

Ship-based MAX-DOAS measurements of tropospheric NO₂, SO₂, and HCHO distribution along the Yangtze River

Qianqian Hong^{1,#}, Cheng Liu^{1,2,3,4,#,*}, Ka Lok Chan^{5,*}, Qihou Hu¹, Zhouqing Xie^{1,2,3,4}, Haoran Liu², Fuqi Si¹, Jianguo Liu^{1,3}

5 ¹Key Lab of Environmental Optics and Technology, Anhui Institute of Optics and Fine Mechanics, Hefei Institutes of Physical Science, Chinese Academy of Sciences, Hefei, 230031, China

²School of Earth and Space Sciences, University of Science and Technology of China, Hefei, 230026, China

³CAS Center for Excellence in Regional Atmospheric Environment, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen, 361021, China

10 ⁴Anhui Province Key Laboratory of Polar Environment and Global Change, USTC, Hefei, 230026, China

⁵Remote Sensing Technology Institute (IMF), German Aerospace Center (DLR), Oberpfaffenhofen, Germany

[#]This two authors contributed equally

^{*}Correspondence to: Ka Lok Chan (ka.chan@dlr.de), Cheng Liu (chliu81@ustc.edu.cn)

Abstract. In this paper, we present ship-based Multi-Axis Differential Optical Absorption Spectroscopy (MAX-DOAS) measurements of tropospheric trace gases distribution along Yangtze River during winter 2015. The measurements were performed along Yangtze River between Shanghai and Wuhan covering major industrial areas in eastern China. Tropospheric vertical column densities (VCDs) of nitrogen dioxide (NO₂), sulfur dioxide (SO₂), and formaldehyde (HCHO) were retrieved using air mass factor calculated by radiative transfer model. Enhanced tropospheric NO₂ and SO₂ VCDs were detected over downwind areas of industrial zones over Yangtze River. In addition, spatial distributions of atmospheric pollutants are strongly affected by meteorological conditions, i.e., positive correlations were found between concentration of pollutants and wind speed over these areas indicating strong influence of transportation of pollutants from high-emission upwind areas along Yangtze River. Comparison of tropospheric NO₂ VCDs between ship-based MAX-DOAS and OMI satellite observations shows good agreement with each other with Pearson correlation coefficient (R) of 0.82. In this study, NO₂/SO₂ ratio was used to estimate the relative contributions of industrial sources and vehicle emissions to ambient NO₂ levels. Analysis results of NO₂/SO₂ ratio shows that higher contribution of industrial NO₂ emissions in Jiangsu province, while NO₂ levels in Jiangxi and Hubei provinces are mainly related to vehicle emissions. These results indicate that different pollution control strategies should be applied in different provinces. In addition, multiple linear regression analysis of ambient carbon monoxide (CO) and odd oxygen (O_x) indicated that the primary emission and secondary formation of HCHO contribute $54.4 \pm 3.7\%$ and $39.3 \pm 4.3\%$ to the ambient HCHO, respectively. The largest contribution from primary emissions in winter suggested that photochemically induced secondary formation of HCHO is reduced due to lower solar

irradiance in winter. Our findings provide an improved understanding of major pollution sources along the eastern part of Yangtze River which are useful for designing specific air pollution control policies.

1 Introduction

Nitrogen dioxide (NO_2), sulfur dioxide (SO_2), and formaldehyde (HCHO) are important atmospheric constituents playing important roles in tropospheric chemistry. Nitrogen oxides (NO_x), defined as the sum of nitric oxide (NO) and NO_2 , is one of the major pollutant in the troposphere, playing a key role in both tropospheric and stratospheric chemistry. It takes part in the catalytic formation of tropospheric ozone (O_3), while being a catalyst for the destruction of stratospheric O_3 (Crutzen, 1970). Major sources of NO_x are high-temperature combustions (e.g. fossil fuel burning, biomass burning) and natural processes (e.g. soil microbial activity, lightning events (Lee et al., 1997)). NO_2 in high concentration is harmful to human health, especially for immune and respiratory systems. In addition, NO_2 can lead to the formation of nitrate aerosols, which is an important component of fine suspended particles in the urban environment. Sulfur dioxide (SO_2) is the most abundant anthropogenic sulfur containing air pollutant. In urban areas, SO_2 is produced mainly through the combustion of sulfur-containing fossil fuels for power generation and domestic heating, which accounts for more than 75% of the total SO_2 emissions (Chin et al., 2000). Atmospheric SO_2 causes similar environmental problems as NO_2 , such as acidification of the natural aqua system, formation of secondary aerosols and causing negative impacts on human health (Chiang et al., 2016). The atmospheric lifetime of both NO_2 and SO_2 are relatively short, ranging from few hours up to few days (Krotkov et al., 2016), therefore, their spatial distributions are highly influenced by the emission sources.

Formaldehyde (HCHO) is one of most abundant volatile organic compounds (VOCs) in the atmosphere, playing an important role in air quality and atmospheric photochemistry. Incomplete combustion processes including industrial emissions and vehicle exhaust have been identified as the major HCHO sources in the urban atmosphere (Garcia et al., 2006). Formaldehyde can also be produced from the atmospheric photochemical oxidation of methane (CH_4) and non-methane hydrocarbons (NMHCs) (Miller et al., 2008). In the polluted regions, terminal alkenes such as isoprene, ethene and propene are the most important HCHO precursors (Goldan et al., 2000). The major sinks of HCHO are photolysis, reaction with OH radical and wet deposition in the atmosphere (Lei et al., 2009). The short atmospheric lifetime of HCHO under sunlight is typically very short (2-4 h), indicating that the daytime ambient HCHO are mostly produced locally (Arlander et al., 1995).

Multi-Axis Differential Optical Absorption Spectroscopy (MAX-DOAS) is a passive remote sensing technique providing indispensable information of atmospheric aerosols and trace gases (Platt and Stutz, 2008). Information of tropospheric trace gases are obtained from the molecular absorption in the ultraviolet and visible wavelength bands by applying the differential optical absorption spectroscopy (DOAS) method to the observations of scattered sun light spectra in several different viewing directions. This method has been widely used for atmospheric NO_2 , SO_2 , and HCHO in the past decades (Lee et al., 1997; Heckel et al., 2005; Wang et al., 2014; Hendrick et al., 2014; Chan et al., 2015). MAX-DOAS observations are not only limited to ground based application, but also can be performed on different mobile platforms like

cars (Johansson et al., 2009;Ibrahim et al., 2010;Shaiganfar et al., 2011), aircrafts (Baidar et al., 2013;Dix et al., 2016) or ships (Sinreich et al., 2010;Peters et al., 2012;Takashima et al., 2012;Schreier et al., 2015). In this study, ship-based MAX-DOAS measurements of NO₂, SO₂, and HCHO were performed along the Yangtze River. Previous ship-based MAX-DOAS measurements were mainly focused on remote and coastal marine environments to obtain boundary layer background concentrations of trace gases, such as in the Indian and Pacific Ocean. In this study, we performed ship-based MAX-DOAS observations along the Yangtze River, the busiest navigable inland waterway in the world to obtain insight spatial distribution information of trace gases in eastern China.

Yangtze River delta (YRD) is one of the most populated regions in China. Due to the rapid industrialization and urbanization in the past two decades, Yangtze River delta (YRD) is facing a series of air pollution problems. As emission sources are not well characterized and the atmospheric processes are rather complex, it is important to measure the spatial distribution of atmospheric pollutants, i.e., NO₂, SO₂, and HCHO, in YRD for the investigation of emission sources and atmospheric processes and provides scientific supports for the prevention and designing control measures of air pollution. In this study, spatial distribution of tropospheric NO₂, SO₂, and HCHO were retrieved from ship-based MAX-DOAS observations along the Yangtze River between Shanghai and Wuhan. The experiment aims to provide improved understanding of emission sources and atmospheric processes over eastern China, which is potentially useful for the formulation of strategic air pollution control and identification of the effectiveness of air pollution control policies.

In this paper, we present ship-based Multi-Axis Differential Optical Absorption Spectroscopy (MAX-DOAS) measurements of tropospheric trace gases distribution along the Yangtze River during winter 2015. The measurements were performed along the Yangtze River between Shanghai and Wuhan covering the major industrial areas in eastern China. Details of the experimental setup, spectral analysis and trace gases retrieval of the ship-based MAX-DOAS measurement is presented in section 2. Comparison with OMI NO₂ and the contribution of major emission sources to NO₂ levels along the Yangtze River, as well as the contribution of primary and secondary sources of HCHO are shown in section 3.

2 Methodology

2.1 The Yangtze River measurement campaign

The Yangtze River campaign took place in winter 2015 along the Yangtze River over eastern China within the framework of the “Regional Transport and Transformation of Air Pollution in Eastern China”. The aims of Yangtze River campaign are to provide better understanding of the transportation and transformation of atmospheric pollution, and to identify the potential impacts on air quality and climate.

Ship-based measurement campaign was carried out along the eastern part of Yangtze River between Shanghai and Wuhan. The campaign includes a departing journey (from Shanghai to Wuhan) and a returning journey (from Wuhan to Shanghai). The measurement campaign started on 21 November 2015 at 19:30 LT from Shanghai (31.36°N, 121.62°E), a major industrial and commercial hub of eastern China, and arrived in Wuhan (30.62°N, 114.32°E) on 29 November 2015 at

95 15:42 LT. The measurement ship was then directly sailing back and finally arrived in Shanghai on 4 December 2015 at 20:30 LT. The journey covered most of the major industrial areas in eastern China including several population dense metropolitan cities, such as Nanjing, Wuhu, and Jiujiang. Detail of the cruise track is shown in Fig. 1.

The ship-based MAX-DOAS instrument was part of the air quality monitoring framework of the Yangtze River measurement campaign. The instrument was installed at the beginning of the measurement campaign and started to provide atmospheric observations on 22 November 2015. A summary of the meteorological conditions during the Yangtze River campaign are shown in Table 1.

2.2 MAX-DOAS measurements

2.2.1 Experimental setup

Ship-based MAX-DOAS measurements were performed during Yangtze River campaign. The ship-based MAX-DOAS instrument was developed at the Anhui Institute of Optics and Fine Mechanics (AIOFM), Chinese Academy of Sciences (CAS) which consists of a telescope, a spectrometer and a computer acting as controlling and data acquisition unit. Viewing directions of the telescope are controlled by a stepping motor, scattered sunlight collected by the telescope is redirected to the spectrometer for spectral analysis through an optical fiber bundle. The field of view of the telescope is estimated to be less than 1° . An imaging spectrometer (Princeton instrument), equipped with a charge-coupled device (CCD) detector (512×2048 pixels) is used to measure spectra in the ultraviolet (UV) wavelength range from 303 nm to 370 nm with a spectral resolution of 0.35 nm full width half maximum (FWHM). Spectral data recorded by the imaging spectrometer were average along the first dimension of the CCD in order to get a better signal to noise ratio. During the measurement campaign, the viewing azimuth angle of the telescope was adjusted to 90° (right) relative to the heading direction of the ship (see Fig. S1). A full measurement sequence includes elevation angles (α) of 30° and 90° (zenith). The exposure time of each measurement is set to 100 ms.

2.2.2 Data processing and filtering

Although the instrument was positioned in front of the exhaust stack (see Fig. S1), the MAX-DOAS measurements could still be influenced by the exhaust from the ship. Therefore, measurement data contaminated by the ship exhaust were filtered out in our analysis. Individual measurements taken under unfavorable wind directions (relative wind directions between 150° and 270° with respect to the heading of the ship) were discarded in the following analysis. Due to the stronger absorptions of stratospheric species and low signal to noise ratio at large SZAs, only measurements with solar zenith angle smaller than 75° were taken into account for the DSCDs retrieval. With these filtering criteria (unfavorable wind directions and SZAs), 5.4% and 15.8% of all data were rejected before DSCDs retrieval, respectively.

As the viewing elevation angles of the measurements were relatively high (30° and 90°), therefore, they are insensitivity

125 to the instability or the movement of the ship. In addition, the exposure time of a measurement is rather short (100 ms), the change of measurement elevation and azimuth angle during one measurement is negligible.

2.2.3 DOAS retrieval

Differential slant column densities (DSCDs) of trace gases are derived from the measurement spectra by applying the differential optical absorption spectroscopy (DOAS) technique (Platt and Stutz, 2008). In this study, MAX-DOAS spectra
130 are analyzed using the QDOAS spectral fitting software suite developed by BIRA-IASB (<http://uv-vis.aeronomie.be/software/QDOAS/>). The wavelength calibration was performed by using a high resolution solar reference spectrum (Chance and Kurucz, 2010). Dark current (DC) spectrum was taken with exposure time of 3000 ms and number of scan of 20 scans while electronic offset spectrum (OFFSET) was taken with exposure time of 3 ms and number of scan of 20000 scans. The dark current and offset spectra were used to correct measurement spectra prior to the spectra analysis.
135 Several trace gas absorption cross sections (Vandaele et al., 1998; Vandaele et al., 2009; Meller and Moortgat, 2000; Serdyuchenko et al., 2014; Thalman and Volkamer, 2013; Fleischmann et al., 2004), the Ring spectrum, a Fraunhofer reference spectrum and a low order polynomial are included in the DOAS fit. Details of the DOAS fit settings are shown in Table 2. In this study, zenith measurement spectrum with the lowest pollutant concentration was selected as the Fraunhofer reference spectrum for the retrieval of measurement spectra taken during the measurement campaign. Similar reference
140 spectrum selection approaches have been used in different mobile measurements studies (Wu et al., 2013; Li et al., 2015).

Figure 2 shows an example of the DOAS analysis of a spectrum recorded on 1 December 2015 at 14:02 LT with an elevation of 30°. The retrieved NO₂ (Fig. 2a), SO₂ (Fig. 2b), and HCHO (Fig. 2c) DSCDs are 1.40×10^{17} , 6.25×10^{16} , and 3.51×10^{16} molec/cm², respectively. In this study, only data with root mean square (RMS) of residuals smaller than 3.0×10^{-3} are considered. This filtering criterion (RMS) removed 18.7%, 20.2%, and 25.2% of data for NO₂, SO₂, and HCHO,
145 respectively.

2.2.4 Determination of the tropospheric VCD

The DOAS spectral retrieval results are the differential slant column densities (DSCDs) which are defined as the difference between the slant column density (SCD) of the measured spectrum and the Fraunhofer reference spectrum:

$$\text{DSCD}_{\text{meas}} = \text{SCD}_{\text{meas}} - \text{SCD}_{\text{Fraunhofer}} \quad (1)$$

150 The SCD is the integrated trace gas concentration along the light path through the atmosphere, which includes both tropospheric and stratospheric part ($\text{SCD}_{\text{meas}} = \text{SCD}_{\text{trop}} + \text{SCD}_{\text{strat}}$). As scattering of photons most likely takes place in the troposphere, it can be assumed that the light path in the stratosphere for zenith and off zenith measurements are very similar, i.e. $\text{SCD}_{\text{strat}}(\alpha) \approx \text{SCD}_{\text{strat}}(90^\circ)$. Then Eq. (1) can be written as:

$$\begin{aligned}
\text{DSCD}_{\text{meas}}(\alpha) &= (\text{SCD}_{\text{trop}}(\alpha) + \text{SCD}_{\text{strat}}(\alpha)) - (\text{SCD}_{\text{trop}}(90^\circ) + \text{SCD}_{\text{strat}}(90^\circ)) \\
&= \text{SCD}_{\text{trop}}(\alpha) - \text{SCD}_{\text{trop}}(90^\circ) \\
&= \text{DSCD}_{\text{trop}}(\alpha)
\end{aligned} \tag{2}$$

155 where $\text{DSCD}_{\text{trop}}(\alpha)$ represents the tropospheric DSCD measured at elevation angle of α .

As the measured DSCDs are dependent on the absorption path in the atmosphere, the measurement has to convert to vertical column density (VCD) in order to compare with each other. For this purpose, a concept so-called air mass factor (AMF) is applied (Solomon et al., 1987), and the tropospheric vertical column density (VCD_{trop}) can be expressed as follows:

$$\text{VCD}_{\text{trop}} = \frac{\text{SCD}_{\text{trop}}(\alpha)}{\text{AMF}_{\text{trop}}(\alpha)} \tag{3}$$

160 Assuming scattering happens above the trace gas layer, the AMF for the zenith and the off-axis view can be estimated as 1 and $1/\sin\alpha$, respectively (Hönninger et al., 2004). This method is so-called “geometric approximation”. However, geometric approximation of AMF could result in large errors under high aerosol load conditions (Wagner et al., 2007). In addition, relative azimuth angle, defined as the angle between the viewing direction and the sun, also plays an important role in the AMF calculation. This effect is particularly important for mobile observations (Wagner et al., 2010). For this reason, we
165 adapted the simultaneous lidar measurement of aerosol profiles for the radiative transfer calculation of AMFs.

In this study, AMFs for SCD to VCD conversion were calculated using the radiative transfer model SCIATRAN 2.2 (Rozanov et al., 2005). Compared to the geometric approach, radiative transfer calculation of AMF is more computational expensive. Vertical distribution profiles of aerosols and trace gases are also important for the AMF calculation. In this study, trace gas profiles (e.g., O_3 , NO_2 , SO_2 , and HCHO) and vertical profiles of pressure and temperature are taken from the
170 Weather Research and Forecasting model coupled with Chemistry (WRF-Chem) simulations for AMF calculations (Liu et al., 2016). Atmospheric profiles obtained from the model simulation were then interpolated in both spatial and temporal dimension to MAX-DOAS measurements location and time for AMF calculation. Hourly averaged aerosol extinction coefficients in the lowest 2 km of the troposphere were taken from the Mie lidar measurements while aerosols above 2 km were not considered in the radiative transfer simulations. Aerosols below the lidar overlap height are considered to be
175 homogeneous in the AMF calculation. In order to estimate the influence of aerosol above 2 km on the AMF calculation, we compared AMFs calculated with and without considering aerosols above 2 km. As the lidar measurement above 2 km has larger uncertainty, aerosols extinction information above 2 km is taken from WRF-Chem simulations. Comparison results show that AMFs calculated with considering aerosol above 2 km are on average 2-4% lower than AMFs without considering aerosol at upper altitudes. The result indicates that ignoring aerosols above 2 km only cause a negligible error on the AMF
180 calculation. Tropospheric AMFs of NO_2 , SO_2 , and HCHO were calculated at the central wavelength of their DOAS fitting windows which are 354 nm, 311 nm, and 347 nm, respectively. The aerosol extinction profiles obtained from the Mie lidar are converted to MAX-DOAS retrieval wavelengths assuming a fix Ångström coefficient (Ångström, 1929) of 1. The aerosol extinction profiles at 354 nm, 311 nm, and 347 nm can be derived using the following formula:

$$\alpha(\lambda_x, z) = \alpha(\lambda_{532}, z) \times \left(\frac{\lambda_x}{\lambda_{532}}\right)^{-\nu} \quad (4)$$

185 where $\alpha(\lambda_x, z)$ is the aerosol extinction coefficient at wavelength λ_x ; $\alpha(\lambda_{532}, z)$ is the aerosol extinction coefficient at 532 nm; ν is the Ångström coefficient which is assigned to a fix value ($\nu=1$) in this study.

A fix set of single scattering albedo (SSA) of 0.95, asymmetry parameter of 0.68 and surface albedo of 0.06 is assumed in the radiative transfer calculations (Chen et al., 2009;Pinker et al., 1995). In this study, all radiative transfer calculations were performed by using the radiative transfer model SCIATRAN 2.2 (Rozanov et al., 2005). Previous studies show that the uncertainties caused by aerosol single scattering albedo (SSA), aerosol asymmetry parameter (AP) and surface albedo assumptions are less than 10% (Chen et al., 2009;Wang et al., 2012b). Uncertainty of lidar measurement of aerosol extinction profiles also contributes to the uncertainty in the AMF calculations. A sensitivity study was performed with aerosol profiles with different AODs (i.e., 0.4, 0.6, 0.8, 1.0, and 1.2) and a single trace gas profile with a constant NO₂, SO₂, and HCHO concentration of 5.4×10^{11} molecules cm⁻³ (equal to 20 ppb at the ground level) to quantify the uncertainty caused by aerosol profiles used in the AMF calculation at different wavelengths. In the sensitivity analysis, aerosols and trace gases are assumed well mixed in the lowest 0.8 km, following an exponential decrease with height. The result shows that the variation of AMFs with different aerosol profiles (SZAs smaller than 75°) are 11%, 13%, and 11% for NO₂, SO₂, and HCHO, respectively (see Fig. S2). Considering the uncertainties caused by the assumptions of SSA, AP and surface albedo and uncertainties of aerosol load in the radiative transfer calculations, we estimated the uncertainties of tropospheric AMFs are ranging between 30-43% for SZAs smaller than 75°.

As the DOAS analysis results are DSCDs, we have to apply the concept of differential air mass factor (DAMF) to convert the measurement to vertical columns as follows:

$$\begin{aligned} \text{DSCD}_{\text{trop}}(\alpha) &= \text{SCD}_{\text{trop}}(\alpha) - \text{SCD}_{\text{trop}}(90^\circ) \\ &= \text{VCD}_{\text{trop}} \times \text{AMF}_{\text{trop}}(\alpha) - \text{VCD}_{\text{trop}} \times \text{AMF}_{\text{trop}}(90^\circ) \\ \Rightarrow \text{VCD}_{\text{trop}} &= \frac{\text{DSCD}_{\text{trop}}(\alpha)}{\text{AMF}_{\text{trop}}(\alpha) - \text{AMF}_{\text{trop}}(90^\circ)} = \frac{\text{DSCD}_{\text{trop}}(\alpha)}{\text{DAMF}_{\text{trop}}(\alpha)} \end{aligned} \quad (5)$$

where DAMF is defined as the difference of air mass factor (AMF) between $\alpha \neq 90^\circ$ and $\alpha = 90^\circ$ (DAMF_{trop}(α) = AMF_{trop}(α) - AMF_{trop}(90°)). This equation (Eq. 5) is regard as the standard method for the determination of the tropospheric trace gas VCDs from MAX-DOAS observations.

Mobile MAX-DOAS observations are strongly influenced by rapid change of air masses and radiative transfer conditions along the navigating route. The standard method (Eqs. 1 to 5) to calculate tropospheric VCDs can result in large errors. An alternative method has been suggested for mobile MAX-DOAS measurements (Wagner et al., 2010). This method has been applied in previous mobile MAX-DOAS observations (Ibrahim et al., 2010;Wu et al., 2015) and reported to be better than the standard method for mobile platforms. Therefore, we adapted the new method in this study for tropospheric VCDs conversion. The VCD_{trop} can be expressed as follows (combining Eqs. 1 and 3):

$$\begin{aligned} \text{VCD}_{\text{trop}} &= \frac{\text{SCD}_{\text{meas}}(\alpha) - \text{SCD}_{\text{strat}}(\text{SZA})}{\text{AMF}_{\text{trop}}(\alpha)} \\ &= \frac{\text{DSCD}_{\text{meas}}(\alpha) + \text{SCD}_{\text{ref}} - \text{SCD}_{\text{strat}}(\text{SZA})}{\text{AMF}_{\text{trop}}(\alpha)} \end{aligned} \quad (6)$$

where SZA denotes the solar zenith angle. We refer to the difference of the two unknowns SCD_{ref} and $\text{SCD}_{\text{strat}}(\text{SZA})$ as $\text{DSCD}_{\text{offset}}(\text{SZA})$ and can be written as follows:

$$\text{DSCD}_{\text{offset}}(\text{SZA}) = \text{SCD}_{\text{ref}} - \text{SCD}_{\text{strat}}(\text{SZA}) \quad (7)$$

The expressions for VCD_{trop} in Eqs. 5 and 6 are set equal:

$$\begin{aligned} &\frac{\text{DSCD}_{\text{meas}}(\alpha) - \text{DSCD}_{\text{meas}}(90^\circ)}{\text{AMF}_{\text{trop}}(\alpha) - \text{AMF}_{\text{trop}}(90^\circ)} \\ &= \frac{\text{DSCD}_{\text{meas}}(\alpha) + \text{SCD}_{\text{ref}} - \text{SCD}_{\text{strat}}(\text{SZA})}{\text{AMF}_{\text{trop}}(\alpha)} \end{aligned} \quad (8)$$

This equation can be solved for $\text{DSCD}_{\text{offset}}(\text{SZA})$ as defined in Eq. 7:

$$\begin{aligned} &\text{DSCD}_{\text{offset}}(\text{SZA}) \\ &= \frac{\text{AMF}_{\text{trop}}(90^\circ) \times \text{DSCD}_{\text{meas}}(\alpha) - \text{AMF}_{\text{trop}}(\alpha) \times \text{DSCD}_{\text{meas}}(90^\circ)}{\text{AMF}_{\text{trop}}(\alpha) - \text{AMF}_{\text{trop}}(90^\circ)} \end{aligned} \quad (9)$$

Since $\text{DSCD}_{\text{offset}}(\text{SZA})$ is a smooth function of the SZA or time, we can fit the time series of calculated $\text{DSCD}_{\text{offset}}(\text{SZA or } t_i)$ by a low order polynomial (second order). t_i indicates the time between the two selected measurements from one elevation sequence i , the time series of the calculated $\text{DSCD}_{\text{offset}}(\text{SZA})$ can be written as:

$$\begin{aligned} &\text{DSCD}_{\text{offset}}(t_i) \\ &= \frac{\text{AMF}_{\text{trop}}(90^\circ, t_i) \times \text{DSCD}_{\text{meas}}(\alpha, t_i) - \text{AMF}_{\text{trop}}(\alpha, t_i) \times \text{DSCD}_{\text{meas}}(90^\circ, t_i)}{\text{AMF}_{\text{trop}}(\alpha, t_i) - \text{AMF}_{\text{trop}}(90^\circ, t_i)} \end{aligned} \quad (10)$$

The fitted polynomial represents the approximation of $\text{DSCD}_{\text{offset}}(t_i)$ and can be inserted into Eq. 8. In this way we can obtain a time series of tropospheric trace gas VCDs essentially without errors introduced by the spatio-temporal variations of the trace gas field (example is shown in Figs. S3-5). The detailed description of the method can be found in Wagner et al. (2010).

2.3 OMI Satellite observations

The Ozone Monitoring Instrument (OMI) was launched onboard the NASA Earth Observing System (EOS)-Aura satellite on 15 July 2004 (Levelt et al., 2006). It is a nadir-viewing imaging spectrometer measuring direct and Earth's reflected sunlight in the ultra violet (UV) and visible (VIS) range from 270 to 500 nm. OMI aims to monitor global atmospheric trace gases distribution with high spatial (up to 13×24 km) and temporal (daily global coverage) resolution. The local overpass time of OMI is between 13:40 and 13:50 (local time) on the ascending node. In this study, USTC's OMI tropospheric NO_2 product is used, which is developed based on OMI's primary product and has proven to be more suitable

235 for the atmospheric conditions in China (Liu et al., 2016;Xing et al., 2017;Su et al., 2017). Slant column densities (SCDs) of
NO₂ are retrieved by applying the DOAS fit to OMI spectra (data source: OMI Level 1B VIS Global Radiances Data product
(OML1BRVG) (https://disc.gsfc.nasa.gov/Aura/data-holdings/OMI/oml1brvg_v003.shtml)). Separation of stratospheric and
tropospheric columns is achieved by the local analysis of the stratospheric field over unpolluted areas (Bucsela et al.,
2013;Krotkov et al., 2017).The OMI NO₂ SCDs are converted to VCDs by using the concept of air mass factor (AMF). The
240 AMFs are calculated based on the NO₂ and atmospheric profiles derived from WRF-Chem chemistry transport model
simulations with a horizontal resolution of 20 × 20 km over eastern China (17-49 °N, 95-124°E) and 26 vertical layers from
the ground level to the height with a pressure of 50 hPa. In this study, the National Centers for Environmental Prediction
(NCEP) Final operational global analysis (FNL) meteorological data are used to drive the WRF-Chem simulations. Details
of the chemistry transport model simulation as well as the satellite data retrieval process can be found in Liu et al. (2016).

245 2.4 Ancillary data

Lidar observations of aerosol vertical distribution were also carried out during the campaign. The lidar system is
equipped with a diode-pumped frequency doubled Nd:YAG laser emitting laser pulses at 532 nm. The typical pulse energy
of the laser is about 20 mJ with a pulse repetition frequency of 20 Hz. The laser beam is emitted with divergence of 1 mrad
and 200 mm off-axis to the receiving telescope with a field of view of 2 mrad, resulting in an overlap height of about 195 m.
250 A constant lidar ratio (S_p , extinction to backscatter ratio) of 50 sr was assumed in the lidar retrieval. Details of the lidar
system and the data retrieval can be found in (Chen et al., 2017;Fan et al., 2018).

Meteorological parameters such as wind direction and wind speed were obtained from an automatic weather station on
board the measurement ship. In-situ trace gas measurements, such as CO, O₃, and NO₂ were performed using Sensor
Networks for Air Quality (SNAQ) during the campaign. SNAQ is a highly portable and low-cost air quality measurement
255 network methodology incorporating electrochemical gas sensors which can be used for high resolution air quality studies at
ppbv levels (Mead et al., 2013). CO, O₃, and NO₂ were monitored by SNAQ with a 20s resolution, and the detection limit of
CO, O₃, and NO₂ were 3 ppbv+5% of measured CO, 2 ppbv+5% of measured O₃, and 2 ppbv+5% of measured NO₂,
respectively, and in special cases 5% of measured values can increase to 10%.

3 Results and discussion

260 MAX-DOAS measurements were conducted during the campaign period from 22 November to 4 December 2015. The
measurements were interrupted occasionally due to power failure of the measurement ship and instrumental problems,
details of the measurement period are listed in Table 1. All the times reported herein are local time (LT=UTC+8).
Measurement spectra taken during daytime between 08:00 and 16:00 (SZAs smaller than 75°), corresponding to the sunshine
period during wintertime in China were used for analysis. In order to avoid unnecessary uncertainties introduced during the

265 VCD conversion, we use the radiative transfer model with lidar aerosol profiles as input for the AMF calculation to convert all the measurements to VCDs.

3.1 General characteristics of tropospheric NO₂, SO₂, and HCHO

Time series of tropospheric NO₂, SO₂, and HCHO vertical column densities (VCDs) for the entire campaign from 22 November to 4 December, 2015 are shown in Figs. 3-4. Missing data are due to power failure of the measurement ship and
270 instrumental problems, measurements taken under unfavorable wind directions and SZAs larger than 75°. The mean NO₂ VCD of the entire campaign is 2.27×10^{16} molec/cm², with an exceptionally large variation range from 1.31×10^{15} molec/cm² to 7.72×10^{16} molec/cm². About half of the NO₂ VCDs are in the range of 5-20 ($\times 10^{15}$ molec/cm²) and high NO₂ VCDs (i.e., $> 5 \times 10^{16}$ molec/cm², about the 95th percentile value) are about 2.2 times higher than mean value (Fig. S6a). The mean SO₂ VCD of the entire campaign is 2.14×10^{16} molec/cm² with a range from 1.05×10^{15} molec/cm² to 9.29×10^{16} molec/cm².
275 Although more than half of the values are in the range of 10-25 ($\times 10^{15}$ molec/cm²), high SO₂ VCDs (i.e., $> 5.5 \times 10^{16}$ molec/cm², about the 95th percentile value) are about 2.5 times higher than mean value (Fig. S6b). It should be noted that three elevated tropospheric NO₂ and SO₂ VCDs events have been observed which are highlighted in gray in Fig. 4. Pollution events were identified with both NO₂ and SO₂ VCDs reached or above the threshold value of 4.0×10^{16} molec/cm². The mean HCHO VCDs of the entire campaign is 9.61×10^{15} molec/cm², ranging from 1.05×10^{15} molec/cm² to 5.37×10^{16}
280 molec/cm². Most of the HCHO VCDs lie between 1-14 ($\times 10^{15}$ molec/cm²) and high HCHO VCDs (i.e., $> 2.6 \times 10^{16}$ molec/cm², about the 95th percentile value) are about 2.7 times higher than mean value (see Fig. S6c).

The spatial distribution of NO₂, SO₂, and HCHO VCDs along the eastern part of the Yangtze River are shown in Fig. 5. Three elevated tropospheric NO₂ and SO₂ VCDs events over Yangtze River were detected around three major industrial cities with large number of heavy emission sources, i.e., Jiujiang (#1), an industrial city located on the southern shores of the
285 Yangtze River in northwest Jiangxi Province, China; Nanjing (#2), the provincial capital and the most populous city in Jiangsu province, Eastern China; and Shanghai (#3), a metropolis located in the Yangtze River Delta with the busiest container port in the world.

The variations of the NO₂ and SO₂ VCDs are closely linked to the spatial distribution of emission sources around industrial cities as well as meteorological conditions (e.g., wind speed and wind direction). Most of the previous studies
290 show an inverse relationship between wind speed and air quality, i.e., the lower the wind speed the higher the pollution level, which suggesting that low wind speed condition is limiting the mixing and dispersion of atmospheric pollutants, and thus in favors of accumulation of local emissions (Chan et al., 2012; Wang et al., 2012b; Chan et al., 2014; Chan et al., 2017; Wang et al., 2017). However, positive correlations ($p < 0.05$, t-test) were found between the mobile MAX-DOAS NO₂ and SO₂ VCDs (red circle and blue square, respectively) and wind speed during these three events (Fig. 6a-6c). The result suggested that
295 these episodes are most likely not related to accumulation of local emission. We further investigated the possible influence of transport on the NO₂ spatial distribution by looking into the backward trajectories during these episodes. We calculated

24h backward trajectories of air masses using the HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) model which is developed by the National Oceanic and Atmospheric Administration-Air Resource Laboratory (NOAA-ARL) (Stein et al., 2015) (<http://ready.arl.noaa.gov/HYSPLIT.php>). Meteorological data from the Global Data Assimilation System (GDAS) with a spatial resolution of $1^{\circ} \times 1^{\circ}$ and 24 vertical levels was used in the model for the trajectory simulations. The 24h backward trajectories (green markers indicate the trajectory point of -6, -12, -18 and -24 h) were calculated for each hour during three pollution episodes using the NOAA HYSPLIT model with end point altitude of 500 m a.g.l.. The result is shown in Fig. 6d. As indicated by the 24h back-trajectories, NO₂ VCDs on 1 December 2015 (Event #1) are prominent when under southwesterly wind condition. This is probably due to an industrial city (Jiujiang) is located on the southern shores of the Yangtze River at the upwind areas of the ship. Backward trajectories (Events #2 and #3, Fig. 6d) indicated prevailing northwesterly wind during 3-4 December 2015. In addition, the backward trajectory analysis suggested that rapid transport of air masses carries significant amount of pollutants from polluted areas in northern China (Krotkov et al., 2016) across the Yangtze River, resulting in higher NO₂ and SO₂ VCDs. The higher the wind speed the higher the NO₂ and SO₂ VCDs under northwesterly wind conditions (Figs. 6b and 6c), which means that the transport from distant sources is more significant than of the contribution from local emission sources. These results suggested that the spatial distributions of pollutants along the Yangtze River are strongly influenced by the meteorological condition. In comparison to these high VCDs events, relatively low NO₂ and SO₂ VCDs were observed in the first few days of the campaign (22 to 25 November), which might due to occasional showers during these days removed pollutants through wet deposition.

Elevated tropospheric HCHO VCDs (up to 2×10^{16} molec/cm²) are observed mostly during clear days (e.g., 26 November, 3 and 4 December), with good visibility and low cloud coverage (see Table 1). This is probably due to the enhancement of photochemical formation of atmospheric HCHO under strong solar irradiation. In contrast, lower HCHO VCDs were observed mainly on rainy, cloudy and haze days, which might be due to stronger wet deposition and weaker solar irradiation during these days. Elevated HCHO VCDs in the HCHO time series was found on 3 December 2015 when the ship was anchored at Yizheng Marine department (32.25°N, 119.15°E). This day is mostly cloud-free with good visibility. In addition, HCHO VCDs show a diurnal pattern with low values in the morning and late afternoon and peaks around noontime. This diurnal pattern indicates the significant contribution of photochemical formation of HCHO. Detailed analysis of the primary sources and secondary formation of HCHO for 3 December 2015 is shown in section 3.4.

3.2 Comparison with OMI NO₂

In order to compare the ship-based MAX-DOAS measurements to OMI observations, the ship-based MAX-DOAS data are temporally averaged around the OMI satellite overpass time from 12:00 to 14:00 (LT). For 22, 25, and 26 November, no MAX-DOAS data were available during the OMI overpass time due to power failure of the measurement ship and instrumental problems (see Table 1). All OMI measurement within 20 km (ship speed: ~10-20 km/h) radius of the ship's averaged position from 12:00 to 14:00 (LT) are averaged and compared to the averaged ship MAX-DOAS data. For 29

November and 1, 3 December, no satellite observations were available at the corresponding ship's location. As a result, 7
330 days (Nov 23, 24, 27, 28 and 30 and Dec 2 and 4) of measurements from both OMI and ship-based MAX-DOAS are used
for data comparison.

Scatter plot of the ship MAX-DOAS and OMI NO₂ measurements is shown in Fig. 7a. The NASA's OMI NO₂ VCDs
are also shown as reference. Compared to the NASA's standard product, the USTC's OMI tropospheric NO₂ VCD agrees
better with ground measurements a Pearson correlation coefficient (R) of 0.82 while the correlation between MAX-DOAS
335 and the NASA OMI product is 0.76. However, the regression analysis indicated that the USTC's and NASA's OMI data
underestimated the tropospheric NO₂ VCD by about 10% and 27%, respectively. Time series of ship-based MAX-DOAS
and OMI NO₂ VCDs is shown in Fig. 7b. The ship-based MAX-DOAS data were higher than the OMI values for most of the
time. Underestimation of tropospheric NO₂ VCDs for OMI might attribute to the averaging effect over large OMI pixel.
Unpolluted or less polluted areas are also included in the OMI pixel and resulting in low values over pollution hotspots.

340 In order to have a better insight of the spatial distribution pattern of tropospheric NO₂ along the Yangtze River, NO₂
VCDs measured by both ship-based MAX-DOAS and OMI are plot on same map which is shown in Fig. 8. OMI
tropospheric NO₂ VCDs are gridded onto a 0.02° × 0.02° grid using the parabolic spline gridding algorithm (Kuhlmann et al.,
2014; Chan et al., 2015; Chan et al., 2017). The gridding routine was reported to provide more realistic continuous spatial
distributions of NO₂ while preserving the details of emission hotspots (Chan et al., 2015; Chan et al., 2017). During clear
345 days (27 November and 4 December, 2015), both ship-based MAX-DOAS and OMI capture similar NO₂ spatial pattern (Fig.
8a and 8d). However, a significant enhancement of NO₂ close to the exit of the Yangtze River was observed by ship-based
MAX-DOAS observation, as shown in Fig. 8d which does not show up in the OMI observation. This is probably due to the
mismatch of OMI overpass time and the ship-based MAX-DOAS measurement time. The spatial coverage of OMI
observation was limited on 30 November 2015 due to cloudy sky condition. On the other hand, NO₂ hotspots can be
350 observed from the ship-based measurement as shown in Fig. 8b. These NO₂ peaks cannot be detected by OMI as cloud
shield NO₂ at the lower troposphere. Different spatial patterns were detected by the ship-based MAX-DOAS and OMI
satellite on 2 December 2015 which was a haze day (Fig. 8c). In order to estimate the influence of ignoring aerosols in
satellite AMF calculation on NO₂ retrieval, we compared OMI NO₂ VCDs calculated with and without considering aerosol
in the satellite AMF calculations. Significant enhancement of OMI NO₂ VCDs is observed over some areas when aerosol is
355 considered in the satellite retrieval. However, the spatial pattern observed by ship MAX-DOAS and OMI are still quite
different. The result indicates the impact of aerosol could not fully explain the discrepancy between MAX-DOAS and OMI
on this day. On the other hand, the MAX-DOAS and OMI observations agree better during OMI overpass time (black star in
Fig. 8) and the agreement decay when the time differences between MAX-DOAS and OMI measurements become larger.
This implies a strong temporal variability of NO₂ on this day and leads to larger differences of NO₂ spatial distribution
360 between OMI and ship MAX-DOAS measurements.

Ship-based MAX-DOAS is more sensitivity to near surface NO₂, however, the measurement is only limited to the area
along the Yangtze River. In order to have a broader coverage of tropospheric NO₂ distribution over Yangtze River delta,

OMI tropospheric NO₂ product is used in this study. Figure 9 shows the averaged tropospheric NO₂ VCDs along Yangtze River and its surrounding regions (26°-34°N, 112°-124°E). Enhanced NO₂ VCDs appeared at the exit of Yangtze River. This area includes southern Jiangsu, eastern Anhui, and northern Zhejiang. It is obvious that the pollution level along Yangtze River (white line in Fig. 9) is higher than surrounding areas, especially areas from Wuhu to Wuhan. This is probably resulting from the fact that most of the industrial activities are concentrated along Yangtze River as the logistic is much more convenience and cost efficient through water transportation. Our observation implies that specific emission control measures should be applied on the highly polluted industry along Yangtze River.

3.3 Possible contributions to ambient NO₂ levels

Fossil fuel consumption is the major source of anthropogenic NO_x emissions, especially in highly industrialized and urbanized regions. Industrial sources (including power plants, other fuel combustion facilities, and non-combustion processes) and vehicle emissions are the two major contributors, which together composed about 90% of the total anthropogenic NO_x emissions in China (Huang et al., 2011; Shi et al., 2014). Understanding the individual contributions of industrial sources and vehicle exhaust to ambient NO₂ is important for designing suitable emission control strategies in polluted areas, like Yangtze River delta. In this study, we estimated contribution of different emission sources to NO₂ levels along the Yangtze River by analyzing the ratio between ambient NO₂ and SO₂.

Figure 1 (green dots) shows a number of power plants are located along the Yangtze River between Shanghai and Wuhan. Industrial zones can also be found close to these power plants along the Yangtze River due to the logistically convenience. Emissions of NO₂ and SO₂ from coal-fired power plants are significant air pollution sources. As the atmospheric lifetime of NO₂ and SO₂ is roughly the same (Krotkov et al., 2016), the ambient NO₂/SO₂ ratio is approximately equal to the emission ratio of NO₂/SO₂. In addition, vehicles mainly emit NO_x and their SO₂ emissions are trivial, while coal-fired power plants, heavy industries and ships mostly use sulfur-containing fossil fuels which emit both NO_x and SO₂. Therefore, lower NO₂/SO₂ ratio implies larger contribution from industrial sources (Zhang et al., 2017), while higher NO₂/SO₂ ratios indicate larger contribution from vehicle exhaust sources toward NO₂ levels (Mallik and Lal, 2014; Krotkov et al., 2016). It should be noted that it is difficult to separate local ship emissions from industrial emissions due to their similar emission components, so industrial sources in this paper including not only coal-fired power plants and heavy industries but also ship emissions. In this study, we analyzed NO₂/SO₂ ratios around coal-fired power plants along the Yangtze River. NO₂/SO₂ ratios are determined by linear regression of NO₂ and SO₂ measurements around power plants which is shown in Fig. 10. NO₂ and SO₂ VCDs measured within 2 km of the power plants (adjacent industrial zones and ships are included) are used for the analysis. Good correlation was found between NO₂ and SO₂ VCDs measured around coal-fired power plants ($R = 0.91$, $N = 195$) which implies the ambient NO₂ and SO₂ are mostly emitted from similar sources (i.e., coal combustion). The slope of linear regression is 0.56 ± 0.02 . Relatively low NO₂/SO₂ ratio indicates large contributions from combustion of high sulfur containing fuel, e.g. coal, which is mainly used for power generation. In

395 addition, the desulfurization filters installed in these power plants are either ineffective or maybe even deactivated during the time.

Assuming the ambient NO₂ is mostly emitted from industrial sources (mainly from power plants, and ship emissions are also included) and vehicle exhaust, other anthropogenic sources like biomass burning and natural sources are negligible. The NO₂/SO₂ ratio (slope) and intercept (offset) of the linear regression of data measured around the power plants can be used to
400 estimate the source contributions of industrial sources and vehicle exhaust to the ambient NO₂ concentration. Assuming the NO₂/SO₂ ratio for industrial emission is constant, we can estimate the industrial and vehicle contribution by using the following equations:

$$\begin{aligned} P_{\text{Industrial sources}} &= \frac{\text{NO}_2(\text{power plants})}{\text{NO}_2(\text{total})} \times 100\% \\ &= \frac{\text{SO}_2 \times \text{Slope} + \text{Intercept}}{\text{NO}_2(\text{total})} \times 100\% \end{aligned} \quad (13)$$

$$\begin{aligned} P_{\text{vehicle exhaust}} &= \frac{\text{NO}_2(\text{vehicle exhaust})}{\text{NO}_2(\text{total})} \times 100\% \\ &= \frac{\text{NO}_2(\text{total}) - (\text{SO}_2 \times \text{Slope} + \text{Intercept})}{\text{NO}_2(\text{total})} \times 100\% \end{aligned} \quad (14)$$

405 where SO₂ represents the SO₂ VCDs, NO₂(total) denotes the NO₂ VCDs, the slope and the intercept of the linear regression are 0.56 and 1.86 (unit: 10¹⁵ molec/cm²), respectively.

During the campaign, the route covered four provinces along the Yangtze River, i.e., Jiangsu, Anhui, Jiangxi, and Hubei. Figure 11 shows the relative contributions of industrial sources and vehicle exhaust to the ambient NO₂ levels over the four provinces. In Jiangsu province, a higher contribution from power generation to NO₂ level was found, which is
410 mainly due to large number of power plant located along the Yangtze River in Jiangsu province. The NO_x emission over the eastern China, including Jiangsu province (15.41 t/(km²·y)) (Shi et al., 2014), is more intensive than other parts of China. In addition, Jiangsu province is one of the province in China with maximum annual NO_x emissions from coal-fired power plants (Zhao et al., 2008; Wang et al., 2012a). In contrast, the contribution of vehicle exhaust to NO₂ level was higher than that of coal-fired power plants in Jiangxi and Hubei provinces, suggesting that traffic emissions have larger impacts on the
415 NO₂ level in these provinces. Previous study shows a dramatic growth of the number of vehicle plays an increasingly significant role for regional NO₂ pollution over past years (Xia et al., 2016). For Jiangxi and Hubei provinces, the number of power plant is less than Jiangsu province. Therefore, the contribution of vehicle exhaust to NO₂ level is expected to be more pronounced along with the dramatic growth of vehicle number. In Anhui province, the contributions of coal-fired power plants and vehicle exhaust to NO₂ level were about the same. Our result suggests that different pollution controlling strategy
420 should be applied in different province: power generation emissions are the major reduction target for Jiangsu province; while more specific control policies are need to reduce the vehicle exhaust pollution in Jiangxi and Hubei provinces.

3.4 Estimation of primary and secondary sources of ambient HCHO

Industrial zones are mainly located along the Yangtze River due to the logistical convenience. Observations along the Yangtze River were constantly influenced by plumes originating from various industrial activities, such as coal burning, crude oil refining and plastic and rubber syntheses. Besides the direct primary emissions, ambient HCHO can also be formed through secondary atmospheric processes. Therefore, it is important to quantify the contribution of primary and secondary HCHO in order to better understand the atmospheric processes as well as the corresponding impacts on the local air quality.

CO is directly emitted to the atmosphere through combustion processes (e.g., incomplete combustion of vehicle engines) and therefore can be used as a tracer for primary emission of HCHO (Friedfeld et al., 2002; Garcia et al., 2006). On the other hand, O₃ reacts with NO emitted from automobiles to form NO₂. Thus, the odd oxygen O_x (O_x = O₃ + NO₂) is often used as a tracer for photochemical processes in urban atmosphere (Wood et al., 2010). In this study, we use CO as the tracer of primary HCHO while O_x being an indicator of secondary HCHO formation. The CO and O_x data were measured by Sensor Networks for Air Quality (SNAQ) during this campaign. In addition, a simplified formula was used to convert mean HCHO DSCDs to mixing ratios (ppbv) (Lee et al., 2008) (detailed formula and parameters are shown in the supplement). Previous study shows that a linear model can be used for the source apportionment analysis of ambient HCHO (Garcia et al., 2006). The measured HCHO was apportioned by a multiple linear regression model which is parameterized by the following equation:

$$[\text{HCHO}] = \beta_0 + \beta_1[\text{CO}] + \beta_2[\text{O}_x] \quad (15)$$

where β_0 , β_1 , and β_2 are the fit coefficients obtained from the multiple linear regression. The analysis was done on a daily basis.

The relative contributions of primary emission, photochemical formation and atmospheric background HCHO to the total atmospheric HCHO are calculated according to the tracer concentrations and corresponding fit coefficients by the following equations:

$$P_{\text{Primary}} = \frac{\beta_1[\text{CO}]_i}{\beta_0 + \beta_1[\text{CO}]_i + \beta_2[\text{O}_x]_i} \times 100\% \quad (16)$$

$$P_{\text{Secondary}} = \frac{\beta_2[\text{O}_x]_i}{\beta_0 + \beta_1[\text{CO}]_i + \beta_2[\text{O}_x]_i} \times 100\% \quad (17)$$

$$P_{\text{Background}} = \frac{\beta_0}{\beta_0 + \beta_1[\text{CO}]_i + \beta_2[\text{O}_x]_i} \times 100\% \quad (18)$$

where P_{Primary} represents the contribution from primary sources (vehicle and industrial emissions); $P_{\text{Secondary}}$ is the contribution of secondary HCHO (photochemical oxidation); and $P_{\text{Background}}$ indicates the background HCHO which is neither classified as primary nor secondary HCHO. According to previous studies in YRD (Wang et al., 2015; Ma et al., 2016), the background level of HCHO is limited to 1 ppbv. Therefore, the regression parameter β_0 is fixed at 1 ppbv in this analysis. $[\text{CO}]_i$ and $[\text{O}_x]_i$ represent the concentrations of CO and O_x at time i , respectively. β_1 and β_2 are the regression coefficients obtained from multiple linear regressions.

As other factors (e.g., meteorological conditions) can also affect the atmospheric HCHO concentration, in order to make

sure the regression model is representative for atmospheric conditions, only data fulfilling the following criteria are used in the analysis (a) correlation coefficient (R) larger than 0.75 (Li et al., 2010) and (b) significance value lower than 0.05. Of the 12 days of measurements, only 2 days fulfill the criteria to be considered in this analysis. The parameters of the multiple linear regression fit and the linear Pearson correlation coefficient (R) for the measured and modeled HCHO are shown in Table 3.

Time series of measured and modeled HCHO of 3 December 2015 is shown in Fig. 12a. Both the measured and modeled HCHO concentrations show similar temporal development with a rising trend in the morning and reached the peak value at noon, then followed by a decrease in the afternoon. The linear regression between measured and modeled HCHO shows a reasonably good agreement with slope of 0.98 and Pearson correlation coefficient (R) of 0.78 on December 3, 2015 (see Fig. 12b). All measurements lie within the 95% prediction interval indicating the best estimate of modeled HCHO. The regression model could not fully reconstruct the measurements, indicating there are other factors influencing the atmospheric HCHO levels. Due to the complexity of emission sources, a constant CO/HCHO factor might not be good enough to represent the HCHO emission from all primary sources. A number of petrochemical-related manufactures and organic synthesis processes industry located along the Yangtze River resulting in higher HCHO emissions and the CO emission factor varies with their emission processes. In addition, as we were measuring on a mobile platform, the composition of emission could change with the measurement location. Future investigation could focus on characterizing the primary industrial emissions of HCHO by different sector.

The diurnal variation of HCHO contribution from primary sources, secondary formation and background contributions on 3 December 2015 is shown in Fig. 13. Background HCHO only accounts for a small portion ($6.2 \pm 0.8\%$, average \pm S.D.) of the total ambient HCHO, while the primary sources contribute the largest fraction of the ambient HCHO, with an average percentage of $54.4 \pm 3.7\%$. The primary sources contributions were relatively stable, which might be due to industrial emission does not show a significant diurnal pattern. The contribution associated with secondary formation accounted for roughly $39.3 \pm 4.3\%$ of the total HCHO on daily average. Secondary formation of HCHO shows two peak values around 10:00 LT and noon time (11:00-14:00 LT). The 24 h backward trajectories on 3 December (Fig. 6d) suggested that rapid transport of air masses carries significant amount of pollutants including formaldehyde precursor from polluted area in northern China. Thus, the peak of relative contribution of secondary sources around 10:00 LT is probably resulted from the transportation of formaldehyde precursor. On the other hand, the peak value of secondary formation of HCHO during noon time (11:00-14:00) is mainly due to enhancement of photochemical reaction during noon time. Our result is consistence with a similar study in Rome, Italy, which the secondary contribution of HCHO is about 35% during winter time (Possanzini et al., 2002). While secondary formation of HCHO has been reported as the largest ambient HCHO source in summer (Parrish et al., 2012; Ling et al., 2017). Reduced photochemical reaction in winter resulting in lower formation rate of HCHO, and therefore, primary emissions become the major source of ambient HCHO in winter.

4 Summary

485 In this paper, we present the ship-based MAX-DOAS measurements along Yangtze River from Shanghai to Wuhan
(22 November to 4 December, 2015). Scattered sunlight spectra were measured to retrieve differential tropospheric slant
column densities (DSCDs) of NO₂, SO₂, and HCHO. DSCDs of NO₂, SO₂, and HCHO were converted to tropospheric
vertical column densities (VCDs) using AMF computed by Radiative Transfer Model with lidar aerosol profile as input.
During the campaign, three significantly enhanced tropospheric NO₂ and SO₂ VCDs events were detected over the
490 downwind areas of industrial zones. Spatial distributions of atmospheric pollutants are strongly affected by meteorological
conditions, i.e., positive correlations were found between the ship-based MAX-DOAS data and wind speed for these three
events, which indicates that the transportation of pollutants from the high-emission areas have a strong influence on the NO₂
and SO₂ distribution along Yangtze River. Comparison of tropospheric NO₂ VCDs between ship-based MAX-DOAS and
OMI satellite observations shows good agreement with Pearson correlation coefficient (R) of 0.82. However, OMI
495 underestimated tropospheric NO₂ by 10% which is mainly due to the averaging effect over large OMI pixels. In addition,
satellite observations have lower sensitivity to near-surface pollutants compared to ground-based measurements.

In this study, NO₂/SO₂ ratio is used to quantify relative contributions of industrial sources and vehicle emissions to
ambient NO₂ levels. The result shows that Jiangsu province has a higher contribution from industrial sources due to the large
number of power plants situated along the Yangtze River in Jiangsu. In contrast, contributions from vehicle emissions to
500 NO₂ level are higher than that of industrial sources in Jiangxi and Hubei provinces. Our result suggested that traffic volume
has large impact on NO₂ level in these provinces. These results indicate that different NO₂ pollution control strategy should
be applied in different provinces. In addition, we estimated the contributions of primary and secondary emission sources to
ambient HCHO levels using a multiple linear regression method. Result from 3 December 2015 indicated that primary
sources have the largest contribution to the ambient HCHO ($54.4 \pm 3.7\%$), while secondary formation contributes $39.3 \pm$
505 4.3% of the total ambient HCHO. The remaining fraction $6.2 \pm 0.8\%$ is attributed to the background. The largest contribution
from primary sources in winter suggested that photochemically induced secondary formation of ambient HCHO is reduced
due to lower solar irradiance in winter. This study provides an improved understanding of the impacts of different emission
sources in different provinces along the eastern part of Yangtze River to the local air quality. Our findings are useful for
designing specific air pollution control and environmental policies.

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References

- 520 Ångström, A.: On the atmospheric transmission of sun radiation and on dust in the air, *Geografiska Annaler*, 11, 156-166, 1929.
- Arlander, D. W., Bruning, D., Schmidt, U., and Ehhalt, D. H.: The tropospheric distribution of formaldehyde during TROPOZ-II, *Journal Of Atmospheric Chemistry*, 22, 251-269, doi:10.1007/bf00696637, 1995.
- Baidar, S., Oetjen, H., Coburn, S., Dix, B., Ortega, I., Sinreich, R., and Volkamer, R.: The CU Airborne MAX-DOAS
525 instrument: vertical profiling of aerosol extinction and trace gases, *Atmospheric Measurement Techniques*, 6, 719-739, doi:10.5194/amt-6-719-2013, 2013.
- Bucsela, E., Krotkov, N., Celarier, E., Lamsal, L., Swartz, W., Bhartia, P., Boersma, K., Veefkind, J., Gleason, J., and Pickering, K.: A new stratospheric and tropospheric NO₂ retrieval algorithm for nadir-viewing satellite instruments: applications to OMI, *Atmospheric Measurement Techniques*, 6, 2607, 2013.
- 530 Chan, K., Ning, Z., Westerdahl, D., Wong, K., Sun, Y., Hartl, A., and Wenig, M.: Dispersive infrared spectroscopy measurements of atmospheric CO₂ using a Fabry-Pérot interferometer sensor, *Science of the Total Environment*, 472, 27-35, 2014.
- Chan, K., Wiegner, M., Wenig, M., and Pöhler, D.: Observations of tropospheric aerosols and NO₂ in Hong Kong over 5 years using ground based MAX-DOAS, *Science of The Total Environment*,
535 doi:https://doi.org/10.1016/j.scitotenv.2017.10.153, 2017.
- Chan, K. L., Pöhler, D., Kuhlmann, G., Hartl, A., Platt, U., and Wenig, M. O.: NO₂ measurements in Hong Kong using LED based long path differential optical absorption spectroscopy, *Atmos. Meas. Tech.*, 5, 901-912, doi:10.5194/amt-5-901-2012, 2012.
- Chan, K. L., Hartl, A., Lam, Y. F., Xie, P. H., Liu, W. Q., Cheung, H. M., Lampel, J., Poehler, D., Li, A., Xu, J., Zhou, H. J.,
540 Ning, Z., and Wenig, M. O.: Observations of tropospheric NO₂ using ground based MAX-DOAS and OMI measurements during the Shanghai World Expo 2010, *Atmospheric Environment*, 119, 45-58, doi:10.1016/j.atmosenv.2015.08.041, 2015.
- Chance, K., and Kurucz, R.: An improved high-resolution solar reference spectrum for earth's atmosphere measurements in the ultraviolet, visible, and near infrared, *Journal of quantitative spectroscopy and radiative transfer*, 111, 1289-1295,
545 2010.
- Chen, D., Zhou, B., Beirle, S., Chen, L. M., and Wagner, T.: Tropospheric NO₂ column densities deduced from zenith-sky DOAS measurements in Shanghai, China, and their application to satellite validation, *Atmospheric Chemistry And*

Physics, 9, 3641-3662, 2009.

- Chen, Z., Liu, C., Liu, W., Zhang, T., and Xu, J.: A synchronous observation of enhanced aerosol and NO₂ over Beijing, China, in winter 2015, *Science Of the Total Environment*, 575, 429-436, doi:10.1016/j.scitotenv.2016.09.189, 2017.
- Chiang, T.-Y., Yuan, T.-H., Shie, R.-H., Chen, C.-F., and Chan, C.-C.: Increased incidence of allergic rhinitis, bronchitis and asthma, in children living near a petrochemical complex with SO₂ pollution, *Environment International*, 96, 1-7, doi:10.1016/j.envint.2016.08.009, 2016.
- Chin, M., Rood, R. B., Lin, S. J., Muller, J. F., and Thompson, A. M.: Atmospheric sulfur cycle simulated in the global model GOCART: Model description and global properties, *Journal Of Geophysical Research-Atmospheres*, 105, 24671-24687, doi:10.1029/2000jd900384, 2000.
- Crutzen, P. J.: The influence of nitrogen oxides on the atmospheric ozone content, *Quarterly Journal of the Royal Meteorological Society*, 96, 320-325, 1970.
- Dix, B., Koenig, T. K., and Volkamer, R.: Parameterization retrieval of trace gas volume mixing ratios from Airborne MAX-DOAS, *Atmospheric Measurement Techniques*, 9, 5655-5675, doi:10.5194/amt-9-5655-2016, 2016.
- Fan, S., Liu, C., Xie, Z., Dong, Y., Hu, Q., Fan, G., Chen, Z., Zhang, T., Duan, J., and Zhang, P.: Scanning vertical distributions of typical aerosols along the Yangtze River using elastic lidar, *Science of The Total Environment*, 628, 631-641, 2018.
- Fleischmann, O. C., Hartmann, M., Burrows, J. P., and Orphal, J.: New ultraviolet absorption cross-sections of BrO at atmospheric temperatures measured by time-windowing Fourier transform spectroscopy, *Journal of Photochemistry and Photobiology A: Chemistry*, 168, 117-132, 2004.
- Friedfeld, S., Fraser, M., Ensor, K., Tribble, S., Rehle, D., Leleux, D., and Tittel, F.: Statistical analysis of primary and secondary atmospheric formaldehyde, *Atmospheric Environment*, 36, 4767-4775, doi:10.1016/s1352-2310(02)00558-7, 2002.
- Garcia, A. R., Volkamer, R., Molina, L. T., Molina, M. J., Samuelson, J., Mellqvist, J., Galle, B., Herndon, S. C., and Kolb, C. E.: Separation of emitted and photochemical formaldehyde in Mexico City using a statistical analysis and a new pair of gas-phase tracers, *Atmospheric Chemistry And Physics*, 6, 4545-4557, 2006.
- Goldan, P. D., Parrish, D. D., Kuster, W. C., Trainer, M., McKeen, S. A., Holloway, J., Jobson, B. T., Sueper, D. T., and Fehsenfeld, F. C.: Airborne measurements of isoprene, CO, and anthropogenic hydrocarbons and their implications, *Journal Of Geophysical Research-Atmospheres*, 105, 9091-9105, doi:10.1029/1999jd900429, 2000.
- Hönninger, G., Friedeburg, C. v., and Platt, U.: Multi axis differential optical absorption spectroscopy (MAX-DOAS), *Atmospheric Chemistry and Physics*, 4, 231-254, 2004.
- Heckel, A., Richter, A., Tarsu, T., Wittrock, F., Hak, C., Pundt, I., Junkermann, W., and Burrows, J.: MAX-DOAS measurements of formaldehyde in the Po-Valley, *Atmospheric Chemistry and Physics*, 5, 909-918, 2005.
- Hendrick, F., Müller, J.-F., Clémer, K., Wang, P., Mazière, M. D., Fayt, C., Gielen, C., Hermans, C., Ma, J., and Pinardi, G.: Four years of ground-based MAX-DOAS observations of HONO and NO₂ in the Beijing area, *Atmospheric Chemistry*

and Physics, 14, 765-781, 2014.

- Huang, C., Chen, C., Li, L., Cheng, Z., Wang, H., Huang, H., Streets, D., Wang, Y., Zhang, G., and Chen, Y.: Emission inventory of anthropogenic air pollutants and VOC species in the Yangtze River Delta region, China, *Atmospheric Chemistry and Physics*, 11, 4105-4120, 2011.
- 585 Ibrahim, O., Shaiganfar, R., Sinreich, R., Stein, T., Platt, U., and Wagner, T.: Car MAX-DOAS measurements around entire cities: quantification of NO_x emissions from the cities of Mannheim and Ludwigshafen (Germany), *Atmospheric Measurement Techniques*, 3, 709-721, 2010.
- Johansson, M., Rivera, C., Foy, B. d., Lei, W., Song, J., Zhang, Y., Galle, B., and Molina, L.: Mobile mini-DOAS measurement of the outflow of NO₂ and HCHO from Mexico City, *Atmospheric Chemistry and Physics*, 9, 5647-5653, 2009.
- 590 Krotkov, N. A., McLinden, C. A., Li, C., Lamsal, L. N., Celarier, E. A., Marchenko, S. V., Swartz, W. H., Bucsela, E. J., Joiner, J., Duncan, B. N., Boersma, K. F., Veefkind, J. P., Levelt, P. F., Fioletov, V. E., Dickerson, R. R., He, H., Lu, Z., and Streets, D. G.: Aura OMI observations of regional SO₂ and NO₂ pollution changes from 2005 to 2015, *Atmospheric Chemistry And Physics*, 16, 4605-4629, doi:10.5194/acp-16-4605-2016, 2016.
- 595 Krotkov, N. A., Lamsal, L. N., Celarier, E. A., Swartz, W. H., Marchenko, S. V., Bucsela, E. J., Chan, K. L., Wenig, M., and Zara, M.: The version 3 OMI NO₂ standard product, *Atmos. Meas. Tech.*, 10, 3133-3149, doi:10.5194/amt-10-3133-2017, 2017.
- Kuhlmann, G., Hartl, A., Cheung, H. M., Lam, Y. F., and Wenig, M. O.: A novel gridding algorithm to create regional trace gas maps from satellite observations, *Atmos. Meas. Tech.*, 7, 451-467, doi:10.5194/amt-7-451-2014, 2014.
- 600 Lee, C., Richter, A., Lee, H., Kim, Y. J., Burrows, J. P., Lee, Y. G., and Choi, B. C.: Impact of transport of sulfur dioxide from the Asian continent on the air quality over Korea during May 2005, *Atmospheric Environment*, 42, 1461-1475, 2008.
- Lee, D. S., Kohler, I., Grobler, E., Rohrer, F., Sausen, R., GallardoKlenner, L., Olivier, J. G. J., Dentener, F. J., and Bouwman, A. F.: Estimations of global NO_x emissions and their uncertainties, *Atmospheric Environment*, 31, 1735-1749, doi:10.1016/s1352-2310(96)00327-5, 1997.
- 605 Lei, W., Zavala, M., de Foy, B., Volkamer, R., Molina, M. J., and Molina, L. T.: Impact of primary formaldehyde on air pollution in the Mexico City Metropolitan Area, *Atmospheric Chemistry And Physics*, 9, 2607-2618, 2009.
- Levelt, P. F., van den Oord, G. H., Dobber, M. R., Malkki, A., Visser, H., de Vries, J., Stammes, P., Lundell, J. O., and Saari, H.: The ozone monitoring instrument, *IEEE Transactions on geoscience and remote sensing*, 44, 1093-1101, 2006.
- 610 Li, A., Zhang, J., Xie, P., Hu, Z., Xu, J., Mou, F., Wu, F., Liu, J., and Liu, W.: Variation of temporal and spatial patterns of NO₂ in Beijing using OMI and mobile DOAS, *Science China-Chemistry*, 58, 1367-1376, doi:10.1007/s11426-015-5459-x, 2015.
- Li, Y., Shao, M., Lu, S., Chang, C.-C., and Dasgupta, P. K.: Variations and sources of ambient formaldehyde for the 2008 Beijing Olympic games, *Atmospheric Environment*, 44, 2632-2639, 2010.
- 615 Ling, Z., Zhao, J., Fan, S., and Wang, X.: Sources of formaldehyde and their contributions to photochemical O₃ formation at

- an urban site in the Pearl River Delta, southern China, *Chemosphere*, 168, 1293-1301, 2017.
- Liu, H., Liu, C., Xie, Z., Li, Y., Huang, X., Wang, S., Xu, J., and Xie, P.: A paradox for air pollution controlling in China revealed by "APEC Blue" and "Parade Blue", *Scientific Reports*, 6, doi:10.1038/srep34408, 2016.
- 620 Ma, Y., Diao, Y., Zhang, B., Wang, W., Ren, X., Yang, D., Wang, M., Shi, X., and Zheng, J.: Detection of formaldehyde emissions from an industrial zone in the Yangtze River Delta region of China using a proton transfer reaction ion-drift chemical ionization mass spectrometer, *Atmospheric Measurement Techniques*, 9, 6101-6116, doi:10.5194/amt-9-6101-2016, 2016.
- Mallik, C., and Lal, S.: Seasonal characteristics of SO₂, NO₂, and CO emissions in and around the Indo-Gangetic Plain, *Environmental Monitoring And Assessment*, 186, 1295-1310, doi:10.1007/s10661-013-3458-y, 2014.
- 625 Mead, M., Popoola, O., Stewart, G., Landshoff, P., Calleja, M., Hayes, M., Baldovi, J., McLeod, M., Hodgson, T., and Dicks, J.: The use of electrochemical sensors for monitoring urban air quality in low-cost, high-density networks, *Atmospheric Environment*, 70, 186-203, 2013.
- Meller, R., and Moortgat, G. K.: Temperature dependence of the absorption cross sections of formaldehyde between 223 and 323 K in the wavelength range 225-375 nm, *Journal of Geophysical Research: Atmospheres*, 105, 7089-7101, 2000.
- 630 Miller, S. M., Matross, D. M., Andrews, A. E., Millet, D. B., Longo, M., Gottlieb, E. W., Hirsch, A. I., Gerbig, C., Lin, J. C., Daube, B. C., Hudman, R. C., Dias, P. L. S., Chow, V. Y., and Wofsy, S. C.: Sources of carbon monoxide and formaldehyde in North America determined from high-resolution atmospheric data, *Atmospheric Chemistry And Physics*, 8, 7673-7696, 2008.
- Parrish, D., Ryerson, T., Mellqvist, J., Johansson, J., Fried, A., Richter, D., Walega, J., Washenfelder, R. d., De Gouw, J., 635 and Peischl, J.: Primary and secondary sources of formaldehyde in urban atmospheres: Houston Texas region, *Atmospheric Chemistry and Physics*, 12, 3273-3288, 2012.
- Peters, E., Wittrock, F., Großmann, K., Frieß, U., Richter, A., and Burrows, J.: Formaldehyde and nitrogen dioxide over the remote western Pacific Ocean: SCIAMACHY and GOME-2 validation using ship-based MAX-DOAS observations, *Atmospheric Chemistry and Physics*, 12, 11179-11197, 2012.
- 640 Pinker, R., Frouin, R., and Li, Z.: A review of satellite methods to derive surface shortwave irradiance, *Remote Sensing of Environment*, 51, 108-124, 1995.
- Platt, U., and Stutz, J.: *Differential absorption spectroscopy: Principles and Applications*, Springer, Berlin, 2008.
- Possanzini, M., Di Palo, V., and Cecinato, A.: Sources and photodecomposition of formaldehyde and acetaldehyde in Rome ambient air, *Atmospheric Environment*, 36, 3195-3201, 2002.
- 645 Rozanov, A., Rozanov, V., Buchwitz, M., Kokhanovsky, A., and Burrows, J.: SCIATRAN 2.0-A new radiative transfer model for geophysical applications in the 175-2400nm spectral region, *Advances in Space Research*, 36, 1015-1019, 2005.
- Schreier, S., Peters, E., Richter, A., Lampel, J., Wittrock, F., and Burrows, J.: Ship-based MAX-DOAS measurements of tropospheric NO₂ and SO₂ in the South China and Sulu Sea, *Atmospheric Environment*, 102, 331-343, 2015.
- Serdyuchenko, A., Gorshelev, V., Weber, M., Chehade, W., and Burrows, J. P.: High spectral resolution ozone absorption

- cross-sections - Part 2: Temperature dependence, *Atmospheric Measurement Techniques*, 7, 625-636, doi:10.5194/amt-7-625-2014, 2014.
- Shaiganfar, R., Beirle, S., Sharma, M., Chauhan, A., Singh, R. P., and Wagner, T.: Estimation of NO_x emissions from Delhi using Car MAX-DOAS observations and comparison with OMI satellite data, *Atmospheric Chemistry and Physics*, 11, 10871-10887, 2011.
- Shi, Y., Xia, Y.-f., Lu, B.-h., Liu, N., Zhang, L., Li, S.-j., and Li, W.: Emission inventory and trends of NO_x for China, 2000-2020, *Journal of Zhejiang University Science A*, 15, 454-464, 2014.
- Sinreich, R., Coburn, S., Dix, B., and Volkamer, R.: Ship-based detection of glyoxal over the remote tropical Pacific Ocean, *Atmospheric Chemistry and Physics*, 10, 11359-11371, 2010.
- Solomon, S., Schmeltekopf, A. L., and Sanders, R. W.: On the interpretation of zenith sky absorption measurements, *Journal of Geophysical Research*, 92, 8311-8319, 1987.
- Stein, A., Draxler, R. R., Rolph, G. D., Stunder, B. J., Cohen, M., and Ngan, F.: NOAA's HYSPLIT atmospheric transport and dispersion modeling system, *Bulletin of the American Meteorological Society*, 96, 2059-2077, 2015.
- Su, W., Liu, C., Hu, Q., Fan, G., Xie, Z., Huang, X., Zhang, T., Chen, Z., Dong, Y., and Ji, X.: Characterization of ozone in the lower troposphere during the 2016 G20 conference in Hangzhou, *Scientific reports*, 7, 17368, 2017.
- Takashima, H., Irie, H., Kanaya, Y., and Syamsudin, F.: NO₂ observations over the western Pacific and Indian Ocean by MAX-DOAS on Kaiyo, a Japanese research vessel, *Atmospheric Measurement Techniques*, 5, 2351-2360, 2012.
- Thalman, R., and Volkamer, R.: Temperature dependent absorption cross-sections of O₂-O₂ collision pairs between 340 and 630 nm and at atmospherically relevant pressure, *Physical Chemistry Chemical Physics*, 15, 15371-15381, doi:10.1039/c3cp50968k, 2013.
- Vandaele, A. C., Hermans, C., Simon, P. C., Carleer, M., Colin, R., Fally, S., Merienne, M.-F., Jenouvrier, A., and Coquart, B.: Measurements of the NO₂ absorption cross-section from 42000 cm⁻¹ to 10000 cm⁻¹ (238-1000 nm) at 220 K and 294 K, *Journal of Quantitative Spectroscopy and Radiative Transfer*, 59, 171-184, 1998.
- Vandaele, A. C., Hermans, C., and Fally, S.: Fourier transform measurements of SO₂ absorption cross sections: II.: Temperature dependence in the 29000-44000 cm⁻¹ (227-345 nm) region, *Journal of Quantitative Spectroscopy and Radiative Transfer*, 110, 2115-2126, 2009.
- Wagner, T., Burrows, J., Deutschmann, T., Dix, B., Friedeburg, C. v., Frieß, U., Hendrick, F., Heue, K.-P., Irie, H., and Iwabuchi, H.: Comparison of box-air-mass-factors and radiances for Multiple-Axis Differential Optical Absorption Spectroscopy (MAX-DOAS) geometries calculated from different UV/visible radiative transfer models, *Atmospheric Chemistry and Physics*, 7, 1809-1833, 2007.
- Wagner, T., Ibrahim, O., Shaiganfar, R., and Platt, U.: Mobile MAX-DOAS observations of tropospheric trace gases, *Atmospheric Measurement Techniques*, 3, 129-140, 2010.
- Wang, M., Chen, W., Shao, M., Lu, S., Zeng, L., and Hu, M.: Investigation of carbonyl compound sources at a rural site in the Yangtze River Delta region of China, *Journal Of Environmental Sciences*, 28, 128-136, doi:10.1016/j.jes.2014.12.001,

2015.

- 685 Wang, S., Zhang, Q., Streets, D., He, K., Martin, R., Lamsal, L., Chen, D., Lei, Y., and Lu, Z.: Growth in NO_x emissions from power plants in China: bottom-up estimates and satellite observations, *Atmospheric Chemistry and Physics*, 12, 4429-4447, 2012a.
- Wang, S., Zhou, B., Wang, Z., Yang, S., Hao, N., Valks, P., Trautmann, T., and Chen, L.: Remote sensing of NO₂ emission from the central urban area of Shanghai (China) using the mobile DOAS technique, *Journal Of Geophysical Research-*
- 690 *Atmospheres*, 117, doi:10.1029/2011jd016983, 2012b.
- Wang, T., Hendrick, F., Wang, P., Tang, G., Clémer, K., Yu, H., Fayt, C., Hermans, C., Gielen, C., and Müller, J.-F.: Evaluation of tropospheric SO₂ retrieved from MAX-DOAS measurements in Xianghe, China, *Atmospheric Chemistry and Physics*, 14, 11149-11164, 2014.
- Wang, Y., Lampel, J., Xie, P., Beirle, S., Li, A., Wu, D., and Wagner, T.: Ground-based MAX-DOAS observations of
- 695 tropospheric aerosols, NO₂, SO₂ and HCHO in Wuxi, China, from 2011 to 2014, *Atmospheric Chemistry And Physics*, 17, 2189-2215, doi:10.5194/acp-17-2189-2017, 2017.
- Wood, E. C., Canagaratna, M. R., Herndon, S. C., Onasch, T. B., Kolb, C. E., Worsnop, D. R., Kroll, J. H., Knighton, W. B., Seila, R., Zavala, M., Molina, L. T., DeCarlo, P. F., Jimenez, J. L., Weinheimer, A. J., Knapp, D. J., Jobson, B. T., Stutz, J., Kuster, W. C., and Williams, E. J.: Investigation of the correlation between odd oxygen and secondary organic aerosol
- 700 in Mexico City and Houston, *Atmospheric Chemistry And Physics*, 10, 8947-8968, doi:10.5194/acp-10-8947-2010, 2010.
- Wu, F.-C., Li, A., Xie, P.-H., Chen, H., Ling, L.-Y., Xu, J., Mou, F.-S., Zhang, J., Shen, J.-C., Liu, J.-G., and Liu, W.-Q.: Detection and distribution of tropospheric NO₂ vertical column density based on mobile multi-axis differential optical absorption spectroscopy, *Acta Physica Sinica*, 64, doi:10.7498/aps.64.114211, 2015.
- Wu, F., Xie, P., Li, A., Chan, K., Hartl, A., Wang, Y., Si, F., Zeng, Y., Qin, M., and Xu, J.: Observations of SO₂ and NO₂ by
- 705 mobile DOAS in the Guangzhou eastern area during the Asian Games 2010, *Atmospheric Measurement Techniques*, 6, 2277-2292, doi:10.5194/amt-6-2277-2013, 2013.
- Xia, Y., Zhao, Y., and Nielsen, C. P.: Benefits of China's efforts in gaseous pollutant control indicated by the bottom-up emissions and satellite observations 2000–2014, *Atmospheric Environment*, 136, 43-53, 2016.
- Xing, C., Liu, C., Wang, S., Chan, K. L., Gao, Y., Huang, X., Su, W., Zhang, C., Dong, Y., and Fan, G.: Observations of the
- 710 vertical distributions of summertime atmospheric pollutants and the corresponding ozone production in Shanghai, China, *Atmospheric Chemistry and Physics*, 17, 14275-14289, 2017.
- Zhang, L., Lee, C. S., Zhang, R., and Chen, L.: Spatial and temporal evaluation of long term trend (2005-2014) of OMI retrieved NO₂ and SO₂ concentrations in Henan Province, China, *Atmospheric Environment*, 154, 151-166, doi:10.1016/j.atmosenv.2016.11.067, 2017.
- 715 Zhao, Y., Wang, S., Duan, L., Lei, Y., Cao, P., and Hao, J.: Primary air pollutant emissions of coal-fired power plants in China: Current status and future prediction, *Atmospheric Environment*, 42, 8442-8452, 2008.

Table 1. Weather and viewing conditions during Yangtze River campaign from 22 November to 4 December, 2015. Interruption of the ship based MAX-DOAS is also listed.

Period	Conditions		
22-25 November	Rain and occasional fog occurred in the morning and night		
26-27 November	Improving weather and viewing conditions, sunny		
28 November	Occasional light rain and partly cloudy around noon		
29 November	Haze		
30 November	Partly cloudy		
1-2 December	Haze		
3-4 December	Good viewing conditions, almost clear sky		
Interruption event	Start time (yyyy/mm/dd, UTC + 8 h)	End time (yyyy/mm/dd, UTC + 8 h)	Reason for interruption
1	2015/11/22 11:00	2015/11/22 14:25	power outages
2	2015/11/25 7:00	2015/11/25 18:00	frequent power outages all day long
3	2015/11/26 11:40	2015/11/26 15:00	instrumental problems

Table 2. Summary of the DOAS retrieval settings used for the NO₂, SO₂, and HCHO slant column densities retrieval.

Parameter	Data source	Fitting interval (nm)		
		NO ₂	SO ₂	HCHO
Wavelength range		338-368 nm	308-314 nm	336.5-359 nm
NO ₂	Vandaele et al. (1998), 220K, 294K, I ₀ -correction* (SCD of 10 ¹⁷ molecules/cm ²)	√	√ (only 294K)	√ (only 294K)
SO ₂	Vandaele et al. (2009), 298K	×	√	×
HCHO	Meller and Moortgat (2000), 297K	√	×	√
O ₃	Serdyuchenko et al. (2014), 223K, 243K, I ₀ - correction* (SCD of 10 ²⁰ molecules/cm ²)	√	√	√
O ₄	Thalman and Volkamer (2013), 293K	√	×	√
BrO	Fleischmann et al. (2004), 223K	√	×	√
Ring	Ring spectra calculated with QDOAS according to Chance and Spurr (1997)	√	√	√
Polynomial degree		Order 5	Order 5	Order 5
Intensity offset		Constant	Order 1	Order 1
Wavelength calibration	Based on a high resolution solar reference spectrum (SAO2010 solar spectra) (Chance and Kurucz, 2010)			

*Solar I₀-correction (Aliwell et al., 2002)

725 **Table 3.** Coefficients of the multiple linear regression and the correlation coefficient (R) for the measured and modeled
HCHO in Eq. (15). β_1 represents the emission ratio of HCHO with respect to CO. β_2 denotes the portion of HCHO from
photochemical production, while β_0 represents HCHO background concentration which is fixed to 1 ppbv.

Date (yyyy/mm/dd)	β_1	β_2	β_0	R	N.Obs
2015/11/26	0.0165±0.0083	0.0765±0.0323	1.0	0.7937	80
2015/12/03	0.0312±0.0097	0.1149±0.0514	1.0	0.7746	139

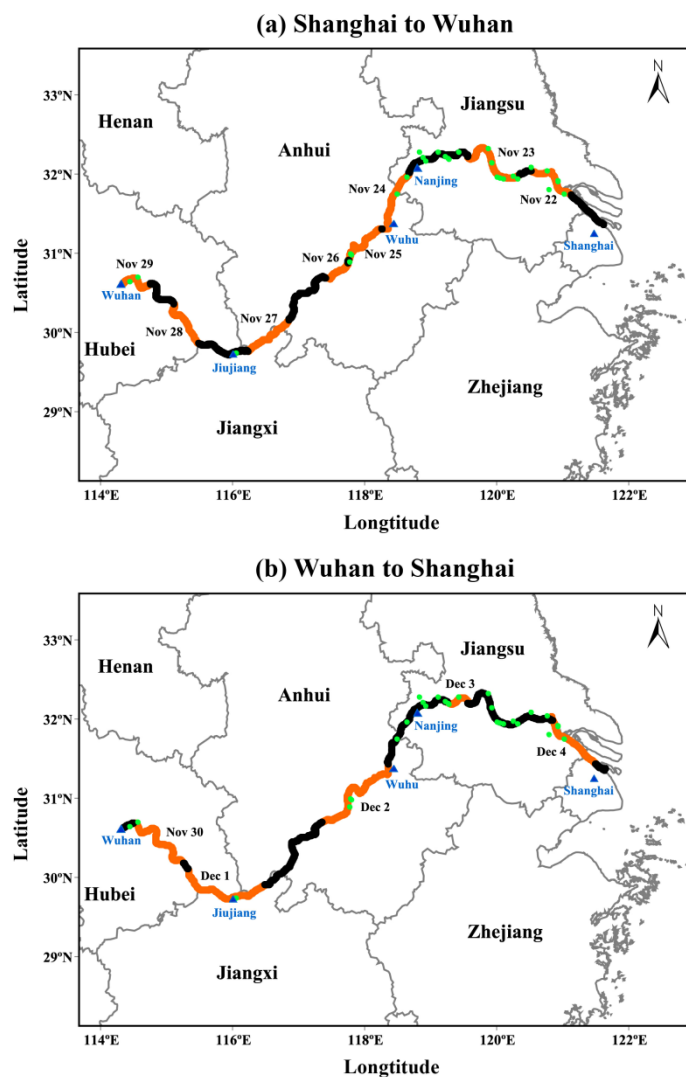


Figure 1. The ship tracks of (a) the departing journey (from Shanghai to Wuhan) and (b) the returning journey (from Wuhan to Shanghai). The sections of the cruise track highlighted in orange indicate the period of MAX-DOAS observations. The green dots represent the major power plants along the Yangtze River.

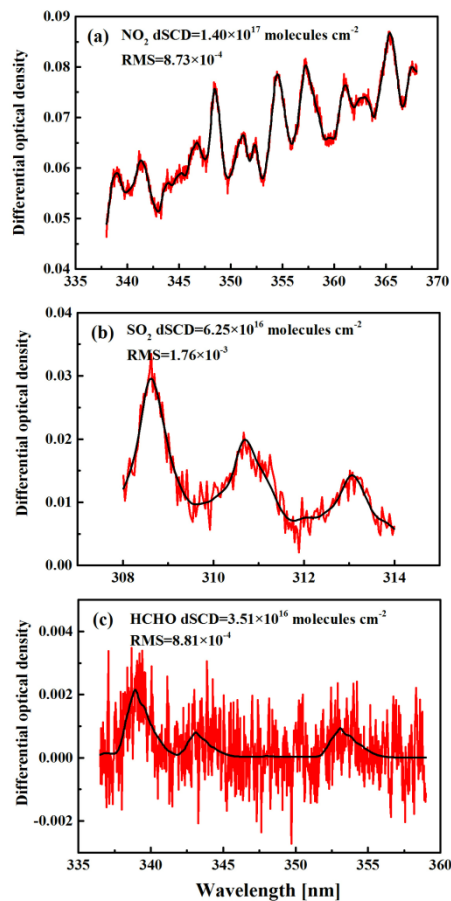


Figure 2. An example of DOAS fit for (a) NO_2 , (b) SO_2 , and (c) HCHO . The spectrum was taken on 1 December 2015 at 14:02 LT with elevation angle of 30° . Red lines show the measured atmospheric spectrum after all other absorbers have been subtracted, and the black line shows the scaled reference absorption cross section.

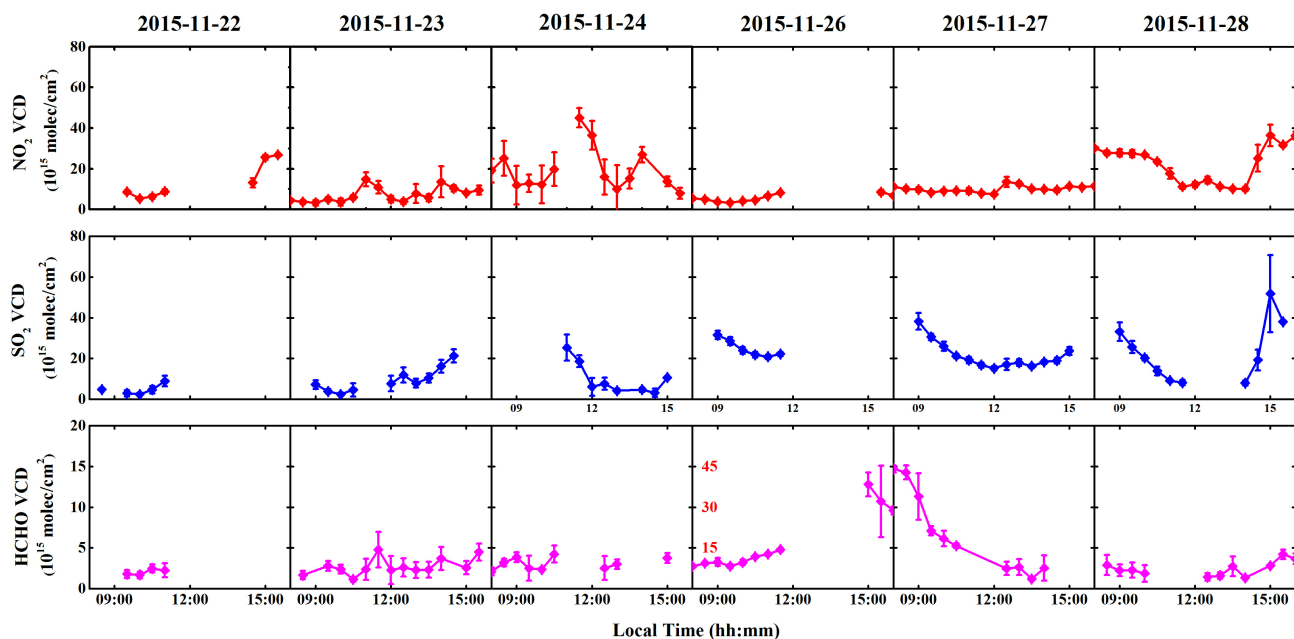


Figure 3. Time series of tropospheric NO₂ (upper panels), SO₂ (middle panels), and HCHO (lower panels) vertical column densities (VCDs) from 22 November to 28 November. The error bars refer to the 1 σ variation of the measurement.

Notes: The data were half-hour averages and individual measurements taken under unfavorable wind directions have been filtered before averaging. No data presented on 25 November due to frequent power outages. The y-axis scale of HCHO on 26 November is different (y-axis scale in red).

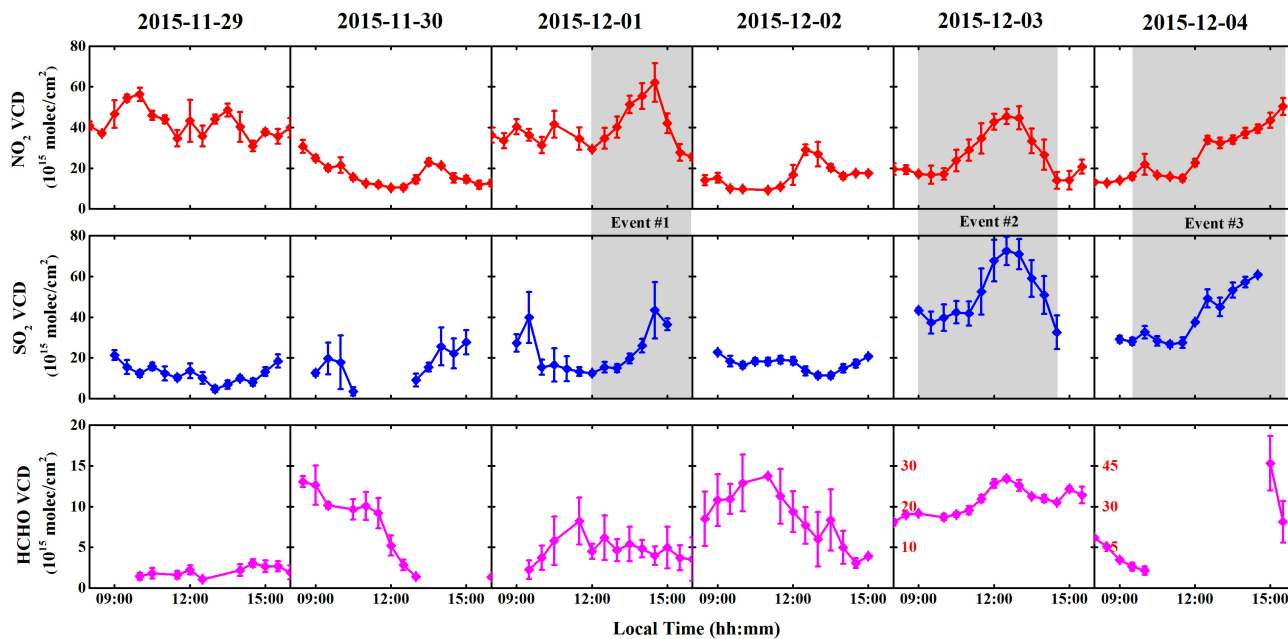
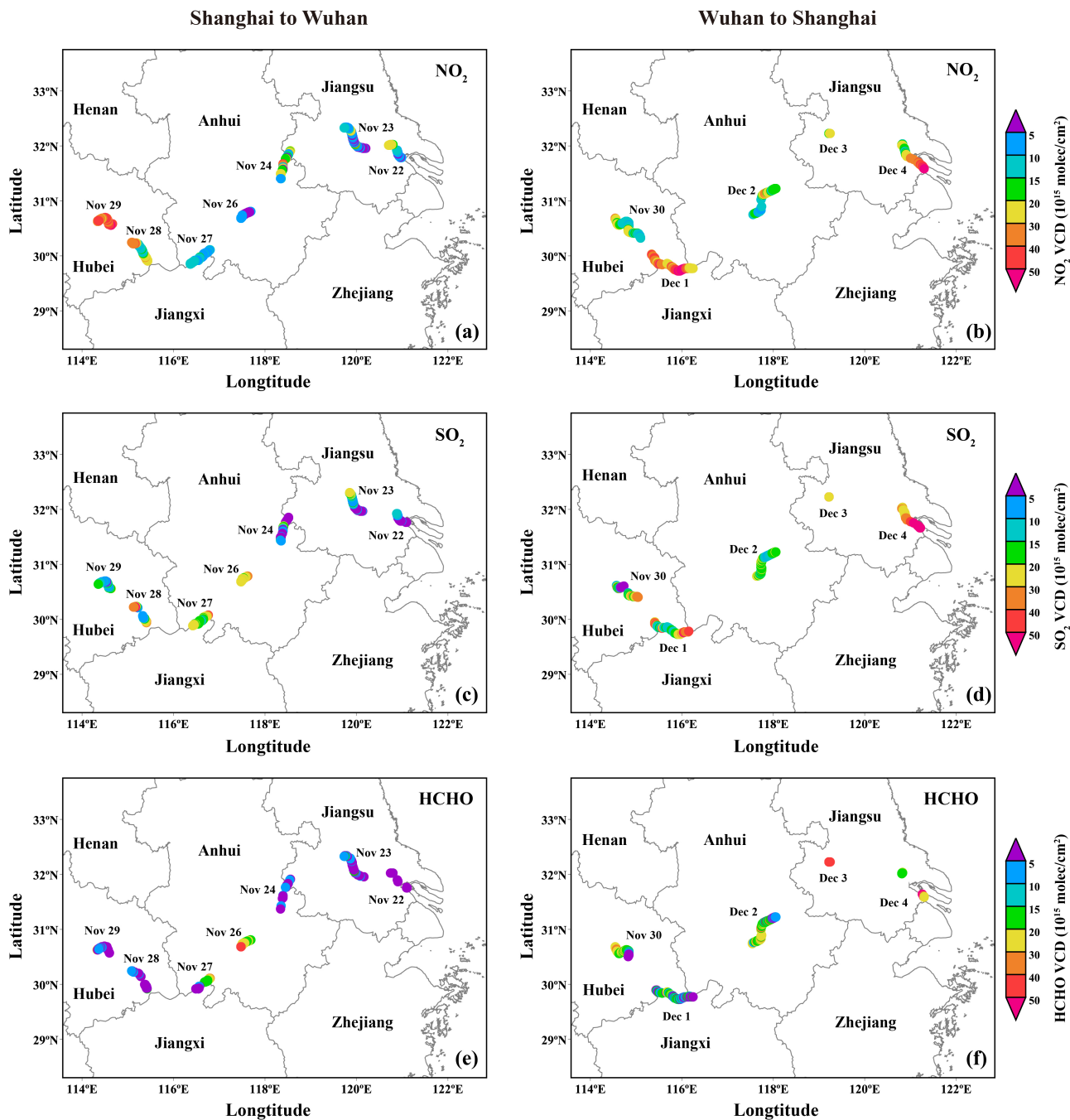


Figure 4. Continue of Fig. 3, but for the time series of tropospheric NO₂ (upper panels), SO₂ (middle panels), and HCHO (lower panels) vertical column densities (VCDs) from 22 November to 28 November. The gray area highlighted the episode periods which NO₂ and SO₂ showed synchronous growth.

Notes: The y-axis scale of HCHO on 3-4 December is different (y-axis scale in red).



755 **Figure 5.** Spatial distribution of tropospheric NO_2 (upper panels), SO_2 (middle panels), and HCHO (lower panels) VCDs along the departing route (left panels, from Shanghai to Wuhan) and returning route (right panels, from Wuhan to Shanghai). Notes: The ship was anchored at Yizheng Marine department on 3 December 2015.

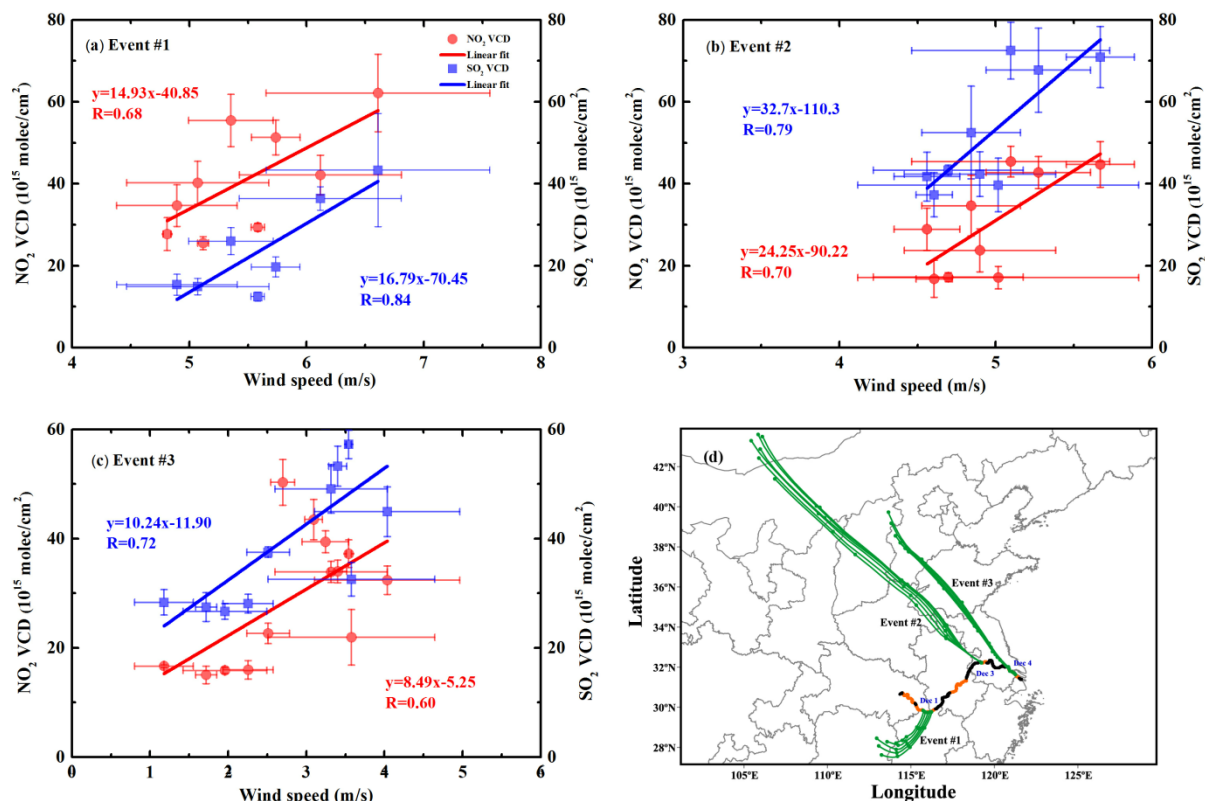


Figure 6. (a-c) Correlation analysis of ship-based MAX-DOAS VCDs (red circle shows the NO $_2$ VCDs and blue square shows the SO $_2$ VCDs) and wind speed for three high VCDs events. (d) Yangtze River Cruise Track and 24 h backward trajectories calculated by the NOAA HYSPLIT model for three events (green marks indicate starting point, -6, -12, -18 and -24 h, respectively). The data were half-hour averages. The error bars show the 1σ standard deviations of mobile DOAS VCDs and wind speed.

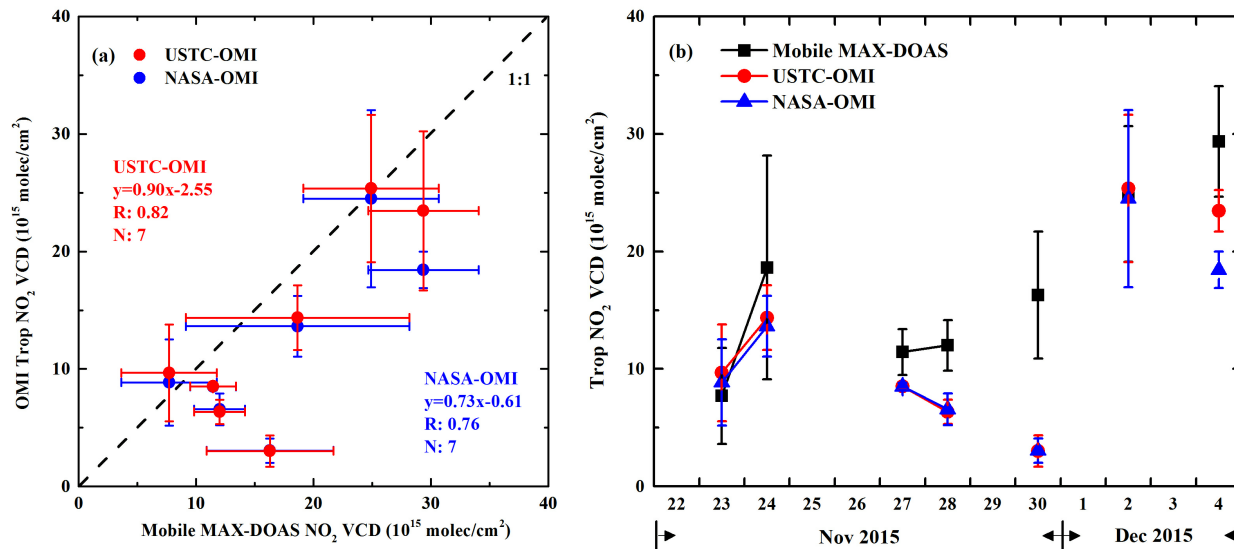


Figure 7. (a) Correlation analysis and (b) time series of tropospheric NO₂ VCDs measured by ship-based MAX-DOAS and OMI during Yangtze River campaign. MAX-DOAS data (black markers) are temporally averaged around the USTC OMI and NASA OMI overpass time (red and blue markers, respectively), while the OMI data are spatially averaged within 20 km radius around the ship's averaged position. The error bars show the 1σ standard deviations of ship-based MAX-DOAS and OMI data.

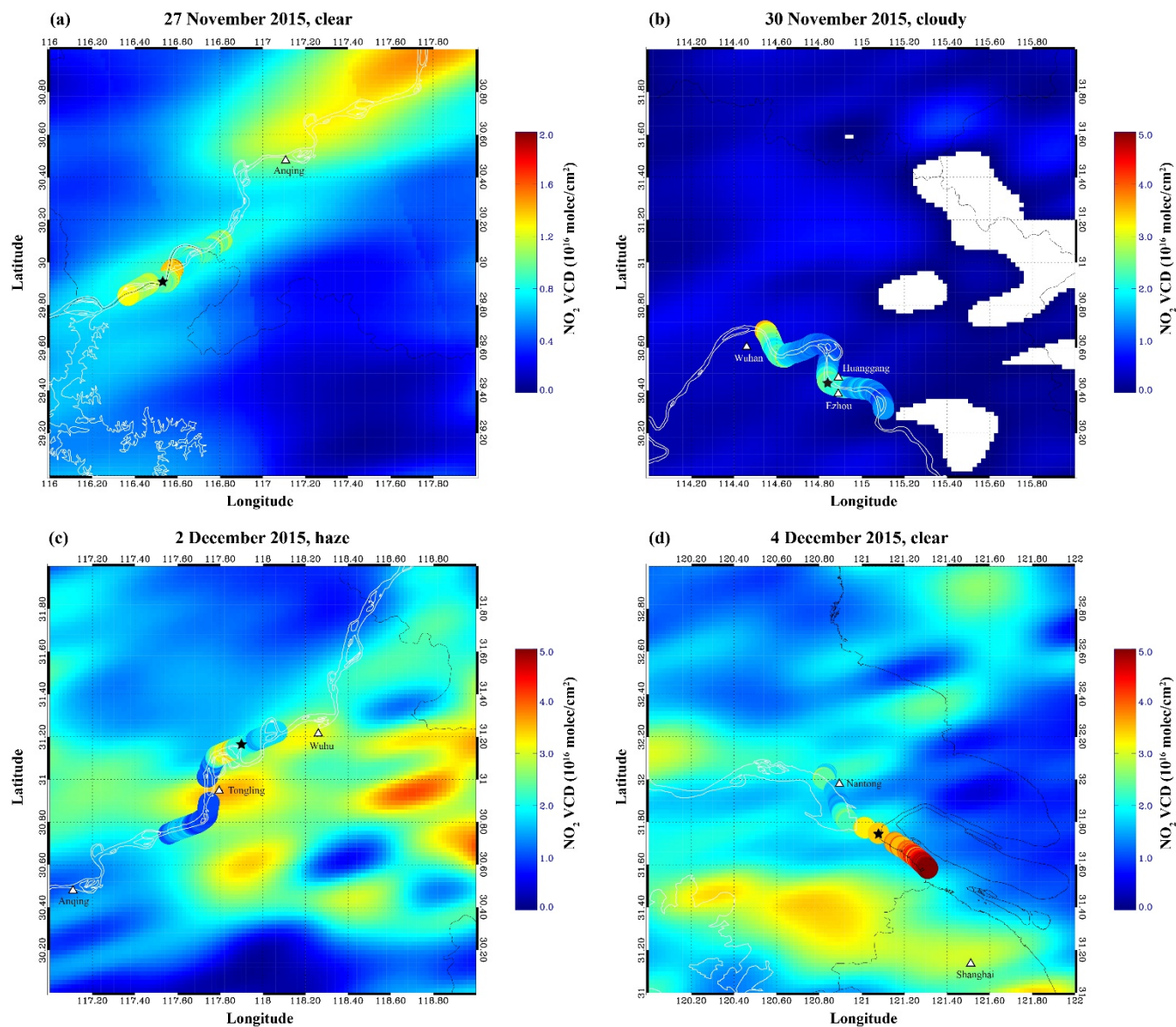
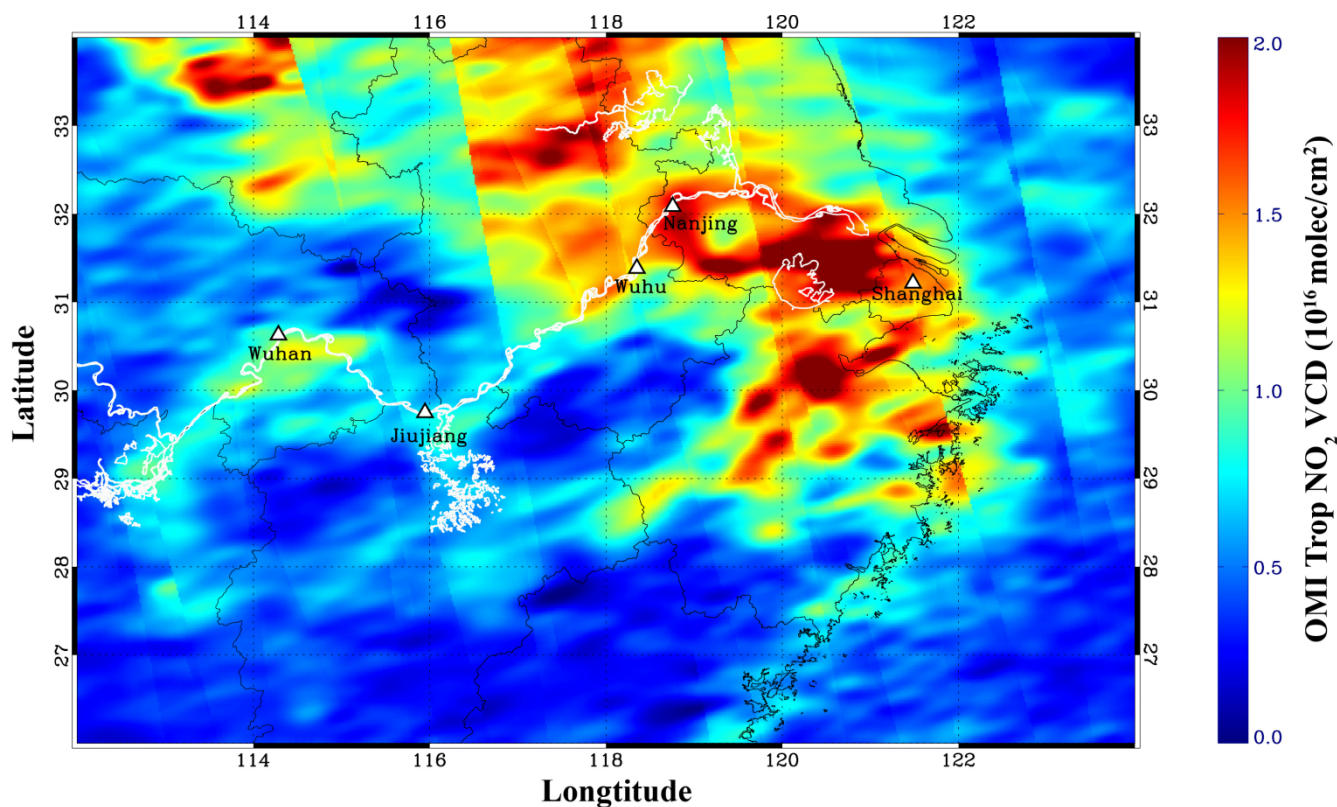


Figure 8. Spatial pattern of tropospheric NO_2 VCD measured by ship-based MAX-DOAS and OMI during four typical days within the Yangtze River campaign. The color-coded circle indicates the ship-based MAX-DOAS observations. Each plot shows an example for relatively clear (a and d), cloudy (b), and haze (c) meteorological conditions along the Yangtze River. The star symbols indicate the ship position during the OMI overpass time (~13:45 LT). The colorbar scale of each panel is different.



780 **Figure 9.** The spatial distribution of averaged tropospheric NO₂ VCDs measured by OMI during Yangtze River campaign (22 November to 4 December, 2015).

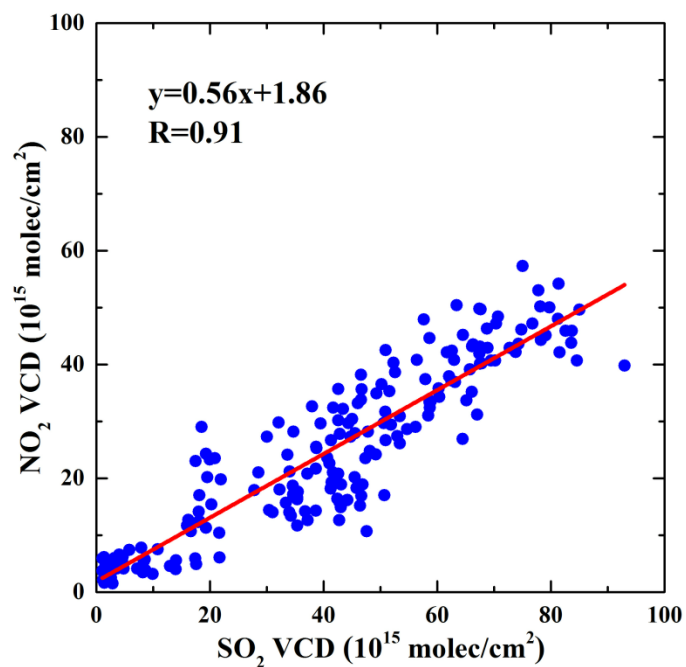


Figure 10. Scatter plot of NO₂ and SO₂ VCDs data around power plants along the Yangtze River. NO₂ and SO₂ VCDs measured within 2 km of the power plants are used for the analysis.

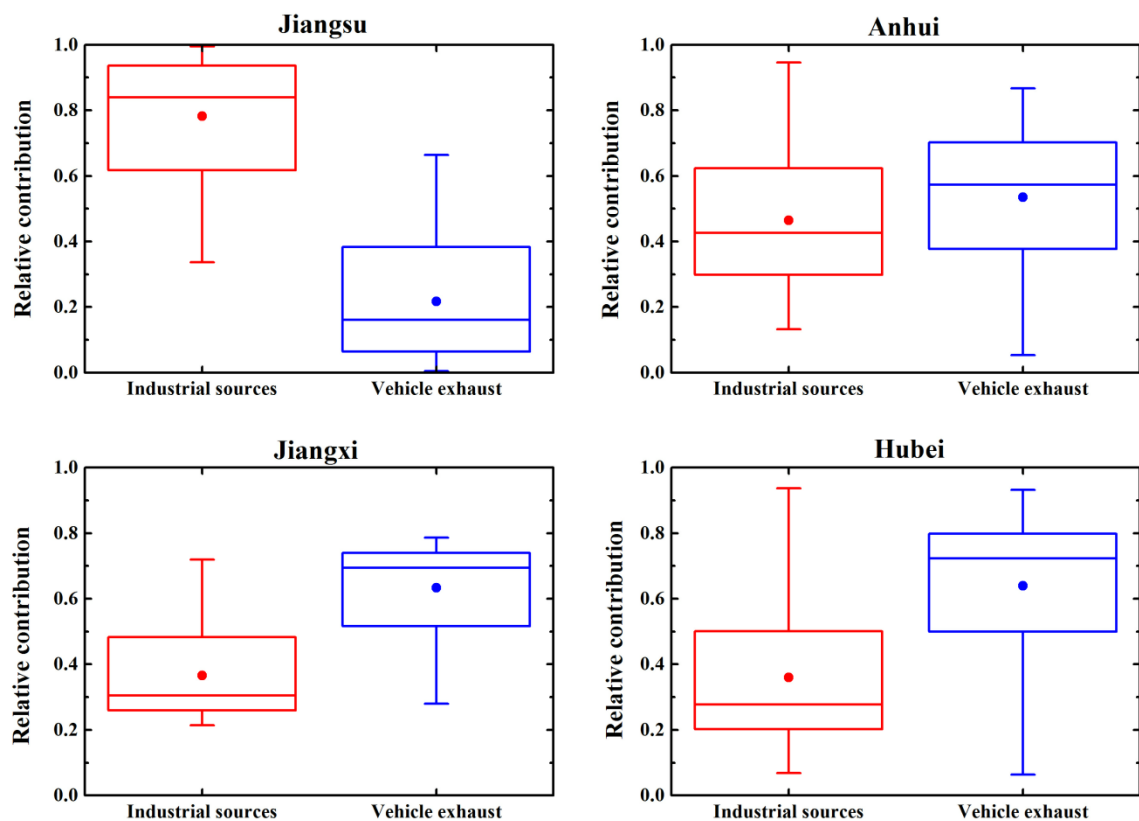


Figure 11. Relative contributions of industrial sources and vehicle exhaust to the ambient NO₂ levels over the four provinces.

Notes: the bottom and top of the box represent the 25th and 75th percentiles, respectively; the line within the box represent the median; the dot represents the mean; the whiskers below and above the box stands for the 10th and 90th percentiles.

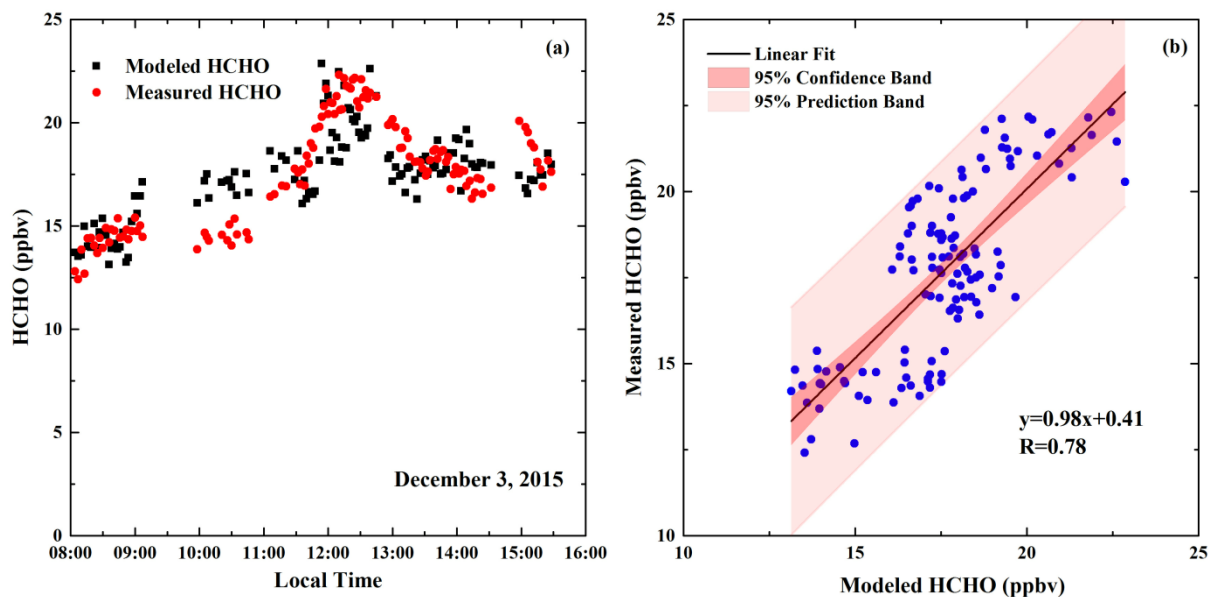


Figure 12. Comparison of the measured and modeled HCHO values from multiple linear regression on 3 December 2015. The left panel shows the modeled and measured HCHO time series. The right panel shows the linear correlation between the modeled and measured HCHO concentrations. The black solid line indicates the linear regression. The red and pink areas denote the 95% confidence interval and the 95% prediction, respectively.

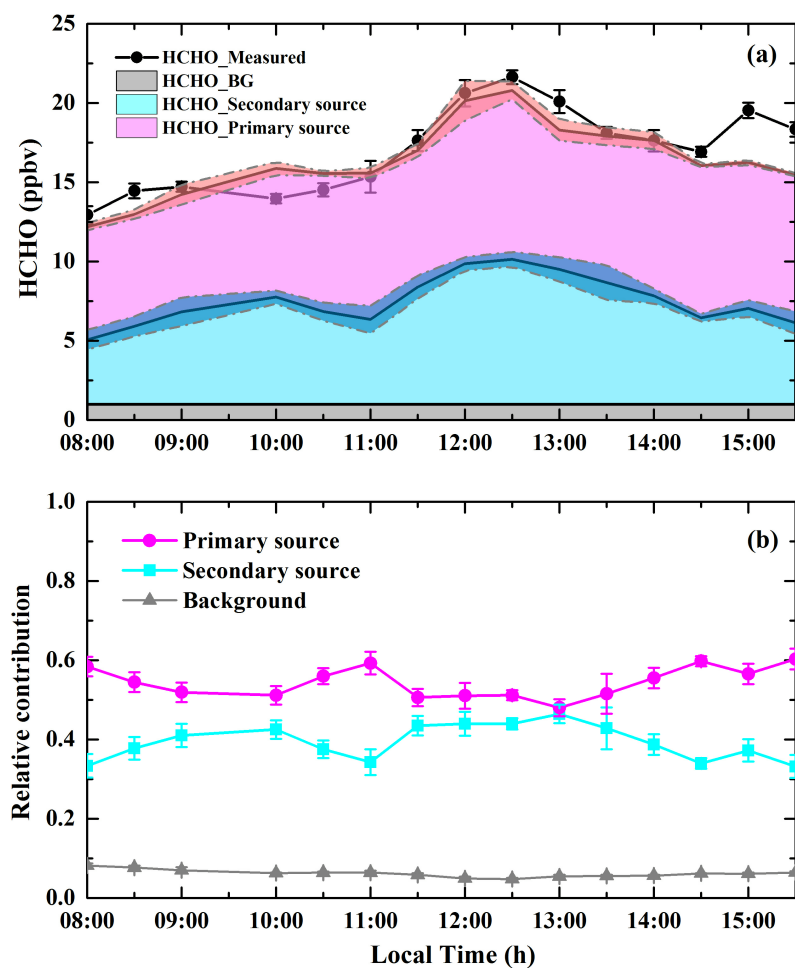


Figure 13. Time series of absolute (upper) and relative (lower) contribution of primary source, secondary source, and atmospheric background to ambient HCHO level on 3 December 2015. The error bars refer to the 1 σ standard variations of the absolute (upper, error bars with fill area) and relative (lower) contribution of primary source, secondary source, and atmospheric background to ambient HCHO.

Responses to Anonymous Referee #1

We thank the reviewer for the constructive suggestions and comments. We appreciate the reviewer's comments and these comments are very helpful for improving the manuscript. We understand that the comments are positive on the scientific content of the manuscript while appropriate revisions and clarifications are necessary.

We have addressed the reviewer's comments on a point to point basis as below for consideration.

General comments:

1) The authors use lidar aerosol profile for AMF calculations to convert SCDs to VCDs for trace gases. However, only aerosol profile at the lowest 2 km is used and aerosol above 2 km are ignored. I think it is necessary to estimate the uncertainty due to ignoring aerosols above 2 km. In addition, the lidar has a blind height of 195m, so how the aerosols at the lowest 195m were treated?

Response: A sensitivity study has been conducted to address the influence from aerosol above 2km to the AMF calculation. Tropospheric NO₂, SO₂ and HCHO AMFs are calculated using lidar aerosol profile at the lowest 2km and WRF-Chem aerosol profile above 2km. The results are compared to AMFs calculated with only lidar aerosol profile at the lowest 2km. Comparison results show that AMFs calculated with considering aerosol above 2km are on average 2-4% lower than AMFs without considering aerosol at upper altitudes. The result indicates that ignoring aerosols above 2 km only cause a negligible error on the AMF calculation. In addition, aerosols at the lowest 195m are considered to be homogeneous in the AMF calculation. These information are now supplemented in the manuscript line 174 to 180.

2) As described in Sect 2.2.4, the authors has finally employed the new method for VCD estimation in the mobile measurements, which is recommended by Wagner et al., 2010. Maybe the authors could shorten the introduction of the geometric approximation and standard method for the VCD estimation. Alternatively, I suggest the authors to provide the comparison of the retrieved VCD results between standard and suggested methods? For example, taking one day as an example, to present the time series of the DSCD_{mea}, DSCD_{offset} and AMF_{trop} as used in the E.q. (12).

Response: We followed the reviewer suggestion and shortened the introduction of the geometric approximation and standard method for the VCD estimation. Changes are listed in the following:

- Line 149-150: we put the formula ($SCD_{meas} = SCD_{trop} + SCD_{strat}$) into the sentence
- Line 151-152: sentence combination: “it can be assumed that the light path in the stratosphere for zenith and off zenith measurements are very similar, i.e. $SCD_{strat}(\alpha) \approx SCD_{strat}(90^\circ)$ ”
- Line 157-158: add description of VCD_{trop} : “and the tropospheric vertical column density (VCD_{trop}) can be expressed as follows”
- Line 193-195: remove this paragraph in the ACPD version

In addition, we have compared the VCD retrieved with both standard and suggested method. Time series of the $DSCD_{meas}$, $DSCD_{offset}$, AMF_{trop} and VCD_{trop} on 28 Nov 2015 are shown in Figure R1. Fig. R1a shows the time series of NO_2 DSCDs for both elevation angles. Higher DSCDs are obtained from the lower elevation angle. The offset caused by the NO_2 absorption in the Fraunhofer reference spectrum and the stratospheric absorption (see Eq. 7 in the revised manuscript) are determined by a polynomial fit. $DSCD_{offset(t)}$ is then calculated following Eq. 10. The tropospheric VCDs of NO_2 calculated with both approaches (corresponding to Eq. 7 and Eq. 8 in the revised manuscript) are shown in Fig. R1d. Comparing with standard method, the temporal development of tropospheric NO_2 VCDs calculated by the new method is less noisy. Similar results can be found for SO_2 and $HCHO$ in Figs. R2-3.

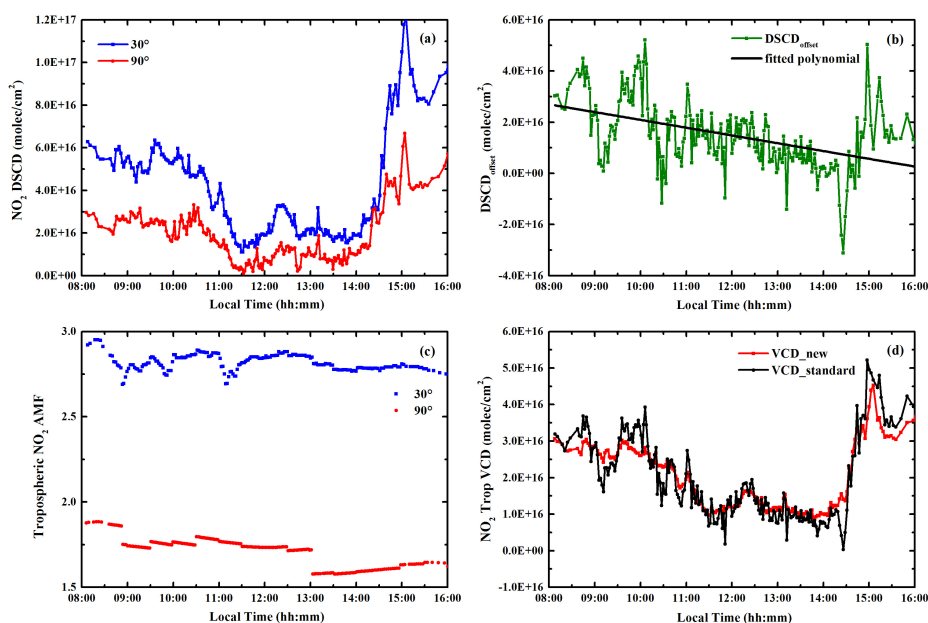


Figure R1. An example of determination of tropospheric NO_2 from the spectra measured on 28

November 2015. (a) NO_2 DSCDs, (b) $\text{DSCD}_{\text{offset}}$ (see Eq. 10) plotted as a function of time (green points), (c) Tropospheric NO_2 AMFs calculated by the radiative transfer model SCIATRAN, (d) The tropospheric VCDs of NO_2 calculated by new and standard method (corresponding to Eq. 7 and Eq. 8).

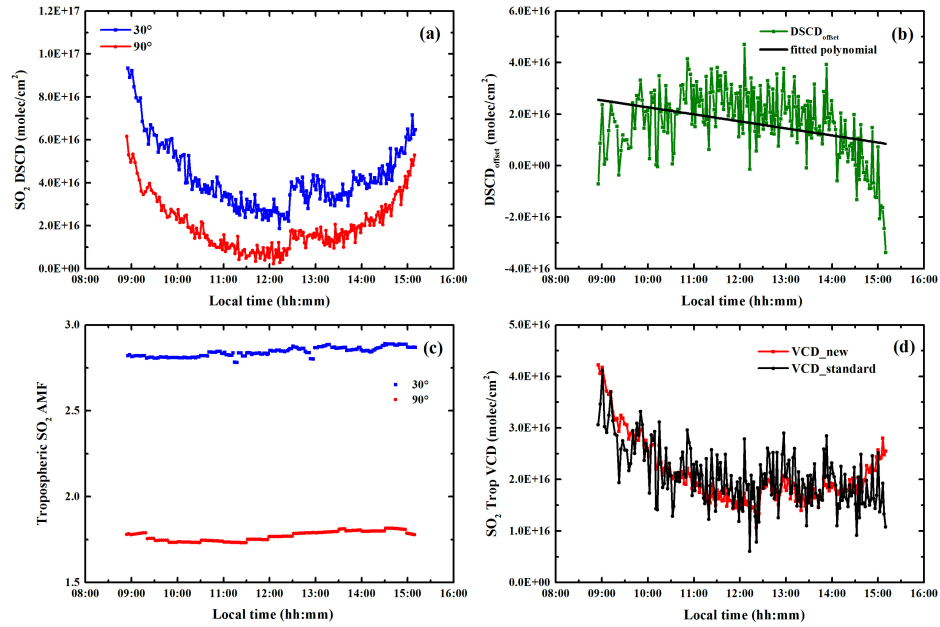


Figure R2. Same as Fig. R1, but for an example of determination of tropospheric SO_2 from the spectra measured on 27 November 2015.

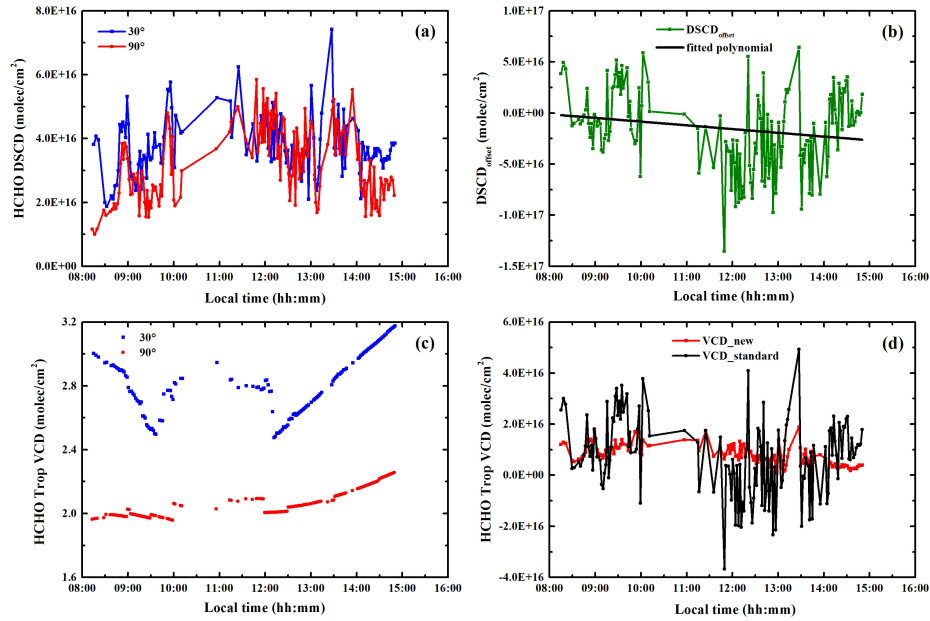


Figure R3. Same as Fig. R1, but for an example of determination of tropospheric HCHO from the spectra measured on 2 December 2015.

3) In this study, OMI VCDs are computed using atmospheric profiles from WRF-Chem simulations. It would be interesting to show how the VCDs are different from other operational products, e.g., NASA product.

Response: In this study, the USTC's OMI tropospheric NO₂ product is used. This product has been reported to be more suitable for atmospheric conditions in China (Liu et al., 2016; Xing et al., 2017; Su et al., 2017). Correlations of daily averaged tropospheric NO₂ VCDs measured by MAX-DOAS with USTC OMI and NASA OMI satellite data are shown in Fig. R4. Compared to the NASA's standard product, the USTC's OMI tropospheric NO₂ VCD agrees better with ground measurements a Pearson correlation coefficient (R) of 0.82 while the correlation between MAX-DOAS and the NASA OMI product is 0.76. The results suggested that accounting for the local atmospheric conditions and use the WRF-Chem model with measured climatology parameter and newest emission inventory to simulate trace gas profile in AMF calculation could improve the accuracy of OMI NO₂ VCD products. The Figure 7 is replaced by Figure R4 in the revised manuscript. These information are now supplemented in the manuscript line 332 to 336.

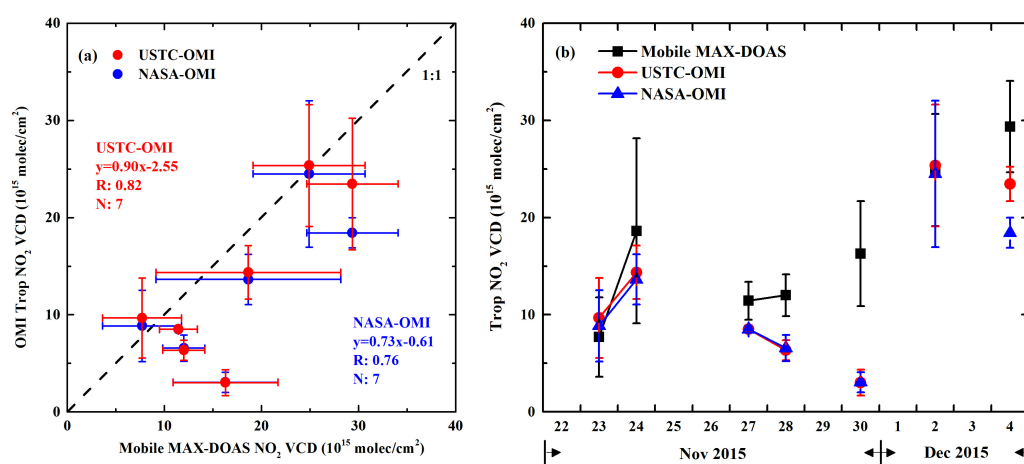


Figure R4. (a) Correlation analysis and (b) time series of tropospheric NO₂ VCDs measured by ship-based MAX-DOAS and OMI during Yangtze River campaign. MAX-DOAS data (black markers) are temporally averaged around the USTC OMI and NASA OMI overpass time (red and blue markers, respectively), while the OMI data are spatially averaged within 20 km radius around the ship's averaged position. The error bars show the 1 σ standard deviations of ship-based MAX-DOAS and OMI data.

4) It is not clear how the pollution events are identified. From Figure 3, the NO₂ VCD on 29 of

Nov is also very high, however, this day is not identified as pollution event. The authors should provide more information on the criterion in selecting pollution events.

Response: Pollution events were identified with both NO₂ and SO₂ VCDs reached or above the threshold value of 4.0×10^{16} molec/cm². Although the NO₂ VCD on 29 November is also very high, but the SO₂ VCD is relatively low. Thus, 29 November is not included in the pollution events analysis. The threshold value for identifying the pollution events is supplemented in the manuscript line 278.

5) In section 3.1, trajectories are calculated to assess the pollutant transportation. However, it is not clear that these backward trajectories are calculated at which altitude level. It would be much better to show the height of the backward trajectories as well, so that readers could better interpret how pollutants are transported.

Response: Considering atmospheric pollutants are mainly concentrated in low altitudes during heavy pollution episodes, the trajectory arrival heights were set to 500 m and assumed to be representative for the entire boundary layer. In this study, 24 h back-trajectories were calculated by the HYSPLIT trajectory model. This information is now included in the manuscript line 302.

6) It's novel and interested to identify the industrial and vehicle contribution by E.q. 13 and 14, which provide the new insights for the sources appointment. As one of the most developed area in China, there were some more studies focusing on the emission inventories and source appointment for YRD areas. Maybe the authors can review previous results and compare with this study a little bit more in the discussion.

Responses: We have updated the section referring to a recent publication (Xia et al., 2016), which show a dramatic growth of the number of vehicle plays an increasingly significant role for regional NO₂ pollution over past years. For Hubei and Jiangxi provinces, the number of power plant is less than Jiangsu province. Therefore, the contribution from vehicle emission to ambient NO₂ level is expected to be more pronounced with the dramatic growth of vehicle number. Changes are applied to line 415 to 418.

7) For the estimation of primary and secondary sources of HCHO, I have two questions: 1) which

kind of the measured HCHO concentrations was used in the regression model? Since the HCHO levels were determined by MAX-DOAS as VCDs, however, the ambient HCHO concentrations were used in the model. How the authors obtain the ground surface concentration HCHO from the VCDs? Otherwise, why the authors can make regression of the HCHO VCDs with in-situ CO, O_x?

2) For the diurnal pattern, the authors inferred that secondary formation of HCHO shows a peak value during noon time (11:00-14:00), however, there was also another peak of relative contribution of secondary sources around 10:00 LT. How to consider this phenomenon?

Response: (1) For the estimation of primary and secondary sources of HCHO, the measured HCHO used in the regression model is ground mixing ratios. Usually, surface HCHO mixing ratios can be obtained from the HCHO vertical profiles (e.g., 0-200 m layer) (Wang et al., 2014). As the viewing elevation angles of the MAX-DOAS measurements only include 30° and 90°, therefore, there is not enough information to retrieve HCHO vertical profiles. In this study, we use a simplified formula introduced by (Lee et al., 2008) to convert mean HCHO DSCDs to mixing ratios (ppbv).

$$M(\text{ppbv}) = 1.25 \times \frac{DSCD(\text{molecule cm}^{-2})}{dAMF} \times \frac{1}{2.688 \times 10^{16} (\text{molecule DU}^{-1})} \times \frac{1}{\Delta P(\text{atom})}$$

where M is the mixing ratio, DSCD is the difference between the SCDs of the measured spectrum and that of the Fraunhofer reference spectrum, dAMF is a differential air mass factor (dAMF=AMF(α=30°)-AMF(α=90°)), and ΔP is the pressure difference between surface and 500 m height of boundary layer. The AMFs for this study were calculated using the radiative transfer model SCIATRAN 2.2 as described in Section 2.2.4.

(2) We agree with the reviewer that there is another peak of relative contribution of secondary sources at around 10:00 LT. The 24 h backward trajectories on 3 December (Fig. 6d in the revised manuscript) suggested that rapid transport of air masses carries significant amount of pollutants including formaldehyde precursor from polluted area in northern China. Thus, the peak of relative contribution of secondary sources around 10:00 LT is probably resulted from the transportation of formaldehyde precursor. The explanation of the diurnal pattern has been modified in the revised manuscript (Line 474-479 in the revised manuscript).

Technical corrections:

1) Introduce abbreviation on the first time used in the manuscript, e.g., line 169 WRFChem.

Response: Abbreviation (WRF-Chem) is now introduced at the first time used in the manuscript (Line 170).

2) Text on Figure 3-6 is too small to read. Considering the similarities of Fig.3 to Fig.5, I suggest to merge them together to show the time series of these three pollutants in each panel with a continuous X-axis.

Response: We have merged Fig.3-5 so that the time series of three pollutants (NO₂, SO₂, and HCHO) in each panel with a continuous X-axis. Considering that a single plot covering all data is a bit difficult to read, so we have now separated it into 2 figures (Fig. 3&4 in the revised manuscript) for two periods (from Nov 22 to Nov 28 and from Nov 29 to Dec 4). In addition, we have enlarged the fonts in figure 6.

3) Put error bars on Figure 13 and 14.

Response: We have now included error bars in Figure 14 (Fig. 13 in the revised manuscript).

4) Please uniform the units of VCDs. It's different in Figures (molec/cm²) and manuscript text (molec cm⁻²) now.

Response: We have uniformed the units of VCDs (molec/cm²) both in Figures and manuscript text.

References:

- Fan, S., Liu, C., Xie, Z., Dong, Y., Hu, Q., Fan, G., Chen, Z., Zhang, T., Duan, J., and Zhang, P.: Scanning vertical distributions of typical aerosols along the Yangtze River using elastic lidar, Science of The Total Environment, 628, 631-641, 2018.
- Lee, C., Richter, A., Lee, H., Kim, Y. J., Burrows, J. P., Lee, Y. G., and Choi, B. C.: Impact of transport of sulfur dioxide from the Asian continent on the air quality over Korea during May 2005, Atmospheric Environment, 42, 1461-1475, 2008.

- Lin, J.-T., Martin, R., Boersma, K., Sneep, M., Stammes, P., Spurr, R., Wang, P., Van Roozendael, M., Clémer, K., and Irie, H.: Retrieving tropospheric nitrogen dioxide from the Ozone Monitoring Instrument: effects of aerosols, surface reflectance anisotropy, and vertical profile of nitrogen dioxide, *Atmospheric Chemistry and Physics*, 14, 1441-1461, 2014.
- Liu, H., Liu, C., Xie, Z., Li, Y., Huang, X., Wang, S., Xu, J., and Xie, P.: A paradox for air pollution controlling in China revealed by "APEC Blue" and "Parade Blue", *Scientific reports*, 6, doi:10.1038/srep34408, 2016.
- Su, W., Liu, C., Hu, Q., Fan, G., Xie, Z., Huang, X., Zhang, T., Chen, Z., Dong, Y., and Ji, X.: Characterization of ozone in the lower troposphere during the 2016 G20 conference in Hangzhou, *Scientific reports*, 7, 17368, 2017.
- Wang, T., Hendrick, F., Wang, P., Tang, G., Clémer, K., Yu, H., Fayt, C., Hermans, C., Gielen, C., and Müller, J.-F.: Evaluation of tropospheric SO₂ retrieved from MAX-DOAS measurements in Xianghe, China, *Atmospheric Chemistry and Physics*, 14, 11149-11164, 2014.
- Xing, C., Liu, C., Wang, S., Chan, K. L., Gao, Y., Huang, X., Su, W., Zhang, C., Dong, Y., and Fan, G.: Observations of the vertical distributions of summertime atmospheric pollutants and the corresponding ozone production in Shanghai, China, *Atmospheric Chemistry and Physics*, 17, 14275-14289, 2017.

Responses to Anonymous Referee #2

We thank the reviewer for the constructive suggestions and comments. We appreciate the reviewer's comments and these comments are very helpful for improving the manuscript. We understand that the comments are positive on the scientific content of the manuscript while appropriate revisions and clarifications are necessary.

We have addressed the reviewer's comments on a point to point basis as below for consideration.

General comments:

1) In section 2.2.2, how many percent of data are removed using the filter wind directions and SZAs?

Response: The wind direction and SZA filtering criterions removed 5.4% and 15.8% of all data, respectively. This information is now supplemented in the revised manuscript line 122 to 123.

2) The authors use the trace gas profiles and vertical profiles of pressure and temperature from WRF-Chem for AMF calculation. What is the spatial resolution and time resolution of the WRF-Chem profiles? Did the authors use a fixed trace gases profile for all the measurements or use the unique profile dependent on the measurement locations and time?

Response: In this study, the WRF-Chem model (version 3.7) was used to simulate the vertical profile of aerosol and trace gases as well as other meteorological parameters. The simulation domain covers large part of East China (17-49 °N, 95-124°E) with a horizontal resolution of 20×20 km and 26 pressure sigma level from ground level up to 50 hPa. The time resolution of the model output is set to 1 h. Details of the configuration of the model can be found in (Liu et al., 2016; Su et al., 2017). Atmospheric profiles obtained from the model simulation were then interpolated in both spatial and temporal dimension to MAX-DOAS measurements location and time for AMF calculation. Details of the model simulation and AMF calculation are now included in the manuscript line 171 to 172.

3) The authors use the aerosol extinction coefficients measured by Mie lidar measurements for the AMF calculations. Did the authors use a fixed aerosol extinction profile (average the aerosol extinction coefficient from all the lidar measurements during the campaign) or use the specified

profile dependent on locations, time and the availability of lidar measurements?

Response: Lidar measurement was carried out together with MAX-DOAS most of the time during the campaign. AMF of the MAX-DOAS observations is calculated using hourly averaged Lidar aerosol extinction profile. This information is now supplemented in the manuscript line 172.

4) A fix set of single scattering albedo (SSA) of 0.95, asymmetry parameter of 0.68 and surface albedo of 0.06 is assumed in the radiative transfer calculations. Please explain why use this setting. Any references?

Response: The single scattering albedo (SSA) of 0.95 and asymmetry parameter of 0.68 are chosen according to the sensitivity study by (Chen et al., 2009). For oceans or rivers, the surface albedo is generally low and keep around 0.06 (Pinker et al., 1995). We have added the references in the revised manuscript line 188.

5) In section 2.2.4, there are too many formula and introduction of the determination of the tropospheric VCD. I suggest shortening the section and combining some of the formula.

Response: We followed the reviewer suggestion and shortened the introduction of the determination of the tropospheric VCD and combined some of the formula. Changes are listed in the following:

- a) Line 149-150: we put the formula ($SCD_{meas} = SCD_{trop} + SCD_{strat}$) into the sentence
- b) Line 151-152: sentence combination: “it can be assumed that the light path in the stratosphere for zenith and off zenith measurements are very similar, i.e. $SCD_{strat}(\alpha) \approx SCD_{strat}(90^\circ)$ ”
- c) Line 157-158: add description of VCD_{trop} : “and the tropospheric vertical column density (VCD_{trop}) can be expressed as follows”
- d) Line 193-195: remove this paragraph about the description of tropospheric vertical column density (VCD_{trop}) in the ACPD version
- e) Line 207: delete the “tropospheric vertical column density”

6) I agree with the comment from Referee #1 about the high NO_2 VCD on Nov. 29. Please explain the reason of high NO_2 and relative low SO_2 concentrations during this day.

Responses: The measurement ship was sailing around Wuhan on 29 November. Elevated tropospheric NO₂ observed around Wuhan is probably related to high emission, i.e., traffic emissions, in Wuhan as it is the largest city in Hubei. A rather low SO₂ level might due to lower SO₂ emissions located along the Yangtze River around Wuhan, e.g., coal-fired power plants.

7) In section 2.3, USTC's OMI tropospheric NO₂ product is used. I suggest showing more detailed information about the USTC OMI product, e.g., the data source of NO₂ slant density (SCD). In addition, USTC shall be explained when appeared for the first time.

Response: We agree with the reviewer suggestion and now included a more detailed description of the USTC's OMI NO₂ product in section 2.3. In this study, USTC's OMI tropospheric NO₂ product is developed based on OMI's primary product and has proven to be more suitable for the atmospheric conditions in China (Liu et al., 2016; Su et al., 2017; Xing et al., 2017). Slant column densities (SCDs) of NO₂ are retrieved by applying the DOAS fit to OMI spectra (data source: OMI Level 1B VIS Global Radiances Data product (OML1BRVG) (https://disc.gsfc.nasa.gov/Aura/data-holdings/OMI/oml1brvg_v003.shtml)). The information of USTC's OMI product are now supplemented in the revised manuscript line 234-237.

8) Figure 7d is a bit confusing, please describe clearly what the green lines represent? Is it 6, 12, 18 or 24 hour backward trajectories? What is the altitude of the backward trajectories?

Response: In Figure 7d, the green lines represent the 24 h backward trajectories during pollution events. The green lines show the backward trajectories calculated for each hour during the detected episodes. For example, five green lines on 1 Dec represent the backward trajectories ending at 04, 05, 06, 07, and 08 UTC on 1 Dec 2015 (corresponding to gray columns in Fig 4). The green markers indicate the location of air masses 6, 12, 18 and 24 h before arriving to the measurement ship. Considering atmospheric pollutants are mainly concentrated in low altitudes during heavy pollution episodes, the trajectory arrival heights were set to 500 m and assumed to be representative for the entire boundary layer. This information is now included in the manuscript line 300-302.

9) The authors mention that the different spatial patterns detected by MAX-DOAS and OMI on

Dec. 2 might be due to the strong influence by the aerosols. This is an interesting episode because it might show that the effect of neglecting aerosol in satellite AMF calculations on satellite NO₂ retrieval. Please prove this hypothesis using the Lidar measurement data.

Response: We agree with the reviewer suggestion and estimated the influence of ignoring aerosols in satellite AMF calculation on NO₂ retrieval. As lidar measurements only cover limited area, therefore, we have recalculated OMI NO₂ VCDs by taking aerosol information from WRF-Chem simulation into account. Figure R1a shows OMI NO₂ VCDs calculated without consider aerosol in the AMF calculation while Figure R1b shows the OMI NO₂ VCDs recalculated using aerosol information from WRF-Chem simulation. The spatial distributions of NO₂ are changed after including aerosol in the radiative transfer calculation. Significant enhancement of NO₂ VCDs can be observed over some areas. However, the spatial patterns of NO₂ detected by MAX-DOAS and OMI are still quite different. The result indicates the impact of aerosol could not fully explain the discrepancy between MAX-DOAS and OMI on this day. On the other hand, the MAX-DOAS and OMI observations agree better during OMI overpass time (black star symbols) and the agreement decay when the time differences between MAX-DOAS and OMI measurements become larger. This implies a strong temporal variability of NO₂ on this day. We have now supplemented the additional information and explanation in the manuscript line 352-360.

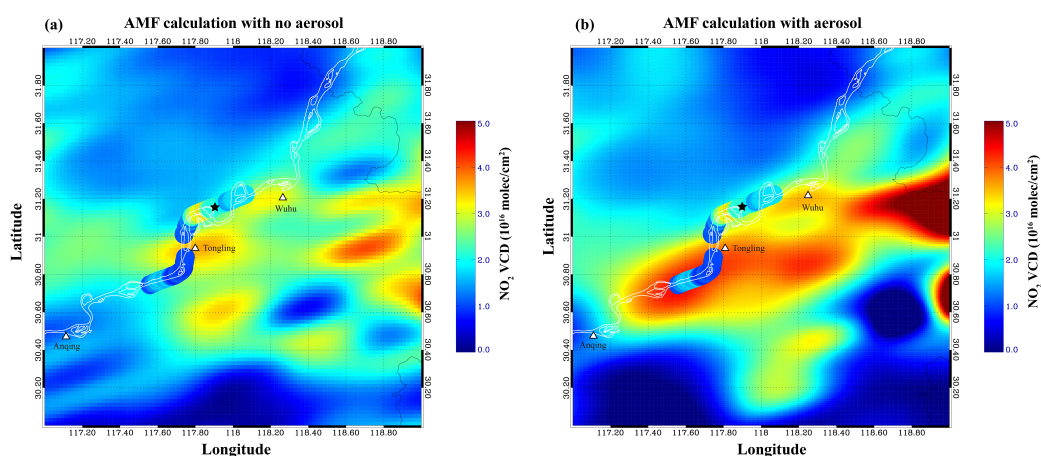


Figure R1. Spatial pattern of tropospheric NO₂ VCD measured by OMI calculated under two different AMFs.

10) In section 3.1, Line 307-308: “In contrast, lower HCHO VCDs were observed mainly on rainy,

cloudy and haze days”. Could the authors explain more about the possible reasons for this phenomenon?

Response: Lower HCHO VCDs were observed mainly on rainy, cloudy and haze days, which might be due to stronger wet deposition and weaker solar irradiation during these days. The possible reasons for this phenomenon are supplemented in the revised manuscript line 316-318.

11) In section 3.4, please explain how to convert HCHO VCD to HCHO concentrations (ppb).

Response: For the estimation of primary and secondary sources of HCHO, the measured HCHO used in the regression model is ground mixing ratios. Usually, surface HCHO mixing ratios can be obtained from the HCHO vertical profiles (e.g., 0-200 m layer) (Wang et al., 2014). As the viewing elevation angles of the MAX-DOAS measurements only include 30° and 90°, therefore, there is not enough information to retrieve HCHO vertical profiles. In this study, we use a simplified formula introduced by (Lee et al., 2008) to convert mean HCHO DSCDs to mixing ratios (ppbv).

$$M(\text{ppbv}) = 1.25 \times \frac{DSCD(\text{molecule cm}^{-2})}{dAMF} \times \frac{1}{2.688 \times 10^{16} (\text{molecule DU}^{-1})} \times \frac{1}{\Delta P(\text{atom})}$$

where M is the mixing ratio, DSCD is the difference between the SCDs of the measured spectrum and that of the Fraunhofer reference spectrum, dAMF is a differential air mass factor (dAMF=AMF($\alpha=30^\circ$)-AMF($\alpha=90^\circ$)), and ΔP is the pressure difference between surface and 500m height of boundary layer. The AMFs for this study were calculated using the radiative transfer model SCIATRAN 2.2 as described in Section 2.2.4. These information are now supplemented in the revised manuscript line 433-434.

12) In section 3.4, Line 430: “As other factors can also affect the atmospheric HCHO concentration”. Please describe the “other factors” in more detail.

Response: In addition to primary emission and secondary formation of HCHO, meteorological conditions, e.g., solar irradiance, could also affect the atmospheric HCHO concentration. This information is now included in the revised manuscript line 451.

Technical corrections:

1) Line 321: 'Dec 1 and 3' > 'Dec 2 and 4'

Response: Corrected.

2) Line 344: 'aerosol' > 'aerosols'

Response: Corrected.

3) Text on Figure 2: change "dSCD" to "DSCD", and please uniform the units of DSCD (molec/cm²).

Response: We have changed "dSCD" to "DSCD" on Figure 2 and uniform the units of DSCD (molec/cm²) in the revised manuscript.

4) Explain the caption 'RTM' in Figure 3-5. Or remove it.

Response: We have removed the caption 'RTM' in Figures 3-5. We have merged Figs.3-5 so that the time series of three pollutants (NO₂, SO₂, and HCHO) in each panel with a continuous X-axis (Fig. 3&4 in the revised manuscript).

5) Text on Figure 6 is too small to read. Please use larger font size and put the colorbar on the right.

Response: We have enlarged the fonts in Figure 6 and put the colorbar on the right (Fig. 5 in the revised manuscript).

6) Improve the quality of Figure 10 (too many stripes).

Response: We have do our best to improve the quality of Figure 10, but too many stripes in Fig. 10 is inevitable which caused by the different satellite orbit.

References:

- Chen, D., Zhou, B., Beirle, S., Chen, L. M., and Wagner, T.: Tropospheric NO₂ column densities deduced from zenith-sky DOAS measurements in Shanghai, China, and their application to satellite validation, *Atmospheric Chemistry And Physics*, 9, 3641-3662, 2009.
- Lee, C., Richter, A., Lee, H., Kim, Y. J., Burrows, J. P., Lee, Y. G., and Choi, B. C.: Impact of transport of sulfur dioxide from the Asian continent on the air quality over Korea during May 2005, *Atmospheric Environment*, 42, 1461-1475, 2008.
- Liu, H., Liu, C., Xie, Z., Li, Y., Huang, X., Wang, S., Xu, J., and Xie, P.: A paradox for air pollution controlling in China revealed by "APEC Blue" and "Parade Blue", *Scientific reports*, 6, doi:10.1038/srep34408, 2016.
- Pinker, R., Frouin, R., and Li, Z.: A review of satellite methods to derive surface shortwave irradiance, *Remote Sensing of Environment*, 51, 108-124, 1995.
- Su, W., Liu, C., Hu, Q., Fan, G., Xie, Z., Huang, X., Zhang, T., Chen, Z., Dong, Y., and Ji, X.: Characterization of ozone in the lower troposphere during the 2016 G20 conference in Hangzhou, *Scientific reports*, 7, 17368, 2017.
- Wang, T., Hendrick, F., Wang, P., Tang, G., Cl  mer, K., Yu, H., Fayt, C., Hermans, C., Gielen, C., and M  ller, J.-F.: Evaluation of tropospheric SO₂ retrieved from MAX-DOAS measurements in Xianghe, China, *Atmospheric Chemistry and Physics*, 14, 11149-11164, 2014.
- Xing, C., Liu, C., Wang, S., Chan, K. L., Gao, Y., Huang, X., Su, W., Zhang, C., Dong, Y., and Fan, G.: Observations of the vertical distributions of summertime atmospheric pollutants and the corresponding ozone production in Shanghai, China, *Atmospheric Chemistry and Physics*, 17, 14275-14289, 2017.