

Supplement of

The representativeness of observed Δt in calculating formation and growth rates of newly formed atmospheric particles – hypothesis and examination

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Text S1 PMF apportionment analysis of robust negative bias associated with the SMPS

Data analysis methods

The positive matrix factorization (PMF) model was employed to identify and apportion the negative bias in N_{total} measured by the SMPS relative to the CPC ($N_{\text{total}}^{\text{(CPC-SMPS)}}$), utilizing indoor PNSDs data. Hourly averaged PNSDs spanning 113 size bins were used as the primary input variables. To reduce uncertainties associated with low counting efficiency and insufficient data acquisition in the largest size range, the observed negative bias (scaled by a factor of 10^{-2}) was incorporated as an additional diagnostic variable by replacing the final size bin. This variable was used as a diagnostic parameter in the PMF analysis rather than representing a physical particle size bin. The optimal number of factors was determined based on the Q/Q_{exp} ratio, residual distributions, and the physical interpretability of the resolved factors (Ogulei et al., 2007; Sun et al., 2024). After 20 independent runs, a robust solution was obtained with a Q/Q_{exp} ratio of approximately 1.1.

PMF-based apportionment analysis results

In this section, we first applied PMF to identify the sources of the 23% negative bias between May 11 and May 20 (Category 1) and to quantify the contribution of each factor to the overall discrepancy (Fig. S2). The same approach was subsequently applied to the more complex cases represented by Category 2a and 2b. For Category 1, four factors were identified and yielded excellent closure between the observed and the predicted N_{total} for both the original PNSDs and the modified PNSDs, in which the last bin was replaced by $N_{\text{total}}^{\text{(CPC-SMPS)}} \times 1/100$ (Fig. S2b, c). The closure analysis of $N_{\text{max-bin}}$ (the last size bin) showed an 8% underprediction by the PMF apportioning with R^2 of 0.81 (Fig. S2d). The closure for $N_{\text{total}}^{\text{(CPC-SMPS)}}$ slightly decreased, i.e., 15% underprediction with $R^2 = 0.71$ (Fig. S2e). Based on the robust result, the apportionment of the negative bias was predominantly driven by Factor 4 and Factor 2, which accounted for 43% and 38% of the total discrepancy, respectively. In contrast, Factor 3 contributed 18%, whereas the contribution of Factor 1 was negligible (1%) (Fig. S2a).

Factor 1 exhibited a unimodal PNSD with a peak at 74 nm and negligible loading at particle sizes ≤ 20 nm. Because the SMPS operates with high transmission efficiency and minimal diffusion losses above 20 nm, this factor contributed negligibly to overall measurement bias. In contrast, Factor 2 displayed a bimodal distribution, consisting of a dominant incomplete nucleation mode peak at particle sizes below 10 nm and a minor accumulation mode peak centered at 163 nm. The strong contribution of this factor to the bias was primarily attributed to the dominant nucleation mode loading, for which the SMPS experiences substantially low transmission efficiency and

diffusion losses. Distinct from the mode characteristics of Factors 1 and 2, Factor 3 exhibited a broad distribution with three comparable modes centered at 11 nm, 79 nm, and 157 nm, respectively. The moderate bias contribution of 18% (or ~4% absolute deviation) could be explained by the same mechanism as Factor 2, although the intrinsic systematic bias between the SMPS and CPC for particles in the size range > 20 nm cannot be completely excluded. However, the 4% likely represents its upper limit by combining the negligible contribution of Factor 1 to the overall bias. Finally, Factor 4 exhibited a unimodal Aitken mode distribution with a peak at 40 nm and contributed the largest fraction of the total measurement bias owing to its dominant particle loading. This large contribution most likely reflects the combined effects of reduced transmission efficiency for smaller particles and the intrinsic systematic differences between the SMPS and CPC.

For Category 2a, the negative bias was more complex, and five factors were identified. Factors 1, 2, 3 and 4 showed profiles closely resembling their corresponding counterparts identified in Category 1, whereas Factor 5 exhibited the lowest loading and likely represented the clean background contribution. Similar to Category 1, the model achieved excellent closure for the observed N_{total} (Fig. S3bc). The closure for $N_{\text{max-bin}}$ (the last size bin) was likewise comparable, with only a 9% underprediction and an R^2 of 0.87 (Fig. S3d). In contrast, the closure for $N_{\text{total (CPC-SMPS)}}$ deteriorated substantially, yielding a weak correlation ($R^2 = 0.30$) and a regression slope of only 0.21 (Fig. S3e). Given this limited predictive capability, the PMF attributed the observed negative bias primarily to Factor 2 (77%) and Factor 1 (23%). This result suggests that the negative bias in Category 2a lacks a coherent physical structure derived from stable source profiles; instead, it represents the manifestation of stochastic fluctuations within the negative domain. As presented in Section 3.2-3.4, the root cause lies in microscale spatial inhomogeneity of State 1 NPF within the indoor environment, where transient concentration gradients caused the collocated instruments to sample instantaneously disparate air parcels. For Category 2b, the perturbation effect from micro-scale spatial inhomogeneity of State 1 NPF likely overwhelmed the systematic bias between the two instruments. The negative values of $N_{\text{total (CPC-SMPS)}}$ were thereby unresolved by the PMF (not shown).

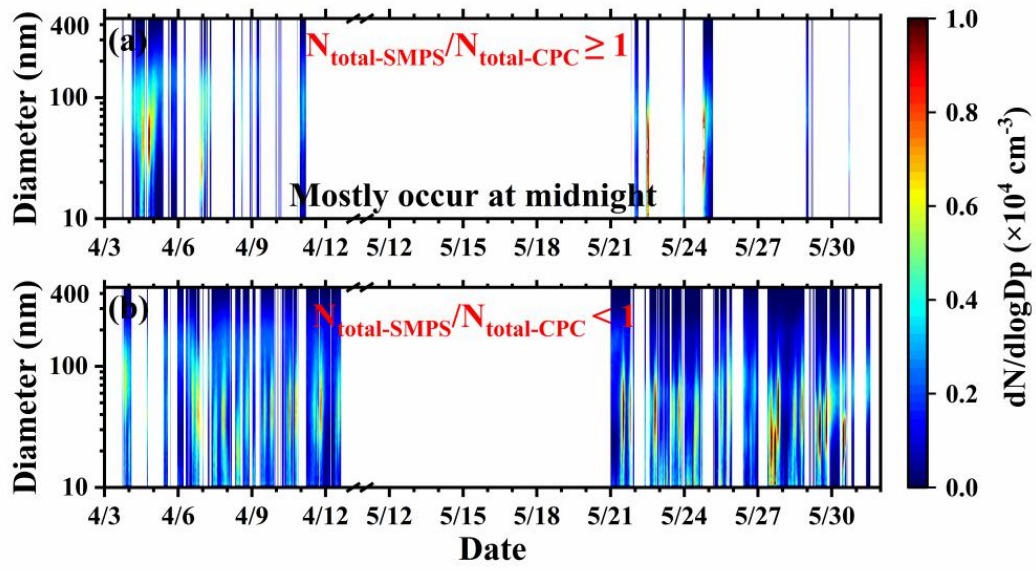


Figure S1. Contour plot of PNSDs for (a) $N_{\text{total-SMPS}} / N_{\text{total-CPC}} \geq 1$ and (b) $N_{\text{total-SMPS}} / N_{\text{total-CPC}} < 1$, based on indoor observations on 3–12 April and 21–31 May, 2025.

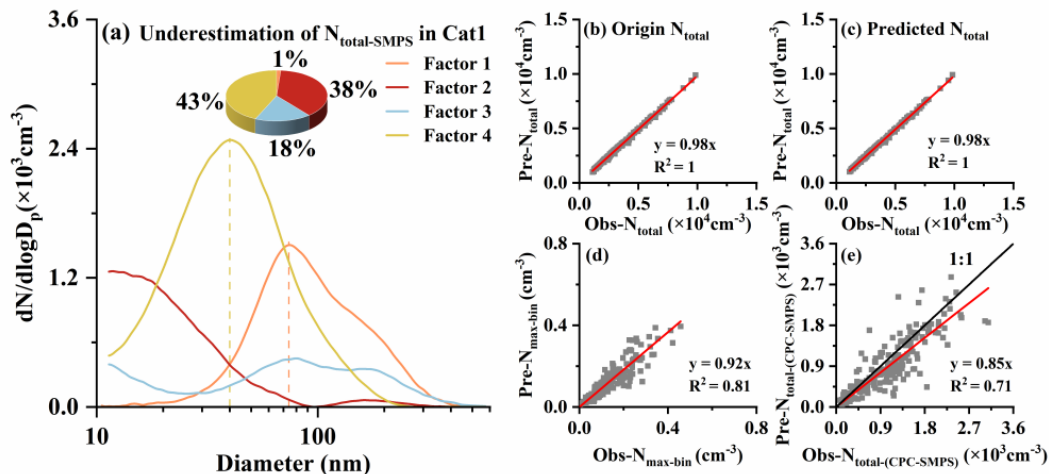


Figure S2. PMF analysis of the negative bias in N_{total} (CPC-SMPS) during 11–20 May 2025 (Category 1). (a) Factor size profiles and relative contributions; (b, c) Closure of total particle number concentrations using original PNSDs and modified PNSDs with N_{total} (CPC-SMPS) assigned to the final diagnostic size bin; (d) Closure of the largest particle size bin in the PNSD; (e) Closure of N_{total} (CPC-SMPS). As described for Factors 1–4 in Text S1, Factors 2 and 4 represented particle populations dominated by nucleation-mode and Aitken-mode particles, respectively, and accounted for 38% and 43% of the negative bias. This indicates that the SMPS underestimation was primarily associated with small particles.

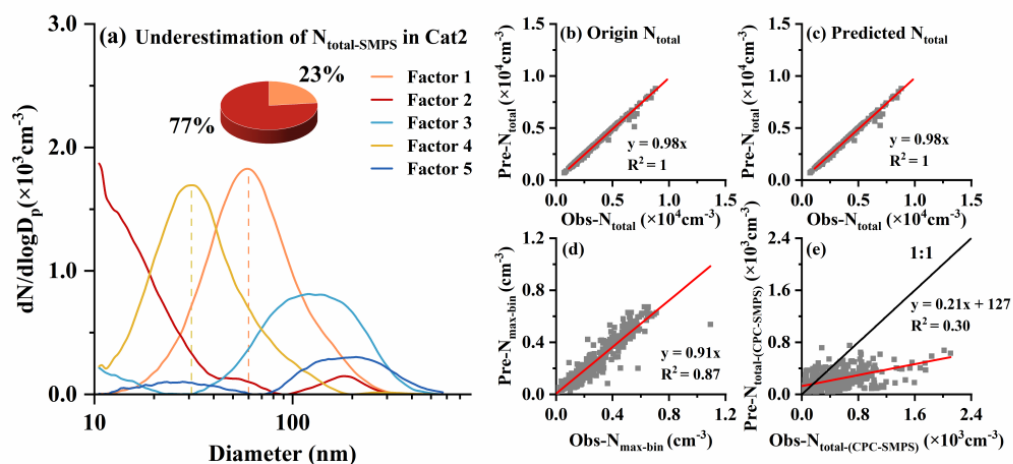


Figure S3. PMF analysis of the negative bias in N_{total} (CPC-SMPS) during 3–12 April and 21–31 May 2025 (Category 2). (a) Factor size profiles and relative contributions; (b, c) Closure of total particle number concentrations using original PNSDs and modified PNSDs with N_{total} (CPC-SMPS) replacing the particle number concentration of the largest particle size bin; (d) Closure of the largest particle size bin in the PNSD; (e) Closure of N_{total} (CPC-SMPS). As described for Factors 1–5 in Text S1, Factor 2 represented a particle population dominated by nucleation-mode particles and accounted for 77% of the negative bias.

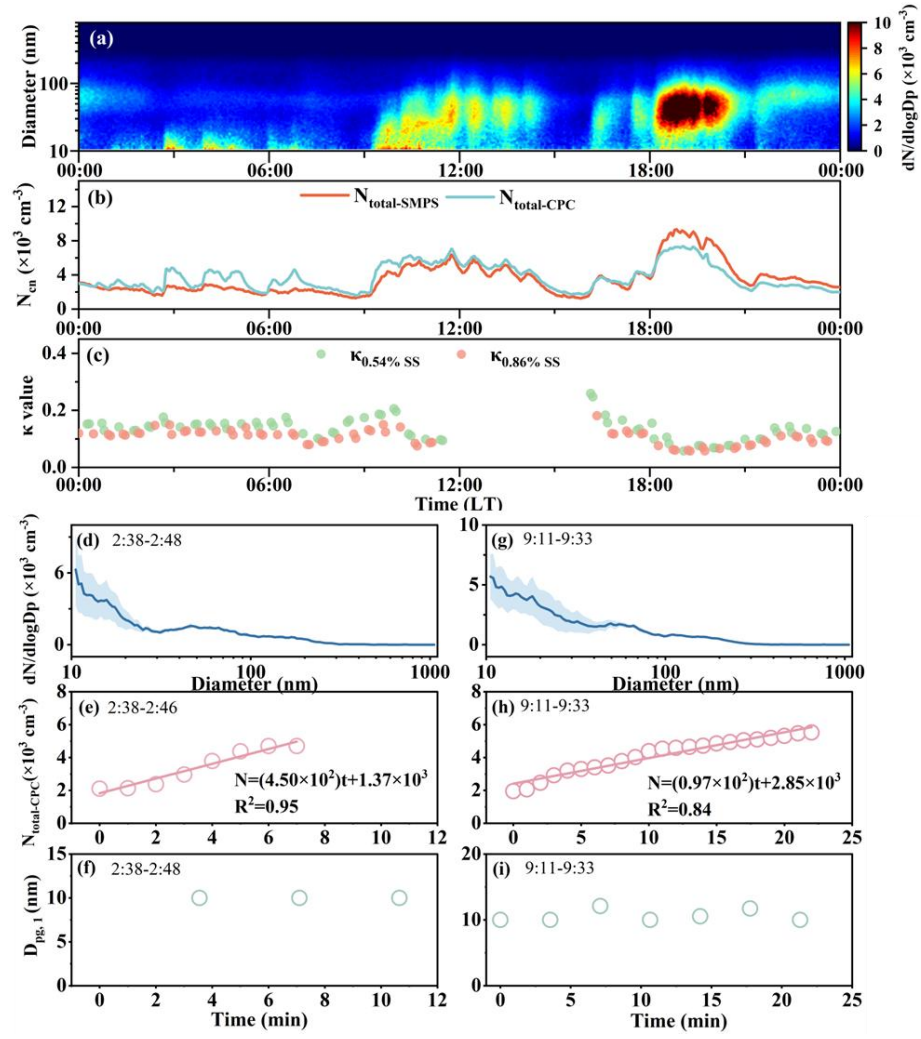


Figure S4. Comparison of two indoor NPF events observed on 24 May 2025 (Case 3 and Case 4). (a) temporal evolution of PNSDs; (b) total particle number concentrations measured by SMPS; (c) κ values retrieved at different SS; (d, g) mean PNSDs with standard deviations; (e, h) temporal evolution and linear regression of newly formed particle number concentration; (f, i) temporal evolution of the $D_{pg,1}$.

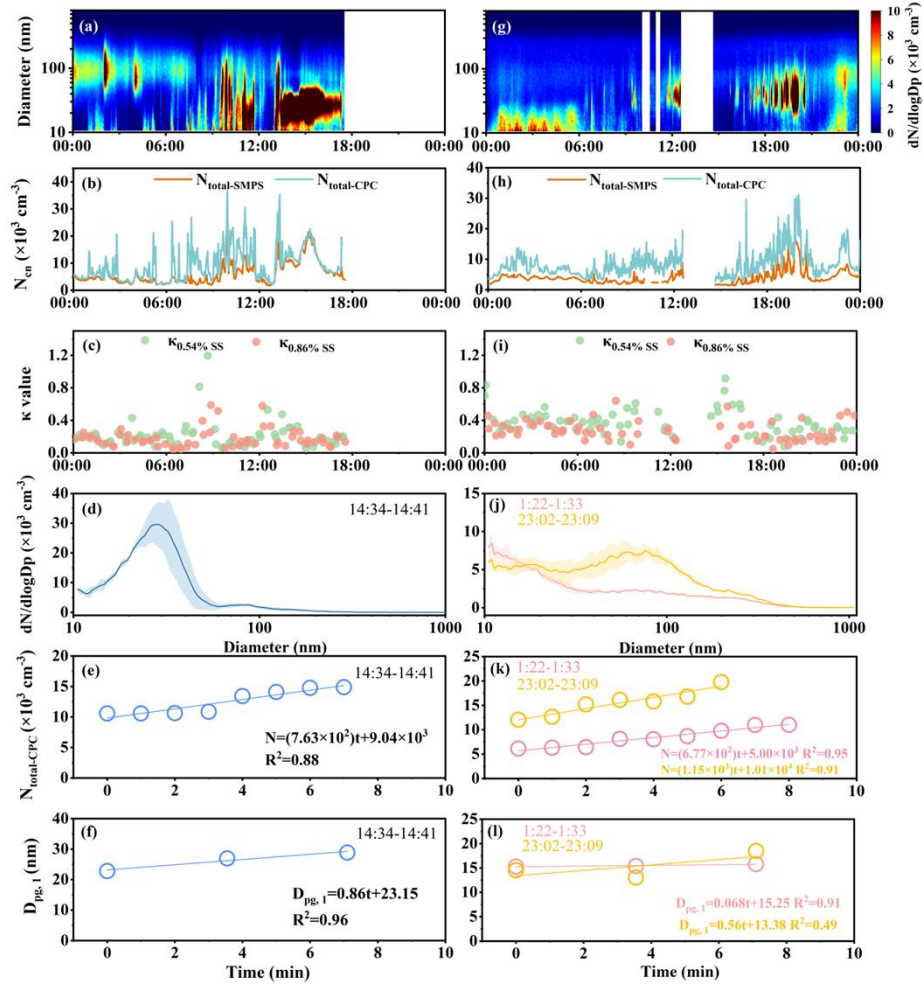


Figure S5. Comparison of three outdoor NPF events observed on 11 May 2025 (Case 5, a–f) and 20 April 2025 (Case 8 and 9, g–l). (a, g) temporal evolution of PNSDs; (b, h) total particle number concentrations measured by SMPS and CPC; (c, i) κ values retrieved at different SS; (d, j) mean PNSDs with standard deviations; (e, k) temporal evolution and linear regression of newly formed particle number concentration; (f, l) temporal evolution and linear regression of the $D_{\text{pg},1}$. In panels (j–l), pink and yellow denote Cases 8 and 9, respectively.

References

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