Supplement of Atmos. Chem. Phys., 23, 3655–3677, 2023
https://doi.org/10.5194/acp-23-3655-2023-supplement

Atmospheric Chemistry and Physics
Open Access

Supplement of

Mobile MAX-DOAS observations of tropospheric NO_2 and HCHO during summer over the Three Rivers' Source region in China

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S1 Radiative transfer simulations

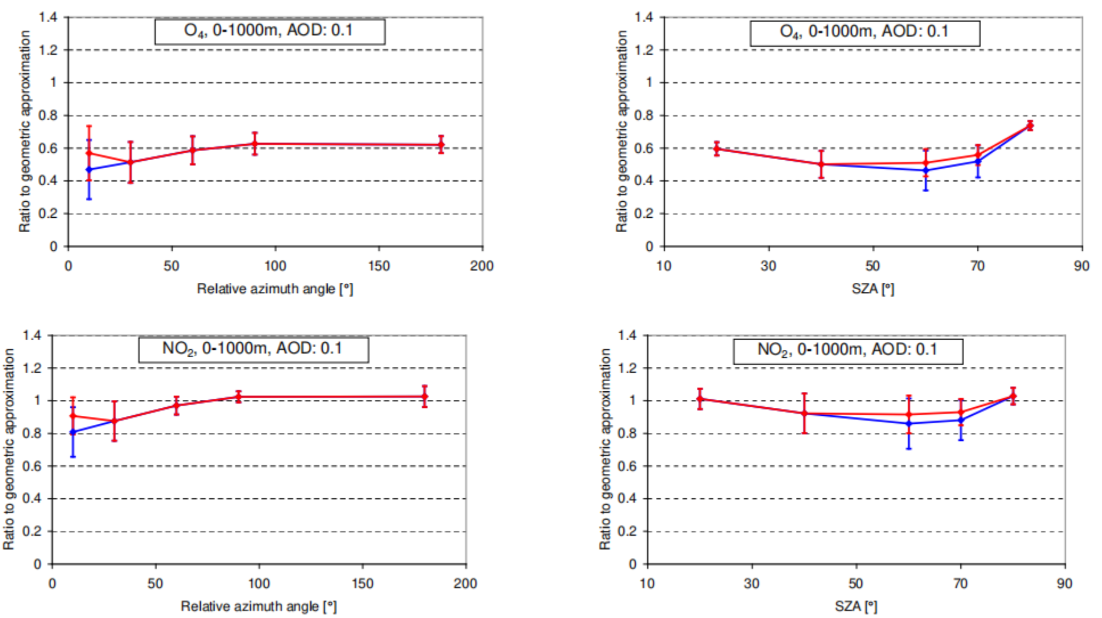
We explored the applicability of the geometric approximation method by radiative transfer simulations. According to the AODs from the AERONET website (https://aeronet.gsfc.nasa.gov, last access: 2 December 2022) at three sites (Mt_WLG, NAM_CO, QOMS_CAS) over the Tibetan Plateau, we estimate the AODs around 0.1 during our field campaign. But similar results are also found for AODs of 0.05 and 0.2. The simulations were performed with the full spherical Monte Carlo radiative transfer model MCARTIM (Deutschmann et al., 2011). The simulation scheme is as the following.

Table S1. Assumptions made for the radiative transfer simulations to test the applicability of the geometric approximation.

Parameters	O_4	NO_2	HCHO
Wavelength (nm)	340	440	340
Layer height (km)	US standard atmosphere	0-1; 0-2	0-1; 0-2
Aerosol height (km)	0-1	same as trace gases	
AOD	0; 0.05; 0.1; 0.2		
Aerosol single scattering albedo	0.95		
Aerosol asymmetry parameter	0.68		
Cloud single scattering albedo	1.0		
Cloud asymmetry parameter	0.85		
Cloud altitude (km)	2-3; 4-5; 8-9		
SZA (°)	20; 40; 60; 70; 80		
RAA (°)	10; 30; 60; 90; 180		
Elevation angle (°)	15		
Terrain height (km)	2; 3; 4; 5		

The VCD ratios of the RTM simulations and the geometric approximation for 15° elevation angle under the condition of AOD=0.1 can be obtained for O_4, NO_2, and HCHO, respectively. The DAMF ratios' means and standard deviations for all geometries (blue symbols) and RAA=10°, SZA=60° and RAA=10°, SZA=70° excluded (red symbols, for these rare measurement scenarios the strongest errors occur) are shown below. The main findings are: (1) The typical errors of the geometric approximation are <20% for NO_2 and HCHO; (2) The errors of the geometric approximation are much larger for O_4 with a systematic underestimation between about 40% and 60%. This underestimation is caused by the low sensitivity for high altitudes (Fig. S1, S3); (3) The large underestimation of the O_4 VCDs indicates that O_4 can not be used for the test if the geometric approximation is justified or not for an individual measurement of NO_2 and HCHO. It should also be noted that HCHO is not only present in the lowest atmospheric layers, but background HCHO levels extend to higher altitudes. We investigated the sensitivity of the geometric approximation also to HCHO concentrations at altitudes above 2km. For that purpose, we used a HCHO concentration profile above the Tibetan plateau from a global chemistry model (Ma et al., 2019) (Fig. S2). The results are shown in Fig. S3 (bottom). Like for O_4, the sensitivity to the background HCHO is reduced by about 60%. Thus the retrieved HCHO VCDs using the geometric approximation will well represent the HCHO located below 2km, but will underestimate the total HCHO VCD by about 8×10^{14} molec cm^{-2}.

We also investigated the effects of clouds. For that purpose, we assumed clouds with an optical depth of 10 at different altitudes (2-3km, 4-5km, 8-9km). The results for O_4 as well as NO_2 and HCHO are shown in Fig. S4. For HCHO and NO_2 only a small cloud effect (even a small increase of sensitivity) is found. In contrast, for O_4 a strong underestimation is found, especially for clouds at low altitudes.



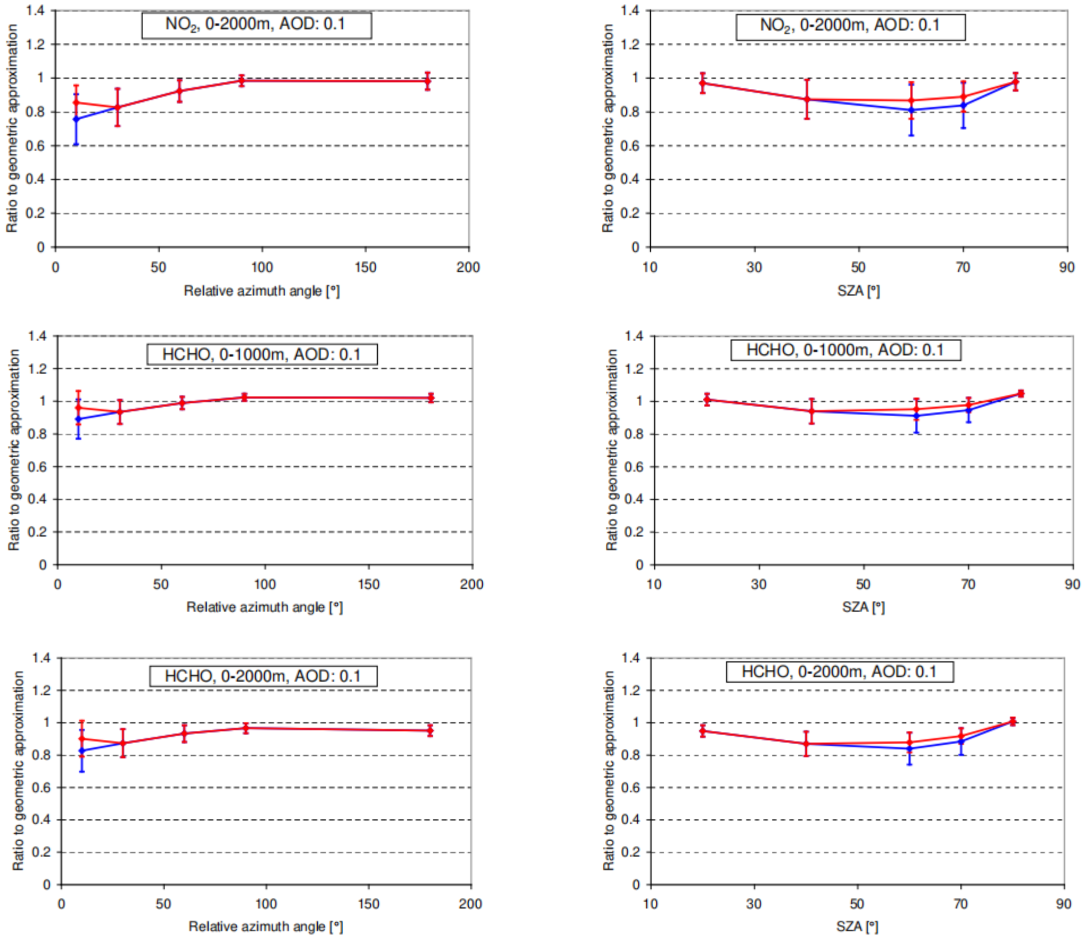


Figure S1. Ratio of the simulated $DAMF_{15°}$ and the corresponding $DAMF_{geom,\,15°}$ (derived from the geometric approximation). Results are calculated for O_4 as well as for NO_2 and HCHO with different layer heights. More details of the radiative transfer settings are presented in Table S1. The results in the left and right are the same, but displayed either as function of the relative azimuth angle (RAA) or SZA. Blue curves represent all scenarios, red curves show results with the most 'problematic scenarios (RAA=10°, SZA=60° and RAA=10°, SZA=70°) excluded. The altitude information in the figures describes the layer height of the aerosols, and for NO_2 and HCHO also the corresponding trace gas layer heights.

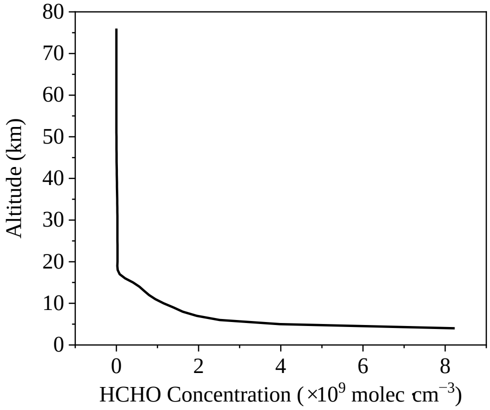
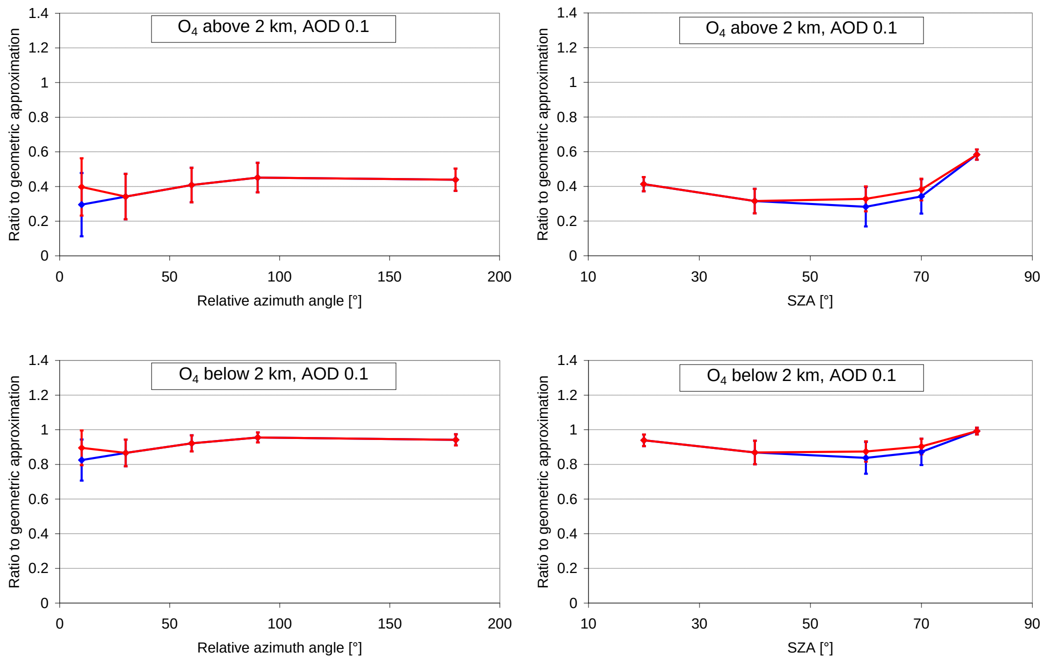


Figure S2. Vertical profile of background HCHO over the experimental area (excluding the region of Xi'ning city) from the simulations of the EMAC global chemistry model in July of 2012 (Ma et al., 2019).



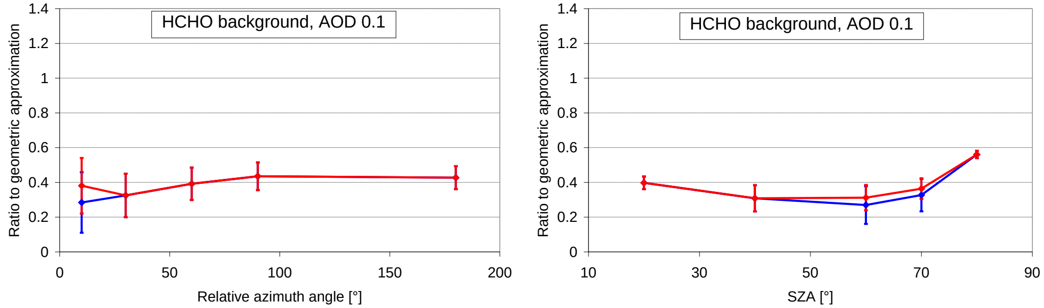
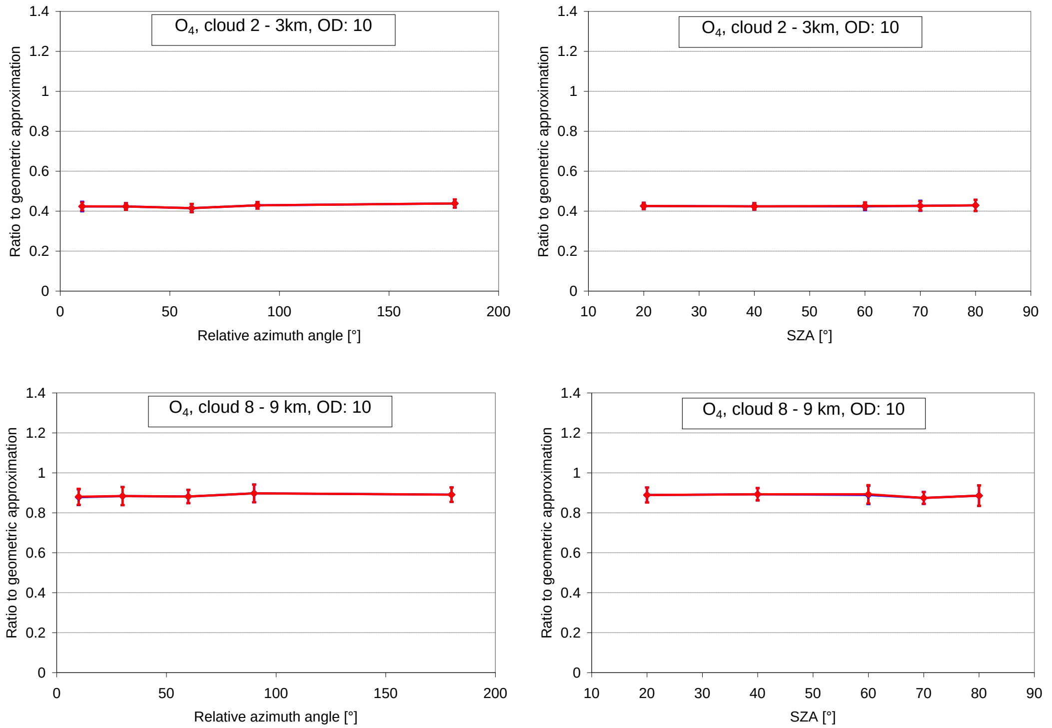
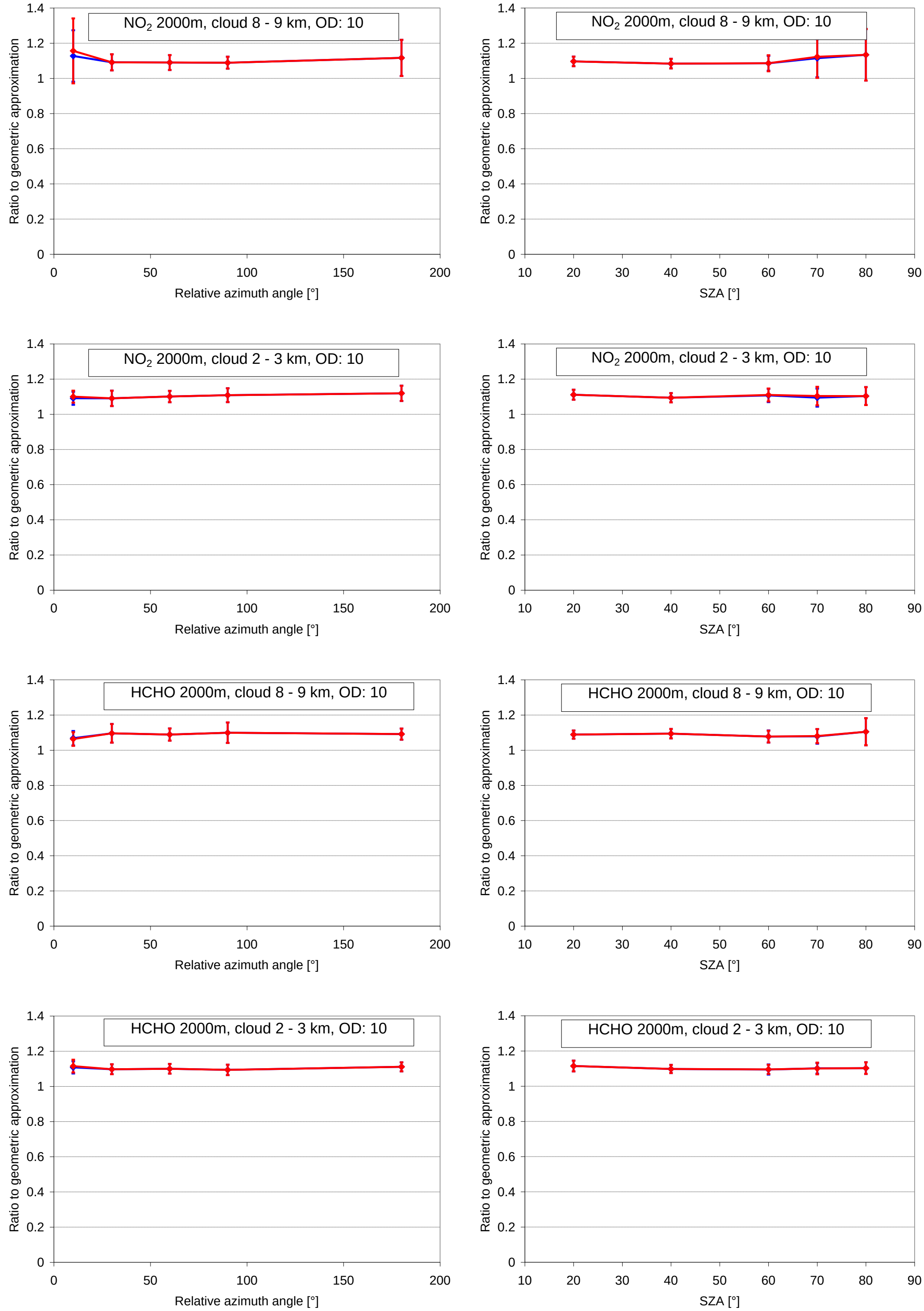


Figure S3. Ratio of the simulated $DAMF_{15°}$ and the corresponding $DAMF_{geom,\ 15°}$ (derived from the geometric approximation) for the part of the O_4 profile above 2km (top) and below 2km (center). The lower panel shows the results for the HCHO background profile with values below 2km set to zero. The aerosol profile ranged from the surface to 2km altitude.





NO_2 2000m, cloud 8 - 9 km, OD: 10
NO_2 2000m, cloud 2 - 3 km, OD: 10
HCHO 2000m, cloud 8 - 9 km, OD: 10
HCHO 2000m, cloud 2 - 3 km, OD: 10
Ratio to geometric approximation
Relative azimuth angle [°]
SZA [°]

Figure S4. Ratio of the simulated $DAMF_{15°}$ and the corresponding $DAMF_{geom,\ 15°}$ (derived from the geometric approximation) in the presence of clouds for O_4 and NO_2 and HCHO located between the surface and 2km.

S2 Profiles of NO_2 and HCHO mixing ratios

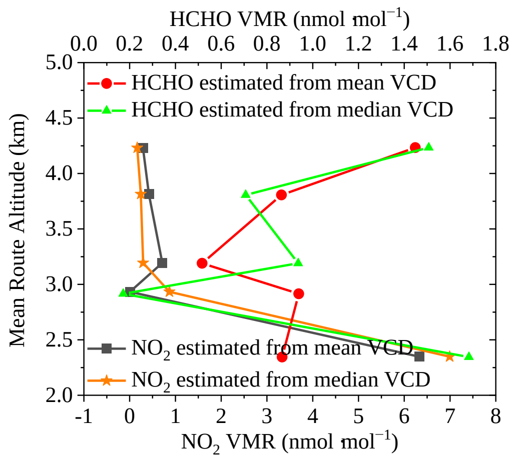


Figure S5. Profiles of NO_2 and HCHO mixing ratios (VMRs) estimated from the corresponding mean and median VCDs along driving routes respectively.

S3 Tropospheric NO_2 introduced by the stratospheric NO_2 absorption

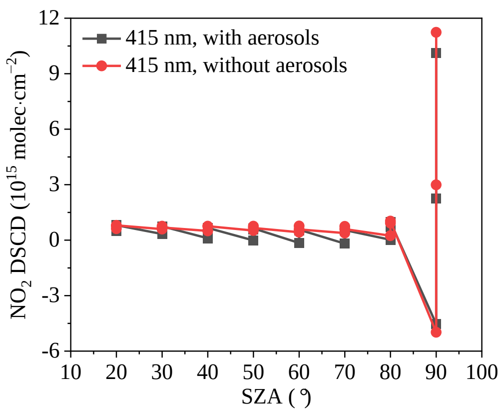


Figure S6. Simulated apparent tropospheric NO_2 DSCDs at different SZAs, introduced by the stratospheric NO_2 absorption. The conditions during radiative transfer simulations include: (1) Simulation wavelength and elevation angle are set as 415 nm and 15° at an altitude of 4 km for three relative azimuth angles (0°, 90°, 180°), respectively; (2) The stratospheric NO_2 VCD is assumed to be 4×10^{15} molec cm^{-2}; (3) The simulations are performed either without aerosols or with aerosols (aerosols from the surface to 1 km above the surface, AOD=0.1, HG phase function with asymmetry parameter=0.68, single scattering albedo=0.95). The DSCDs represent the differences of the SCDs at 15° and 90° elevations.

S4 Spatial distributions of air temperature at 2 m above the land surface

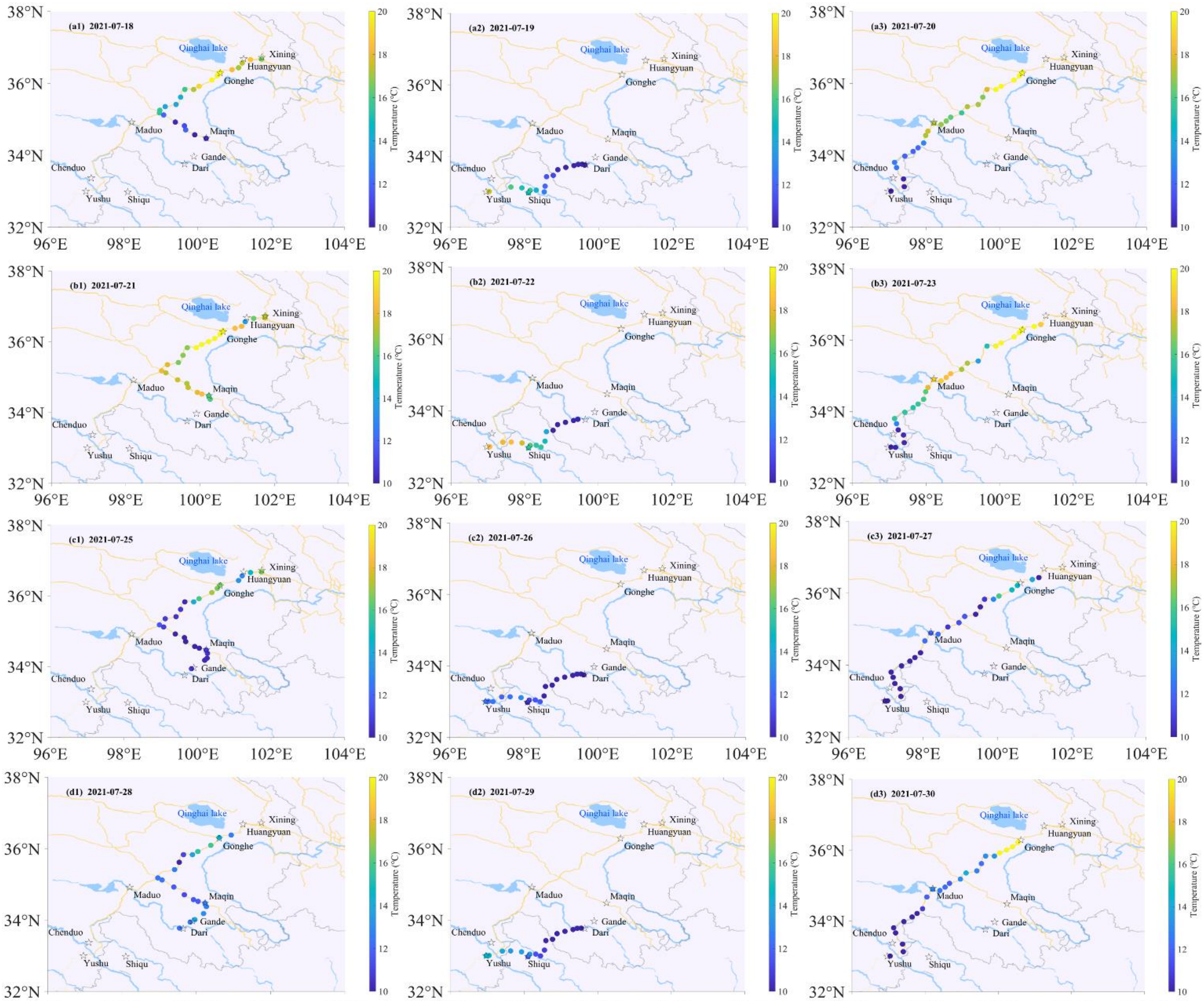


Figure S7. Spatial distributions of ERA5 hourly air temperature at 2 m above the land surface, corresponding to gridded HCHO VCDs with 0.25 °×0.25 ° resolution for three segments **(1, 2, 3)** of four circling journeys **(a, b, c, d)**. The main cities and counties on the driving routes are marked by the black stars. On the background map, the light blue lines and areas represent rivers and lakes (such as, Qinghai Lake), the yellow lines denote the roads, and the grey lines indicate the administrative boundaries.