

This manuscript presents a four-season field investigation of primary IVOCs at an urban site in the Yangtze River Delta and explores the roles of temperature-dependent evaporative emissions and gas/particle partitioning in regulating their seasonal variability. The dataset is valuable, and the observed summer-maximum pattern provides useful insights into the atmospheric behavior of IVOCs. The manuscript is generally well organized and suitable for publication after minor revision. I have several comments that may help improve the clarity and robustness of the manuscript.

Reply: We sincerely appreciate your valuable and constructive comments and suggestions. We have provided our point-by-point responses below.

1. Lines 94–108: The field campaigns covered only approximately one week in each season (April 21–27, July 4–10, October 9–15, and December 14–20). Although this design provides observations across four seasons, short-term meteorological episodes may influence the apparent seasonal differences. The authors are encouraged to briefly discuss the representativeness of these sampling periods. For example, were the temperature, PM_{2.5}, and other meteorological conditions during each campaign generally representative of the corresponding seasonal conditions? This limitation should also be acknowledged when interpreting the seasonal patterns.

Reply: Thank you for the constructive and insightful comments. We fully agree that the relatively short duration of each field campaign (approximately one week per season) warrants careful discussion regarding the representativeness of the sampling periods. For example, the observed seasonal patterns should be interpreted as representative of typical seasonal conditions rather than capturing the full range of seasonal variability. As suggested, we have added a discussion on the representativeness of our sampling periods in the revised manuscript, which are also provided as follows:

“Each seasonal campaign lasted approximately one week, which may not capture the full spectrum of seasonal meteorological variability. Nonetheless, the variation trends of meteorological parameters (e.g., temperature) and air quality parameters (PM_{2.5}, CO, SO₂, NO₂, and O₃) recorded during each campaign broadly agreed with the corresponding seasonal features of this region (Table S2). The seasonal patterns reported herein should thus be interpreted as representative of typical seasonal conditions.” (Lines 97–103)

2. Lines 260–289: The authors attribute the very low gaseous concentrations of nC₁₉–nC₂₂ in winter and their negative relationship with PM_{2.5} primarily to gas/particle partitioning. This interpretation is reasonable given their relatively low volatility. However, PM_{2.5} concentrations can covary with temperature, boundary-layer dynamics, emission intensity,

and other meteorological factors. Therefore, statements such as “a direct consequence” of gas/particle partitioning appear somewhat strong based solely on the observed correlations. The authors are encouraged either to provide additional supporting evidence or to moderate the causal language and briefly discuss possible confounding factors.

Reply: Thank you for carefully reviewing our manuscript. We agree that the observed inverse relationship between gaseous low-volatility IVOCs (nC_{14} – nC_{22}) and $PM_{2.5}$ is a correlation, and that $PM_{2.5}$ concentration can covary on seasonal scales with temperature, BLH and primary emission intensity, any of which might contribute to the decline in gaseous low-volatility IVOCs. In the revised manuscript, we have made three main changes. **First**, we have moderated the causal language throughout the relevant sentences. **Second**, we have added explicit, largely independent lines of evidence that strengthen the partitioning interpretation beyond a single pairwise correlation. **Third**, we have added a dedicated paragraph acknowledging the possible confounding factors and a corresponding limitation statement. The revised texts are provided below:

*“these low-volatility species were nearly undetectable during the cold winter (Figure 3), which was **at least partially** due to their preferential partitioning into the particle phase under low ambient temperature (4.9 ± 1.0 °C, Table S3). This observation was consistent with higher gas/particle partitioning coefficients (K_p) for these species at lower temperature (Fang et al., 2022)”* (Lines 282–287)

“This exponential decline of nC_{14} – nC_{22} from the gas phase was largely consistent with their low saturation vapor pressures, which yield high K_p , and suggested that gas/particle partitioning was a dominant, though not exclusive, control on their gaseous abundances.” (Lines 296–299)

“Notably, $PM_{2.5}$ concentration could covary with ambient temperature, BLH and primary emission intensity on seasonal timescales, any of which may partly contribute to the observed decline in gaseous low-volatility IVOCs. Sensitivity to $PM_{2.5}$ strengthened monotonically with decreasing volatility (nC_{14} – nC_{15} to nC_{20} – nC_{22}), consistent with the expected increase in K_p . In contrast, high-volatility nC_{12} – nC_{13} remained insensitive to $PM_{2.5}$ loading, even though they were subject to identical emission and meteorological drivers. This species-selective, K_p -dependent pattern, alongside with the independent gas/particle partitioning factor resolved via PMF, cannot be attributed merely to generic covariation. Nevertheless, particle-bound IVOCs were not measured here. Next work is therefore recommended to conduct concurrent measurements of both gas- and particle-phase IVOCs to further elucidate the linkage between $PM_{2.5}$ and low-volatility IVOCs.” (Lines 306–317)

3. Lines 290–324: Both evaporative emissions and gas/particle partitioning are interpreted as

strongly temperature-dependent processes, particularly for the lower-volatility IVOCs. Therefore, it would be helpful if the authors could clarify how the relative roles of these two processes were distinguished based on the current observational dataset. In particular, the authors should explain more explicitly which observational evidence supports enhanced primary evaporative emissions versus particle-to-gas repartitioning. This clarification would strengthen the proposed “temperature–volatility dual-control framework.”

Reply: Thank you for the valuable comments. Although both evaporative emission and gas/particle partitioning are temperature-dependent, there are some differences existing between these two contributors.

1) Gas/particle partitioning is governed by the equilibrium between the gas phase and the particle phase and is therefore intrinsically tied to the amount of absorbing particulate matter through the gas/particle partitioning coefficient (K_p). Evaporative emission, in contrast, injects new gas-phase mass directly from sources and does not require an aerosol reservoir. We exploit this by examining the response of each volatility bin to $PM_{2.5}$ at a given temperature. Moderate- and low-volatility IVOCs (nC_{14} – nC_{22}) decayed exponentially with rising $PM_{2.5}$, with the sensitivity strengthening monotonically as volatility decreases (K_p increases), whereas high-volatility nC_{12} – nC_{13} remain unaffected (Section 3.2, Fig. 4a). This volatility-ordered, K_p -tracking dependence on aerosol loading is the fingerprint of partitioning. A purely emission-driven signal cannot reproduce it, because emission strength is set by source activity and temperature, not by $PM_{2.5}$ concentration. The high-volatility nC_{12} – nC_{13} serve as an internal control: they share the same sources and seasonal meteorology, but having low K_p , are insensitive to $PM_{2.5}$.

2) Isopentane, a recognized tracer of evaporative emissions (Zhang et al., 2013), showed significantly higher concentrations in summer than in the other three seasons ($p < 0.05$; Fig. S4). Because its summer enhancement can arise from temperature-dependent evaporative emission and not from repartitioning, it provides direct, partitioning-independent support that warmer seasons enhance primary evaporative emissions, which together with the exponential IVOC–temperature relationship underlies the observed summer maximum.

According to your comments and suggestions, we have added some sentences to explain how to distinguish these two contributors. The added text is also provided as follows:

“Overall, this volatility-ordered, K_p -tracking dependence on $PM_{2.5}$ concentration serves as a fingerprint of partitioning rather than an emission-driven signal. The latter is controlled by source activity and temperature, not by $PM_{2.5}$ concentrations.” (Lines 317–319)

“As a typical gaseous tracer for evaporative emissions (Zhang et al., 2013), isopentane is not subject to gas/particle partitioning and exhibits pronounced summertime enhancement

(Figure S4), indicative of temperature-dependent evaporative emission processes.” (Lines 326–329)

Reference

Zhang, Y.L., Wang, X.M., Zhang, Z., Lv, S.J., Shao, M., Lee, F.S.C., and Yu, J.Z.: Species profiles and normalized reactivity of volatile organic compounds from gasoline evaporation in China. *Atmos. Environ.*, 79, 110–118, <https://doi.org/10.1016/j.atmosenv.2013.06.029>, 2013.

4. Lines 349–378: The interpretation of Factor 3 as “gas/particle partitioning” deserves further clarification. Unlike vehicle exhaust, evaporative emissions, and industrial emissions, gas/particle partitioning is an atmospheric process rather than an emission source. The manuscript itself acknowledges that this factor “did not represent a conventional primary emission source.” The authors should therefore explain more clearly how PMF can quantitatively separate this process from temperature-dependent evaporative emissions and why the resulting 14.8% can be interpreted alongside conventional source contributions. It may also be more appropriate to consistently refer to the PMF results as “contributors” rather than “sources” when this factor is included.

Reply: Thank you for the valuable comments. We fully agree with the distinction you draw between atmospheric processes and primary emission sources, and recognize the necessity of standardizing terminology for describing PMF results. We have revised the manuscript accordingly and address this concern from following aspects below:

(a) How PMF quantitatively separates the gas/particle partitioning factor from evaporative emissions.

PMF resolved Factor 3 (gas/particle partitioning) from Factor 2 (evaporative emissions), as the two factors exhibit some differences in their chemical fingerprints, tracer couplings, and variation characteristics. Factor 3 is dominated by the low-volatility species (nC_{19} – nC_{22}), which are highly susceptible to phase transfer. This factor shows a pronounced exponential decay with increasing $PM_{2.5}$ concentrations, reflecting the condensation sink effect under high aerosol loading. In contrast, Factor 2 is dominated by lighter alkanes (nC_{12} – nC_{16}), and correlates with isopentane, a permanent gas with a gas/particle partitioning coefficient $K_p \sim 0$ that exists exclusively in the gas phase. Furthermore, Factor 2 displays no significant $PM_{2.5}$ dependence. Collectively, these distinct chemical fingerprints and response patterns demonstrate that our PMF model effectively differentiated evaporative emissions (a primary source) from gas/particle partitioning (an atmospheric process), even though both are temperature-sensitive.

(b) Why the resulting 14.8% can be interpreted alongside conventional source contributions. In PMF receptor model, the G matrix returns the contribution of each factor to the observed receptor concentration in mass units, regardless of whether the factor represents a primary emission source or an atmospheric process. For example, secondary formation has also frequently been identified as an important contributor in PMF-resolved aerosol sources (Zhao et al., 2023; Cai et al., 2026). The 14.8% attributed to Factor 3 is therefore comparable, in dimensionality and in physical meaning, to the contributions of the direct emission sources (e.g. 38.9% for evaporative emissions and 37.7% for vehicle exhaust). We would like to clarify that this 14.8% reflects the net impact of gas/particle partitioning on gas-phase IVOCs, not a distinct primary emission source.

As suggested, we have replaced “sources” with “contributors” when interpreting the PMF results in the revised manuscript. We have also added the following sentences to the Results and Discussion section:

“Notably, this factor was dominated by low-volatility $nC_{19} - nC_{22}$, which are susceptible to phase transfer. Furthermore, the IVOCs attributed to Factor 3 exhibited a strong positive correlation with temperature ($r = 0.79$, $p < 0.01$, Figure S9), consistent with the temperature-driven repartitioning of low-volatility organics from the particle phase to the gas phase (Zhou et al., 2024). This factor also showed a pronounced exponential decay with increasing $PM_{2.5}$ concentrations, reflecting the condensation sink effect under high aerosol loading. Hence, Factor 3 was interpreted as reflecting gas/particle partitioning processes, rather than a conventional primary source.” (Lines 405–412)

References

- Cai, M.F., Yuan, B., Hu, W.W., Chenshuo, Y., Huang, S., Yang, S.X., Chen, W., Peng, Y.W., Deng, Z.X., Zhao, J., Chen, D.H., Sun, J.R., and Shao, M.: New insight into the formation and aging processes of organic aerosol from positive matrix factorization (PMF) analysis of ambient FIGAERO-CIMS thermograms, *Atmos. Chem. Phys.*, 26, 769–788, <https://doi.org/10.5194/acp-26-769-2026>, 2026.
- Zhao, Y.Y., Hu, K., Wang, J., Wang, Q.Q., Wang, P., Chen, N., Zhu, B., Zhang, H.L., and Yu, H.: Quantifying new sources of ambient organic aerosol and their roles in particle growth using oxygenated organic molecule (OOM) tracers, *Environ. Sci. Technol. Lett.*, 11, 988–995, <https://doi.org/10.1021/acs.estlett.4c00536>, 2024.
- Zhou, Z.Y., Wang, Z.S., Feng, W., Qin, C., Liao, H., Wang, Y.H., and Xie, M.J.: Simulation of gas-particle partitioning of semi-volatile n-alkanes and PAHs in Nanjing, China, and Denver, United States: effects of vapor pressure and surface adsorption estimation, *J. Geophys. Res. Atmos.*, 129, e2024JD041368, <https://doi.org/10.1029/2024JD041368>, 2024.

5. Lines 383–397: The assignment of Factor 2 to evaporative emissions is supported by high loadings of Pr and Ph, low levels of combustion tracers, correlation with isopentane, and temperature dependence. However, evaporative emissions can originate from multiple sources, including fuel evaporation, asphalt, and volatile chemical products, as subsequently discussed by the authors. Therefore, the authors are encouraged to clarify whether the PMF factor specifically represents petroleum/fuel evaporation or a broader category of temperature-dependent evaporative sources. Consistent terminology throughout the manuscript would avoid overinterpretation of this factor.

Reply: Thank you for the insightful comments. As suggested, we have clarified the terminology regarding evaporative emissions in the PMF analysis and updated the manuscript accordingly. Please see the revised text below:

“Moreover, evaporative IVOCs are also from asphalt (itself petroleum-derived) and volatile chemical products (VCPs) (McDonald et al., 2018; Khare et al., 2020; Wan et al., 2026). PMF model cannot further sub-partition this factor to separate contributions from fuel evaporation, asphalt, and VCPs. Therefore, Factor 2 resolved by PMF was primarily attributed to bulk evaporative emissions, with fuel evaporation as the important constrained contributor, based on its significant correlations with isopentane, Pr, and Ph.” (Lines 399–404)

References

- McDonald, B.C., de Gouw, J.A., Gilman, J.B., Jathar, S.H., Akherati, A., Cappa, C.D., Jimenez, J.L., Lee-Taylor, J., Hayes, P.L., McKeen, S.A., Cui, Y.Y., Kim, S.W., Gentner, D.R., Isaacman-VanWertz, G., Goldstein, A.H., Harley, R.A., Frost, G.J., Roberts, J.M., Ryerson, T.B., Trainer, M., Jimenez, J.L., Lee-Taylor, J., Hayes, P.L., McKeen, S.A., Cui, Y.Y., Kim, S.W., Gentner, D.R., Isaacman-VanWertz, G., Goldstein, A.H., Harley, R.A., Frost, G.J., Roberts, J.M., Ryerson, T.B., and Trainer, M.: Volatile chemical products emerging as largest petrochemical source of urban organic emissions, *Science*, 359, 760–764, <https://doi.org/10.1126/science.aag0524>, 2018.
- Khare, P., Machesky, J., Soto, R., He, M., Presto, A.A., and Gentner, D.R.: Asphalt-related emissions are a major missing nontraditional source of secondary organic aerosol precursors, *Sci. Adv.*, 6, eabb9785, <https://doi.org/10.1126/sciadv.abb9785>, 2020.
- Wan, Z.C., Guo, S., Ni, X.S., Zhou, Q.Q., Hu, K., Chen, S.Y., Yao, M.S., and Donahue, N.M.: Urban activity shifts reshape S/IVOC composition and SOA formation: insights from wintertime observations in Beijing, *Environ. Sci. Technol.*, 60, 17927–17937, <https://doi.org/10.1021/acs.est.5c17863>, 2026.

6. Lines 452–468: The authors appropriately note that industrial emissions may contain

substantial oxygenated IVOCs that were not included in the current measurements. Since the study targets only 16 representative compounds, mainly hydrocarbon IVOCs, the derived concentrations and PMF contributions may not represent the entire atmospheric IVOC pool. I suggest that the authors more explicitly acknowledge this limitation and consistently use terms such as “measured IVOCs” or “targeted IVOCs”, particularly when discussing source contributions and broader implications.

Reply: We sincerely thank you for this constructive and precise comment regarding the compound coverage of our measurements. Following your suggestions, we have revised the manuscript by (a) making this limitation explicit and (b) consistently adopting the qualifiers “measured IVOCs” or “targeted IVOCs” throughout the text, especially where source contributions and broader implications are discussed. The corresponding changes have been listed as follows:

“Additionally, this study focused on 16 representative hydrocarbon IVOC species. The reported concentrations and PMF-resolved relative contributions are therefore specific to these measured compounds and cannot fully capture the entire atmospheric IVOC pool. Nevertheless, our findings regarding temperature-dependent evaporation and gas/particle partitioning are generalizable to the broader IVOC continuum, since the measured compounds span the IVOC volatility window.” (Line 537–542)