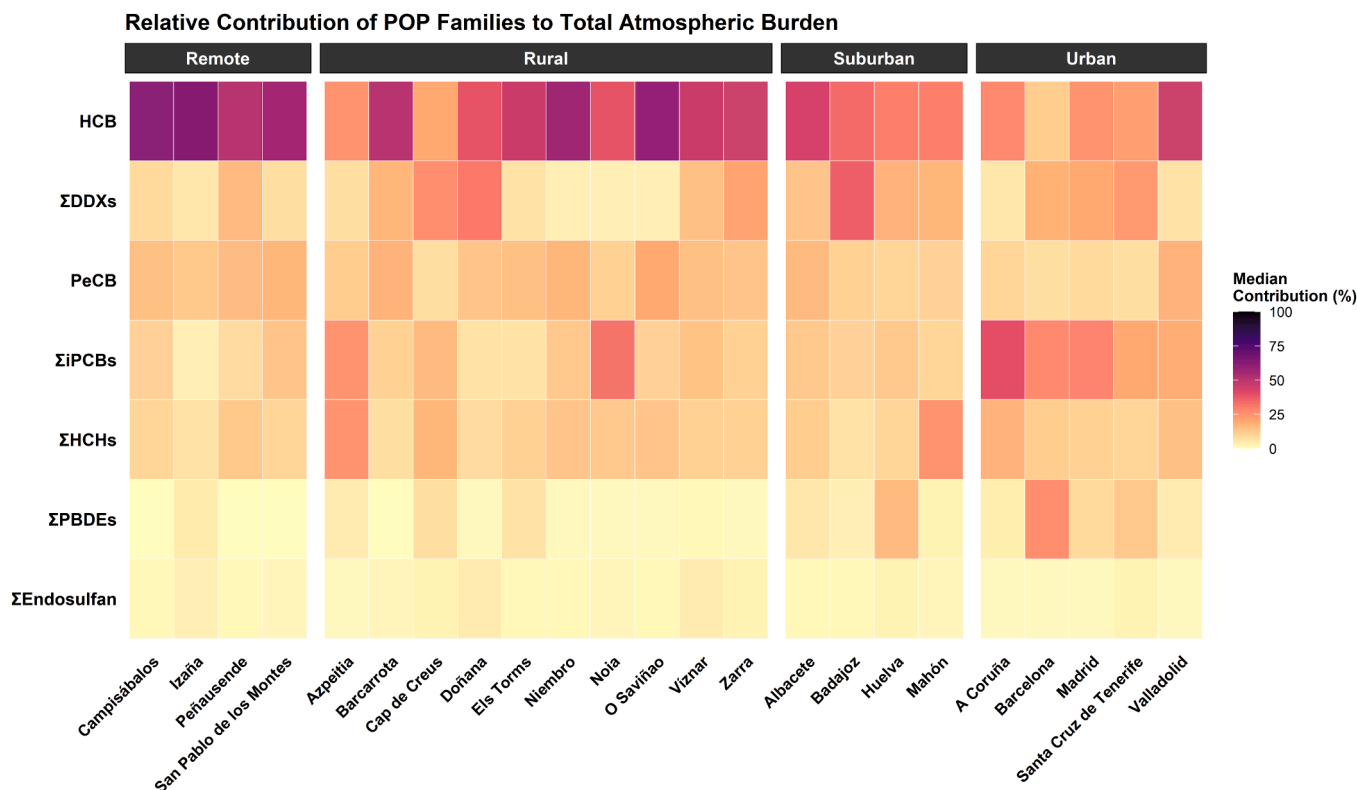


Fig. 2. Relative contribution (%) of POP families to the total atmospheric burden across 23 monitoring sites. Stacked bar chart represents the median relative contribution of each family at location. Sites are categorized by urbanization level (Remote, Rural, Suburban, and Urban) and sorted alphabetically within each group. POP families are ordered according to their global median contribution.

POP inventory at remote and rural sites, whereas profiles become notably more diverse in suburban and urban environments due to the increasing contribution of other chemical families, justifying a more detailed analysis based on site classification.

The chemical pattern of POPs varied significantly according to site classification (Fig. S2; Table S5 and S6). Although urban areas consistently acted as primary emission hotspots, the spatial gradients presented family-specific nuances. While median concentrations of Σ PBDEs exhibited a strict stepwise increase across all urbanization levels (Remote: $0.4 < \text{Rural}: 1.0 < \text{Suburban}: 4.1 < \text{Urban}: 12.9 \text{ pg/m}^3$), Σ iPCBs and Σ HCHs showed comparable intermediate levels between the rural and suburban categories (ranging from 10.8 to 12.7 pg/m^3). Similarly, Σ DDXs displayed a clear spatial dichotomy, with significantly higher concentrations in suburban and urban areas (20.0 and 21.0 pg/m^3 , respectively) compared to remote and rural sites (8.4 and 8.7 pg/m^3). Conversely, HCB, PeCB, and Σ endosulfan exhibited no pronounced urban-remote gradients, indicating a well-mixed atmospheric distribution across the network. Their median concentrations ranged from 36.6 to 53.1 pg/m^3 for HCB, 12.3 – 14.1 pg/m^3 for PeCB, and 1.3 – 2.0 pg/m^3 for Σ endosulfan. While this urbanization-based classification provides a valuable framework, the high internal variability observed within sampling sites (Table S7) indicates that certain dynamics transcend broad geographical labels. A compelling example emerges when comparing the two most densely populated urban centers: Barcelona and Madrid. Five of the seven highest median concentrations in the entire network were recorded in Barcelona, including Σ iPCBs (90.6 pg/m^3), Σ PBDEs (68.5 pg/m^3), Σ DDXs (59.4 pg/m^3), Σ HCHs (37.0 pg/m^3), and PeCB (18.3 pg/m^3). Notably, for PBDEs, concentrations in Barcelona are 3.5 times higher than those in Madrid (19.6 pg/m^3). These discrepancies can be attributed to Barcelona's coastal location, favoring soil volatilization through higher humidity and temperature, and its intense port and industrial activities. Furthermore, the microenvironments differ significantly: the Madrid station

represents an urban background (consistent with Directive (EU) 2024/2881), whereas the Barcelona sampler is positioned in a high-traffic zone acting as a pollution hotspot. This dense urban environment acts as a continuous primary source, as combustion from both on-road vehicular traffic and off-road machinery has been identified as a massive unintentional emitter of PCBs and highly brominated PBDEs like BDE-209 [13,14]. Therefore, a granular approach is necessary to account for unique local characteristics.

3.1. PeCB and HCB

HCB and PeCB exhibited generally uniform atmospheric distribution across the 23 monitoring sites (Fig. S3 and S4). This behavior is consistent with their high volatility (vapor pressures of 0.015 and 0.065 Pa , respectively; Table S2), which favors their persistence in the gas phase and minimizes local deposition. However, a closer examination of the site categorization reveals a clear-cut divergence between the two. While PeCB showed no discernible urban-remote gradient, HCB displayed a statistically reverse spatial trend (Remote: $53.1 > \text{Urban}: 42.5 \approx \text{Rural}: 39.9 \approx \text{Suburban}: 36.6 \text{ pg/m}^3$; Table S6). This remote enrichment provides strong empirical evidence of the global distillation effect (or cold condensation). Driven by its environmental persistence and large-scale background reservoir, HCB can undergo LRAT and preferentially condenses in colder, high-altitude or remote environments. As shown in Fig. 3, this spatial dynamic is consistent with CC relationships, where significant positive slopes (indicating higher partial pressures at lower temperatures) were systematically identified. For HCB, this temperature dependence was significant at 9 of the 23 stations (e.g., $p < 0.001$ at Campisábalos, Niembro, and O Saviñao), while PeCB exhibited positive CC relationships at 10 locations (e.g., $p < 0.001$ at Cap de Creus, Doñana, Badajoz, and Mahón; Table S8 and Fig. S5). Positive CC slopes can arise from both the regional advection of cold, contaminated air masses (LRAT) and enhanced primary emissions from

Atmospheric Dynamics: Clausius-Clapeyron and Temporal Trends



Fig. 3. Coupled atmospheric dynamics and temporal trends for POP families. Marker shapes represent temperature dependence (Clausius-Clapeyron) based on median congener ΔH values: upward triangles for volatilization ($\Delta H > 0$, $p < 0.05$), downward triangles for deposition/LRAT ($\Delta H < 0$, $p < 0.05$), and circles for non-significant relationships ($p \geq 0.05$). Marker fill colors represents the Annual Percentage Change (APC, % yr⁻¹) calculated from total family concentration. Only significant trends ($p < 0.05$ and statistical power > 0.5) are colored, using a scale from green (decrease) to orange (increase). Transparent markers denote non-significant trends or insufficient statistical power. Median values for families were derived from: *o,p'*- and *p,p'*-DDE (Σ DDEs); *o,p'*- and *p,p'*-DDD (Σ DDD); *o,p'*- and *p,p'*-DDT (Σ DDTs); PCB-28, -52, and -101 (Σ L-PCBs); PCB-138, -153, and -180 (Σ H-PCBs); BDE-47, -99, and -100 (Σ PBDEwo209); and BDE-47, -99, -100, and -209 (Σ PBDEs).

domestic heating during winter [15–18]. However, for HCB, the aforementioned reverse spatial trend (enrichment at remote sites rather than urban centers) effectively rules out localized urban winter combustion as the driving force. Instead, its positive CC slopes are fundamentally governed by regional-scale LRAT and global distillation dynamics, which overwhelm local soil-air exchange signals.

Despite sharing these thermodynamic signatures, their long-term temporal trends diverge sharply. HCB showed a consistent decline across the network, with 13 locations exhibiting APCs ranging from -6% to -9% (Fig. 3, S6 and Table S9). In contrast, PeCB concentrations remained much more stable, with only Niembro (APC -6%) and Valladolid (APC -5%) registering significant downward trends. This divergence, characterized by distinct temporal trajectories despite

highly synchronized spatial and thermodynamic behaviors, can be explained by their inter-compound correlations. HCB and PeCB exhibited significant positive correlations across all 23 monitoring stations (r_s ranging from 0.51 to 0.91, $p < 0.01$; Fig. S17), completely independent of the site classification. This ubiquitous covariance indicates that both compounds are co-transported within the same background air masses and governed by identical meteorological factors. Therefore, their temporal divergence highlights the fundamental nature of their global inventories: while they travel together in the regional atmosphere, the global pool of HCB is slowly depleting due to strict long-term bans. Conversely, the baseline levels of PeCB are continuously maintained by contemporary active sources that counterbalance its atmospheric removal.

This reliance on large-scale background dynamics is best exemplified by the vertical distribution on Tenerife Island, which reveals a complex dissociation from local processes. The lack of significant CC relationships at both Santa Cruz de Tenerife (urban: 28 m a.s.l.) and Izaña (remote: 2390 m a.s.l.) may reflect that their presence is primarily driven by LRAT. Nevertheless, a compelling finding arises from the altitudinal gradient: while PeCB levels remained uniform across both elevations (9 pg/m³; median), HCB concentrations were significantly higher at the high-altitude site of Izaña (47.8 pg/m³) than in coastal Santa Cruz (27.8 pg/m³; Fig S3, Table S4). This enrichment suggests that Izaña effectively captures the HCB burden of the free troposphere, consistent with recent global observations showing that HCB tends to exhibit higher, more stable concentrations at elevated altitudes due to its persistence and stronger coupling to the free-tropospheric background [19,20]. Furthermore, despite a synchronized annual decline of HCB at both sites (−6%), PeCB levels remained stable. This local altitudinal divergence mirrors the network-wide observations, which may be indicative that while HCB is successfully being gradually scrubbed from the global atmosphere, PeCB remains a continuously replenished background pollutant.

Interestingly, our observation of steady PeCB levels contrasts with recent continent-wide evaluations across Europe. [21] reported a widespread decline in atmospheric PeCB (median annual change of −9%) across the MONET network between 2003 and 2019. The decoupling observed in the SMP-POPs could be attributed to specific regional and temporal factors. First, although the overall study spans from 2009 to 2023, PeCB was incorporated into the network later, in 2016. This recent temporal window (2016–2023) suggests that PeCB had already reached a steady-state baseline in southwestern Europe following the initial regulatory drops that occurred shortly after its inclusion in the SC in 2009. Remarkably, this temporal plateau has been recently mirrored in decadal observations from East Asia [22,23], confirming a global phenomenon where historical HCB is successfully declining while PeCB reaches a steady state. The primary sources of PeCB have shifted towards thermal processes, including solid waste incineration, coal and biomass combustion, coking processes, and non-ferrous industrial processes [23–26]. Furthermore, it is still released as a chemical impurity in currently or formerly applied agricultural pesticides, such as pentachloronitrobenzene, endosulfan, chlorpyrifos-methyl, atrazine, and clopyralid [17,27]. In Spain, these baseline levels are likely further sustained by the higher frequency of severe forest fires and biomass combustion, both from winter domestic heating (supported by CC observations) and agricultural residue burning, which act as continuous secondary sources [28]. Finally, the higher solar radiation in Spain could favor the photochemical degradation of the abundant HCB, a process that may yield PeCB as a primary byproduct via reductive dechlorination, thereby providing a potential supplementary secondary source that effectively sustains its atmospheric baseline.

3.2. Endosulfan

Endosulfan exhibits a partitioned environmental behavior governed by marked physico-chemical differences between its isomers. α -endosulfan is volatile (vapor pressure (P_L) of 0.0012 Pa; log K_{OA} = 7.94; Table S2), partitioning primarily into the gas phase, and dominates the atmospheric load with a well-mixed spatial distribution (Fig. S7). Conversely, the less volatile β -isomer (P_L =0.00011 Pa; log K_{OA} = 9.12) presents a higher affinity for atmospheric particles and remains closer to historical application areas. This mobility constraint is perfectly illustrated in Tenerife (Fig. S8): α -endosulfan levels were identical at the high-altitude Izaña observatory and coastal Santa Cruz (both showing a median of 2.4 pg/m³; Table S4), confirming homogeneous free troposphere transport via LRAT. However, β -endosulfan was significantly depleted at Izaña (0.1 pg/m³) compared to Santa Cruz (0.8 pg/m³), confirming a strictly local terrestrial origin.

The origin and age of these atmospheric residues can be further elucidated through their isomeric profile. The commercial technical mixture contained an α/β ratio of 2.0–2.3 [10,29]. However, observed atmospheric α/β ratios across the SMP-POPs were overwhelmingly > 3.0 (medians of 4.8, 4.8, 4.5 and 3.6 for Remote, Rural, Suburban and Urban, respectively; Table S5). Beyond differential volatility, this α enrichment is accentuated by the irreversible environmental isomerization of the β -isomer into α -endosulfan, coupled with its higher water solubility, which increases its susceptibility to wet deposition scavenging [30–33]. Consequently, this isomeric profile serves as a diagnostic tracer of weathered emissions, indicating that the baseline is sustained by secondary re-volatilization from agricultural soils. CC analysis supports this result: individual isomers exhibited significant negative slopes (indicating higher atmospheric concentrations at higher ambient temperatures) at 8 (α -endosulfan) and 12 (β -endosulfan) locations (Fig. 3). This thermodynamic behavior contrasts with HCB and PeCB, indicating endosulfan is likely sustained by summer volatilization from historically contaminated soils.

Nevertheless, while Σ endosulfan exhibited a generalized temporal decline (Fig. S8), a closer examination reveals distinct trajectories. Historically applied extensively in southern Spain and the Mediterranean coast, endosulfan's current atmospheric presence relies heavily on local soil-air exchange from finite legacy reservoirs rather than continuous global emissions. Following its market withdrawal (2006–2007) and global ban (2011; SC), the 15-year SMP-POPs dataset captures the immediate environmental depletion phase of these anthropized soils. α -endosulfan showed a steep decline at 22 of the 23 network stations (APCs: −13% to −33%; Figs. 3 and S8). The β -isomer also declined significantly at 16 locations (APCs: −12% to −31%). These pronounced decreases are consistent with the rapid global atmospheric decline of endosulfan, which responds much faster to international regulations than older legacy POPs and exhibits some of the steepest annual declines worldwide [21,34–37]. Interestingly, β -endosulfan depletion rates exhibit a clear latitudinal gradient across SMP-POPs. The most significant and steepest declines occur in lower latitudes, encompassing historical southern and Mediterranean hotspots. In contrast, β -levels have already stalled at northern sites and Mahón. Owing to lower historical usage and cooler baseline temperatures that limit secondary volatilization, these smaller soil reservoirs have likely reached a steady-state equilibrium. This temporal disparity is exemplified by the Tenerife sites: α -endosulfan declined identically at Izaña (−33%) and Santa Cruz (−32%), reflecting global tropospheric depletion, while the β -isomer dropped half as much at the remote Izaña site (−17%) compared to the coastal source (−30%).

This dissociation from ongoing primary emissions is further reflected in the Spearman matrices (Fig. S17). Notably, neither endosulfan isomer correlated with PeCB, corroborating their distinct origins: contemporary combustion processes versus legacy agricultural sources. Interestingly, α -endosulfan systematically displayed stronger correlations with HCB than the β -isomer at western Atlantic sites (e.g., Noia, A Coruña, Huelva, Santa Cruz and Izaña). In contrast, eastern Mediterranean sites (Barcelona, Cap de Creus and Mahón) showed no such covariance. This Atlantic-Mediterranean dichotomy mirrors prevailing atmospheric circulation patterns over the Iberian Peninsula. Atlantic sites predominantly receive older, well-mixed marine air masses (Westerlies), where volatile legacy pesticides (α -endosulfan and HCB) act as co-varying trace components of the hemispheric background. Conversely, the Mediterranean basin features lower synoptic ventilation, strong land-sea breeze recirculation, and intense regional agricultural pressure [38]. In these eastern locations, continuous secondary emissions from local soils completely overwhelm the global background signal, disconnecting endosulfan's atmospheric dynamics from HCB.

3.3. DDT and its main metabolites

Following a trajectory similar to endosulfan, the atmospheric

presence of DDT and its primary metabolites (DDE and DDD) is entirely governed by historical legacy sources. Banned in Spain in 1977, their contemporary levels rely strictly on progressive degradation and temperature-driven secondary volatilization from environmental reservoirs. This aged state is robustly confirmed by the isomer profiles. Given that p,p' -DDE is the primary aerobic degradation product of p,p' -DDT [33,39], atmospheric p,p' -DDE/ p,p' -DDT ratios > 1 indicate historical residues devoid of fresh inputs. Across the SMP-POPs, this ratio was consistently high (median of 5.9), reaching extreme values indicative of intense degradation in southern hotspots like Badajoz (21.9) and Doñana (21.8). Consequently, the continuous outgassing of the massive historical reservoirs drives highly significant downward atmospheric trends. As illustrated in Fig. 3, Σ DDTs, Σ DDDs, and Σ DDEs are undergoing rapid depletion, exhibiting significant annual decreases at 10, 12, and 13 locations, respectively (with APCs reaching up to -14% , -21% , and -15% ; Fig S9). These background depletion rates align with continental observations from the European MONET network [21]. However, the high spatial resolution of the SMP-POPs reveals critical local deviations from this generalized atmospheric clearance. A notable exception to this widespread decline is the apparent increase of Σ DDDs in O Saviñao (APC $+35\%$). However, its time series reveals a sudden step-change rather than a progressive trend: concentrations were low until 2011, followed by an abrupt increase that established a higher, persistent baseline for the subsequent decade. This localized anomaly likely reflects a discrete terrestrial disturbance in the site's vicinity, such as deep agricultural plowing or earthworks, that suddenly exposed a buried, anoxic DDD reservoir to secondary volatilization [40]. Furthermore, altitudinal data from Tenerife provides compelling insights into the progressive clearance of the free troposphere: absolute DDXs levels were substantially lower at the high-altitude Izaña observatory (4.2 pg/m^3 ; Fig S9) compared to the coastal Santa Cruz site (27.9 pg/m^3). While the coastal source exhibits significant depletion across all metabolites, only the parent Σ DDTs decreased at Izaña. This suggests that the global free troposphere is being cleared of the residual parent compound, whereas the coastal boundary layer remains strictly governed by local terrestrial degradation.

While heavily degraded profiles in southern and central regions (DDT $< 10\%$ of the Σ DDXs concentration) confirm the depletion of historical agricultural applications, a pronounced spatial anomaly emerged in northern and eastern coastal hubs. Industrialized and port-influenced stations (Azpeitia, A Coruña, and Barcelona) exhibited unexpectedly large proportions of the parent compound (p,p' -DDE/ p,p' -DDT ratios < 1.9), indicating unadulterated DDT signatures. This phenomenon can be attributed to two region-specific factors. First, the influence of dicofol impurities remains a significant factor [20]. To verify this, isomeric relationship between o,p' -DDT and p,p' -DDT was evaluated throughout the network (Table S4). Median values consistently exceeded the theoretical technical DDT threshold of 0.2–0.3 [41], with results ranging from 0.62 to 1.34 across the sites. This underscores that, even decades after restricted use, dicofol-type signatures continue to govern the DDT baseline within Spanish atmosphere. Second, the historical use of technical DDT in marine antifouling paints should be considered as a plausible secondary source in maritime settings [30]. In major hubs, routine port maintenance, dredging, and shipyard operations could potentially re-expose anoxic sediments, liberating preserved parent DDT into the coastal boundary layer [42]. While this pathway remains difficult to quantify directly, the concurrence of low degradation signatures in port-cities suggests that sediment remobilization may complement the broader regional influence of dicofol-related inputs.

Despite its legacy origin, DDXs present an urban enrichment, diverging fundamentally from endosulfan. While DDE and DDD showed generally elevated concentrations in populated environments, total DDT exhibited a statistically significant positive gradient with population density (Remote: $1.3 < \text{Rural}$: $1.6 < \text{Suburban}$: $2.9 < \text{Urban}$: 6.5 pg/m^3 ; Table S5). Consequently, major hubs (e.g., Barcelona, Madrid, and Santa Cruz de Tenerife) emerged as primary hotspots for the parent compound

(Fig. S9). This urban trapping primarily stems from the sealing of former agricultural lands beneath contemporary infrastructure, supplemented by minor historical contributions from structural spraying [37,43]. This effect is exacerbated by the urban heat island, which forces the continuous volatilization of trapped residues. CC analysis agrees with this mechanism, with Σ DDTs exhibiting significant negative slopes in 16 of the 23 locations (Fig. 3). A notable rural exception to this urban pattern is Cap de Creus, which recorded exceptionally high, aged Σ DDXs levels (ratio of 6.8). This localized hotspot could be the legacy of massive historical aerial fumigations over adjacent Mediterranean wetlands (e.g., Aiguamolls de l'Empordà) to eradicate malaria vectors [44–47], potentially exacerbated by coastal breeze circulations that favor the retention and accumulation of aged air masses.

Inter-compound correlations further elucidate these temperature-driven dynamics. The parent p,p' -DDT correlated positively with endosulfan isomers across the SMP-POPs, likely reflecting synchronized outgassing from regional soils. Additionally, p,p' -DDE positively correlated with HCB at 19 locations, indicating that substantial HCB inventories (historically applied as seed fungicides) [48] persist in Spanish soils and co-volatilize alongside degraded DDT. Notably, HCB and p,p' -DDE completely decoupled only at sites where DDT inputs are driven by distinct local factors (A Coruña and Cap de Creus). Although PeCB lacks a direct agricultural history, it correlated with p,p' -DDE at several sites (e.g., Huelva, O Saviñao, Zarra, Madrid, Niembro), suggesting both compounds, historically present as impurities in other organochlorine fungicides, share secondary emissions from managed soils. Finally, Tenerife's altitudinal profile highlights a perfect mechanistic dissociation. At the remote Izaña observatory, PeCB correlated strongly with primary DDXs, reflecting homogeneous mixing within the free troposphere (LRAT). Conversely, at Santa Cruz, PeCB decoupled entirely from DDXs, supporting that the coastal boundary layer is dominated by independent local sources for PeCB (combustion) and DDXs (urban soil volatilization).

3.4. HCHs

In contrast to other legacy pesticides like DDTs and endosulfan, the atmospheric burden of HCH isomers across the continental boundary layer exhibits a highly localized and generally weak temperature dependence, pointing to a complex interplay between limited secondary outgassing and regional advection. The evaluation of the α - γ -HCH ratio provides evidence regarding historical usage patterns. While the technical HCH mixture is inherently dominated by the α -isomer (ratio 3–7), pure lindane ($>99\% \gamma$ -HCH) yields ratios < 1 [49,50]. Across the continental network, median ratios consistently fell well below 1 (Table S4), suggesting that Spanish agriculture and public health programs heavily relied on lindane. A singular exception is the remote high-altitude Izaña observatory, which exhibited a median α - γ -HCH ratio of 3.3. This α -enrichment is the chemical signature of highly aged, global background air masses within the free troposphere, where the photochemically stable α -isomer accumulates.

Despite their legacy origins, specific HCH isomers exhibited an enrichment comparable to DDT. Both γ - and β -HCH displayed significant positive gradients with population density (e.g., Remote: $4.5 < \text{Rural}$: $6.2 = \text{Suburban}$: $7.4 < \text{Urban}$: 15.0 pg/m^3 for γ -HCH; Table S6), identifying major urban centers such as Barcelona, Madrid, and A Coruña as hotspots within the monitoring network (Fig. S10), alongside regional anomalies like Azpeitia and Mahón. Rather than widespread agriculture, this urban enrichment is plausibly linked to the re-volatilization of historical residues within urban and peri-urban zones. This baseline is sustained by the historical use of lindane in domestic and public health applications (e.g., scabies and lice treatments or pet shampoos) [29,31, 51,52], which acts as persistent secondary sources exacerbated by the aforementioned urban soil sealing and the heat island effect forcing continuous outgassing. Conversely, α -HCH lacked a clearly defined urban gradient, reflecting a stronger dependence on regional advection

and the hemispheric background.

The divergent physicochemical properties of the isomers profoundly affect their local secondary emission dynamics. As indicated by the CC analyses (Fig. 3 and Table S8), the temperature-driven volatilization of HCHs is highly localized. The volatile α -HCH lacked widespread negative slopes, exhibiting significant positive temperature dependences in only two locations, suggesting its baseline is heavily influenced by advection (LRAT) rather than exclusive local soil-air exchange. Similarly, the γ -HCH exhibited significant negative slopes (active volatilization) in only three locations. Despite this scattered thermodynamic response, the active depletion of legacy reservoirs is driving a generalized atmospheric depletion. All isomers are declining at comparable rates: α -HCH decreased significantly at 10 peninsular locations (APCs from -5% to -10% ; Figs. 3, S6 and S10), β -HCH at 12 sites (-5% to -34%), and γ -HCH at 13 sites (-5% to -16%). These pronounced depletion rates are highly consistent with European and global observations, where HCHs currently exhibit some of the most rapid and sustained atmospheric declines among legacy POPs following their regulation [21,53,54]. Crucially, against this backdrop of widespread continental decline, α -HCH concentrations at Izaña remain completely stagnant, corroborating its isolation from local depleting sources and continuous replenishment by the global tropospheric background.

Spearman matrices capture the co-occurrence of these residual legacy sources. In historically agricultural and peri-urban environments (e.g., Zarra, Campisábalos, Barcarrota, Valladolid, Albacete; Fig. S17), the more volatile α - and γ -HCH isomers exhibited robust positive correlations with other legacy agricultural pesticides (DDXs, HCB, and endosulfan). This confirms that historical multi-pesticide applications created thoroughly mixed soil reservoirs. Site-specific anomalies further highlight distinct local phenomena: in Azpeitia, while the γ -isomer maintains a significant covariance with DDTs and endosulfan, the α -HCH correlates with endosulfan but completely decouples from DDXs, pointing to specific historical co-applications or complex industrial dumping. Nevertheless, the definitive contrast between local soil emissions and the global background is well exemplified in Tenerife. At Santa Cruz, α - and γ -HCH co-volatilize tightly with local legacy soil reservoirs (endosulfan, HCB, DDXs); remarkably, neither correlates with β -HCH, confirming its higher retention in local soils. Conversely, at the high-altitude Izaña observatory, the simultaneous covariance of HCHs with all legacy pesticides results solely from the homogeneous mixing of aged global backgrounds within the free troposphere.

3.5. iPCBs

Unlike legacy agricultural pesticides, the spatial distribution of iPCBs maps the footprint of contemporary urbanization and industrialization. Across the SMP-POPs, Σ iPCBs and all individual congeners exhibited a highly significant positive gradient with population density (Remote: $8.1 < \text{Rural} < 11.3 = \text{Suburban} < 12.7 < \text{Urban} < 45.2 \text{ pg/m}^3$; Figs. S2 and S11). Consequently, major metropolitan hubs emerged as the primary hotspots, led by Barcelona (90.6 pg/m^3) and Madrid (62.6 pg/m^3) (Fig. S12). This urban footprint is the direct environmental legacy of the massive mid-20th-century consumption of commercial PCB mixtures, such as Aroclors, Clophens, Pyralenes, and Phenoclor [55–57].

The physicochemical properties of the individual congeners, where vapor pressure drops by a factor of ~ 400 from the PCB-28 to PCB-180 while $\log K_{\text{OA}}$ proportionally increases (Table S2), induce a profound thermodynamic fractionation. Although a general decrease in iPCB levels with increasing chlorination is expected (as observed in Azpeitia and Els Torms; Fig. S13), evaluating median concentrations reveals distinct atmospheric patterns. In remote and rural sites like O Saviñao and San Pablo de los Montes, the load is dominated by lighter, gas-phase congeners (PCB-28, PCB-52, and PCB-101). Historically prevalent in lighter commercial formulations (e.g., Aroclor 1242) used in open applications such as building sealants and paints, their high volatility allows them to dominate the regional background [58]. Conversely, a

completely different profile emerges in Noia, Barcelona, Madrid, and Cap de Creus, characterized by significantly higher proportions of heavy congeners (PCB-153, PCB-138, and PCB-180) typically associated with heavier dielectric fluids (e.g., Aroclor 1260 [33]). Given their extreme affinity for atmospheric particles ($\log K_{\text{OA}} > 9.5$) and negligible LRAT capabilities, these heavy congeners serve as a strong indicator of proximity to historically burdened sources.

This local emission dynamic is consistent with the striking thermodynamic behavior observed in the CC analyses (Fig. 3 and Table S8). Impressively, the heaviest congeners (PCB-138, -153, and -180) simultaneously exhibited strongly significant negative slopes across seven highly urbanized or industrial environments (Madrid, Barcelona, Valladolid, Albacete, Azpeitia, Huelva, and Santa Cruz de Tenerife). However, active secondary volatilization (negative slopes) for some heavy congeners was also detected at specific remote (San Pablo de los Montes and Campisábalos) and rural sites (Zarra, Vízmar, and O Saviñao). This thermodynamic anomaly physically confirms that while heavy PCB presence is strongly sustained by the urban heat island effect, where extreme temperatures force the outgassing of urban surfaces, including buildings, pavements and technical infrastructures, localized historical residues in rural soils or legacy substations also actively volatilize into the boundary layer under elevated summer temperatures.

Following decades of international prohibitions (e.g., Directive 96/59/EC), the atmospheric depletion of iPCBs has significantly slowed. This generalized plateau confirms that primary emissions have ceased, and contemporary levels are now sustained by continuous secondary outgassing from massive environmental reservoirs. To unravel these active atmospheric removal dynamics, temporal trends were evaluated by grouping congeners into lighter (Σ L-iPCBs: PCB-28, -52, -101) and heavier (Σ H-iPCBs: PCB-138, -153, -180) homologues. The more volatile Σ L-iPCBs are rapidly depleting from the global free troposphere at Izaña (-10% ; Table S9), as well as from specific urban and industrial hotspots (Azpeitia, Barcelona, and A Coruña; APCs from -5% to -8%). Incipient potential increases ($+6\%$) of Σ L-iPCBs were observed at San Pablo de los Montes and Vízmar; however, their moderate statistical power ($0.5\text{--}0.8$) indicates that these specific trajectories require further long-term validation. Concurrently, the Σ H-iPCBs are only undergoing localized depletion in Azpeitia, Niembro, Noia, and Barcelona (APCs from -7% to -15%). These compound-specific trajectories are highly consistent with global and European observations, where lighter PCBs exhibit faster depletion rates driven by rapid OH radical degradation and long-range transport, whereas heavy, particle-bound congeners deplete more slowly and locally due to the gradual dissipation of historically contaminated sinks [21,35,54,59,60].

The diverse origins and atmospheric trajectories of PCBs are further unraveled by Spearman correlation matrices. Across a heterogeneous subset of locations (e.g., Noia, Madrid, Barcelona, A Coruña, Santa Cruz, and Campisábalos), heavy PCBs showed surprising positive correlations with legacy agricultural pesticides (DDTs and/or endosulfan). Rather than a shared physical source, this synchronization points to meteorological trapping and local atmospheric stagnation events, which indiscriminately accumulate all regional soil and urban emissions within the boundary layer. Meanwhile, at the high-altitude Izaña observatory, PCBs correlate strictly with highly degraded DDEs and parent DDTs, but notably lack any correlation with the modern endosulfan isomers. This perfectly reflects the homogeneous mixing of aged, globally distributed legacy pollutants via LRAT. Finally, the rural coastal hotspot of Cap de Creus presents again a notable anomaly: iPCBs exhibited strong correlations with the DDEs and DDTs while completely decoupling from volatile endosulfans. Given the heavily weathered legacy reservoirs previously identified in this exact location, this unique covariance provides physical evidence of a distinct emission mechanism. Rather than pure gaseous volatilization, the continuous outgassing in this Mediterranean hotspot may force the joint secondary emission and particle resuspension of heavy PCBs and agricultural legacy POPs from the exact same historically contaminated local soils.

3.6. PBDEs

Building on the urban footprint of legacy PCBs, PBDEs act as definitive tracers of contemporary human settlements and legacy consumer products. Although their production was regulated over the past two decades, their extensive historical incorporation into long-lasting consumer goods (e.g., plastics, textiles, and electronics) ensures that modern urban centers remain massive emission reservoirs. Across the SMP-POPs, PBDEs exhibited the most extreme spatial gradient of all analyzed POPs. Σ PBDEs levels surged sharply with population density, escalating from minimal baselines in remote sites (0.4 pg/m³; median) to massively enriched levels in strictly urban environments (12.9 pg/m³), representing a staggering 35-fold increase. Consequently, major metropolitan areas completely dominate the network hotspots (Figs. S14 and S15). Barcelona stands out as the absolute network maximum (68.5 pg/m³), virtually tripling the concentration of the second-highest cities (Madrid and Santa Cruz de Tenerife, 19.6 and 16.0 pg/m³, respectively), followed closely by Huelva (12.7 pg/m³).

A congener-specific evaluation reveals that atmospheric partitioning is dictated by specific local emission mechanisms rather than general location categories. In urban and suburban environments, the profile is overwhelmingly monopolized by the heaviest congener, BDE-209 (Fig. S16). Isolating the lighter fraction, all PBDEs without 209 (Σ PBDEwo209) still reveals a clear urban footprint (Remote: 0.2 < Rural: 0.3 < Suburban 0.8 < Urban: 1.7 pg/m³), but at concentrations an order of magnitude lower than the BDE-209 burden. This stark difference accurately reflects European regulatory history: while lighter Penta- and Octa-BDE commercial formulations were banned in 2004, the Deca-BDE mixture (mainly BDE-209) was not included in the SC until 2017. Outside metropolitan hubs, divergent profiles emerge. In specific rural and remote sites (e.g., San Pablo de los Montes, Peñausende, Barcarrota), the load is dominated by lighter congeners (BDE-47, -99, -100), pointing to the localized outgassing of older Penta-BDE treated materials. However, this physical fractionation is driven by a profound thermodynamic divide and is consistent with the patterns observed in the CC analyses (Fig. 3). The Σ PBDEwo209 fraction exhibited highly significant negative slopes in 16 of the 23 locations. These lighter PBDEs actively and continuously volatilize from contemporary materials and infrastructures into the local atmosphere under temperature-driven forcing. Conversely, BDE-209 possesses an extremely low vapor pressure and massive log K_{OA} , rendering its gaseous volatilization negligible under ambient temperatures. Accordingly, BDE-209 lacked widespread temperature-driven volatilization slopes across the network, showing active secondary emission exclusively in Vízcar. Its substantial presence in the lower boundary layer is strictly largely driven by the physical abrasion of plastics and the mechanical resuspension of contaminated urban particulate matter.

These distinct emission trajectories are unraveled by the Spearman matrices. In major urban and industrial epicenters, lighter, volatile PBDEs showed strong and statistically significant correlations with iPCBs. Interestingly, this co-emission profile varies across hubs depending on local infrastructural reservoirs: while PBDEs co-vary with almost all PCB homologues in cities like A Coruña, Azpeitia, and Barcelona, they correlate strictly with heavier congeners (PCB-101 to -180) in Madrid, and with lighter homologues (PCB-52 and -101) in Huelva. Regardless of the specific congener, this widespread synchronization underscores their continuous co-emission from shared contemporary urban infrastructures and consumer goods [60]. A completely different physical mechanism is captured at the rural coastal hotspot of Cap de Creus, where the particle-bound BDE-209 exhibited correlations with specific mid-to-heavy PCBs (PCB-101, -138, and -153) and the DDX family, while completely decoupling from volatile endosulfan. Given the heavily weathered legacy reservoirs previously identified in this location, this unique covariance suggests that the dry Mediterranean climate forces the joint atmospheric resuspension of historically contaminated soil dust containing a complex mixture of

legacy agricultural POPs, industrial PCBs, and contemporary flame retardant tracers. Finally, at the high-altitude observatory of Izaña, the profile is again dominated by BDE-209 (Fig. S16). Rather than a local source, its dominance and correlation with specific highly weathered legacy POPs (*o,p*-DDE and α -endosulfan) likely points towards the LRAT of BDE-209 bound to fine global background aerosols within the free troposphere [61–63].

The profound impact of regulatory lag times between Penta-/Octa- and Deca-BDE commercial mixtures is captured by the temporal trends (Fig. 3, Table S9). The stricter 2004 regulations are finally driving an active environmental reduction of the lighter fraction. The Σ PBDEwo209 is declining significantly at 8 locations across the monitoring network, without exhibiting any upward trends. Notably, this fraction dropped at an identical rate (–15%) at both the remote Izaña site and coastal Santa Cruz (Fig. S15), indicating a synchronized depletion of the global free troposphere background rather than strictly local coastal sources. However, a highly distinct scenario emerges for BDE-209. Due to its late restriction, BDE-209 continues to show steady or rising atmospheric levels globally, even in remote environments such as the Norwegian Arctic [21,35,64]. Within the SMP-POPs, BDE-209 increased significantly in several locations (e.g., Noia, Mahón, and A Coruña), but most notably in the southwest, specifically in Huelva (APC +25%) and the adjacent Doñana National Park (+45%). The localized surge in the Huelva-Doñana region strongly suggests the presence of ongoing local emissions of BDE-209. The Huelva industrial pole is one of the largest metallurgical and chemical complexes in southern Europe, historically associated with heavy industrial processing and waste management. The continuous mechanical degradation of Deca-BDE-treated plastics in this industrial hub likely acts as a primary emitter of particle-bound BDE-209 [65,66], which is subsequently advected by regional sea breezes directly into the neighboring protected area of Doñana, completely masking any regulatory-driven decline.

4. Conclusions

The continuous 15-year monitoring of atmospheric POPs across the SMP-POPs provides strong evidence of the overall success of the SC while highlighting critical ongoing environmental challenges. The rapid, generalized depletion of early-banned compounds, specifically HCB, legacy pesticides (endosulfan, DDXs, and HCHs), and lighter PBDEs, aligns with ongoing depletion of historically burdened environmental reservoirs. However, this regulatory success is starkly contrasted by the persistence of PeCB and iPCBs, alongside localized surges in BDE-209. These resistant atmospheric loads appear to be sustained by a combination of continuous unintentional combustion emissions, extended regulatory lag times associated with active consumer goods, and the urban heat island effect promoting the secondary volatilization of legacy sinks. Furthermore, our thermodynamic analyses reveal that while local secondary re-emissions strictly govern regional boundary layers, high-altitude remote observatories reflect the gradual clearing of the global free troposphere. Ultimately, this long-term dataset reinforces that while historical bans are highly effective, sustained national-scale monitoring is essential to track unintentional emissions, identify contemporary urban and industrial hotspots, and inform future environmental policies.

CRedit authorship contribution statement

Begoña Jiménez: Writing – review & editing, Validation, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Data curation, Conceptualization. **María Ángeles Martínez:** Writing – review & editing, Validation, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Data curation, Conceptualization. **Adrián de la Torre:** Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation.

Juan Muñoz-Arnanz: Writing – review & editing, Validation, Methodology, Investigation, Data curation. **Irene Navarro:** Writing – review & editing, Validation, Methodology, Investigation, Data curation. **Pere Colomer-Vidal:** Writing – review & editing, Validation, Methodology, Investigation, Formal analysis, Data curation. **Covadonga Alonso:** Writing – review & editing, Validation, Methodology, Investigation, Data curation. **Roscales José Luis:** Validation, Methodology, Investigation, Data curation. **Ángeles Jiménez:** Funding acquisition, Conceptualization. **Ana García:** Funding acquisition, Conceptualization.

Statement of significance

Persistent organic pollutants (POPs), including PBDEs, PCBs, and legacy pesticides, are toxic, bioaccumulative hazardous materials posing severe risks to ecosystems and human health. This 15-year atmospheric monitoring study evaluates the effectiveness of the Stockholm Convention. While early-banned POPs show rapid environmental depletion, we demonstrate that urban areas remain critical emission hotspots. We identify the urban heat island effect as a key thermodynamic driver for the secondary outgassing of trapped residues. By uncovering these mechanisms and identifying stalled depletion for late-regulated POPs like BDE–209, this work provides crucial empirical evidence to refine mitigation strategies and safeguard populated regions.

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.

Acknowledgments

This work has been supported by the Spanish Ministry for the Ecological Transition and the Demographic Challenge (MITECO) under the projects “Protocolo de Actuación entre la Dirección General de Calidad y Evaluación Ambiental del MITECO y el CIEMAT en materia de contaminación atmosférica y contaminantes orgánicos persistentes”, Ref.: P2021/10195 and “Protocolo general de actuación entre la Dirección General de Calidad y Evaluación ambiental y la Agencia Estatal CSIC en materia de contaminación atmosférica y por contaminantes orgánicos persistentes”, Ref. 2018TE003. We thank all partners involved in field sampling and analytical activities across the IQOG-CSIC and CIEMAT teams.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jhazmat.2026.143155](https://doi.org/10.1016/j.jhazmat.2026.143155).

Data availability

Data will be made available on request.

References

- [1] UNEP, 2025. Stockholm Convention on Persistent Organic Pollutants (POPS), Text and Annexes, Revised in 2025.
- [2] De la Torre, A., Sanz, P., Navarro, I., Martínez, M.Á., 2016. Time trends of persistent organic pollutants in Spanish air. *Environ Pollut* 217, 26–32. <https://doi.org/10.1016/j.envpol.2016.01.040>.
- [3] Muñoz-Arnanz, J., Roscales, J.L., Vicente, A., Ros, M., Barrios, L., Morales, L., Abad, E., Jiménez, B., 2018. Assessment of POPs in air from Spain using passive sampling from 2008 to 2015. Part II: Spatial and temporal observations of PCDD/Fs and dl-PCBs. *Sci Total Environ* 634, 1669–1679. <https://doi.org/10.1016/j.scitotenv.2018.04.164>.
- [4] Roscales, J.L., Muñoz-Arnanz, J., Ros, M., Vicente, A., Barrios, L., Jiménez, B., 2018. Assessment of POPs in air from Spain using passive sampling from 2008 to 2015. Part I: Spatial and temporal observations of PBDEs. *Sci Total Environ* 634, 1657–1668. <https://doi.org/10.1016/j.scitotenv.2018.03.043>.
- [5] Muñoz-Arnanz, J., Roscales, J.L., Ros, M., Vicente, A., Jiménez, B., 2016. Towards the implementation of the Stockholm Convention in Spain: Five-year monitoring (2008–2013) of POPs in air based on passive sampling. *Environ Pollut* 217, 1–7. <https://doi.org/10.1016/j.envpol.2016.01.052>.
- [6] UNEP, 2025. Guidance on the global monitoring plan for persistent organic pollutants. UNEP/POPS/COP.12/INF/43.
- [7] Wania, F., Shunthirasingham, C., 2020. Passive air sampling for semi-volatile organic chemicals. *Environ Sci Process Impacts* 22, 1925–2002. <https://doi.org/10.1039/d0em00194e>.
- [8] Eng, A., Hsu, Y.M., Harner, T., Mastin, J., Wheadon, S., 2026. Twenty-Five Years of Research and Monitoring Using PUF Disk Passive Air Samplers. *Environ Sci Technol* 60, 11833–11870. <https://doi.org/10.1021/ACS.EST.5C17602>.
- [9] Harner, T., 2025. Template Calc PUF SIP Disk Sample air Vol June9. <https://doi.org/10.13140/RG.2.2.28436.00643>.
- [10] Ding, Y., Song, Z., Li, Y., Zhan, F., Du, L., Tang, H., Huang, H., Zhang, Y., Qi, S., 2026. Occurrence and health risks of persistent organic pollutants in urban environments on the Tibetan Plateau: Insights from one-year monitoring of soil and air across four elevation-gradient county seats. *J Hazard Mater* 501, 140632. <https://doi.org/10.1016/j.jhazmat.2025.140632>.
- [11] AMAP, 2014. Trends in Stockholm Convention Persistent Organic Pollutants (POPS) in Arctic Air, Human Media and Biota. AMAP Technical Report to the Stockholm Convention. AMAP Technical Report No. 7 (2014), Arctic Monitoring and Assessment Programme (AMAP), Oslo, Norway. Arctic Monitoring and Assessment Programme.
- [12] OSPAR, 2023. CEMP Assessment Manual: Coordinated Environmental Monitoring Programme. OSPAR Commission, London. Available at: www.ospar.org.
- [13] Chen, S.J., Tsai, J.H., Chang-Chien, G.P., Huang, K.L., Wang, L.C., Lin, W.Y., Lin, C. C., Yeh, C.K.J., 2017. Emission factors and congener-specific characterization of PCDD/Fs, PCBs, PBDD/Fs and PBDEs from an off-road diesel engine using waste cooking oil-based biodiesel blends. *J Hazard Mater* 339, 274–280. <https://doi.org/10.1016/j.jhazmat.2017.06.045>.
- [14] Wang, L.C., Lee, W.J., Lee, W.S., Chang-Chien, G.P., 2010. Emission estimation and congener-specific characterization of polybrominated diphenyl ethers from various stationary and mobile sources. *Environ Pollut* 158, 3108–3115. <https://doi.org/10.1016/j.envpol.2010.06.041>.
- [15] Wang, C., Wang, X., Gong, P., Yao, T., 2018. Long-term trends of atmospheric organochlorine pollutants and polycyclic aromatic hydrocarbons over the southeastern Tibetan Plateau. *Sci Total Environ* 624, 241–249. <https://doi.org/10.1016/j.scitotenv.2017.12.140>.
- [16] Mao, S., Zhang, G., Li, J., Geng, X., Wang, J., Zhao, S., Cheng, Z., Xu, Y., Li, Q., Wang, Y., 2020. Occurrence and sources of PCBs, PCNs, and HCB in the atmosphere at a regional background site in east China: Implications for combustion sources. *Environ Pollut* 262, 114267. <https://doi.org/10.1016/j.envpol.2020.114267>.
- [17] Gong, W., Fiedler, H., Liu, X., Wang, B., Yu, G., 2017. Emission factors of unintentional HCB and PeCBz and their correlation with PCDD/PCDF. *Environ Pollut* 230, 516–522. <https://doi.org/10.1016/j.envpol.2017.05.082>.
- [18] Martínez Valenzuela, C., Gavilán García, A., Conde Avila, V., Barrientos Alemán, D., Apodaca Avalos, M., Luna Valdez, J.G., Castro Carranza, G., Masías Ambríz, L.O., 2022. Applying the Global Monitoring Plan and analysis of POPs results in atmospheric air in Mexico (2017–2018). *Chemosphere* 303, 135154. <https://doi.org/10.1016/j.chemosphere.2022.135154>.
- [19] Fiedler, H., de Boer, J., Abad, E., 2024. Persistent organic pollutants in air across the globe using a comparative passive air sampling method. *TrAC - Trends Anal Chem* 171, 117494. <https://doi.org/10.1016/j.trac.2023.117494>.
- [20] Wang, L., Ma, W.L., Yang, P.F., Huo, C.Y., Hu, P.T., Li, W.L., Fu, M.Q., 2025. Occurrence, spatial-seasonal variation and air-soil exchange of traditional and novel organochlorine pesticides across 30° latitude in Eastern China: Old tales and new realities. *J Hazard Mater* 490, 137772. <https://doi.org/10.1016/j.jhazmat.2025.137772>.
- [21] White, K.B., Kalina, J., Scheringer, M., Příbylová, P., Kukučka, P., Kohoutek, J., Prokeš, R., Klánová, J., 2023. Spatial and Temporal Trends of Persistent Organic Pollutants across Europe after 15 Years of MONET Passive Air Sampling. *Environ Sci Technol* 57, 11583–11594. <https://doi.org/10.1021/acs.est.3c00796>.
- [22] Prithiviraj, B., Lee, H.Y., Khuman, S.N., Kim, H.J., Hwang, S.M., Lee, C.H., Choi, S. D., 2025. Spatio-temporal variations of air- and soil-borne hexachlorobenzene and pentachlorobenzene: A decadal nationwide assessment in South Korea. *Atmos Environ* 356, 121306. <https://doi.org/10.1016/j.atmosenv.2025.121306>.
- [23] Lee, H.Y., Choi, S.D., Park, M.K., Lee, Y.S., Kim, C.S., Kim, C.H., Chang, L.S., 2025. Long-range atmospheric transport of organochlorine pesticides from China to South Korea: Evidence from Deokjeok Island. *Chemosphere* 370. <https://doi.org/10.1016/j.chemosphere.2024.143964>.
- [24] Chen, P., Gong, W., Yu, G., Fiedler, H., 2019. Preliminary release inventories of unintentionally generated dl-PCB and HCB from sources in China: Base year 2015. *Chemosphere* 219, 875–881. <https://doi.org/10.1016/j.chemosphere.2018.12.098>.
- [25] Bailey, R.E., 2001. Global hexachlorobenzene emissions. *Chemosphere* 43, 167–182.
- [26] Liu, G., Liu, W., Cai, Z., Zheng, M., 2013. Concentrations, profiles, and emission factors of unintentionally produced persistent organic pollutants in fly ash from coking processes. *J Hazard Mater* 261, 421–426. <https://doi.org/10.1016/j.jhazmat.2013.07.063>.
- [27] Liu, X., Fiedler, H., Gong, W., Wang, B., Yu, G., 2018. Potential sources of unintentionally produced PCB, HCB, and PeCBz in China: A preliminary overview. *Front Environ Sci Eng* 12. <https://doi.org/10.1007/s11783-018-1036-9>.

- [28] Gong, P., Wang, X., 2021. Forest fires enhance the emission and transport of persistent organic pollutants and polycyclic aromatic hydrocarbons from the central Himalaya to the Tibetan Plateau. *Environ Sci Technol Lett* 8, 498–503. <https://doi.org/10.1021/acs.estlett.1c00221>.
- [29] Birgül, A., Kurt-Karakuş, P.B., 2024. Air monitoring of organochlorine pesticides (OCPs) in Bursa Türkiye: Levels, temporal trends and risk assessment. *Sci Total Environ* 912. <https://doi.org/10.1016/j.scitotenv.2023.169397>.
- [30] Hao, Y., Li, Y., Han, X., Wang, T., Yang, R., Wang, P., Xiao, K., Li, W., Lu, H., Fu, J., Wang, Y., Shi, J., Zhang, Q., Jiang, G., 2019. Air monitoring of polychlorinated biphenyls, polybrominated diphenyl ethers and organochlorine pesticides in West Antarctica during 2011–2017: Concentrations, temporal trends and potential sources. *Environ Pollut* 249, 381–389. <https://doi.org/10.1016/j.envpol.2019.03.039>.
- [31] Lunder Halvorsen, H., Bohlin-Nizzetto, P., Eckhardt, S., Gusev, A., Moeckel, C., Shatalov, V., Skogeng, L.P., Breivik, K., 2023. Spatial variability and temporal changes of POPs in European background air. *Atmos Environ* 299. <https://doi.org/10.1016/j.atmosenv.2023.119658>.
- [32] Lunder Halvorsen, H., Bohlin-Nizzetto, P., Eckhardt, S., Gusev, A., Krogseth, I.S., Moeckel, C., Shatalov, V., Skogeng, L.P., Costa, P.G., de Azevedo, A., Gonzalez, M., Miglioranza, K.S.B., Ondarza, P.M., Costa, P.G., de Azevedo, A., Gonzalez, M., Shimabukuro, V.M., Grondona, S.I., Milton, F.M., Barra, R.O., Wania, F., Fillmann, G., 2021. Spatial and temporal distribution of Persistent Organic Pollutants and current use pesticides in the atmosphere of Argentinean Patagonia. *Chemosphere* 266. <https://doi.org/10.1016/j.chemosphere.2020.129015>.
- [33] UNEP, 2021. Global monitoring plan for persistent organic pollutants. Third regional monitoring report (GMP-3) Western Europe and others group (WEOG) Region.
- [34] Wong, F., Hung, H., Dryfhout-Clark, H., Aas, W., Bohlin-Nizzetto, P., Breivik, K., Mastrodonato, M.N., Lundén, E.B., Ólafsdóttir, K., Sigurðsson, A., Vorkamp, K., Bossi, R., Skov, H., Hakola, H., Barresi, E., Sverko, E., Fellin, P., Li, H., Vlasenko, A., Zapevalov, M., Samsonov, D., Wilson, S., 2021. Time trends of persistent organic pollutants (POPs) and Chemicals of Emerging Arctic Concern (CEAC) in Arctic air from 25 years of monitoring. *Sci Total Environ* 775. <https://doi.org/10.1016/j.scitotenv.2021.145109>.
- [35] Luarte, T., Hirmas-Olivares, A., Höfer, J., Giesecke, R., Mestre, M., Guajardo-Leiva, S., Castro-Nallar, E., Pérez-Parada, A., Chiang, G., Lohmann, R., Dachs, J., Nash, S.B., Pulgar, J., Pozo, K., Příbylová, P.P., Martín, J., Galbán-Malagón, C., 2024. Occurrence and diffusive air-seawater exchanges of organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) in Fildes Bay, King George Island, Antarctica. *Sci Total Environ* 908. <https://doi.org/10.1016/j.scitotenv.2023.168323>.
- [36] Guida, Y., Carvalho, G.O. de, Capella, R., Pozo, K., Lino, A.S., Azeredo, A., Carvalho, D.F.P., Braga, A.L.F., Torres, J.P.M., Meire, R.O., 2021. Atmospheric Occurrence of Organochlorine Pesticides and Inhalation Cancer Risk in Urban Areas at Southeast Brazil. *Environ Pollut* 271. <https://doi.org/10.1016/j.envpol.2020.116359>.
- [37] Massagué, J., Torre-Pascual, E., Carnerero, C., Escudero, M., Alastuey, A., Pandolfi, M., Querol, X., Gangoli, G., 2024. Extreme ozone episodes in a major Mediterranean urban area. *Atmos Chem Phys* 24, 4827–4850. <https://doi.org/10.5194/ACP-24-4827-2024>.
- [38] Lee, M., Lee, S., Noh, S., Park, K.S., Yu, S.M., Lee, S., Do, Y.S., Kim, Y.H., Kwon, M., Kim, H., Park, M.K., 2022. Assessment of organochlorine pesticides in the atmosphere of South Korea: spatial distribution, seasonal variation, and sources. *Environ Monit Assess* 194. <https://doi.org/10.1007/s10661-022-10335-x>.
- [39] Spencer, W.F., Singh, G., Taylor, C.D., Lemert, R.A., Cliath, M.M., Farmer, W.J., 1996. DDT Persistence and Volatility as Affected by Management Practices after 23 Years. *J Environ Qual* 25, 815–821.
- [40] Qiu, X., Zhu, T., Yao, B., Hu, J., Hu, S., 2005. Contribution of Dicofof to the Current DDT Pollution in China. *Environ Sci Technol* 39, 4385–4390. <https://doi.org/10.1021/ES050342A>.
- [41] Pozo, K., Gómez, V., Tucça, F., Galbán-Malagón, C., Ahumada, R., Rudolph, A., Klánová, J., Lamm, G., 2022. Multicompartmental analysis of POPs and PAHs in Concepción Bay, central Chile: Part II – Air-sea exchange during Austral summer. *Mar Pollut Bull* 177. <https://doi.org/10.1016/j.marpolbul.2022.113518>.
- [42] Hites, R.A., Venier, M., 2023. Good News: Some Insecticides Have Been Virtually Eliminated in Air near the Great Lakes. *Environ Sci Technol* 57, 2199–2204. <https://doi.org/10.1021/acs.est.2c08318>.
- [43] Marañés Antonanzas, I., López Gallardo, Y., García de Oro, Á., Gutiérrez González, C., Peyró Sánchez, R., Sánchez Martínez, S., 2025. Historical evolution of the epidemiology of Malaria in Spain and Europe. Future perspectives. *Eur J Clin Microbiol Infect Dis* 44, 2597–2607. <https://doi.org/10.1007/s10096-025-05246-x>.
- [44] Ordóñez, J.M., De La O Álvarez, M., González, M.L., 2018. Evolution of the legal vector control framework in Spain: 1945–2017. Proposals for the future. *Span J Environ Health* 18, 19–28. <https://doi.org/www.ojs.diffundit.com/index.php/rsa/article/view/898>.
- [45] Salvadó, V., Quintana, X.D., Hidalgo, M., 2006. Monitoring of nutrients, pesticides, and metals in waters, sediments, and fish of a wetland. *Arch Environ Contam Toxicol* 51, 377–386. <https://doi.org/10.1007/s00244-005-0107-7>.
- [46] Salvadó, V., Alcaide, A., Carandell, N., Hidalgo, M., 2001. Evaluation of Extraction Procedures of Organochlorine Pesticides from Natural Waters and Sediments. *Int J Environ Anal Chem* 81, 243–256. <https://doi.org/10.1080/03067310108044247>.
- [47] Barber, J.L., Sweetman, A.J., Van Wijk, D., Jones, K.C., 2005. Hexachlorobenzene in the global environment: Emissions, levels, distribution, trends and processes. *Sci Total Environ* 349, 1–44. <https://doi.org/10.1016/j.scitotenv.2005.03.014>.
- [48] Llanos, Y., Cortés, S., Martínez, A., Pozo, K., Příbylová, P., Klánová, J., Jorquera, H., 2022. Local and regional sources of organochlorine pesticides in a rural zone in central Chile. *Atmos Pollut Res* 13. <https://doi.org/10.1016/j.apr.2022.101411>.
- [49] Khoury, D., Jabali, Y., Delhomme, O., Millet, M., 2024. Pesticide occurrence and distribution in fogwater collected at four sites at Strasbourg metropolitan between 2015 and 2021. *Environ Pollut* 359. <https://doi.org/10.1016/j.envpol.2024.124564>.
- [50] Tominaga, M.Y., Silva, C.R., Melo, J.P., Niwa, N.A., Plascak, D., Souza, C.A.M., Sato, M.I.Z., 2016. PCDD, PCDF, dl-PCB and organochlorine pesticides monitoring in São Paulo City using passive air sampler as part of the Global Monitoring Plan. *Sci Total Environ* 571, 323–331. <https://doi.org/10.1016/j.scitotenv.2016.07.173>.
- [51] Surejav, E., Fiedler, H., 2023. POPs in the Mongolian environment. *Emerg Contam* 9. <https://doi.org/10.1016/j.emcon.2023.100251>.
- [52] Fiedler, H., Abad, E., de Boer, J., 2023. Preliminary trends over ten years of persistent organic pollutants in air - Comparison of two sets of data in the same countries. *Chemosphere* 324. <https://doi.org/10.1016/j.chemosphere.2023.138299>.
- [53] Kalina, J., White, K.B., Scheringer, M., Příbylová, P., Kukučka, P., Audy, O., Klánová, J., 2019. Comparability of long-term temporal trends of POPs from co-located active and passive air monitoring networks in Europe. *Environ Sci Process Impacts* 21, 1132–1142. <https://doi.org/10.1039/c9em00136k>.
- [54] Santa-Marina, L., Barroeta, Z., Irizar, A., Alvarez, J.L., Abad, E., Muñoz-Arnan, J., Jiménez, B., Ibarluzea, J., Urbieto, N., Jimeno-Romero, A., Zubero, M.B., Lertxundi, A., 2023. Characterization of PCDD/F and dl-PCB levels in air in Gipuzkoa (Basque Country, Spain). *Environ Res* 228. <https://doi.org/10.1016/j.envres.2023.115901>.
- [55] Mastin, J., Harner, T., Schuster, J.K., South, L., 2022. A review of PCB-11 and other unintentionally produced PCB congeners in outdoor air. *Atmos Pollut Res* 13. <https://doi.org/10.1016/j.apr.2022.101364>.
- [56] Barbas, B., de la Torre, A., Sanz, P., Navarro, I., Artíñano, B., Martínez, M.A., 2018. Gas/particle partitioning and particle size distribution of PCDD/Fs and PCBs in urban ambient air. *Sci Total Environ* 624, 170–179. <https://doi.org/10.1016/j.scitotenv.2017.12.114>.
- [57] Breivik, K., Sweetman, A., Pacyna, J.M., Jones, K.C., 2002. Towards a global historical emission inventory for selected PCB congeners-a mass balance approach 1. Global production and consumption. *Sci Total Environ* 290, 181–198. [https://doi.org/10.1016/S0048-9697\(01\)01075-0](https://doi.org/10.1016/S0048-9697(01)01075-0).
- [58] Fernandez, P., van Drooge, B.L., Arellano, L., Grimalt, J.O., 2021. Atmospheric deposition of semivolatile organic pollutants in European high mountains: Sources, settling and chemical degradation. *Sci Total Environ* 784. <https://doi.org/10.1016/j.scitotenv.2021.147099>.
- [59] Dien, N.T., Hirai, Y., Koshiba, J., Sakai, S., 2021. Factors affecting multiple persistent organic pollutant concentrations in the air above Japan: A panel data analysis. *Chemosphere* 277. <https://doi.org/10.1016/j.chemosphere.2021.130356>.
- [60] Breivik, K., Wania, F., Muir, D.C.G., Alae, M., Backus, S., Pacepavicius, G., 2006. Empirical and modeling evidence of the long-range atmospheric transport of decabromodiphenyl ether. *Environ Sci Technol* 40, 4612–4618. <https://doi.org/10.1021/es060730s>.
- [61] Xie, Z., Möller, A., Ahrens, L., Sturm, R., Ebinghaus, R., 2011. Brominated flame retardants in seawater and atmosphere of the Atlantic and the southern ocean. *Environ Sci Technol* 45, 1820–1826. <https://doi.org/10.1021/es103803t>.
- [62] Li, Y.F., Qiao, L.N., Ren, N.Q., Sverko, E., Mackay, D., Macdonald, R.W., 2017. Decabrominated diphenyl ethers (BDE-209) in Chinese and global air: Levels, gas/particle partitioning, and long-range transport: Is long-range transport of BDE-209 really governed by the movement of particles? *Environ Sci Technol* 51, 1035–1042. <https://doi.org/10.1021/acs.est.6b05395>.
- [63] de Boer, J., van Dijk, R., Abalos, M., Abad, E., 2023. Persistent organic pollutants in air from Asia, Africa, Latin America, and the Pacific. *Chemosphere* 324. <https://doi.org/10.1016/j.chemosphere.2023.138271>.
- [64] Li, H., Wang, Z., He, J., Zhang, N., Mao, X., Ma, J., Gao, H., Yang, Z., Ma, H., 2023. Deca-BDE emissions, validation, and environmental fate in China. *J Hazard Mater* 459, 132223. <https://doi.org/10.1016/J.JHAZMAT.2023.132223>.
- [65] Redfern, F.M., Lee, W.J., Yan, P., Mwangi, J.K., Wang, L.C., Shih, C.H., 2017. Overview and Perspectives on Emissions of Polybrominated Diphenyl Ethers on a Global Basis: Evaporative and Fugitive Releases from Commercial PBDE Mixtures and Emissions from Combustion Sources. *Aerosol Air Qual Res* 17, 1117–1131. <https://doi.org/10.4209/AAQR.2016.12.0579>.