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Ozone seasonal evolution and photochemical production regime in the polluted troposphere in eastern China derived from high-resolution Fourier transform spectrometry (FTS) observations

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Section S1: Theoretical basis for retrieval and error analysis

The basic principle of SFIT4 is using an Optimal Estimation Method (OEM) to fit the calculated-to-observed spectra with an iterative Newton scheme (Rodgers, 2000). The retrieved profile $\boldsymbol{x}$ is expressed as,

$$\mathrm{x}_{i+1} = \mathrm{x}_a + \mathrm{G}_y([\mathrm{y} - \mathrm{F}(\mathrm{x}_i, \mathrm{b})] + \mathrm{K}_i[\mathrm{x}_i - \mathrm{x}_a]) \tag{S1}$$

where $\boldsymbol{x}$ is retrieved profile, $\boldsymbol{x}_a$ is *a priori* profile, $\boldsymbol{y}$ is measured spectra, and $\mathbf{F}(\boldsymbol{x}, \mathbf{b})$ is forward model calculated spectrum. The $m \times n$ matrix $\mathbf{K}_i = \Delta\mathbf{F}(\boldsymbol{x}_i, \mathbf{b})/\Delta\boldsymbol{x}_i$ is weighting function matrix or Jacobian matrix for the *i*-th iteration. $\mathbf{G}_y$ is the contribution function matrix,

$$\mathrm{G}_y = (\mathrm{K}_i^T \mathrm{S}_\varepsilon^{-1} \mathrm{K}_i^T + \mathrm{S}_a^{-1})^{-1} \mathrm{K}_i^T \mathrm{S}_\varepsilon^{-1} \tag{S2}$$

where $\mathbf{S}_\varepsilon$ and $\mathbf{S}_a$ are measurement noise covariance matrices and *a priori* profile covariance matrices, respectively. The averaging kernel matrix $\mathbf{A}$ can be calculated as (Rodgers, 2000),

$$\mathrm{A} = \mathrm{G}_y \mathrm{K} = (\mathrm{K}^T \mathrm{S}_\varepsilon^{-1} \mathrm{K}^T + \mathrm{S}_a^{-1})^{-1} \mathrm{K}^T \mathrm{S}_\varepsilon^{-1} \mathrm{K} \tag{S3}$$

The degrees of freedom for signal (DOFs) is calculated as the trace of $\mathbf{A}$,

$$d_s = tr(\mathrm{A}) = tr((\mathrm{K}^T \mathrm{S}_\varepsilon^{-1} \mathrm{K}^T + \mathrm{S}_a^{-1})^{-1} \mathrm{K}^T \mathrm{S}_\varepsilon^{-1} \mathrm{K}) \tag{S4}$$

An error analysis and characterization is of great importance for a retrieval algorithm. Errors are traditionally classified as systematic or random according to whether they are constant between consecutive measurements, or vary randomly. The total error covariance matrix ($\mathbf{E}$) can be expressed as the sum of the contributions from (a) the measurement error due to measurement noise ($\mathbf{E}_m$), (b) the smoothing error due to the limited altitude resolution of the FTS system ($\mathbf{E}_s$), (c) the model parameter error due to uncertainties of forward model parameters ($\mathbf{E}_{model}$), and (d) forward model error due to the error of the model in physical process simulation ($\mathbf{E}_f$):

$$\mathrm{E} = \mathrm{E}_m + \mathrm{E}_s + \mathrm{E}_{\mathrm{model}} + \mathrm{E}_f \tag{S5}$$

The forward model error is hard to evaluate because it requires a model which includes the correct physics. In this study, we neglect the forward model error. The smoothing error $\mathbf{E}_s$ is calculated via equation (S6), the measurement error $\mathbf{E}_m$ is calculated via equation (S7), and the model parameter error $\mathbf{E}_{model}$ is calculated via equation (S8) (Rodgers, 2000).

$$\mathrm{E}_s = (\mathrm{A} - \mathrm{I}) \mathrm{S}_a (\mathrm{A} - \mathrm{I})^T \tag{S6}$$

$$\mathrm{E}_{m} = \mathrm{G}_{y}\mathrm{S}_{\varepsilon}\mathrm{G}_{y}^{T} \tag{S7}$$

$$\mathrm{E}_{\mathrm{model}} = \mathrm{G}_{y}\mathrm{K}_{\mathrm{var}}\mathrm{S}_{\mathrm{var}}\mathrm{K}_{\mathrm{var}}^{T}\mathrm{G}_{y}^{T} \tag{S8}$$

where $\mathbf{S}_{\mathrm{var}}$ is the error covariance matrix of the model parameter vector *var*, and $\mathbf{K}_{\mathrm{var}}$ is the corresponding weighting function matrix. Here *var* refers to one of the error items listed in Table 1 except smoothing error and measurement error. In Eq. (S6), to estimate $\boldsymbol{E}_{\mathrm{s}}$ correctly, $\mathbf{S}_{\mathrm{a}}$ should represent natural variability of the target gas in the atmosphere, and thus should be evaluated from climatological data. In this study, the diagonal elements of $\mathbf{S}_{\mathrm{a}}$ are set to standard deviation of a dedicated WACCM run from 1980 to 2020, and its non-diagonal elements are set to zero. The model parameter error contains the error from retrieved parameters, namely the interference error, and the error from non-retrieved forward model parameters.

Section S2: Data filtering

For the tropospheric O_3, CO, and HCHO columns derived from FTS measurements, we established a specific filter criterion to remove the outliers by setting certain thresholds for measurement intensity, fitting error, DOFS, and fitting residuals. Measurements satisfying the criteria as follows were classified as valid and were subsequently used in the analysis.

1) Spectra recorded with too low incident signals are discarded to ensure adequate SNRs. Meanwhile, spectra recorded with too high incident signals are discarded because of non-linearity in the detector. Specifically, for O_3 spectra recorded with MCT detector, the signal intensity should lie in between 5,000 and 11,000 ADCs, and for CO and HCHO spectra recorded with InSb detector, the signal intensity should lie in between 10,000 and 20,000 ADCs.

2) The auxiliary data such as solar intensity and meteorological data (at least surface pressure and temperature) should be recorded synchronously with the measurement. Otherwise, the measurements are screened out.

3) The observed scene must be nearly cloud-free and not seriously affected by smog or unknown opaque object. The spectra recorded with a solar intensity variation (SIV)

of larger than 10% were not used in this study. The SIV within the duration of a spectrum is the ratio of the standard deviation to the average of the sun intensities.

4) The root mean square error (RMS) of the residual difference (relative difference between measured and calculated spectra after the fit) in all fitting windows has to be less than 2.5%.

5) The retrievals should be converged and the concentrations of the target and interfering gases at each sub layer should be positive.

6) The tropospheric DOFs should be larger than 0.8, the SZA should be less than 85°.

Section S3: Extra figures

Figure S1 Locations of the FTS stations. The background image is the Blue Marble: Next Generation, produced by Reto Stockli, NASA Earth Observatory (NASA Goddard Space Flight Center) (Wunch et al, 2015).

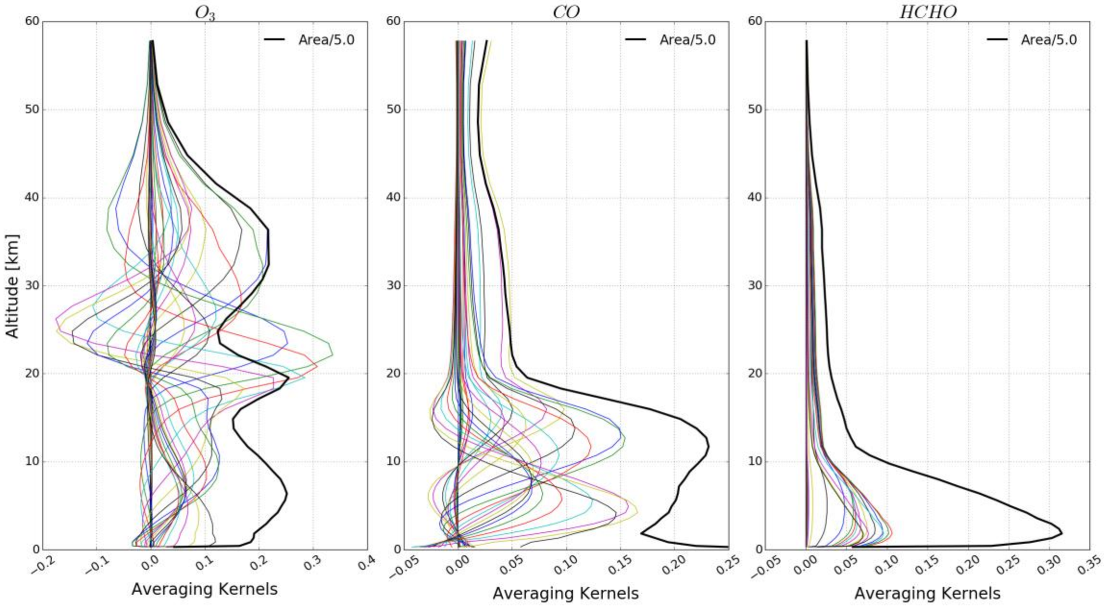

Figure S2. Averaging kernels (ppmv/ppmv) of O_3, CO, and HCHO (color fine lines), and their area scaled by a factor of 0.2 (black bold line). The atmosphere (0 – 120 km) is unevenly divided into 48 layers, and each curve reflects the retrieval sensitivity at each layer. They are deduced from the spectra recorded in Hefei on March 15, 2016 with a measured instrumental line shape (ILS).

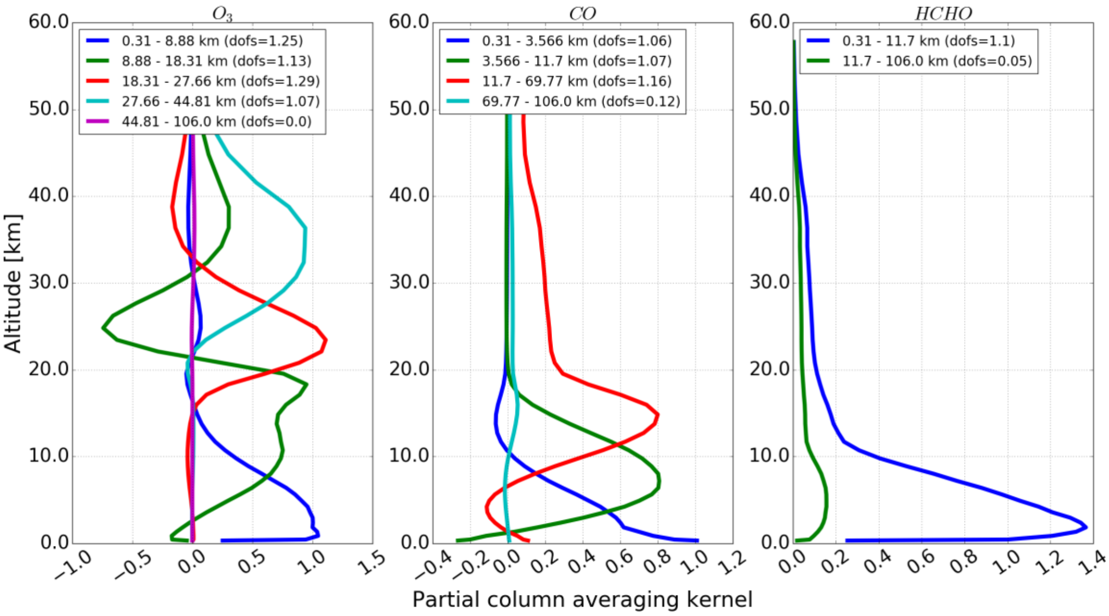

Figure S3. Partial column averaging kernels (PAVK) (ppmv / ppmv) for O_3, CO, and HCHO retrievals. For all gases, large PAVKs in certain altitude range are not relevant for the results because they have low content in the respective regions.

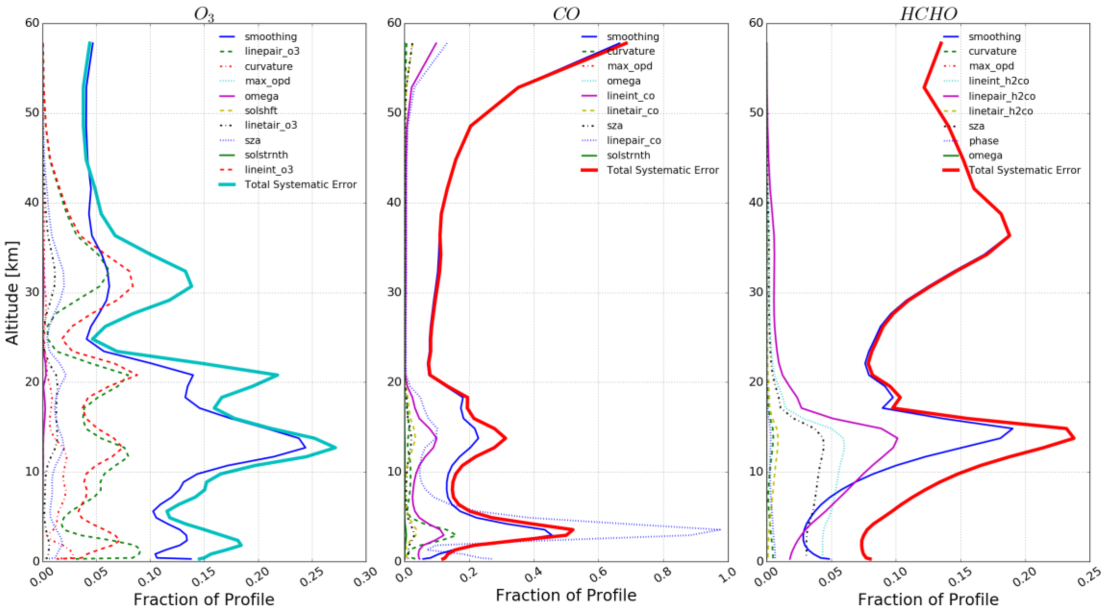

Figure S4. Ground-based FTS systematic errors for O_3, CO, and HCHO retrievals. Descriptions for the acronyms in the legend are listed in Table 1.

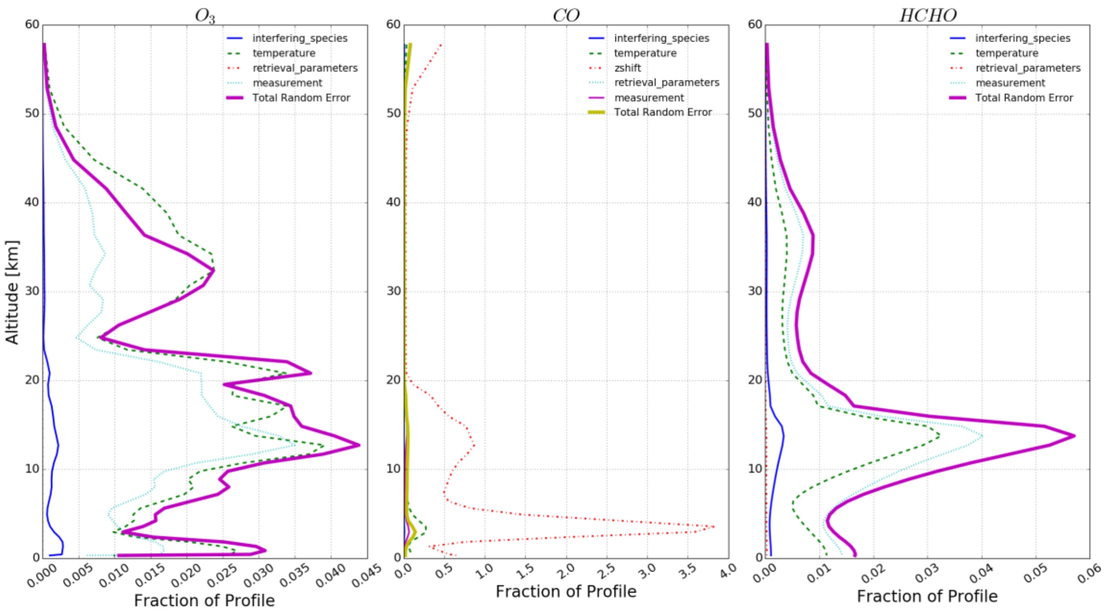

Figure S5. The same as Figure S4 but for random errors. Descriptions for the acronyms in the legend are listed in Table 1.

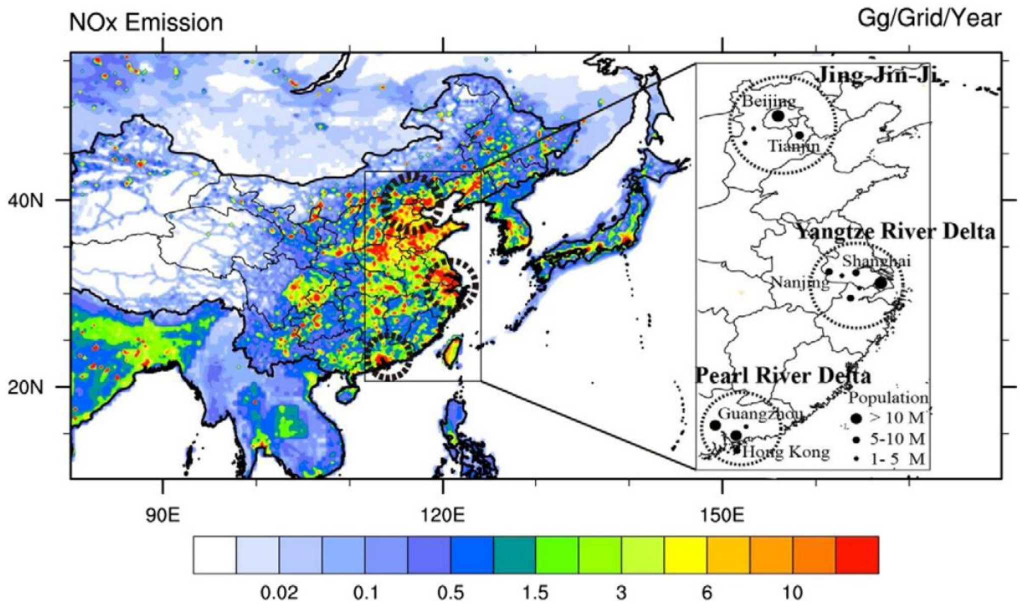

Figure S6. Map of China showing the three most developed regions—Jing-Jin-Ji (Beijing-Tianjin-Hebei), Yangtze River Delta (including Shanghai), and Pearl River Delta (including Guangzhou and Hong Kong–Shenzhen)—and NOx emission intensity for 2013 with resolution of 0.25 ° × 0.25 °(Wang et al., 2017). Emission data is from Tsinghua University available at http://meicmodel.org/. Also shown are major cities in three regions.

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