



# Article Observations by Ground-Based MAX-DOAS of the Vertical Characters of Winter Pollution and the Influencing Factors of HONO Generation in Shanghai, China

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Abstract: Analyzing vertical distribution characters of air pollutants is conducive to study the mechanisms under polluted atmospheric conditions. Nitrous acid (HONO) is a kind of crucial species in photochemical cycles. Exploring the influence and sources of HONO in air pollution at different altitudes offers some insights into the research of tropospheric oxidation chemistry processes. Ground-based multi-axis differential optical absorption spectroscopy (MAX-DOAS) measurements were conducted in Shanghai, China, from December 2017 to March 2018 to investigate vertical distributions and diurnal variations of trace gases (NO2, HONO, HCHO, SO2, and water vapor) and aerosol extinction coefficient in the boundary layer. Aerosol and NO2 showed decreasing profile exponentially, SO2 and HCHO concentrations were observed relatively high values in the middle layer. SO2 was caused by industrial emissions, while HCHO was from secondary sources. As for HONO, below 0.82 km, the heterogeneous reactions of NO<sub>2</sub> impacted on forming HONO, while in the upper layers, vertical diffusion might be the dominant source. The contribution of OH production from HONO photolysis at different altitudes was mainly controlled by the concentration of HONO. MAX-DOAS measurements characterize the vertical structure of air pollutants in Shanghai and provide further understanding for HONO formation, which can help deploy advanced measurement platforms of regional air pollution over eastern China.

Keywords: MAX-DOAS; vertical profiles; HONO sources



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# 1. Introduction

Over the past decades, people paid more and more attention to air pollution, since this problem did have multifarious devastating impacts on human health [1–4]. It is particularly serious in China, including the Yangtze River Delta (YRD), it is the consequence of the fast-paced progress of the economy and industrialization [5–11]. Shanghai is one of the four directly controlled municipalities in China, with a large number of vehicles and factories. Heavy industrial activities and growing vehicle numbers have continued to deteriorate the air quality. The meteorological environment in winter is relatively stable, which is not conducive to the dissipation of pollution. Then the pollution is getting worse in winter [12–14]. What's more, nitrous acid (HONO) has long been recognized as significant to atmospheric photochemistry [15,16]. A high-level concentration of HONO would lead to the formation of secondary pollutants and accelerate air pollutions [15,17]. Previous studies showed that the concentration of HONO in winter is higher than that in summer [16]. Therefore, it is particularly important to formulate specific air pollution prevention and control strategies for the winter of Shanghai.

Monitoring temporal and spatial concentrations of atmospheric species is the premise of pollution control. Traditional atmospheric environment monitoring technology mainly relies on automatic monitoring stations in urban cities, so the coverage is limited. Vertical distributions of precursor trace gases (e.g., NO<sub>2</sub>, SO<sub>2</sub>, HCHO, and so on) and aerosols in regional pollution studies are also short of research. Multi-axis differential optical absorption spectroscopy (MAX-DOAS) is a passive remote sensing technique that measures the tropospheric aerosol extinctions and trace gas concentrations [18–23], hence provides the information of temporal and spatial characters of air pollutants. Fengxian, the site we set the instrument in, is one of the sub-districts of Shanghai, located in the southeast of YRD and the north of Hangzhou Bay. This area is mainly affected by the Subtropical marine monsoon, the prevailing winds are mainly southeasterly and there are always rainy days in winter. Notably, the measurement site is surrounded by agricultural areas with only a few industrial and traffic emissions.

In this paper, MAX-DOAS observations were conducted from December 2017 to March 2018 for measuring the vertical distribution and diurnal variations of aerosol extinction and trace gases in the lower troposphere, where conducted a majority of chemical and physical reactions. The VCDs and profiles were retrieved by the HEIPRO (Heidelberg Profile) algorithm and also validated by USTC-OMI (University of Science and Technology of China-Ozone Monitoring Instrument) products, CNEMC (the China National Environmental Monitoring Center), and NCDC (the National Climatic Data Center) measurements. In the following, this study also focuses on studying winter HONO sources and the contribution of OH production from HONO photolysis at different altitudes in Shanghai by analyzing the vertical nitrous acid distribution during the whole campaign.

#### 2. Materials and Methodologies

2.1. The MAX-DOAS Observations

# 2.1.1. Setup of Observations

The MAX-DOAS instrument was set up in the Fengxian campus of East China University of Science and Technology (30.8336°N 121.5025°E; Elevation: 20 m) from 16 December 2017 to 6 March 2018, located in shanghai (Figure 1).

The instrument contains a telescope, two spectrometers, a computer acting as a controlling and data acquisition unit. The viewing elevation angles of the telescope are controlled by a stepping motor. Scattered sunlight collected by the telescope is redirected to the spectrometer through a prism reflector and quartz fibers for spectral analysis. Two imaging spectrometers (Ocean Optics HR2000C and a Maya2000 Pro spectrometer) were used to measure spectra in both the UV (303–370 nm) and visible (390–608 nm) wavelength ranges, the spectral resolution of full width half maximum (FWHM) is 0.5 nm and 0.3 nm respectively. The operating temperature of spectrometers is stabilized to 20 °C with the help of Peltier. The field of view (FOV) of the telescope is estimated to be less than 1°.



**Figure 1.** The position of the MAX-DOAS observation sites in Shanghai. The instrument was set up on the roof of the Environmental Science Building in the Fengxian campus of East China University of Science and Technology (30.8336°N 121.5025°E). Figure 1 was captured from online Google Map.

During the whole observation period, the viewing azimuth direction of the telescope was kept to the north. The elevation angles of a full measurement scan sequence consist of  $1^{\circ}$ ,  $2^{\circ}$ ,  $3^{\circ}$ ,  $4^{\circ}$ ,  $5^{\circ}$ ,  $8^{\circ}$ ,  $10^{\circ}$ ,  $15^{\circ}$ ,  $30^{\circ}$ , and  $90^{\circ}$ , each sequence lasts about 15 min automatically depending on the intensity of scattered sunlight. A spectral software in the combined computer collected the measurement data only when the Solar Zenith Angle (SZA) is less than  $75^{\circ}$  in order to avoid the influence from the stratospheric absorptions. Dark current and offset spectra were removed from the measured spectrum automatically through a script at night [14,24,25].

# 2.1.2. Spectral Analysis

The solar scattering spectra observed by MAX-DOAS were analyzed to derive the differential slant column densities (DSCDs) at different elevation angles via QDOAS spectral fitting software. Detailed DOAS fit settings for the trace gases have been presented in Table 1. The fitting wavelength interval of  $O_4$  (oxygen dimer), NO<sub>2</sub>, HONO, HCHO, SO<sub>2</sub>, and H<sub>2</sub>O are 338–367 nm, 338–367 nm, 335–373 nm, 336.5–359 nm, 305–317.5 nm, and 433–462 nm, respectively. And  $O_4$  has an additional wavelength (460–490 nm) especially for analysis of H<sub>2</sub>O. Several trace gases absorption cross-sections, the Ring spectrum, the Frauenhofer reference spectrum (FRS), and a low order polynomial are applied in the DOAS parameters. The wavelength calibration was typically used in form of a high-resolution solar spectrum [26]. Then we will get the results of the differential slant column densities (DSCDs), which means the difference of the slant column density between the off-aix spectrum and the zenith-sky reference spectrum. These DSCDs will be converted to vertical profile retrieval subsequently. Before profile retrieval, DOAS fit results with a root mean square (RMS) of residuals larger than 0.002 or a solar zenith angle (SZA) larger than 75° were filtered for quality control.

Parameter	Data Source				Trace Gases			
		<b>O</b> <sub>4</sub>	$O_4$	NO <sub>2</sub>	HONO	нсно	SO <sub>2</sub>	H <sub>2</sub> O
Fitting Wavelength Range (nm)		338-367	460-490	338-367	335–373	336.5-359	307.5-315	433-462
	[27] 220 K, 294 K,							
NO <sub>2</sub>	I <sub>0</sub> -correction * (SCD of 10 <sup>17</sup>	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	√(294 K)	√(294 K)	$\checkmark$
SO <sub>2</sub>	molecules/cm <sup>2</sup> ) [28] 298 K							
HCHO HONO	[29], 297 K [30], 296 K	$\checkmark$		$\checkmark$		$\checkmark$		
	[31], 223 K, 243 K,				v			
O <sub>3</sub>	I <sub>0</sub> -correction * (SCD of 10 <sup>20</sup>	$\checkmark$	√(223 K)	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	√(223 K)
0	molecules/cm <sup>2</sup> )	,	/	,	,	,		,
$O_4$ BrO	[32], 293 K [33], 223 K		$\checkmark$					$\checkmark$
Glyoxal	[34], 298 K	V		V	V	V		
H <sub>2</sub> O	[ <mark>35</mark> ], 293 K, 1021 hPa							$\checkmark$
Dina	Ring spectra	/	/	/	/	/	/	/
King	ODOAS [36]	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$
Polynomial degree	~ 1 1	5th order	5th order	5th order	5th order	5th order	5th order	3rd order
Intensity offset		constant	constant	constant	1st order	1st order	1st order	constant
Wavelength calibration		Based on a high resolution solar reference spectrum (SAO2010 solar spectra) [26]						

Table 1. Summary of retrieval settings for the O<sub>4</sub>, NO<sub>2</sub>, HONO, HCHO, SO<sub>2</sub>, and H<sub>2</sub>O DOAS spectral analyses.

\* Solar I0-correction [37].

The primary results (i.e., DSCDs) are affected by the absorption path in the atmosphere, so the calculated results need to convert to the tropospheric Vertical Column Density (VCD) by using tropospheric Differential Air Mass Factors (DAMFs) [38,39], the equation is:

$$VCD_{trop} = \frac{DSCDs}{DAMFs} = \frac{DSCDs(\alpha)}{AMF(\alpha) - AMF(90^{\circ})}$$
(1)

The Air Mass Factors (AMFs) is calculated by the so-called geometric approximation method [18,38], and is simply expressed in a transfer simulation [39,40]:

$$AMF(\alpha) = \frac{1}{\sin(\alpha)}$$
(2)

So, the tropospheric VCD can be figured out by:

$$VCD_{trop} = \frac{DSCDs(\alpha)}{\frac{1}{\sin(\alpha)} - 1}$$
(3)

# 2.1.3. Profile Retrievals of Aerosol and Trace Gases

Vertical profiles of aerosol and trace gases (NO<sub>2</sub>, HONO, HCHO, SO<sub>2</sub>, water vapor) are retrieved from DSCDs at different elevation angles by the HEIPRO (Heidelberg Profile) retrieval algorithm [20,41,42]. The equation consisting of different elevation SCD and different layer concentrations will be overdetermined. It is hard to obtain a unique solution for this equation, in order to solve this problem, the HEIPRO algorithm is developed basing on the Optimal Estimation Method (OEM) [43], and the radiative transfer model SCIATRAN [44] is applied as a forward model to simulate the measurement vector y

through the atmospheric state vector x. An a priori state vector  $x_a$  is introduced into the optimal estimation method, and the minimum value function  $\chi^2(x)$  is used to solve the optimally estimated state vector x between the measurement and the prior, so as to invert the statement that is closest to the real atmospheric concentration, i.e., the so-called maximum a posteriori (MAP) solution.

$$\chi^{2}(x) = [y - F(x,b)]^{T} S_{\epsilon}^{-1} [y - F(x,b)] + [x - x_{a}]^{T} S_{a}^{-1} [x - x_{a}]$$
(4)

where x represents observed gas or aerosol concentrations. Parameter b represents system parameters that are not involved in retrieval but have an influence on results such as meteorological statements (i.e., pressure and temperature vertical profiles). The measurement vector y (DSCDs at different elevation angles), which is a function of x and b. F(x, b) is a radiative transfer model or forward model, which corresponds to the measurement vector y as a function of the atmospheric state vector x, which is also dependent on parameters b. The a priori state vector  $x_a$  serves as an initial profile to constrain the range of the solution. S $\varepsilon$  and Sa denote the covariance matrices of the measurement error and the a priori uncertainty, respectively.

HEIPRO has two steps to retrieve profiles. Firstly, aerosol extinction profiles are retrieved according to the measured  $O_4$  DSCDs. The concentration of  $O_4$  in the atmosphere is positively proportional to the square of  $O_2$  monomer concentration, and its vertical concentration and profile are basically stable. SCD of  $O_4$  is not only affected by geometric observation angle but also affected by aerosol concentration. The absorption band of  $O_4$  with different wavelengths can reflect the aerosol extinction, so  $O_4$  can be used as an indicator of aerosol. A fixed set of aerosol optical properties with single-scattering albedo (SSA) of 0.90, asymmetry parameter of 0.69, and ground surface albedo of 0.05 is assumed here [14].

Then the retrieved aerosol extinction profiles serve as the forward model parameters coupled with the measured trace gas DSCDs to retrieve trace gases (i.e., NO<sub>2</sub>, HONO, HCHO, SO<sub>2</sub>, and water vapor) vertical profiles. The retrieval processes of trace gases are nearly similar to that of aerosols. As for NO<sub>2</sub>, HONO, HCHO, and SO<sub>2</sub>, their retrievals depend on the wavelength of O<sub>4</sub> ranged from 338–367 nm, the lowest 3.0 km of the troposphere were divided into 20 layers, with 100 m grid below 1 km and 200 m grid from 1–3 km. But as for water vapor, the forward O<sub>4</sub> wavelength ranges from 460–490 nm, the profiles were divided into 30 layers that the first 20 layers (below 2 km) are on a 100 m grid, and the last ten layers (between 2 km and 4 km) are on a 200 m grid. Considering a full scan- sequence lasts around 13 min, a fixed time interval of 15 min was set to cover all the measured DSCDs. The retrieved profiles with degrees of freedom (DFS) less than 2.0 were filtered out for quality control.

### 2.2. Backward Trajectory

To calculate backward trajectories of air masses, the HYSPLIT (Hybrid Single particle Lagrangian Integrated Trajectory) model coupled with the Global Data Assimilation System (GDAS) [45,46] was used. Both the National Oceanic and Atmospheric Administration Air Resource Laboratory (NOAA-ARL) and the Australian Weather Bureau developed the model. It can simulate and analyze the trajectory of air pollutant transport and diffusion and has been widely used in many studies [24,47] over the past 20 years.

In this study, backward trajectory frequencies were simulated online in order to determine the source of air masses and the physical transport pathway of atmospheric pollutants. Meteorological data from the Global Data Assimilation System (GDAS) (spatial resolution of 0.5 degrees) was inputted in the model for simulations. The HYSPLIT model functions real-time calculation and fine analysis.

# 2.3. TUV Model

The NCAR Tropospheric Ultraviolet and Visible (TUV) radiation model was used to compute the photolysis frequencies of J (HONO) in the absence of direct observations.

The ozone density was got from the Total Ozone Mapping Spectrometer, the typical single scattering albedo (SSA) is 0.95 [48], the mean value of optical depth (AOD) was derived from DOAS retrieval results, and others were set as defaults.

#### 2.4. Ancillary Data for Validation

The Ozone Monitoring Instrument (OMI) flies onboard NASA's Earth Observing System (EOS) Aura satellite launched on 15 July 2004 into a Sun synchronous polar orbit (98° inclination) [49]. OMI is a passive imaging spectrometer equipped with two-dimensional array charge-coupled devices (CCDs) to measure the solar spectra which are reflected by the earth's surface in the ultraviolet and visible (UV-VIS) wavelength range from 270 nm to 500 nm. OMI has a high spatial resolution (13 km (along-track)  $\times$  24 km (cross-track)) and daily global coverage because of a large 114° swath along with a 2600 km wide spatial sampling for one orbit. The local overpass time is between 13:40 LT and 13:50 LT. The algorithm for the retrieval of total column and NO2, SO2, and HCHO is based on the DOAS method. In this study, USTC-OMI tropospheric products were derived from three processes. The trace gas SCDs were derived from OMI Level 1B VIS Global 190 Radiances Data (OML1BRVG). Then the SCDs were converted into vertical column densities (VCDs) using the air mass factors (AMFs) [39]. AMFs were calculated based on the atmospheric temperature and pressure profiles derived from WRF-Chem chemistry transport model simulations. Albedo data are from the climatology albedo database derived from 5 years of OMI observations [50]. VCDs of stratospheric and tropospheric were separated by the assimilation model [51]. More details of the retrieval method can refer to [52–54].

The concentration of NO<sub>2</sub>, SO<sub>2</sub>, and HCHO retrieved from USTC-OMI and the concentration of NO<sub>2</sub>, SO<sub>2</sub>, and PM<sub>2.5</sub> collected from the China National Environmental Monitoring Center (CNEMC) network were both used to validate the MAX-DOAS retrieved data.

The public FTP server of the National Climatic Data Center (NCDC) provided the daily surface meteorological data (temperature, pressure, dew point, wind direction, and speed), at the HONGQIAO INTL site (USAF ID: 583670; 31.198° N, 121.336° E) approximately 42 km north-east of the MAX-DOAS instrument. The RH data were converted to the molecular number density of water vapor to validate the MAX-DOAS retrieved data.

# 3. Results

The whole observation lasted for 81 days from 16 December 2017 to 6 March 2018. According to the principle of MAXDOAS retrieval, the observation results are valid only when sunlight appears. Therefore, the diurnal variations in this study referred specifically to diurnal variations during daytime (08:00 to 17:00 LT (local time)). There are only 37 days available (Table S1) with relatively consecutive data of February 2018 after screening by weather conditions since Shanghai is always rainy and cloudy in winter. Figures S1–S6 shows the relatively consecutive time series of vertical profiles of aerosol extinction and trace gases during February 2018 measured by MAX-DOAS using the QDOAS software and HEIPRO algorithm. According to China Meteorological Center, the datasets were distinguished into haze days when the AQI was >100 and clear days when the AQI was <100. There are 9 days are defined as haze days among all the valid days (Table S1).

#### 3.1. Validation of VCDs Measured by MAX-DOAS

USTC-OMI measurements were obtained by spatially averaging the grid data with a radius of 20 km around the instrument location ( $30.8336^{\circ}$  N  $121.5025^{\circ}$  E) considering the grid is >10 km [55–58]. It is necessary to exclude satellite data for accuracy with larger error (relative error > 100%) and cloud impacts (could fraction > 0.3). The MAX-DOAS retrieved VCDs were averaged around 13:00-14:00 LT according to the OMI overpass time for Shanghai for a correspondent temporal and spatial comparison. All the MAX-DOAS retrieval VCDs were filtered with an error of more than  $1 \times 10^{22}$  molecule/cm<sup>2</sup>, a chi-square of more than 100, or less than 1 degree of freedom (DOF) [59] (-25% of the data).

As shown in Figure 2, the Pearson correlation coefficient (R) of NO<sub>2</sub>, SO<sub>2</sub>, and HCHO is 0.84, 0.64, and 0.61 respectively, Significance level (p) < 0.05, indicating a good agreement between MAX-DOAS and USTC-OMI observation. As for  $NO_2$  (number of data points = 12,  $VCD_{MAX-DOAS} = 1.10 \times VCD_{OMI} - 1.38 \times 10^{15}$ ), the in situ MAX-DOAS VCDs ranges from 1.89  $\times$   $10^{15}$  to 6.27  $\times$   $10^{16}$  , and the USTC-OMI VCDs ranges from 3.57  $\times$   $10^{15}$  to  $4.38 \times 10^{16}$ . The regression analysis suggested that USTC-OMI data was underestimated a little because the NO<sub>2</sub> retrieval VCDs by USTC-OMI subtracting the stratospheric part is only tropospheric VCDs, however, MAX-DOAS was much more sensitive to the surface, leading to higher and more accurate results of VCD. As for  $SO_2$  (number of data points = 21,  $VCD_{MAX-DOAS} = 0.81 \times VCD_{OMI} + 1.97 \times 10^{15}$ ), the in situ MAX-DOAS VCDs ranges from  $9.62 \times 10^{14}$  to  $2.97 \times 10^{16}$ , and the USTC-OMI VCDs ranges from  $9.42 \times 10^{14}$  to  $2.07 \times 10^{16}$ . As for HCHO (number of data points = 23, VCD<sub>MAX-DOAS</sub> =  $0.89 \times VCD_{OMI} + 1.07 \times 10^{15}$ ), the in situ MAX-DOAS VCDs ranges from  $2.34 \times 10^{15}$  to  $1.78 \times 10^{16}$ , and the USTC-OMI VCDs ranges from  $2.64 \times 10^{15}$  to  $2.01 \times 10^{16}$ . Here, all the VCD values are in units of molecule/cm<sup>2</sup>. The regression analysis indicated that SO<sub>2</sub> and HCHO by USTC-OMI both overestimated a little because they were integrated VCDs including stratospheric and tropospheric segments, however, the VCDs by MAX-DOAS just covered from surface to 3 km's height less than that of OMI data. In a word, the MAX-DOAS retrieval VCDs are reliable according to the comparison results.



**Figure 2.** Correlation analysis between tropospheric VCDs measured by the in-situ MAX-DOAS and OMI satellite. (**a**–**c**) is NO<sub>2</sub>, SO<sub>2</sub>, and HCHO columns respectively.

# 3.2. Validation of Surface Concentrations Measured by MAX-DOAS

The first layer of the retrieved data can reflect the concentration near ground. As shown in Figure 3a-c, the hourly averaged NO<sub>2</sub>, SO<sub>2</sub> surface concentrations and aerosol extinction observed by MAX-DOAS were validated using the averaged measurements of in-situ instruments from CNEMC sites of Shanghai under clear sky conditions. For NO<sub>2</sub> (number of data points = 258,  $NO_{2CNEMC}$  ( $\mu g/cm^3$ ) = 1.46 ×  $NO_{2MAX-DOAS}$  (ppb) + 25.46, Pearson correlation coefficient (R) = 0.75, Significance level (p) < 0.001), SO<sub>2</sub> (number of data points = 268, SO<sub>2CNEMC</sub> ( $\mu$ g/cm<sup>3</sup>) = 1.85 × SO<sub>2MAX-DOAS</sub> (ppb) + 11.34, Pearson correlation coefficient (R) = 0.79, Significance level (*p*) < 0.001), and aerosol extinction (number of data points = 255, PM2.5<sub>CNEMC</sub> ( $\mu$ g/cm<sup>3</sup>) = 0.01 × AE<sub>MAX-DOAS</sub> (km<sup>-1</sup>) + 0.20, Pearson correlation coefficient (R) = 0.80, Significance level (p) < 0.001), there existed obvious good coincidence between them, although the CNEMC sites are far away from the position of the MAX-DOAS instrument (as showed in Figure S7). The daily averaged results of water vapor surface concentration measured by MAX-DOAS and NCDC in-situ instrument were displayed in Figure 3d, we can see good correlation between them(number of data points = 35, Water vapor <sub>NCDC</sub> (molecule/cm<sup>3</sup>) =  $0.98 \times$  Water vapor <sub>MAX-DOAS</sub> (molecule/cm<sup>3</sup>)  $- 3.2 \times 10^{14}$ , Pearson correlation coefficient (R) = 0.82, Significance level (p) < 0.001). All of these results demonstrated dependable data quality and robustness of the MAX-DOAS measurements in Shanghai.



**Figure 3.** Correlation analysis between NO<sub>2</sub>, SO<sub>2</sub> surface concentrations, aerosol extinction, water vapor observed by MAX-DOAS and CNEMC, NCDC datasets. (**a**–**d**) is NO<sub>2</sub>, SO<sub>2</sub>, aerosol extinction, and water vapor respectively.

# 3.3. Vertical Distribution Characters and Diurnal Variations of Tropospheric Aerosol Extinction, NO<sub>2</sub>, HONO, HCHO, SO<sub>2</sub>, and Water Vapor

Figures 4–6 were the diurnal variations of the vertical profiles from 08:00 to 17:00 LT (local time) at the height of 0–3 km. Figure 4 is the averaged profiles of tropospheric aerosol extinction, HONO, NO<sub>2</sub>, HCHO, SO<sub>2</sub>, water vapor during the whole campaign. And the averaged diurnal variations of profiles on clear days and haze days are depicted in Figures 5 and 6, respectively. By comparing the differences between Figures 4–6, typical information of polluted cases could be found.

The averaged ground-level of aerosol extinction, HONO, HCHO, SO<sub>2</sub>, NO<sub>2</sub>, and water vapor were 0.86 km<sup>-1</sup>, 18.63 ppb, 0.27 ppb, 3.00 ppb, 4.35 ppb, 1.58 × 10<sup>17</sup> molecule/cm<sup>3</sup> respectively. As for haze days: aerosol extinction 1.63 km<sup>-1</sup>, NO<sub>2</sub> 24.70 ppb, HONO 0.43 ppb, HCHO 4.98 ppb, SO<sub>2</sub> 6.66 ppb, water vapor 1.36 × 10<sup>17</sup> molecule/cm<sup>3</sup> and for clear days: aerosol extinction 0.64 km<sup>-1</sup>, NO<sub>2</sub> 16.63 ppb, HONO 0.22 ppb, HCHO 2.43 ppb, SO<sub>2</sub> 3.69 ppb, water vapor 1.61 × 10<sup>17</sup> molecule/cm<sup>3</sup>, it is obvious that aerosol extinction and all the trace gases except water vapor were much higher in haze days than those in clear days. Emissions of primary pollutants reacted to generate secondary products through the gas to particle transformation in the atmosphere, thus resulting in the enhancement of aerosols [60].



**Figure 4.** Diurnal variations of the vertical distribution characters of tropospheric aerosol extinction coefficient, and HONO, SO<sub>2</sub>, NO<sub>2</sub>, HCHO, and water vapor vertical mixing ratios during the whole campaign.



**Figure 5.** Diurnal variations of the vertical distribution characters of tropospheric aerosol extinction coefficient, and HONO, SO<sub>2</sub>, NO<sub>2</sub>, HCHO, and water vapor vertical mixing ratios during clear days.



**Figure 6.** Diurnal variations of the vertical distribution characters of tropospheric aerosol extinction coefficient, and HONO, SO<sub>2</sub>, NO<sub>2</sub>, HCHO, and water vapor vertical mixing ratios during haze days.

The diurnal variations can potentially be derived by the interaction of miscellaneous emissions, chemical and physical reaction processes in the boundary layer. The boundary layer height is generally high at noon, but low in the morning & evening [61], which can directly influence the diurnal variations of the vertical characters of those trace gas pollutants. It is noted that the individual pollutant has their own specific peak time because of their various lifetimes and chemical and physical behaviors. As shown in Figure 7, aerosol extinction coefficients and NO<sub>2</sub> concentrations are both linear fitting well with altitudes, which means the vertical profiles of NO2 and aerosol extinction coefficient decreased exponentially with the increase of height (i.e., highest NO<sub>2</sub> and aerosol concentrations at the surface, and decreased gradually). It was probably owing to the close approach of their emission sources to the ground. NO<sub>2</sub> mainly concentrated near the ground, and there were two small peaks, one was in the morning and the other was in the afternoon, which were exactly during the rush hour (8:00–10:00; 16:00–17:00 LT), due to the direct emission of vehicles. The decrease NO<sub>2</sub> at noon was the result of the increase of the boundary layer. As for  $SO_2$ , it is also concentrated near the ground like  $NO_2$ , moreover, they were both observed in the upper layer from 13:00 to 15:00 LT. A possible explanation is that  $NO_2$ and SO<sub>2</sub> were emitted predominantly from elevated point sources due to the discharges of burning fossil fuels (e.g., power plants) and long-term transport from other regions which can bring higher  $NO_2$  and  $SO_2$  concentrations at the height of hundreds of meters [62–65]. A similar phenomenon (i.e., SO<sub>2</sub> has been observed at a high-level concentration in the upper layer) has also been found in previous aircraft experiments [66]. Most of HONO was distributed below 0.6 km, and its diurnal variation is characterized by high in the morning & evening and low at noon, with a U shape. Occasionally, there existed a small peak at noon. The heterogeneous reaction of nitrogen oxides generating HONO occurred at night, which caused the HONO accumulation till early morning. However, HONO was gradually decomposed along with the enhanced radiation in the daytime. What is noteworthy is that, similar to NO<sub>2</sub> and SO<sub>2</sub>, HCHO also appeared at an elevated concentration in the upper layer, probably predicting that there was a strong photochemical generation of secondary HCHO rather than primary HCHO emissions. There were also two small peaks during

the rush hour (8:00–10:00; 16:00–17:00 LT), which was the primary source. The vertical character of HCHO was not obvious as others, which possibly was the consequence of preponderant secondary sources from photochemical production. The concentration of HCHO was higher in hazy conditions, demonstrating severe photochemical oxidation processes during haze pollution days. HCHO and NO<sub>2</sub>, which were known as the typical precursor compounds of  $O_3$ , were both relatively sufficient at noon in the upper layer, so it is expected that there will be significant  $O_3$  production, and bring a stronger impact to the atmospheric oxidizing capacity than HONO. In winter, the water vapor concentra-

(a)(b Y=-0.62X+1.73 2.0 Y=-0.54X+0.03 2.0 N=16 N=16 R=0.98 R=0.99 1.5 Altitude (km) Altitude (km) 1.0 1.0 0.5 0.5 0.0 0.0 e<sup>-3</sup> e<sup>-2</sup> e e<sup>2</sup> e-1 AE (km<sup>-1</sup>) NO<sub>2</sub>(ppb)

tion is lower than in other seasons. It showed a decreasing profile and the concentration is negatively correlated to the solar irradiance, thus the concentration in the afternoon (12:00–16:00 LT) was relatively low during the whole daytime. In general, increased concentration of water vapor contributed to the generation of secondary pollutants, but the water vapor concentration observed in haze days was lower than that in clear days, which was different from others' research. A possible explanation for it may be the increase of moisture absorption of aerosol particles, as we have known, it is a process of consuming

**Figure 7.** (a) Linear fitting between averaged aerosol extinction coefficients and altitudes, here X is natural logarithmic coordinate; (b) Linear fitting between averaged NO<sub>2</sub> concentrations and altitudes, here X is natural logarithmic coordinate. Significance level (p) < 0.001.

#### 4. Discussion

water vapor [67–69].

# 4.1. Trajectory Clustering and Potential Pollution Evolution

To distinguish the influence and source of regional transport on air pollutants, the HYSPLIT model helps simulating the backward trajectories. The trajectory frequency option is used. It starts a trajectory every 6 h from a position and a height, then sums the frequency with the trajectory passing through the grid cells, and then normalizes with the total number of trajectories or endpoints. The backward trajectory frequency of the whole campaign was shown in Figure 8a, moreover, according to the AQI (air quality index), the whole campaign was classified into haze days or clear days respectively. Figure 8b–h described the backward trajectory frequency of each period in chronological order.

The backward trajectories indicate that air mass mainly came from the north and northwest. The results portrayed absolute differences between different air qualities, especially on haze days, which were much more air mass transported from other regions. The north and northwest of the observed site are the urban districts of Shanghai, there were many factories and heavy traffic pollutions. In addition, Shanghai could be influenced by emissions from neighboring provinces. The trajectory extended in the northerly and northwesterly direction pointed to Zhenjiang, Nantong, and Yangzhou, were also covered many industries, so the pollution of the observed site in Shanghai was transported from both locality and other regions in the north and northwest. At the same time, it is worth noting that sometimes pollution is transported from southern areas, such as Zhejiang



Province. Even though the wind direction in Shanghai is mainly southeast in winter, there is a sea in the southeast, so the pollution from this direction is not obvious as we saw.

**Figure 8.** The backward trajectory frequency of this campaign. (**a**) is the whole campaign; and from (**b**–**h**) is in chronological order: 15–22 December 2017 clear period; 29 December 2017–1 January 2018 haze period; 7–14 January 2018 clear period; 28 January 2018–2 February 2018 haze period; 3–7 February 2018 clear period; 7–10 February 2018 haze period; 17 February 2018–1 March 2018 clear period, respectively.

## 4.2. Vertical Characters of Tropospheric HONO

Nitrous acid (HONO) is known as a vital precursor of tropospheric hydroxyl radical (OH), an important oxidant, which can react with organic matters and form multiple secondary productions like ozone and aerosols [15,70,71]. The role of HONO in photochemical cycles had been underestimated before, recent studies revealed that HONO not only affects daytime atmospheric chemistry early in the morning but also has a dominant effect in generating OH radicals throughout the whole day [72–76]. The current observations of HONO were mainly set up at a surface level, there are few focuses in the upper atmospheric layers. Direct observations of HONO at high altitudes are scanty. This constrained better comprehending for distribution in vertical dimension and transmission mode of HONO. In this study, vertical characters of tropospheric HONO are analyzed.

Table 2 compares the HONO concentration levels in this study with those measured at various surface sites as well as in the high-elevation atmospheres around the world. The mean concentration of HONO at the surface and the height of 1 km is  $0.27 \pm 0.085$  ppb and  $0.013 \pm 0.0077$  ppb. In contrast to previous studies, the concentrations in this study were lower than others and were obviously lower than those polluted sites in China, but in approximate order of magnitude as most of them. These are within expectation and indicate reasonable measurements of HONO in this study. Moreover, the low level of HONO concentration may imply the HONO sources of high altitudes were from diffusion considering the short lifetime of HONO, which are discussed below.

Туре	Site Location	Period	HONO (ppb) Mean $\pm$ SD	References
	Beijing, China (urban)	3 January–27 January 2016	$1.05\pm0.89$	[25]
	Ji'nan, China (urban)	December 2015–February 2016	$1.75\pm1.62$	[16]
Ground level	Wangdu, China (rural)	June–July 2014	$0.91\pm0.48$	[77]
observations	Guangzhou, China (urban)	June 2006	2.80	[78]
in China	Xinken, China (rural)	13 October-2 November 2004	1.20	[79]
	Back Garden, China (rural)	July 2006	0.76	[80]
	Shanghai, China (urban)	October 2004–January 2005	$1.1 \pm 1.0$	[81]
	Whiteface Mountain, USA (1483 m a.s.l.)	14 June-20 July 199	0.046	[82]
	Hohenpeissenberg, Germany (980 m a.s.l.)	3 July-12 July 2002	0.039	[83]
	Mt.Brocken, Germany (1142 m a.s.l.)	19 June-4 July 1999	0.056	[84]
Observations at	Northern Michigan (1000–1900 m.)	30 July-6 August 2007	0.009	[85]
high altitude	Northern Italy (300–1000 m a.g.l.)	12 July 2012	~0.15	[86]
	Mt. Tai, China (1534 m a.s.l)	November–December 2017 March–April 2018	$\begin{array}{c} 0.15 \pm 0.15 \\ 0.13 \pm 0.15 \end{array}$	[87]

Table 2. Comparison of HONO concentration observed at Shanghai with previous studies at surface and high altitudes.

HONO diurnal variations of all the valid days, clear days, and haze days at different altitudes were shown in Figure 9. For the sake of description, the vertical profiles of HONO were divided into four representational sections as follows: (1) the bottom layer (0.02 km) represents the surface layer nearest to the ground, (2) the lower layer (0.12–0.42 km) represents the lower boundary layer, (3) the middle layer (0.52–0.82 km) represents the middle boundary layer, (4) the higher layer (0.92–1.82 km) representing the upper boundary layer.

As shown in Figure 9, HONO was remarkably in higher concentration levels when the pollution was severer. By comparing Figure 9b,c, a distinction can be found that the HONO concentration was exceedingly high in the morning of haze days. The diurnal variation patterns of those three conditions were fairly close at the bottom layer, i.e., HONO concentrations were high in the morning & evening and low at noon, with a U shape, occasionally, there existed a small peak at noon, indicating there will be an unknown source. With the increase of height, the concentration of HONO decreased, which means the HONO of upper layers was prevailingly diffused from lower layers. However, the diurnal variation patterns of the upper layer did not retain the characteristics of that of the bottom layer, that is to say, from morning to noon, there was no obvious downward trend, and even appeared higher concentration at noon, especially in the middle and higher layers. Reasonable speculation is that the consumption of HONO at the bottom layer is stronger than that in the upper layers, and the photolysis of HONO, dry deposition, and wet deposition of HONO are the dominant sinks of the bottom layer. To confirm this, the HONO vertical transport distance ( $\sigma$ ) caused by turbulent diffusion was estimated by Equation (5) [88]:

$$\sigma = \left(2K_Z \tau_{\text{HONO}}\right)^{1/2} \tag{5}$$

where  $\sigma$  is the vertical transport distance,  $K_Z$  is the turbulent diffusion coefficient,  $\tau_{HONO}$  is HONO chemical lifetime. In the morning,  $K_Z$  is usually  $10^2-10^5$  cm<sup>2</sup>/s [85].  $\tau_{HONO}$  is assumed as 79.1 min (according to a J(HONO) of  $2.1 \times 10^{-4}$  s<sup>-1</sup>, which is simulated from TUV model), then  $\sigma$  of the ground HONO is calculated in the range of 9.7–308.0 m. While around noontime, the PBL has been lifted and  $K_Z$  is generally in the range of  $2-8 \times 10^6$  cm<sup>2</sup>/s [89].  $\tau_{HONO}$  is assumed as 17.0 min (according to a J(HONO) of  $9.8 \times 10^{-4}$  s<sup>-1</sup>, which is simulated from TUV model), then  $\sigma$  of the ground HONO is calculated in the range of 451.7–903.3 m. According to the results, the HONO vertical transport distance ( $\sigma$ ) at noon is much higher than in the morning. Due to the effective and uniform PBL mixing,  $\Delta c/\Delta h$  of high altitude at noon is lower, which is consistent with the observation ( $\Delta c/\Delta h$  at noon is ~0.11 ppb/km;  $\Delta c/\Delta h$  in the morning is ~0.60 ppb/km).



**Figure 9.** Diurnal variations of HONO at different altitudes. (**a**) is average of all the valid days; (**b**) is clear days; (**c**) is haze days. Different colored lines represent different altitudes: 0.02 km black; 0.12–0.42 km red; 0.52–0.82 km blue; 0.92–1.82 km green.

# 4.3. The Impact Factors on HONO Formation at Different Altitude

HONO can promote forming air pollutions [15], so, studying the HONO formation mechanism can help to understand the complex process of atmospheric chemistry. Generally, the adopted sources of HONO included: (a) emitting directly from combustion [90–94], (b) reaction of NO with OH in gas phase [37,95], (c) NO<sub>2</sub> heterogeneous reduction on various surfaces including aerosol surfaces, ground surface, and reductive surfaces [96–99], (d) photolysis of nitrate (pNO<sub>3</sub>) [100–102], (e) biotic emissions [103,104]. The direct emission sources were not that important except rush hours [80]. The reaction of NO and OH in gas phase was also relatively insignificant due to its low production rate [70]. While heterogeneous reactions of NO<sub>2</sub> were regarded as a considerable contributor to generating HONO, and the efficiency of the reaction depended on the compositions of surfaces and the content of absorbed water [105,106]. HONO/NO<sub>2</sub> ratios could indicate the extent of heterogeneous reaction of NO<sub>2</sub> [80,96], normally, it was in the range of 0.01 to 0.13 near the ground surface [107–112].

In this study, the variations of diurnal HONO/NO<sub>2</sub> ratios during the whole observed period, clear days, and haze days were plotted in Figure 10. The mean HONO/NO<sub>2</sub> ratios in each layer were 0.013, 0.010, 0.004, 0.008 respectively, and for clear days were 0.013, 0.010, 0.004, 0.0010 respectively, and for haze days were 0.017, 0.014, 0.005, 0.009 respectively. HONO/NO<sub>2</sub> ratios of these conditions suggested that the efficiencies of heterogeneous reactions of NO<sub>2</sub> in haze days were much more abundant. Aerosols provided more surfaces for reactions. Below 800 m, HONO/NO<sub>2</sub> ratios showed a decreasing trend as the height increased. The surface and lower layer provided more surfaces including concrete, glass, foliage, and aerosols for reacting. However, in this measurement, HONO/NO<sub>2</sub> ratios of the higher layer were not the lowest; a possible explanation for this phenomenon was that there might be an unknown source such as vertical diffusion for generating HONO. Future work might be expected to include tropospheric Doppler Lidar measurements with MAX-DOAS to calculate pollutant fluxes and verify the HONO source of the higher layer.



**Figure 10.** Diurnal variations of HONO/NO<sub>2</sub> at different altitudes. (**a**) is average of all the valid days; (**b**) is clear days; (**c**) is haze days. Different colored lines represent different altitudes: 0.02 km black; 0.12–0.42 km red; 0.52–0.82 km blue; 0.92–1.82 km green.

The NO<sub>2</sub> concentration, absorbed water, and reaction surfaces would impact HONO heterogeneous generations. In order to study these effects, the relationships between HONO and NO<sub>2</sub> concentrations in each layer were depicted in Figure 11. The Pearson correlation coefficient (R) was 0.69, 0.50, 0.54, 0.33, which means, when the height was below 0.82 km, HONO formation was affected by NO<sub>2</sub> to some extent. As seen in Figure 11a,c,e, the HONO concentrations were increasing with the increase of aerosol extinction because of more reaction surfaces. While in Figure 11b,d,f, water vapor inhibited the generation of HONO. The wet deposition could account for the decrease of HONO because of the oversaturation of water vapor, although high RH might bring more opportunities for reactions. When above 0.82 km (Figure 11g,h), there is no obvious correlation between HONO and NO<sub>2</sub>, aerosol extinction, and water vapor. It is speculated that vertical diffusion might be the dominant factor of HONO at high altitudes, which is agreed with the previous analysis.

#### 4.4. Contribution of OH Production from HONO Photolysis at Different Altitude

Growing researches suggest that HONO photolysis contributes to producing OH not only in the morning but also throughout the whole daytime [72–76]. HONO appeared low concentrations at daytime because of the fast rate of its photolysis (R1) and hence HONO photolysis provides a great contribution in generating OH radicals. Measuring HONO in the boundary layer rather than just on the ground is really important for getting the access of the knowledge in the field of tropospheric oxidation photochemistry.

$$HONO + hv \rightarrow NO + OH (320 \text{ nm} < \lambda < 400 \text{ nm})$$
(R1)

The OH production rate of HONO is figured up by Equation (6)

$$P_{OH}(HONO) = J_{HONO} \times [HONO]$$
(6)



**Figure 11.** Correlations between HONO and NO<sub>2</sub> concentrations in each layer, (**a**,**b**) is the bottom layer 0.02 km; (**c**,**d**) is the lower layer 0.12–0.42 km; (**e**,**f**) is the middle layer 0.52–0.82 km; (**g**,**h**) the higher layer 0.92–1.82 km.

Figures 12 and 13 are the case analysis of OH production rate from HONO photolysis for a clear day (11 January 2018) and a haze day (10 February 2018) respectively. J<sub>HONO</sub> was simulated by TUV model, and [HONO] was retrieved from MAX-DOAS measurements using the HEIPRO algorithm. The results of POH displayed fairly close patterns whether it's a hazy day or a clean day. (P<sub>OH</sub> value up to 1.27 ppb/h and 0.67 ppb/h respectively)  $J_{HONO}$  increased with the increase of height, on the contrary, [HONO] usually decreased with the increase of height. These two parameters have an opposite effect on  $P_{OH}$ . [HONO] changed substantially when the height elevated, while  $J_{HONO}$  changed relatively in a smaller amplitude. So, it is evident that  $P_{OH}$  had a similar variation trend with [HONO], which means  $P_{OH}$  was mainly controlled by [HONO], especially below 0.7 km. However, with the decrease of [HONO],  $P_{OH}$  was controlled both by [HONO] and  $J_{HONO}$  when the height was up to 0.7 km.



**Figure 12.** Case analysis of OH production rate from HONO photolysis for a clear day (11 January 2018). (**a**–**c**) is the correlation between [HONO], J<sub>HONO</sub>, P<sub>OH</sub>, and altitude at different times in one day. Different colored lines represent different times. (**d**–**f**) is the profile of [HONO], J<sub>HONO</sub>, and P<sub>OH</sub> respectively.



**Figure 13.** Case analysis of OH production rate from HONO photolysis for a haze day (10 February 2018). (**a**–**c**) is the correlation between [HONO],  $J_{HONO}$ ,  $P_{OH}$ , and altitude at different times in one day. Different colored lines represent different times. (**d**–**f**) is the profile of [HONO],  $J_{HONO}$ , and  $P_{OH}$  respectively.

# 5. Conclusions and Summaries

This paper described the diurnal variation and vertical distribution of trace gases (NO<sub>2</sub>, HONO, HCHO, SO<sub>2</sub>, and water vapor) and aerosol extinction of Shanghai based on in-situ MAX-DOAS measurements from December 2017 to March 2018, and characterized their vertical profiles retrieved using the HEIPRO algorithm. The VCDs and surface concentrations are validated with the USTC-OMI, CNEMC, and NCDC measurements, gaining good correlation coefficients and proving good data quality of MAX-DOAS. The HYSPLIT model helps to simulate the backward trajectories, indicating that air mass mainly came from north and northwest, and sometimes southeast.

Aerosol and NO<sub>2</sub> both showed an exponentially downward trend, and the high concentration was concentrated near the surface, indicating that the main emission sources were at surface level.  $SO_2$  profiles showed high concentration levels at the altitude of 0.12–0.82 km, which is the same height as the chimneys of power plants, showing direct effects by industrial emissions. However, as for HCHO, it was also observed a peak concentration at the middle layer in the afternoon, probably manifesting that there existed strong photochemical formation, and HCHO was principally from secondary sources. The water vapor concentration observed in haze days was lower than that in clear days, which might be caused by the increase of moisture absorption of aerosol particles. Then, we also emphasized the analysis of influencing factors of HONO generation and contribution of OH production from HONO photolysis at different altitudes. Below 0.82 km, various surfaces, such as ground, aerosol surfaces, reductive surfaces, provided more opportunities for the heterogeneous reactions of  $NO_2$  to form HONO, while in the upper layers, vertical diffusion might be the dominating source of HONO. NO<sub>2</sub> promoted the formation of HONO, however, water vapor inhibited. The contribution of OH production from HONO photolysis at different altitudes was influenced by both the concentration of HONO and the HONO photolysis frequencies, however, the results showed that it was mainly controlled by the former factor.

**Supplementary Materials:** The following are available online at https://www.mdpi.com/article/ 10.3390/rs13173518/s1, Table S1: All the defined haze days and clear days during the whole campaign, Figure S1: Time series of aerosol extinction vertical profiles during February 2018 retrieved from MAX-DOAS measurements, Figure S2: Time series of NO<sub>2</sub> vertical profiles during February 2018 retrieved from MAX-DOAS measurements, Figure S3: Time series of HONO vertical profiles during February 2018 retrieved from MAX-DOAS measurements, Figure S4: Time series of HCHO vertical profiles during February 2018 retrieved from MAX-DOAS measurements, Figure S5: Time series of SO2 vertical profiles during February 2018 retrieved from MAX-DOAS measurements, Figure S6: Time series of water vapor vertical profiles during February 2018 retrieved from MAX-DOAS measurements, DOAS measurements, Figure S7: The location of the MAX-DOAS instrument and CNEMC sites in urban Shanghai. The CNEMC sites are far away from the instrument.

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