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Abundance of volatile organic compounds and their role in ozone pollution management: evidence from multi-platform observations and model representation during the 2021–2022 field campaign in Hong Kong

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Sect. S1: Quality assurance and quality control (QA/QC) for VOCs

Land-based HKEPD AQMS has implemented online gas chromatography (GC) for monitoring NMHCs (Mai et al., 2024; Ou et al., 2015) and high-performance liquid chromatography with ultra-violet spectroscopy (HPLC-UV) for monitoring OVOCs. Shipborne measurements used offline GC for NMHCs (Sun et al., 2024) and ultra-high-performance liquid chromatography with mass spectrometry (UPHLC-MS) for OVOCs (Xu et al., 2023; Chen et al., 2025). Strict QA/QC procedures were followed to ensure data quality; detailed sampling and analysis methods are explicitly described in our above-cited peer-reviewed publications. Below, we list some key information.

(1) Online GC for NMHCs:

NMHCs speciation data were collected by an online GC-photo ionization detector (PID)/flame ion detector (FID) system (Syntech Spectras GC955 series 611/811). The analyzer was equipped with built-in computerized programs, such as auto-linearization and autocalibration. Weekly calibrations were conducted by injecting certified calibration gas (NPL span gas, National Physical Laboratory). Additionally, independent comparisons with offline canister samples analyzed by HKUST were regularly carried out as a benchmark for audit. In general, the detection limits of the target NMHCs ranged from 2 to 787 pptv, with measurement accuracy of ~ 1%–10% and measurement precision of ~ 2.5%–20% (Mai et al., 2024; Ou et al., 2015).

(2) Offline GC for NMHCs:

Whole air canister samples were collected using 2 L electropolished stainless-steel canisters and analyzed with a GC-mass selective detector (MSD)/electron capture detector (ECD)/flame ion detector (FID) system. To ensure sampling quality, NMHC samples were collected following the QA/QC procedures outlined in the equipment user manuals and in accordance with the United States Environmental Protection Agency (USEPA) Methods TO-14A and TO-15, as detailed in the "Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air". Whole air standards were analyzed for recalibration every eight runs. Each sample was validated against a standard analyzed on the same day to account for inter-day fluctuations. When an analyte was detected across multiple detectors, its concentration was further validated among them. The method detection limits (MDLs) for NMHCs were ≤0.5 ppbv, and replicate precision for target NMHC species was within 25% (Sun et al., 2024).

(3) HLPC-UV for OVOCs

To ensure the quality of the samplings, OVOC samples were collected in accordance with the QA/QC procedures specified in the equipment user manuals and USEPA Method TO-11A. One field blank was collected through an individual channel without airflow through the cartridge for each sailing trip. For chemical analysis, solvent blanks, field blanks, and quality control standards were analyzed on each analysis day. A multiple-point calibration, consisting of at least five concentration levels, was performed. Linear regression analysis was conducted using concentration and average area counts to determine the regression correlation coefficient (R^2), which must exceed 0.995 to be considered sufficiently linear. The HPLC was calibrated using

working standards of five different concentrations (0.25, 0.5, 1, 2.5, and 5 μg/mL) for target OVOC species, achieving a linearity of at least 0.999 in this study. Method detection limits (MDLs) ranged from 0.028 to 0.127 μg/m³ across different carbonyl species (0.24 m³ of air), and replicate precision for target species ranged from 0.20% to 3.85%.

(4) UHPLC-MS for OVOCs

The UHPLC-MS calibration is detailed in our publications (Xu et al., 2023; Chen et al., 2025). A series of standard solutions containing 47 carbonyl-DNPH derivatives were prepared at concentrations ranging from 5 μg/L to 1000 μg/L. Calibration curves were established based on the analysis of these standards, demonstrating good linearity with correlation coefficients (R^2) greater than 0.99. Method detection limits (MDLs) were determined from seven replicate analyses of the lowest concentration standard, ranging from 0.003 to 0.1 μg/m³ across different carbonyl species, based on a sampling flow rate of 1 L/min over 2 hours (equivalent to 0.12 m³ of air). The limits of quantification (LOQ), defined by a signal-to-noise ratio of 10, ranged from 0.01 ng/mL to 0.08 μg/mL. The precision of the method was assessed using relative standard deviations (RSD), which ranged from 0.36% to 6.14% across the target compounds.

Supplement Figures & Tables:

Figure S1. 18 Air Quality Monitoring Station (AQMS) and 1 supersite (Cape D'Aguilar Supersite (CDSS) at Hok Tsui) from HKEPD. Three types of sites are represented as follows: background sites as squares, roadside sites as triangles, and general sites as circles. Red color represents sites with volatile organic compound (VOC) measurements.

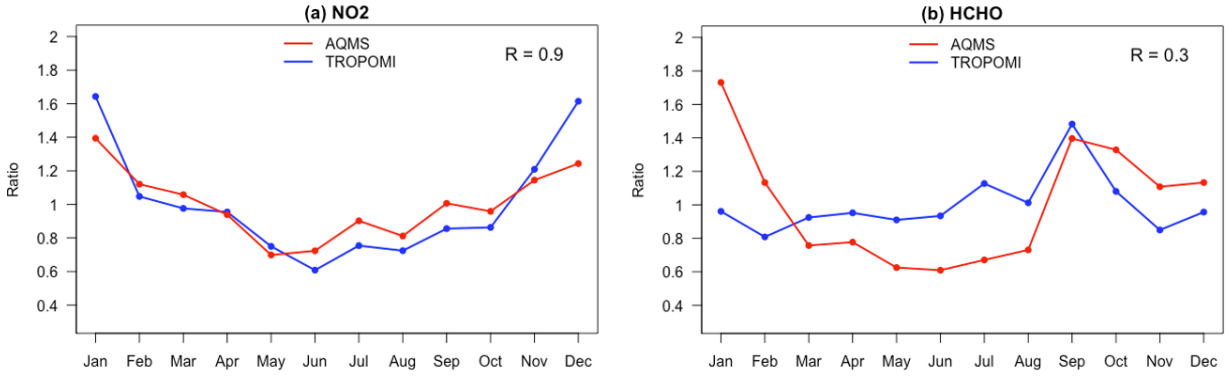

Figure S2. Monthly variations of (a) NO_2 and (b) HCHO recorded by surface land-based AQMS sites and spaceborne TROPOMI during 2021–2022. Measurements from AQMS and TROPOMI were normalized using their respective annual mean.

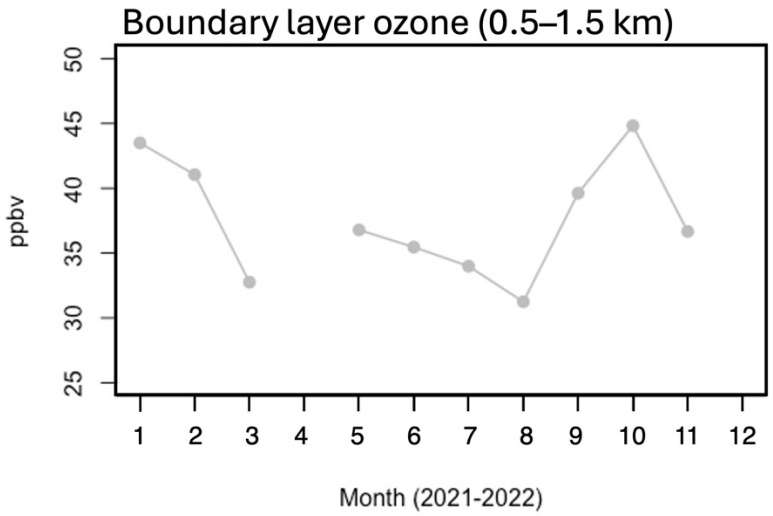

Figure S3. Monthly variations of boundary layer ozone, averaged from 0.5–1.5 km aloft, recorded by the ozone lidar at the Hok Tsui site in Hong Kong during 2021–2022.

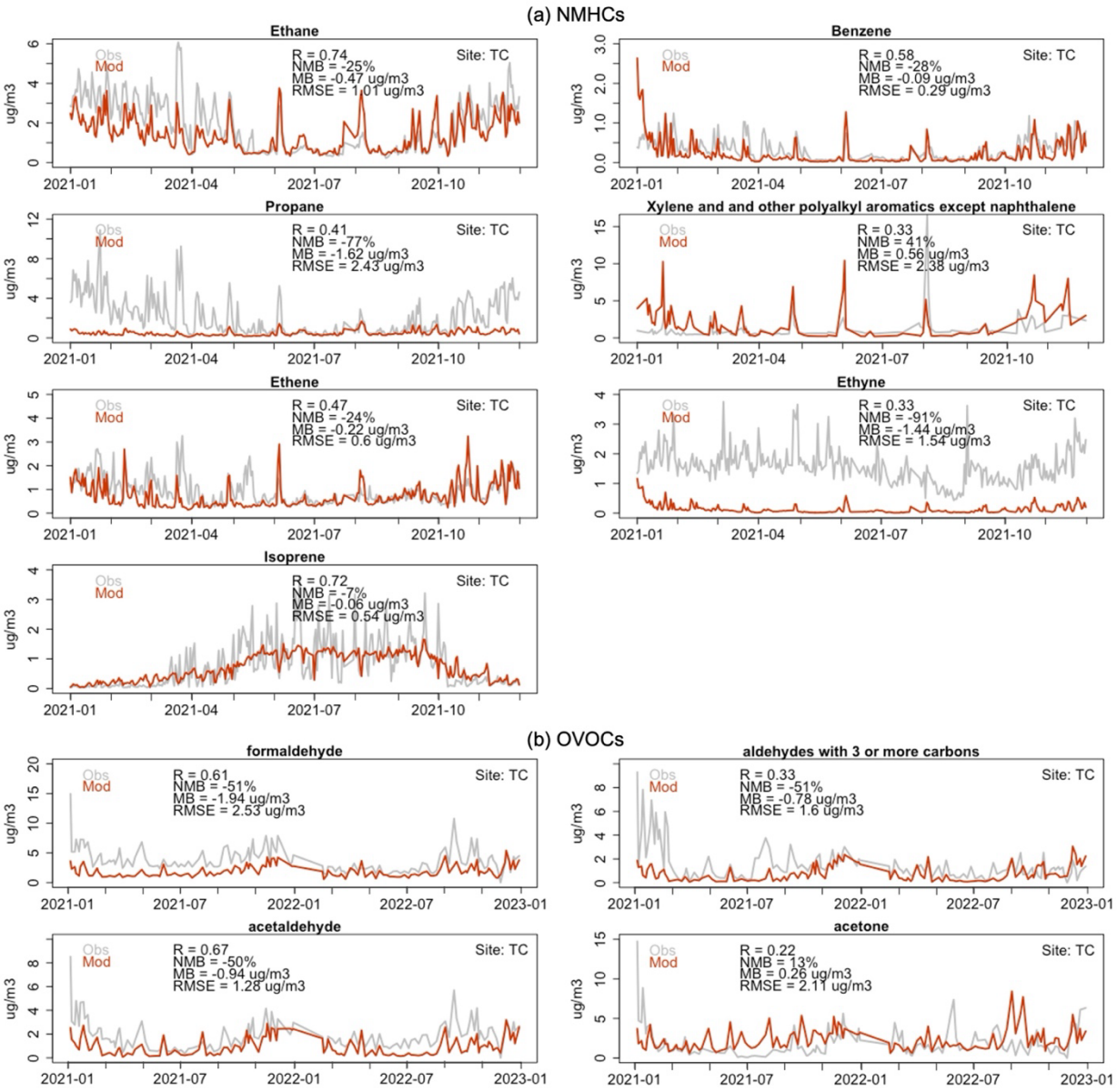

Figure S4. NMHC and OVOC observations at the Tung Chung (TC) site compared to the CMAQ model.

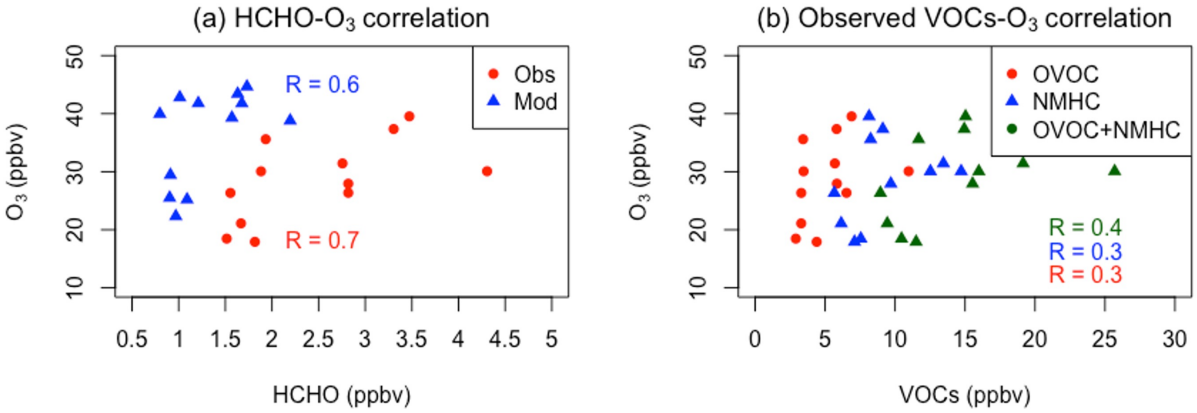

Figure S5. Correlation between monthly variability of ozone and VOCs at land-based sites.

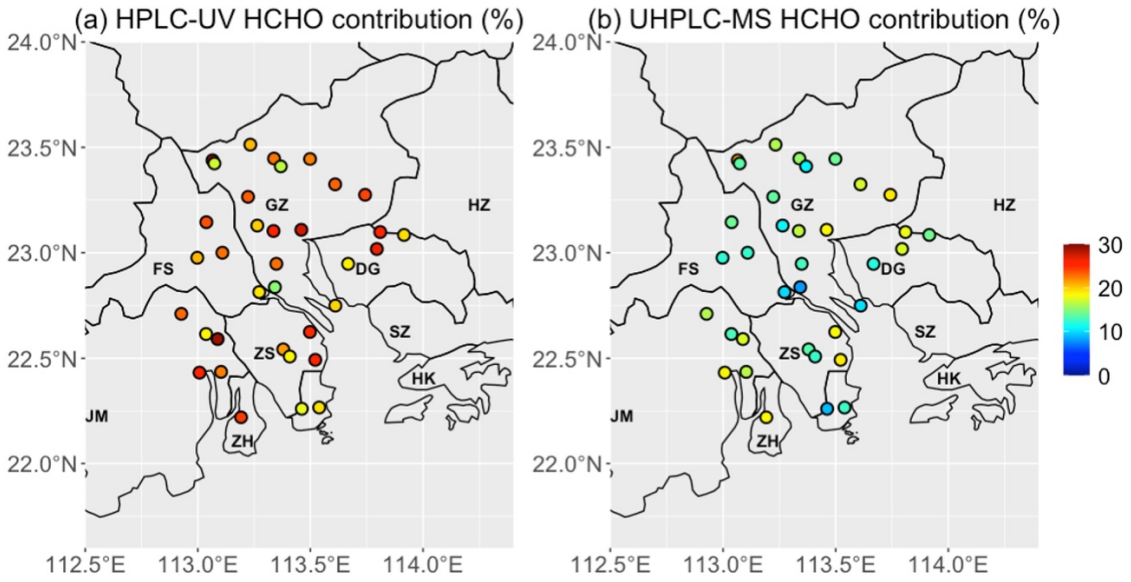

Figure S6. The contribution of HCHO to the total concentration of all observed VOCs during September 4–5, 2022. OVOCs were measured using (a) HPLC-UV for 16 species and (b) UHLPC-MS for 43 species. NMHCs were measured using the same method in both (a) and (b), totaling 38 species. Overall, there are 54 observed VOC species in (a) and 81 in (b).

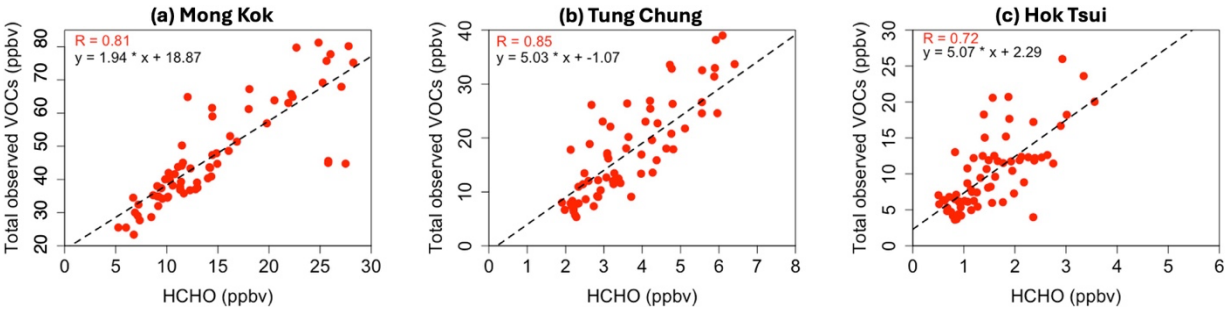

Figure S7. Correlation between HCHO and total observed VOCs at three land-based sites.

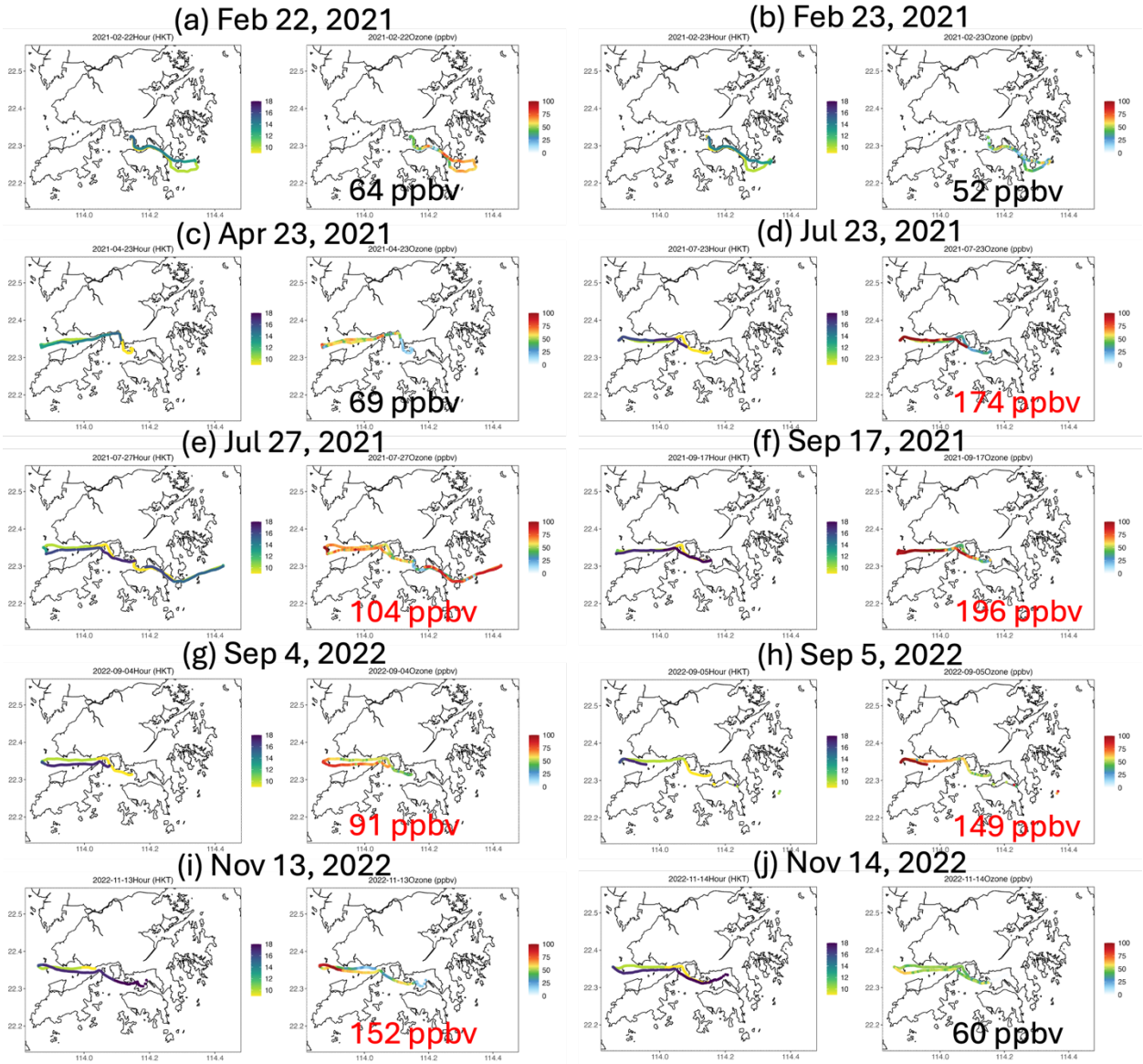

Figure S8. Mobile ship measurements of ozone and the corresponding sampling times for each day. Maximum hourly mean ozone concentrations are inserted.

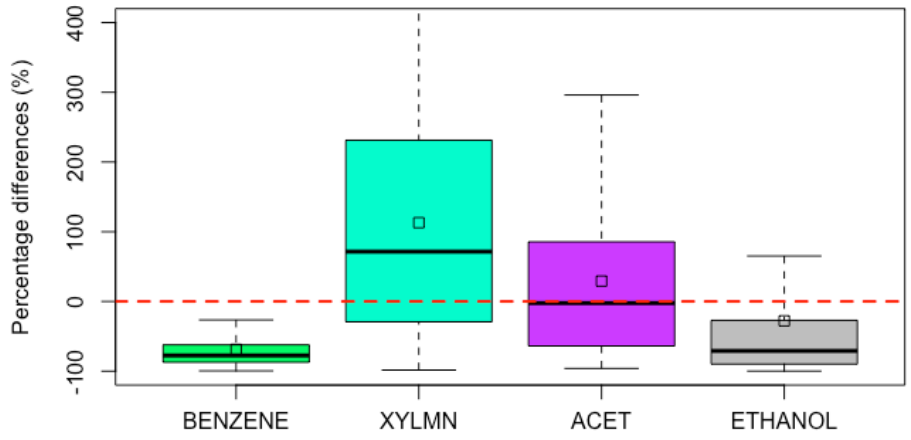

Figure S9. The percentage differences between the observation and model for individual VOC species measured at the HKUST supersite.

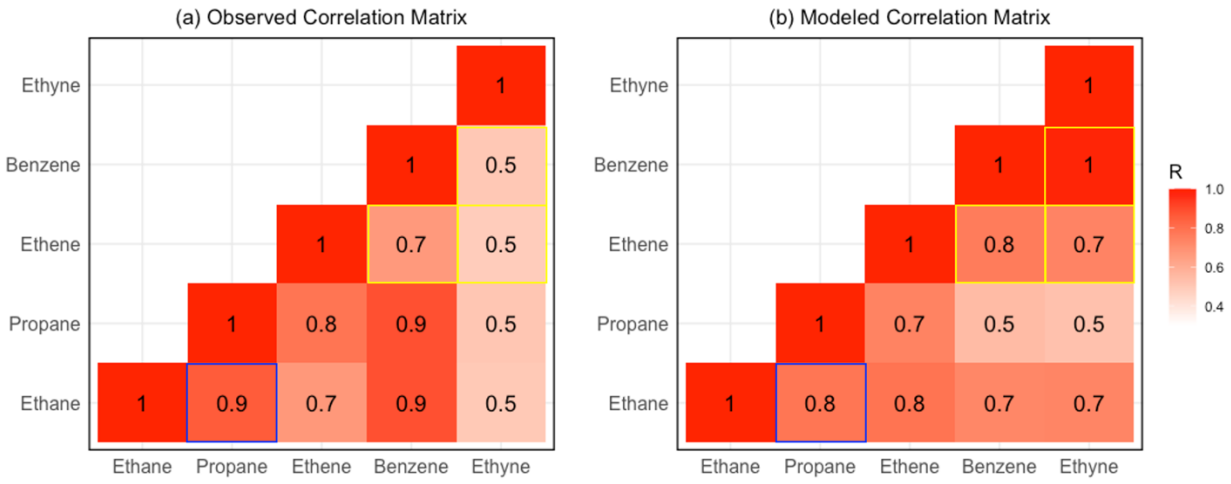

Figure S10. Correlation matrix for anthropogenic NMHCs at the land-based Tung Chung site. Blue boxes indicate that the model accurately represents the strong correlation between co-emitted propane and ethane. Yellow boxes highlight discrepancies between the observed and modeled correlations of ethyne with ethene and benzene.

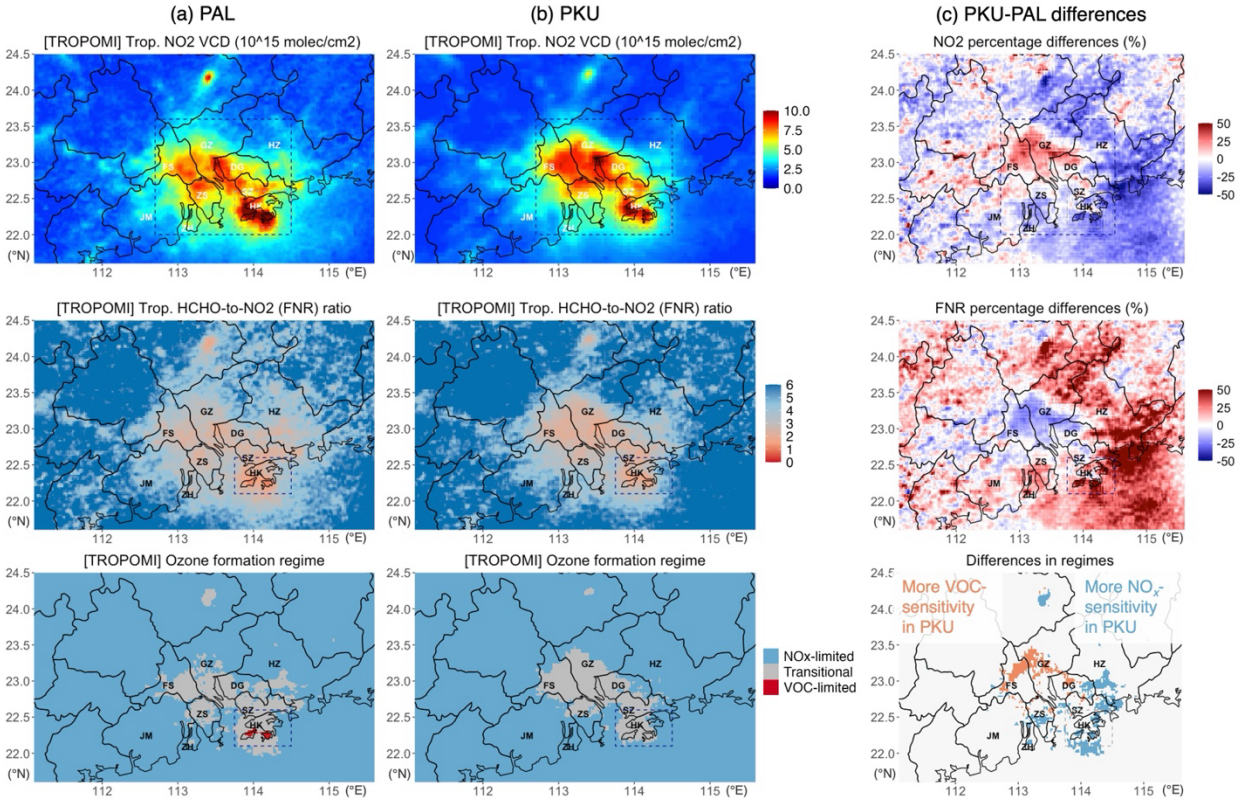

Figure S11. Differences between two TROPOMI NO_2 products retrieved by (a) Product Algorithm Laboratory (PAL) and (b) Peking University (PKU; Liu et al., 2020), along with their associated FNR and ozone formation regimes.

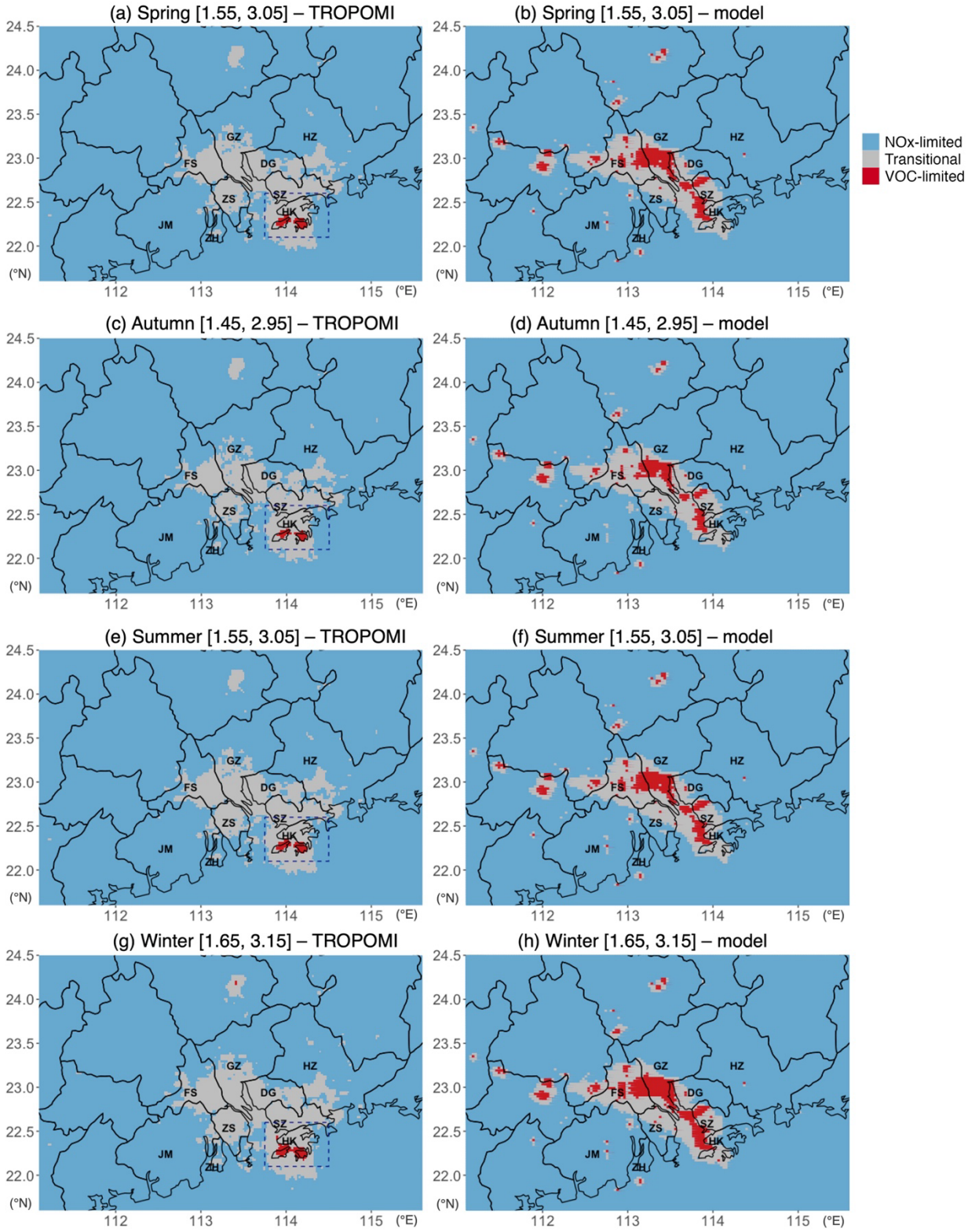

Figure S12. Ozone formation regimes classified using Pearl River Delta region-specific FNR thresholds derived for different seasons, including spring and summer [1.55, 3.05], autumn [1.45, 2.95], and winter [1.65, 3.15], as in Wang Y et al. (2023).

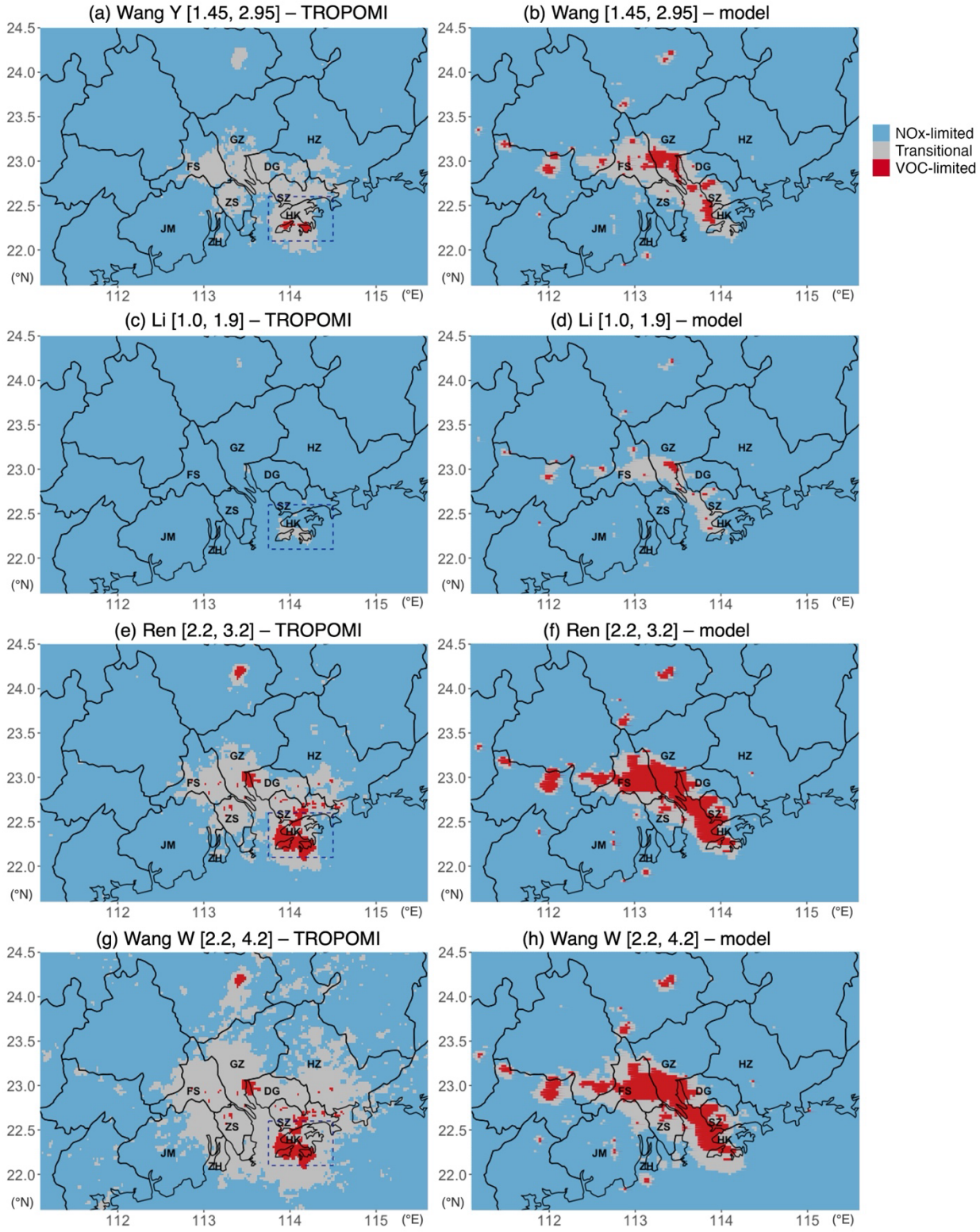

Figure S13. Ozone formation regimes classified using various FNR thresholds derived from different studies, including (a) [1.45, 2.95] from Wang Y. et al. (2023), (b) [1.0, 1.9] from Li et al. (2021), (c) [2.2, 3.2] from Ren et al. (2022), and (d) [2.2, 4.2] from Wang W. et al. (2021).

Table S1. Comparison between observed VOCs and modeled counterparts by 3-D chemical transport models. Negative values indicate model underestimation.

	Ge et al. (2024)	Rowlinson et al. (2024)						She et al. (2024)	Chen et al. (2019)	This study	
	Europe	Europe	North America	Southern Hemisphere	Pacific Ocean	Atlantic Ocean	Asia	China	USA	HK (land)	HK (water)
Unspeciated VOC total								–30%	–37%	–47% for NMHCs; –45% for OVOCs	–48% for NMHCs; –70% for OVOCs
Ethyne (C2H2)	–7% ~ –13%							–45%		–88%	–73%
Ethene (C2H4)	–5% ~ –29%							–40%		–19%	–2%
Isoprene (C5H8)										–18%	–21%
Alpha-Pinene (C10H16)											–7%
Ethane (C2H6)	–12% ~ –14%	–4% ~ –38%	–4% ~ –38%	–23% ~ –32%	–2% ~ –34%	–16% ~ –50%	–19% ~ +26%			–16%	+9%
Propane (C3H8)	–49% ~ –56%	–39% ~ –60%	–45% ~ –64%	–78% ~ –79%	–38% ~ –56%	–56% ~ –76%	–32% ~ –49%			–57%	–76%
n-butane (nC4H10)	+45% ~ +55%										
i-butane (iC4H10)	–30% ~ –38%							–41%			
n-Pentane (nC5H12)	+26% ~ +44%	+24% ~ +45%	–4% ~ +3%	–60%	–10% ~ +5%	–12% ~ –15%	+55% ~ +86%				
i-Pentane (iC5H12)	–53% ~ –59%										
n-Hexane (nC6H14)	–8% ~ +9%										
Benzene	–12% ~ –17%									–13%	–34%
Toluene	–33% ~ –39%							–60%			
Xylene	–13% ~ +3%									+93%	–23%
HCHO								+66%		–23%	–42%
Acetaldehyde										–58%	–57%
Aldehydes with 3 or more carbons										–53%	–69%
Acetone										+26%	–65%
Glyoxal											+30%
Methylglyoxal											–27%

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