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Seasonal Investigation of MAX-DOAS and In Situ Measurements of Aerosols and Trace Gases over Suburban Site of Megacity Shanghai, China

Aimon Tanvir¹, Muhammad Bilal² , Sanbao Zhang¹, Osama Sandhu³, Ruibin Xue¹, Md. Arfan Ali² , Jian Zhu¹, Zhongfeng Qiu² , Shanshan Wang^{1,4} and Bin Zhou^{1,4,5,*}

- ¹ Shanghai Key Laboratory of Atmospheric Particle Pollution and Prevention (LAP3), Department of Environmental Science and Engineering, Fudan University, Shanghai 200433, China; 19110740045@fudan.edu.cn (A.T.); 18210740015@fudan.edu.cn (S.Z.); 21110740017@fudan.edu.cn (R.X.); 20110740023@fudan.edu.cn (J.Z.); shanshanwang@fudan.edu.cn (S.W.)
- ² School of Marine Sciences, Nanjing University of Information Science and Technology, Nanjing 210044, China; muhammad.bilal@connect.polyu.hk (M.B.); md.arfanali@nuist.edu.cn (M.A.A.); zhongfeng.qiu@nuist.edu.cn (Z.Q.)
- ³ National Center for Meteorology and Seismology, Department of Aviation Meteorology, Dubai International Airport, Dubai 35595, United Arab Emirates; osandhu@ncms.ae
- ⁴ Institute of Eco-Chongming (SIEC), No. 20 Cuinia Road, Shanghai 200062, China
- ⁵ Institute of Atmospheric Sciences, Fudan University, Shanghai 200433, China
- * Correspondence: binzhou@fudan.edu.cn



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Abstract: Shanghai has gained much attention in terms of air quality research owing to its importance to economic capital and its huge population. This study utilizes ground-based remote sensing instrument observations, namely by Multiple AXis Differential Optical Absorption Spectroscopy (MAX-DOAS), and in situ measurements from the national air quality monitoring platform for various atmospheric trace gases including Nitrogen dioxide (NO₂), Sulfur dioxide (SO₂), Ozone (O₃), Formaldehyde (HCHO), and Particulate Matter (PM; PM₁₀: diameter ≤ 10 μm, and PM_{2.5}: diameter ≤ 2.5 μm) over Shanghai from June 2020 to May 2021. The results depict definite diurnal patterns and strong seasonality in HCHO, NO₂, and SO₂ concentrations with maximum concentrations during winter for NO₂ and SO₂ and in summer for HCHO. The impact of meteorology and biogenic emissions on pollutant concentrations was also studied. HCHO emissions are positively correlated with temperature, relative humidity, and the enhanced vegetation index (EVI), while both NO₂ and SO₂ depicted a negative correlation to all these parameters. The results from diurnal to seasonal cycles consistently suggest the mainly anthropogenic origin of NO₂ and SO₂, while the secondary formation from the photo-oxidation of volatile organic compounds (VOCs) and substantial contribution of biogenic emissions for HCHO. Further, the sensitivity of O₃ formation to its precursor species (NO_x and VOCs) was also determined by employing HCHO and NO₂ as tracers. The sensitivity analysis depicted that O₃ formation in Shanghai is predominantly VOC-limited except for summer, where a significant percentage of O₃ formation lies in the transition regime. It is worth mentioning that seasonal variation of O₃ is also categorized by maxima in summer. The interdependence of criteria pollutants (O₃, SO₂, NO₂, and PM) was studied by employing the Pearson's correlation coefficient, and the results suggested complex interdependence among the pollutant species in different seasons. Lastly, potential source contribution function (PSCF) analysis was performed to have an understanding of the contribution of different source areas towards atmospheric pollution. PSCF analysis indicated a strong contribution of local sources on Shanghai's air quality compared to regional sources. This study will help policymakers and stakeholders understand the complex interactions among the atmospheric pollutants and provide a baseline for designing effective control strategies to combat air pollution in Shanghai.

Keywords: MAX-DOAS; trace gases; seasonal characteristics; ozone sensitivity; source contribution

1. Introduction

Anthropogenic activities are a major source of deterioration in air quality. With advancements in technology, the extent of air quality deterioration has increased manifolds owing to the enhanced fossil fuel combustion by various kinds of transport to meet the modern-day requirements [1,2]. Air pollution has gained much attention in China owing to the fast-paced industrialization, economic growth, urbanization, and massive population. According to the World Health Organization (WHO) standards, only 1% of China's megacities meets the safe city criteria in terms of air quality [3]. Atmospheric quality directly influences the earth's radiation budget as well as the ecological environment. It also has pronounced effects on regional climate, agriculture, and human health [4,5].

Sulphur dioxide (SO_2), Nitrogen oxides (NO_x), and formaldehyde (HCHO) are important constituents of the atmosphere and are known to have a strong influence on air quality and regional climate [6]. NO_x comes from a variety of sources, though essentially from electric utilities, combustion processes, transportation, and industry. Photochemical reactions that involve NO_2 are vital for tropospheric ozone production [7], which severely impacts air quality and human health. SO_2 is a crucial primary atmospheric pollutant that plays an important function in defining the atmospheric chemistry and climate at the regional level. This gas is supposed to be a potential threat to human health as it severely affects human respiratory health [8]. The removal pathways include dry and wet deposition (either as settling with dust or acid rain) or by oxidation, which contributes to the formation of sulphate aerosols [9]. Anthropogenic SO_2 emissions generally come from fuel consumption for domestic heating or power generation, etc., in the urban environment, while the minor sources include shipping, oil refining, and metal smelting [10]. Anthropogenic SO_2 emissions are usually restricted to the atmospheric boundary layer, whereas the regional emission and transport sources are characterized by the vertical distribution of SO_2 in various atmospheric layers.

Formaldehyde (HCHO) is one of the simplest hydrocarbons (HC) in the atmosphere. It has a short life span and comes from the oxidation of VOCs [11,12]. Therefore, the tropospheric variability of HCHO largely depends on VOC oxidation. Direct emissions result from fossil fuel combustion, natural vegetation, and biomass burning [13]. Both HCHO and NO_2 are very important trace gas species in the atmosphere and are definitive of the atmospheric chemistry. Complex photochemical reactions involving NO_x and VOCs play a substantial role in the formation of tropospheric Ozone (O_3) [14]. As an oxidation product of VOCs, HCHO is usually employed as a proxy for VOC reactivity [15] while NO_2 concentrations in the troposphere are closely related to NO_x [16]. Therefore, the ratio of HCHO to NO_2 (RFN) is employed as a proxy to study O_3 - NO_x -VOC sensitivity [5,17,18]. The aforementioned trace gas species, along with other atmospheric trace gas molecules, have been extensively observed by employing Multiple AXis Differential Optical Absorption Spectroscopy (MAX-DOAS) owing to its ubiquity in an urban environment and strong UV absorption [19–22]. Particulate Matter (PM) is another crucial air pollutant which is classified into PM_{10} (diameter $\leq 10 \mu\text{m}$) and $\text{PM}_{2.5}$ (diameter $\leq 2.5 \mu\text{m}$). PM pollution has become a major cause of concern owing to adverse health impacts (e.g., respiratory and cardiovascular diseases) and deterioration in air quality (e.g., haze formation), [23].

Shanghai is called the economic capital of China owing to its huge economic activity and the warm water seaport. It is one of the largest metropolitan areas, with a population of 24.87 million as of 2020 (National Bureau of Statistics of China, 2021). Due to the fast-paced urbanization and industrialization of Shanghai and the surrounding cities, the air quality of the city has deteriorated thereby gaining much attention in terms of air quality and public health research [24]. The aforementioned facts render Shanghai a prime location for the continuous monitoring of air pollution to assist in the policymaking process and joint control strategies to cap anthropogenic emissions. The continuous monitoring of trace gas species is crucial not only towards understanding environmental footprints but also their social implications.

Ozone (O_3) is a species of concern with respect to atmospheric pollution across the globe). A series of regulations and strategies were issued by the Chinese government to mitigate air pollution. For example, the Air Pollution Prevention Action Plan [25,26] and the Win the Blue Sky three-year action plan, in 2013 and 2018, respectively, focused on reducing the concentration of $PM_{2.5}$ [27,28]. These efforts were effective, with a recorded reduction in annual mean concentrations of $PM_{2.5}$ from 74 mg/m^3 to 39 mg/m^3 for 31 provincial capitals during 2013–2018 (<http://english.mee.gov.cn/> (accessed on 28 February 2022)). The average annual concentrations of other pollutants including NO_2 , SO_2 , CO , and PM_{10} declined by 9.7%, 54.1%, 28.2%, and 27.8%, respectively, over 74 big cities, with O_3 concentration observed to increase by a whopping 20.4% [12,26,29,30]. Hence, O_3 production strongly depends on the ratio of VOCs and NO_x [31]. Previous strategies to combat O_3 pollution focused on controlling NO_x emissions [32], while a higher O_3 concentration occurs in a VOC-limited regime [33]. Therefore, this study may serve as a guide for government agencies regarding the control policies of O_3 pollution based on $HCHO/NO_2$. O_3 sensitivity studies over Shanghai have been reported in the literature; however, these studies were limited only to a specific time period of the year or a single season [11,20], creating gaps in holistic analysis and understanding. To the author's best knowledge, this is the first study that tries to analyze O_3 sensitivity across the year with ground-based observations while emphasizing the seasonal trends of other atmospheric species including $HCHO$, SO_2 , and NO_2 species.

For the current study, MAX-DOAS observations at a suburban site in Shanghai were utilized to evaluate the variation in trends of different trace gas species, including SO_2 , NO_2 , and $HCHO$, from June 2020 to May 2021. The organization of the study is as follows: Section 2 describes the study site, instrument specifications, and the DOAS methodology used for the analysis and retrieval. The additional datasets used for further assessments and analysis have also been referenced. A time series of daily mean concentrations for $HCHO$, NO_2 , and SO_2 was generated (Section 3.1) based on the described methodology, which provided the basis for performing additional analysis including the monthly, seasonal, and diurnal variations (Section 3.2). The study was complemented by the dependence on meteorology (including temperature and humidity; Section 3.3) as well as the enhanced vegetation index (EVI) (Section 3.4), which was followed by sensitivity analysis for tropospheric Ozone (O_3) production (Section 3.5). The interdependence of different pollutants using in situ measurements was also studied (Section 3.6). Finally, the potential source contribution function (PSCF) was analyzed (Section 3.7), succeeded by a scientific conclusion.

2. Materials and Methods

2.1. Observation Site

Shanghai is one of the largest cities of China in terms of population and economic activities, with one of the world's largest container ports. The city has witnessed several episodes of high pollution to date which are attributed to massive fossil fuel combustion to meet the energy and transport requirements of the city's huge population. The observations for the current study were made at the Shanghai Nanhui Environment Monitoring Station (121.807003°E , 31.054963°N), which is a suburban site in Shanghai located away from the city center, near to shore, and south of Pudong International Airport by a distance of 11 km (Figure 1).

2.2. MAX-DOAS Instrument

The ground based remote sensing instrument MAX-DOAS used in this study entails a scanning telescope which is governed by a stepping motor, a spectrometer (Ocean Optics, Orlando, FL, USA, QE65 Pro), and a computer that acts as an operating system. Optical fiber has been employed in the telescope to collect scattered sunlight. The spectrometer is geared up with a charged coupled device (CCD) detector (with a resolution of $1044 \text{ Horizontal} \times 64 \text{ vertical}$ and cooling up to -15°C) which has been used for the measurements in wavelength ranging from 300 nm to 480 nm. This spectrometer has a spectral resolution

of 0.5 nm full-width half maximum (FWHM). The telescope is directed north clockwise at an azimuthal angle of 2° to avoid direct sunlight and is capable of scanning at ten different elevation angles (EA). The sequence includes measurements 2° , 3° , 5° , 7° , 9° , 12° , 15° , 20° , 30° , 45° , and 90° . The whole cycle of scanning takes around five minutes to complete. Background measurements were taken each night, and the signal for the dark current was automatically extracted from them. Validation of MAX-DOAS instrument has been performed by several previously reported studies [20,22] and shows good agreement with both space-based and ground-based trace gas monitoring instruments. The position of the instrument is shown in Figure 1.

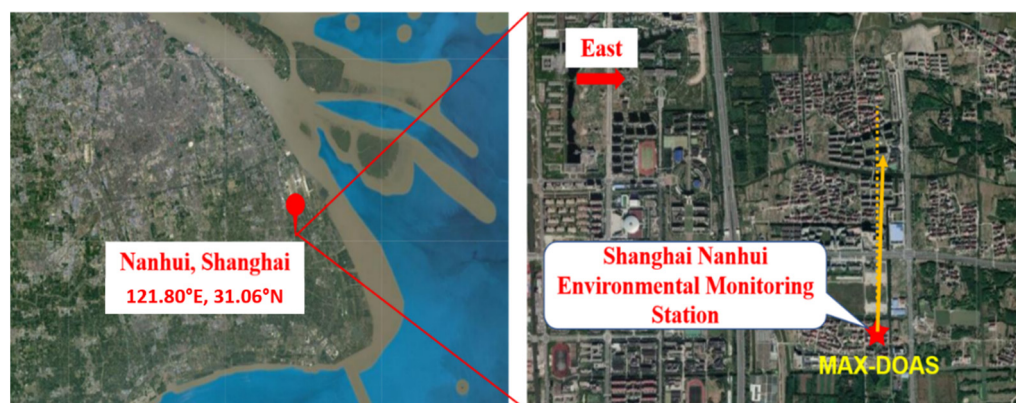


Figure 1. The region surrounding the measurement station (31.05°N , 121.81°E) is shown by the topography map (Google Maps). The arrow points towards the direction of the telescope of the Multiple AXis Differential Optical Absorption Spectroscopy (MAX-DOAS) instrument.

2.2.1. DOAS Analysis

Accurate column measurements for the trace gases in the atmosphere are possible only because the MAX-DOAS instrument can measure dispersed sunlight at several elevation angles, known as EVAs. A Fraunhofer reference spectrum was selected as the zenith measurements for each measurement sequence, which was then subtracted from the off-zenith spectrum to obtain differential slant column densities (DSCDs). DSCDs refer to the integrated number density for any trace gas along the effective light path. The process essentially minimizes the stratospheric interference to the tropospheric measurements [19]. The DOAS technique is used to recover DSCDs of SO_2 , NO_2 , and HCHO from the obtained spectra [34], which involves the analysis of the recorded spectra utilizing the QDOAS software version 3.2 (<http://uv-vis.aeronomie.be/software/QDOAS/> (accessed on 17 September 2021)). The configuration of the DOAS retrievals is based on previous studies [35,36] and the MAD-CAT campaign (http://joseba.mpchmainz.mpg.de/mad_analysis.htm (accessed on 17 September 2021)). Table 1 describes the configurations for SO_2 , NO_2 , and HCHO retrieval from DOAS, where “parameters” refer to the absorption cross-sections of interfering compounds and “data source” refers to the source and temperature at which absorption cross-sections are measured. A high-resolution solar spectrum was used to calibrate the wavelength [37]. Owing to the scattering processes in the atmosphere, the quality of data is likely to be impacted. To avoid this, certain filters are applied to maintain quality. The data with a root mean square (RMS) greater than 0.002 and a solar zenith angle greater than 75° were filtered out for this study. The RMS represents the average error in spectral analysis for MAX-DOAS. The detection limit for DSCDs is estimated based on the typical DOAS fit errors of discrete species under characteristic measurement circumstances.

Table 1. Retrieval settings for trace gases spectral analysis.

Parameters	Data Source	Trace Gases		
		NO ₂	SO ₂	HCHO
		337–370 (nm)	307–325 (nm)	325–350 (nm)
HCHO	297 K [38],	✓	✓	✓
SO ₂	298 K [39],	×	✓	✓
NO ₂	220 K [39],	✓	✓	✓
NO ₂	298 K [39],	✓	×	✓
BrO	223 K [40],	✓	✓	×
O ₃	223 K [40],	✓	✓	✓
O ₃	243 K [41],	✓	✓	×
O ₄	293 K [42],	✓	×	✓
Ring	Calculation made by QDOAS	✓	✓	✓
Polynomial degree		5	5	5

2.3. Ancillary Data

The Aqua-Moderate Resolution Imaging Spectrometer (MODIS) has been employed here to obtain the vegetation index, which was used as a proxy for biogenic emission sources. MODIS vegetation index products are unique as they provide spatial as well as temporal comparisons for the vegetation cover over any area. Enhanced vegetation index (EVI) at 250 m resolution from the Aqua-MODIS vegetation product (MYD13Q1 V006) was used to support our analysis.

The daily mean concentrations were taken for the criteria pollutants, including SO₂, NO₂, O₃, PM₁₀, and PM_{2.5}, from June 2020 to May 2021 from China's air quality online monitoring and analysis platform (downloaded from: <https://www.aqistudy.cn/> (accessed on 25 September 2021)).

Meteorological data including temperature, wind speed, relative humidity, and wind direction were obtained from the automatic weather station installed at Pudong International airport to determine the impact of meteorological parameters on pollutant concentrations.

2.4. PSCF Analysis

Backward trajectory analysis was performed to determine the origin of air masses using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model developed by National Oceanic and Atmospheric Administration (NOAA) [43]. The model offers a comprehensive understanding of the transport of air masses, their dispersion, and their chemical transformation [44], along with highlighting the likely causes of aerosol pollutants which affect the air quality. The Potential Source Contribution Function (PSCF) analysis was integrated with the HYSPLIT back trajectory model and daily NO₂, SO₂, and HCHO measurements over a grid of 0.5 × 0.5 degrees. The HYSPLIT model backward trajectory at a height of 500 m above the ground level (AGL) for 72-h was computed every 6-h by using the Global Data Assimilation System (GDAS) meteorological data at a spatial resolution of 1° × 1° (accessible at <ftp://arlftp.arlhq.noaa.gov/pub/archives/gdas1> (accessed on 23 December 2021)) at seasonal scales from June 2020 to May 2021.

The height 500 m is the estimated height of the boundary layer; therefore, it is reported to have been very useful when used as AGL for the trajectory analysis [45,46]. Assuming that the endpoint for the trajectory is located inside the grid (*i,j*), the PSCF value was enumerated. It was also assumed that the trajectory collects pollutants coming from diverse sources of emission within that cell (*i,j*). Therefore, by definition, the PSCF value is the conditional probability which is definitive of the potential contribution of extraordinary pollutant loading at the receptor location for the grid cells. Equation (1) defines the calculation of the PSCF value for the *ij*th grid cell:

$$PSCF(i, j) = m_{ij}/n_{ij} \quad (1)$$

where n_{ij} signifies the frequency of endpoints falling or passing through the ij th cell and m_{ij} represents the frequency of endpoints in the ij th cell that have a higher pollutant load than the 24-h Air Quality Standards. Small n_{ij} may cause uncertainty in the calculations and results. Multiplying an arbitrary weight function $W_{i,j}$ to the PSCF greatly reduces this uncertainty. Equation (2) gives the weight function for the current analysis:

$$W_{i,j} = \begin{cases} \text{if } n_{ij} > 3n \rightarrow 1.00 \\ \text{if } 1.5n < n_{ij} \leq 3n \rightarrow 0.70 \\ \text{if } n < n_{ij} \leq 1.5n \rightarrow 0.42 \\ \text{if } n_{ij} \leq n \rightarrow 0.15 \end{cases} \quad (2)$$

Here, n signifies the average numeral of endpoints for each cell, computed for each cell with a minimum of one endpoint. Equation (3) expresses the Weighted PSCF, which is given as:

$$WPSCF = W_{i,j} \times PSCF(i, j) \quad (3)$$

3. Results and Discussion

3.1. MAX-DOAS Observations

Figure 2 shows the time series for daily averaged HCHO, SO₂, and NO₂ and monthly averaged concentrations, which are represented by red dots. There are certain gaps in the observations owing to instrumental error and maintenance as well as the quality filters. The data, which qualified a certain quality standard (mentioned under Section 2.2.1), were used for the analysis. The daily HCHO minimum, maximum, and mean concentrations of 1.26×10^{16} molecules/cm², 6.31×10^{16} molecules/cm², and 2.48×10^{16} molecules/cm² were observed, respectively (Figure 2a). Minimum SO₂ concentration was observed to be 1.92×10^{16} molecules/cm², while 1.57×10^{17} molecules/cm² was the peak value observed depicting an average of 3.97×10^{16} molecules/cm² (Figure 2b). The average NO₂ remained to be 7.51×10^{16} molecules/cm² with a minimum of 5.16×10^{15} molecules/cm² and a maximum of 2.24×10^{17} molecules/cm² (Figure 2c). HCHO shows higher values during summer, with peak values occurring during August, while both NO₂ and SO₂ depicted opposite trends with peaks in January. This trend complies with the previous studies reported for these species in different regions [6,47–49].

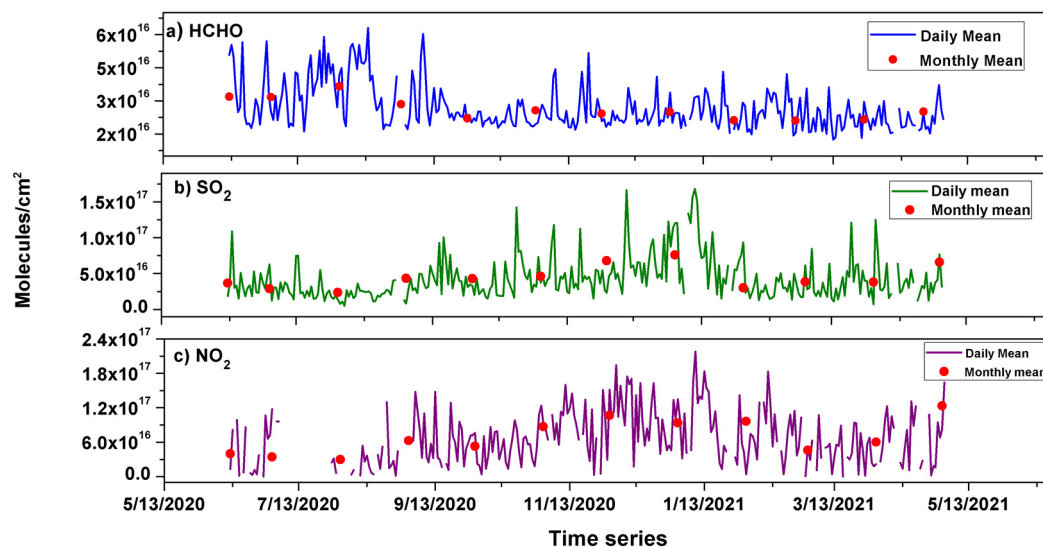


Figure 2. Daily and monthly averages of (a) HCHO, (b) SO₂, and (c) NO₂ from June 2020 to May 2021.

3.2. Seasonal Variations and Diurnal Cycles

The seasonal variation in pollutant concentration is meticulously connected to meteorological conditions in conjunction with the characteristics of diverse sources of emission.

The diurnal variability of any pollutant is affected by the solar intensity, a planetary boundary layer (PBL), emission sources, and wind pattern [50]. Seasonal variations in HCHO, NO₂, and SO₂ over suburban Shanghai are depicted in Figure 3. HCHO depicted the highest values during summer followed by autumn, winter, and spring. The surge in HCHO emissions for the summer months is said to be the result of its production by photochemical reactions and biomass burning, while the emissions from biogenic sources during the growing season, i.e., spring and autumn, also contribute towards its emissions [51]. The impact of biogenic emissions has been discussed separately under Section 3.5. For SO₂ and NO₂, however, the opposite trend was observed with the highest values observed during winter, followed by spring, autumn, and summer. These characteristics are already well recognized and reported over various metropolitan areas in China [52,53] and in other regions [46].

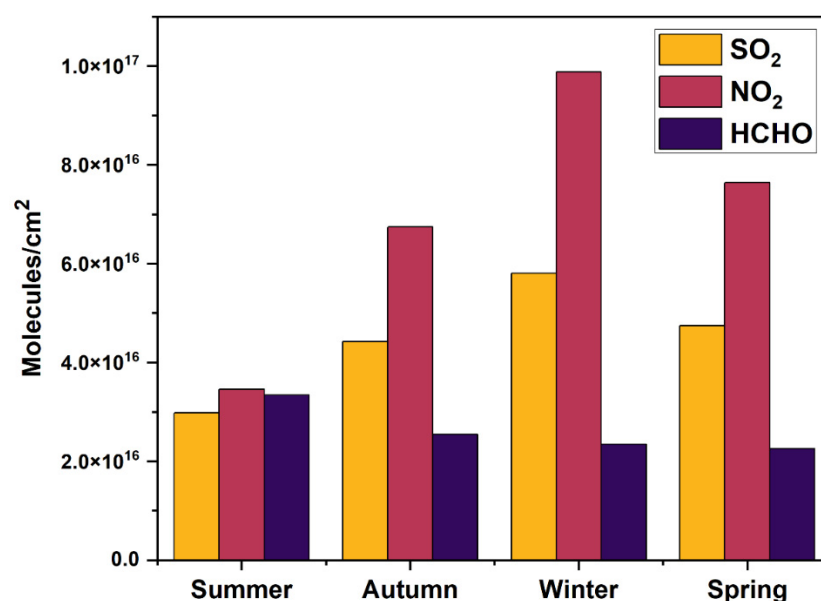


Figure 3. Seasonal variation in SO₂, HCHO, and NO₂ over Shanghai.

Higher NO₂ in winters is associated with a longer atmospheric lifetime and higher emission during winters owing to domestic heating and power consumption [51]. A high mixing ratio and less solar intensity during winters are associated with a higher atmospheric lifetime of NO₂ compared to summer. Solar intensity is crucial towards initiating the breakdown reactions for NO₂; consequently, NO₂ persists for a longer period in the atmosphere during winter compared to summer [46]. Less turbulence and less surface heating in winter, which are attributed to lower solar intensity, cause the formation of a stable boundary layer with a low height. Moreover, owing to the effect of local heating close to the top of the boundary layer, the atmospheric stability is increased owing to high concentrations of light-absorbing aerosols, especially black carbon (BC), which causes the boundary layer height (BLH) to lower further [54]. Shallow BLH, coupled with lower wind speed, causes stable atmospheric conditions and is crucial towards restricting the transport of aerosols, which further causes the aerosol buildup and enrichment of near-surface particle concentrations. Consequently, the lifetime of anthropogenic aerosols such as those coming from the combustion of fossil fuel and certain industrial and urban activities may be increased [46,55].

Transport from the highly polluted areas is essentially crucial towards determining the seasonal behavior of SO₂, especially in winters, owing to its long residence time in the atmosphere (<1 h to 2 weeks, as reported in the literature [56], owing to the fact that elongated residence time will allow for transport of greater distance with turbulence). In summary, the removal pathway including oxidation by OH radicals is crucial in defin-

ing the seasonality of NO_2 which depicts maxima in winter and minima in summer [57]. The seasonality of SO_2 is also partly linked to a similar removal mechanism [58], while heterogeneous reactions play a further role [59]. HCHO seasonality trends are the opposite owing to enhanced sunlight in summer months, which enhances its formation by the photochemical reactions [60]. Figure 3 depicts seasonally averaged SO_2 , HCHO, and NO_2 for Shanghai from June 2020 to May 2021. The average concentrations during winter remained to be 5.63×10^{16} molecules/cm², 2.14×10^{16} molecules/cm², and 9.71×10^{16} molecules/cm² for SO_2 , HCHO, and NO_2 , respectively. For autumn, the concentrations were observed to be 4.80×10^{16} molecules/cm², 2.47×10^{16} molecules/cm², and 7.63×10^{16} molecules/cm², respectively, while, for spring, the seasonally averaged concentrations were 4.20×10^{16} molecules/cm², 1.94×10^{16} molecules/cm², and 6.98×10^{16} molecules/cm², respectively. For summers, the seasonally averaged concentrations depicted 2.98×10^{16} molecules/cm², 3.40×10^{16} molecules/cm², and 3.17×10^{16} molecules/cm² for SO_2 , HCHO, and NO_2 .

The diurnal variations in HCHO depicted an increase in concentrations from morning to noon and declining from afternoon to evening (Figure 4a). Only a weak cycle is visible for autumn and winter (black and green curves), and an opposite or no clear trend is observed for summer and spring (blue and red curves). This is attributed to the enhanced photolytic oxidation of VOCs to form HCHO with an increase in light intensity during the day [51]. A similar diurnal trend has been observed in different regions in various previously published studies [6,60]. The seasonal variation in HCHO diurnal trends shows peak value during the summer, followed by autumn, winter, and spring. A similar diurnal trend for different seasons has been reported by other studies [13]. SO_2 shows an opposite diurnal trend as that of HCHO (Figure 4b), with peak values occurring in the morning and evening. This might be because there is enhanced anthropogenic activity during morning and evening hours, with more vehicle flux consuming more fuel and generating more pollutant gases [61]. The diurnal variation in SO_2 concentrations can also be explained by the strengthened emission sources during this time [62,63]. The results suggest strong seasonality in SO_2 concentrations with peak values occurring in winter, followed by spring, autumn, and summer. Similar diurnal trends for different seasons have been reported earlier [64].

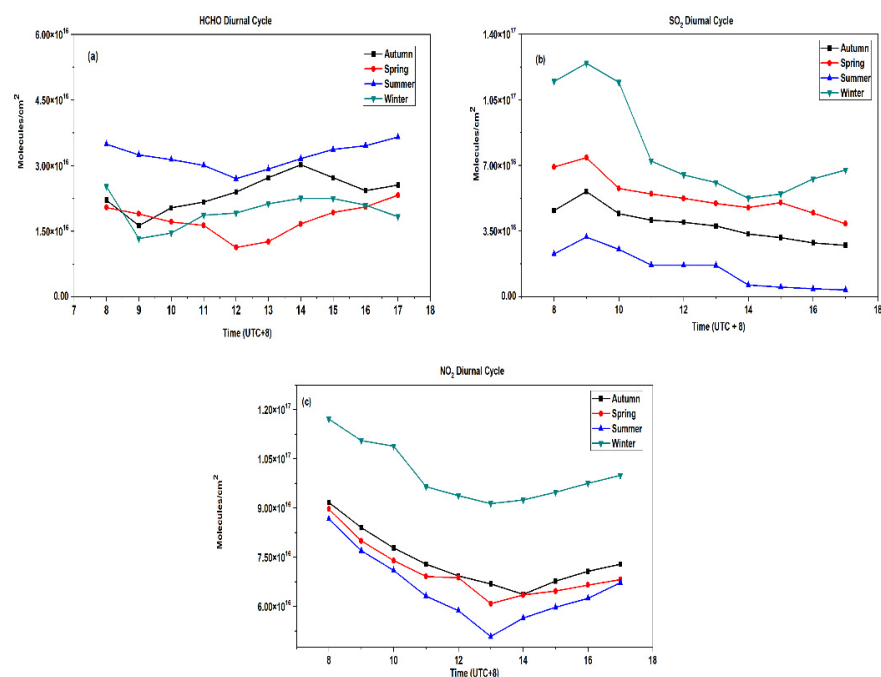


Figure 4. Diurnal cycle of (a) HCHO, (b) SO_2 , and (c) NO_2 for different seasons as obtained from MAX-DOAS observations.

A similar diurnal trend was observed for NO_2 (Figure 4c). Owing to an increase in solar intensity during the daytime, photolytic oxidation is enhanced, which acts as a sink for NO_2 [61], justifying a sharp decline in NO_2 concentrations, especially in summers when sunlight intensity is highest of all the seasons. Moreover, higher levels of NO_x during morning and evening hours can be attributed to low PBL, which weakens the mixing process for air pollutants, while lower pollutant levels during the day result from high PBL, which increases the diffusion of pollutants in the atmosphere. Similar results are reported by earlier studies [61,65]. The seasonal diurnal trend for NO_2 shows the highest values in winter followed by autumn, spring, and summer. This trend complies with the studies reported earlier [64,66].

3.3. Relationship with Meteorological Parameters

Aerosol and trace gas distributions along with the residence time and chemical behavior are largely affected by the meteorological settings over the vicinity [5,6]. Figure 5 shows the time series of temperature ($^{\circ}\text{C}$), relative humidity (RH%), and wind speed (m/s) for the study period. These parameters are pivotal in determining trace gas concentrations.

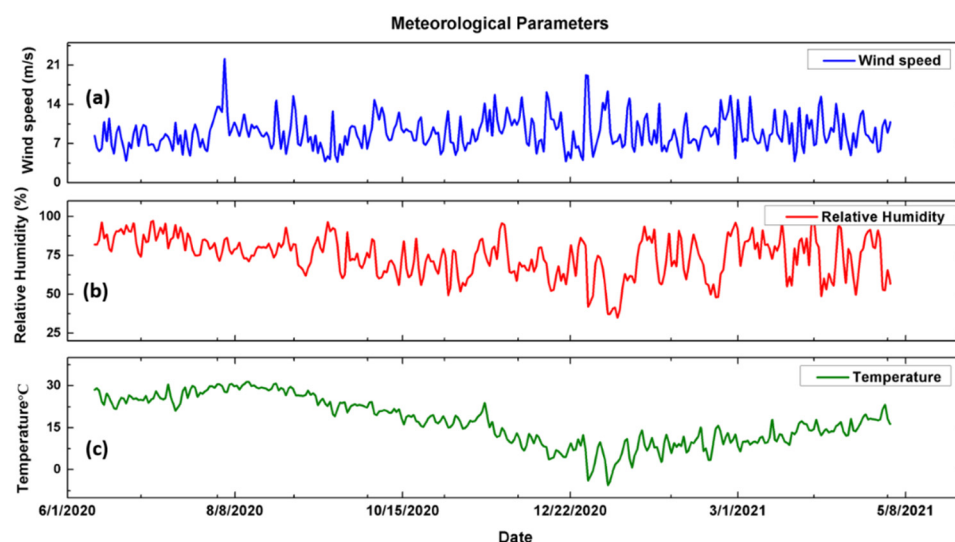


Figure 5. Time series for (a) wind speed (m/s), (b) relative humidity (%), and (c) temperature ($^{\circ}\text{C}$).

The correlation coefficient of weekly mean SO_2 , NO_2 , and HCHO with RH is shown in Figure 6A. As the MAX-DOAS instrument is capable of observation during daytime hours, only daytime values for temperature and RH were averaged in order to make correlations. HCHO shows a slight positive correlation coefficient of 0.42 (Figure 6(Aiii)), suggesting an increase in HCHO concentration with enhanced humidity, while both NO_2 and SO_2 have a negative correlation coefficient of 0.65 (Figure 6(Ai)) and 0.72 (Figure 6(Aii)) with RH, respectively, implying that both NO_2 and SO_2 concentrations decline at high RH, or that both SO_2 and NO_2 can have higher concentrations at low RH and that this is the reason higher concentrations were observed during winter compared to summer (please see Section 3.2). This is probably because of the OH oxidation of SO_2 and NO_2 at a higher humidity, where NO_x removal mechanisms are particularly affected by the increase in humidity [67]. It is conceivable that aerosol particles in the atmosphere will swell with increasing humidity, and thus the contact area for gas-particle exchange will increase. Therefore, gaseous species (i.e., SO_2 and NO_2) can more frequently enter the particle phase and will be removed. Liu, Zhou, and Lu, 2020 [68], reported a similar correlation coefficient for SO_2 and NO_2 with RH.

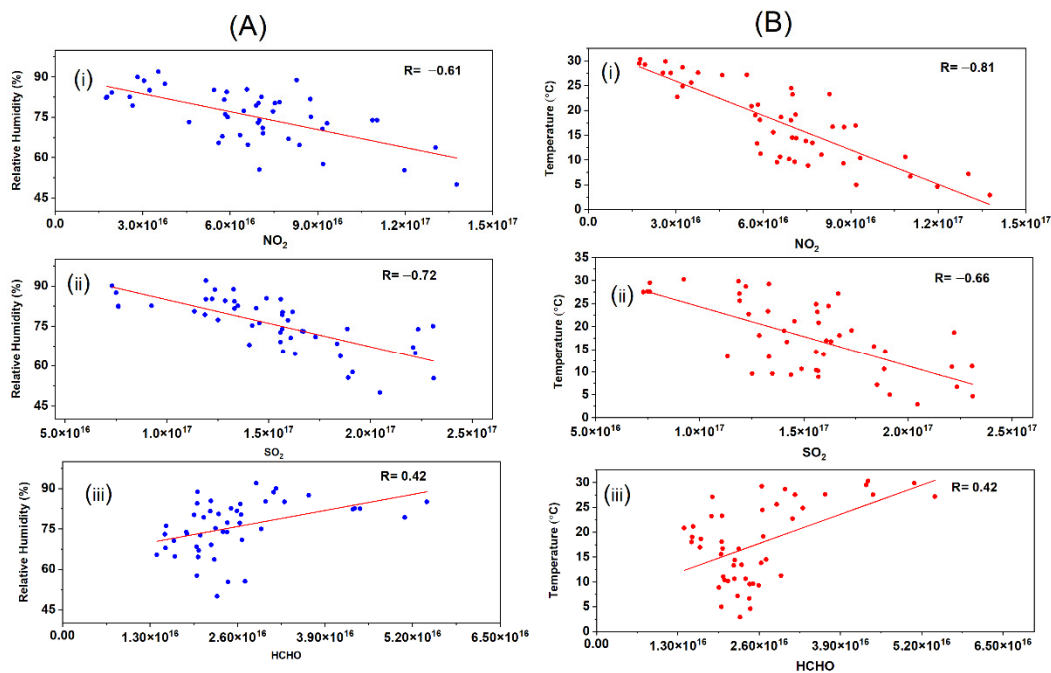


Figure 6. Relationship of RH (A) and T (B) with weekly averaged (i) NO_2 , (ii) SO_2 , and (iii) HCHO .

Temperature is another crucial factor in determining trace gas concentration and atmospheric chemistry. HCHO shows an enhanced concentration with increased temperature ($R = 0.52$; Figure 6(Biii)), suggesting that the photo-oxidation of VOCs is the main source of HCHO formation [6,69]. NO_2 and SO_2 depicted a negative correlation coefficient of 0.81 and 0.66 (Figure 6(Bi,ii)) with temperature, respectively. This is because an increase in temperature is usually associated with enhanced photo intensity, which in turn leads to photolytic degradation of SO_2 , NO_2 , and VOCs. HCHO concentrations increase because VOC oxidation is the major source of its formation in the atmosphere [51].

3.4. Impact of Biogenic Emissions

During the growing season (spring to autumn), biogenic emissions tend to have a stronger influence on trace gas chemistry. According to the literature, the relative contribution of biogenic emissions to the overall VOCs is predicted to be about 13% [70]. High-quality spatial and temporal coverage of the vegetation cover can be obtained from the MODIS vegetation index products [71–73]. During summer, EVI values were observed to be high, indicating the presence of vegetation. Here, we analyzed the linkage between EVI and the formation of HCHO , NO_2 , and SO_2 to assess the impact of biogenic emissions on the concentrations of these trace gases.

A moderately positive correlation is exhibited by HCHO with EVI (Figure 7a), which is indicative of the fact that the formation of HCHO is associated with the oxidation of isoprene, which is a common VOC [6,74], whereas both NO_2 and SO_2 depicted a negative correlation (Figure 7b,c), implying that these two species do not come from biogenic sources. Vrekoussis et al. [75] reported an anti-correlation of NO_2 with EVI, while Guo et al. [76] argued that SO_2 decreases with an increase in vegetation as it enhances the absorbing capability for SO_2 . In conclusion, HCHO emissions are impacted by anthropogenic as well as biogenic emissions, which are indicated by a moderately positive correlation between the two, whereas both NO_2 and SO_2 come from anthropogenic sources. These results are consistent with previous studies [6,75].

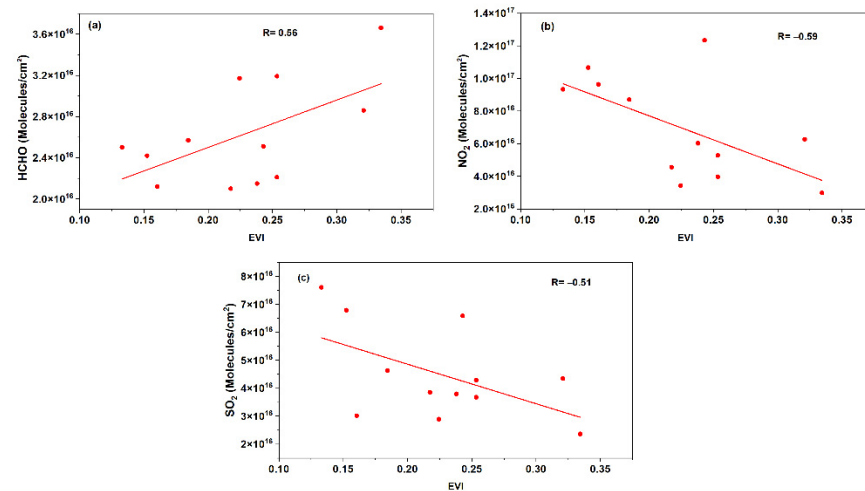


Figure 7. Relationship of monthly mean (a) HCHO, (b) NO₂, and (c) SO₂ with monthly mean EVI.

3.5. O₃–NO_x–VOC Sensitivity

The conditions for O₃ formation by VOCs or NO_x have broadly been categorized into three regions: (1) a VOC-limited regime, where VOCs are the major precursor for O₃ formation; (2) a NO_x-limited regime, where the levels of NO_x determine the levels of O₃; (3) a transition regime, where both NO_x and VOC contribute equally towards O₃ formation [77]. Several studies have utilized the ratio of HCHO to NO₂ (RFN) as a proxy to study the sensitivity of tropospheric O₃ formation to these species [20,78]. The linkage between RFN and O₃ formation was described by Duncan et al. [76], and the study suggested that the RFN values for the aforementioned regimes where an RFN less than 1 corresponds to a VOC-limited regime, an RFN of more than 2 characterizes an NO_x-limited regime, while an RFN value of between 1 and 2 corresponds to transition regimes. Figure 8 shows the RFN for Shanghai over the observation period. For most of the observation period (about 68%), the O₃ production remained in the VOC-limited regime. While 20% of the time, the O₃ production lay in the transitional regime, and it was NO_x-limited for only 12%. These results imply that VOCs are a major player for O₃ formation in Shanghai.

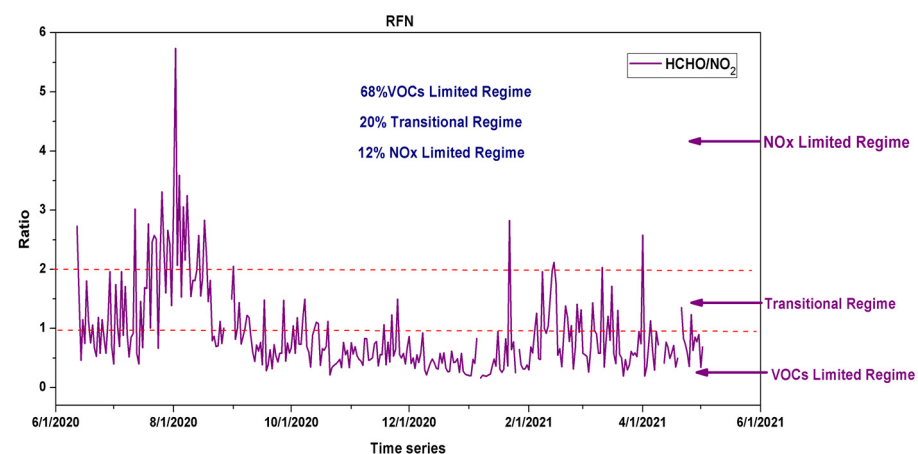


Figure 8. Daily mean RFN over Shanghai from June 2020 to May 2021.

Further, seasonal variations in RFN were analyzed. Table 2 depicts the mean, standard deviation, minimum, maximum, and median values of RFN for different seasons along with the percentage of O₃ formation regimes over Shanghai. The mean value for RFN shows very little variation for winter, spring, and autumn (between 0.63 and 0.73), while, for summer, the mean RFN was observed to be higher (>1.38). This is because significant O₃ formation lay in the VOC–NO_x-limited regime or transition regime (about 31%) during

this season. It is worth noting here that O_3 peaks are also observed during the summer season [66]. Yet, O_3 formation predominantly remained in the VOC-limited regime for all the seasons. This trend is consistent with previously reported studies [74,79,80].

Table 2. Seasonal variation in RFN calculated for the analysis of O_3 sensitivity.

Season	Mean	Standard Deviation	Minimum	Maximum	Median	VOC-Limited	VOC- NO_x -Limited (Transition Regime)	NO_x Limited
Winter	0.63593	0.49349	0.16212	2.82642	0.47576	86%	12%	2%
Spring	0.73219	0.432	0.19491	2.57558	0.6197	85%	12%	3%
Summer	1.3823	0.91103	0.28631	5.73799	1.1142	47%	31%	22%
Autumn	0.67106	0.29097	0.21438	1.49756	0.60024	82%	18%	-

3.6. Relationship among Different Pollutants

In situ daily mean concentrations were used to study the correlations among five criteria pollutants, including NO_2 , SO_2 , O_3 , $PM_{2.5}$, and PM_{10} over the study area for different seasons. Pairwise Pearson's correlation coefficient was employed for this analysis, which has been depicted in Figure 9. $PM_{2.5}$ depicted a strongly positive correlation with PM_{10} for all seasons ($R = 0.76$ for summer, $R = 0.74$ for autumn, and $R = 0.64$ for winter) except during spring, where it showed a weak negative correlation ($R = -0.13$). This is most likely because of the occurrence of sandstorms in eastern China during the spring months, which substantially enhance PM_{10} concentrations in the atmosphere [81]. $PM_{2.5}$ also depicted moderate positive correlations with primary pollutants (NO_2 and SO_2) for all the seasons ($R > 0.48$ with NO_2 and $R > 0.34$ with SO_2 for all seasons). This is indicative of the similar sources of emissions (such as fossil fuel combustion and vehicular exhausts) for these pollutants. PM_{10} also depicted weak positive correlations with NO_2 and SO_2 for all seasons ($R > 0.30$ for NO_2 and $R > 0.17$ for SO_2 for all seasons) except spring, where the correlation between NO_2 and PM_{10} was found to be negative ($R = -0.56$). This can be attributed to high PM_{10} content resulting from sandstorms, as stated above. These results are consistent with the findings reported by Sulaymon et al. [81].

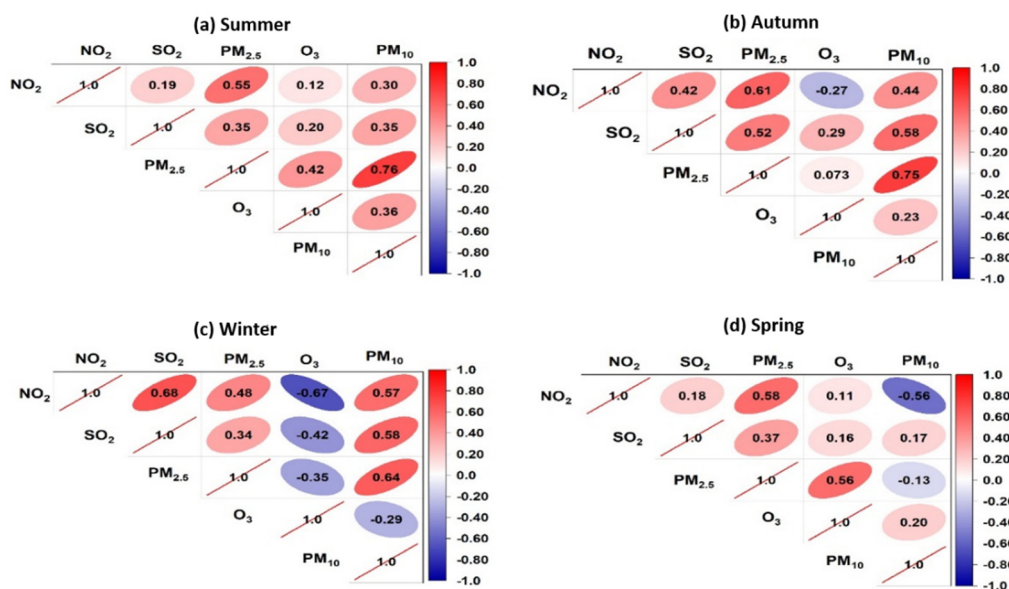


Figure 9. Pearson's correlation coefficients among different pollutants for (a) summer, (b) autumn, (c) winter, and (d) spring over Shanghai.

The positive correlation of $PM_{2.5}$ with SO_2 and NO_2 is attributed mainly to the coal-fired power plants and huge emissions from traffic [82]. Moreover, it can be argued that the positive correlation of PM (PM_{10} and $PM_{2.5}$) with SO_2 and NO_2 might be because these primary gaseous pollutants act as a precursor for the formation of major components (nitrates and sulfates) of PM [83]. A significantly weak correlation has been observed between NO_2 and SO_2 for summer ($R = 0.19$) and spring ($R = 0.18$) while a moderate correlation was found among the two during autumn ($R = 0.42$). During winter, however, the correlation between NO_2 and SO_2 was fairly strong ($R = 0.68$). These findings indicate varied and multiple sources of emission for these two atmospheric species during different seasons [84]. The correlation of O_3 with all other species was found to be negative during winter. During other seasons, however, the correlation was slightly positive except for NO_2 (negative during autumn as well) and $PM_{2.5}$ (fairly positive during spring). Chen et al. [85] reported a negative correlation between $PM_{2.5}$ and O_3 during winter, while a significantly positive correlation was reported for summer over the East China region. The least correlation coefficients of O_3 were observed, with NO_2 depicting a negative correlation during winter and autumn, while, for spring and summer, the correlation was positive, albeit insignificant. The negative correlation of O_3 with NO_2 is explained through studying the tropospheric chemistry, where the reaction of O_3 with NO leads to the formation of NO_2 , thereby depleting O_3 [86]. Additionally, these results imply that O_3 formation over Shanghai mainly lies in the VOC-limited regime. These results comply with previously reported findings [51,87].

3.7. Potential Source Regions of Pollutants

PSCF analysis was based on HCHO, NO_2 , and SO_2 , grouped by season (summer; autumn; winter; spring), over Shanghai, using 72-h back trajectories attained from the NOAA HYSPLIT model and ground-based data to detect the potential source areas of HCHO, NO_2 , and SO_2 . The HYSPLIT-derived back-trajectories over Shanghai were used to compute PSCF for each air pollutant and show the major likely sources of pollution. It is important to mention that the significant differences between sources and seasons were observed over Shanghai. The high values of PSCF (>0.50) in summer indicate that the contribution of local sources (e.g., Anhui, Fujian, Guangdong, Guangxi, Hainan, Hong Kong, Jiangsu, Jiangxi, Macao, Shandong, and Zhejiang) is much stronger than outside sources (Myanmar and Vietnam), which is more observable for HCHO than NO_2 and SO_2 concentrations (Figure 10a). These local sources of HCHO concentration more significantly affect the air quality of Shanghai than regional sources. As in summer, local sources (i.e., Anhui, Beijing, Hebei, Hubei, Inner Mongolia, Jiangsu, Jiangxi, Shandong, and Zhejiang) of the three concentrations (HCHO, NO_2 , and SO_2) also substantially affect the autumn (Figure 10b) air quality over Shanghai more than distant regional sources such as Mongolia do, as indicated by the higher values of PSCF (>0.50). In winter, the contribution of local sources (e.g., Anhui, Beijing, Fujian, Guangdong, Guangxi, Hebei, Henan, Hubei, Inner Mongolia, Jiangsu, Jiangxi, Liaoning, Shandong, Shanxi, Shaanxi, Tianjin, and Zhejiang) is much stronger than outside sources (Mongolia and Russia), which is more observable for NO_2 and SO_2 than HCHO concentrations (Figure 10c). The springtime air quality over Shanghai is also significantly impacted by local pollution sources (Figure 10d). Overall, the results show that local sources from mainland China are the major contributors of air pollution over Shanghai, with NO_2 and SO_2 pollution levels being higher in winter than in other seasons, whereas HCHO pollution is higher in summer.

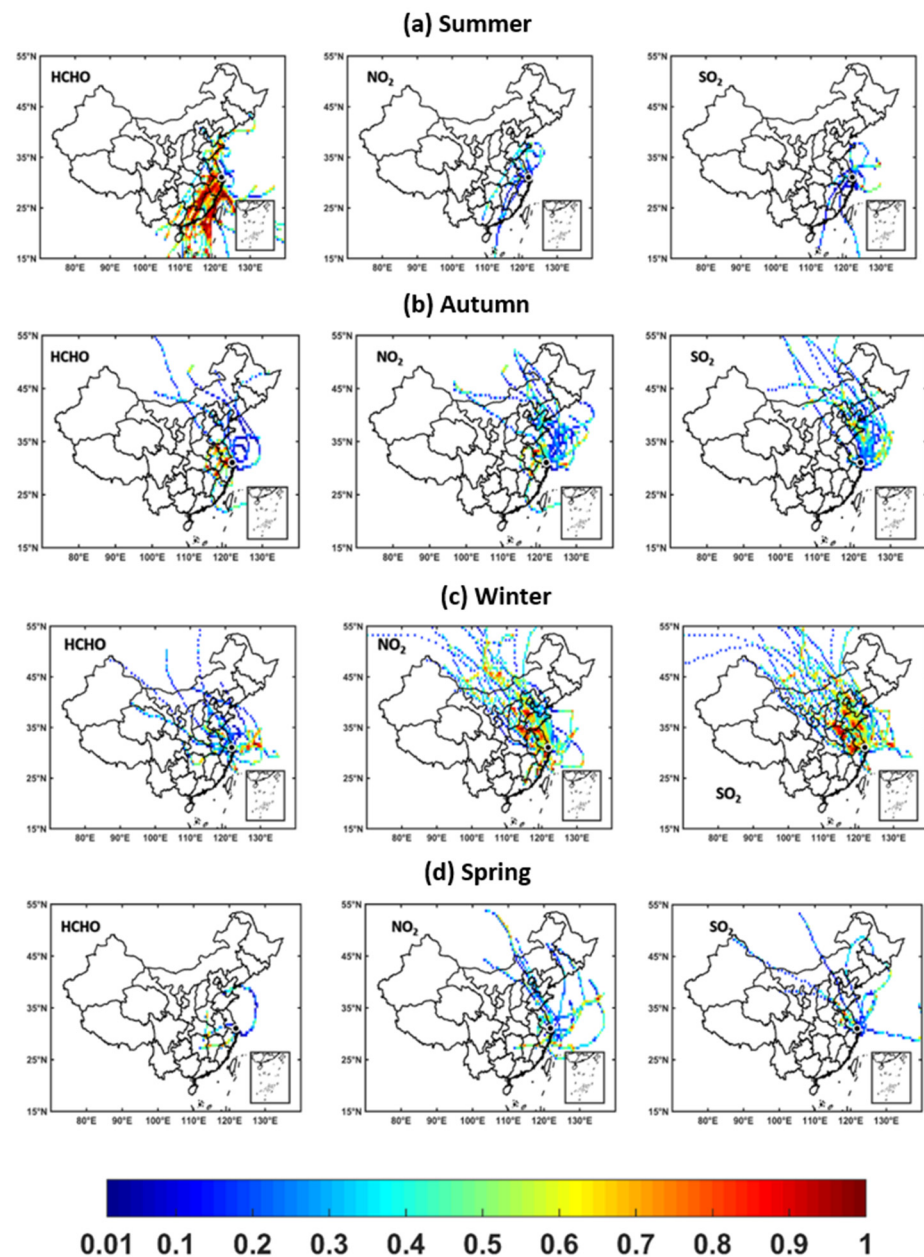


Figure 10. PSCF analysis based on HCHO, NO₂, and SO₂, grouped by seasons (a) summer, (b) autumn, (c) winter, and (d) spring over Shanghai: Here, the color bar indicates the weights of the pollution source regions (WPSCF). Regions with WPSCF < 0.4 are termed a low-polluted source regions, regions with WPSCF between 0.4 and 0.5 are considered medium-polluted source regions, while the WPSCF > 0.5 indicate high-polluted source regions.

4. Conclusions

The current study was conducted to monitor various trace gas species over a sub-urban site in Shanghai for one year. Ground-based MAX-DOAS observations were recorded, spanning from June 2020 to May 2021. The spectra were analyzed using QDOAS, and the time series was obtained for HCHO, NO₂, and SO₂. The results indicated strong seasonality for these trace gas species, with both NO₂ and SO₂ being higher during winter while HCHO concentrations were higher during the summer season. These results can be explained by the correlation of these species with temperature, where HCHO shows a strong positive correlation ($R = 0.78$), while both NO₂ and SO₂ depict a negative correlation ($R = -0.66$ and $R = -0.57$, respectively). Similar correlations have been found with RH,

where an increase in humidity causes a decline in NO₂ and SO₂ concentrations. Diurnal variations in SO₂ and NO₂ showed a similar pattern, with concentrations being higher during the morning and evening while declining in the afternoon owing to an enhanced rate of photolysis. HCHO concentrations were lower during the morning and evening while higher during noon, arguably because of the secondary formation of HCHO from the oxidation of VOCs. Further, HCHO depicted a moderately positive correlation with EVI, implying that the concentrations are influenced by the biogenic sources of emissions. The results of the sensitivity analysis showed that the majority of the O₃ formation in Shanghai is VOC-limited while a significant percentage (31%) lies in the VOC-NO_x-limited regimes during the summer season. Pearson's correlation coefficients among different species depicted complex relationships with strong seasonal impacts. The relationship of PM₁₀ with PM_{2.5} was mostly positive, and both of these species depicted a positive correlation with SO₂ and NO₂, whereas the relationship between SO₂ and NO₂ varied from weakly positive to fairly positive. The relationship of O₃ with all these species was negative or negligibly weak, with the lowest correlation being found for NO₂, which further confirms that the O₃ formation in Shanghai is VOC-limited. These results indicate that the currently employed strategies to combat air pollution over Shanghai are not significantly sufficient and that there is a dire need to combat the precursor species in order to achieve the objective of controlling O₃ pollution, keeping in view the HCHO/NO₂ ratio. The results of the PSCF analysis reveal that the atmospheric pollution over the study area is mostly impacted by the contribution from local sources with lesser contributions from regional sources, which implies local O₃ production at this suburban site. In conclusion, this study provides an insight into the multifaceted nature of atmospheric pollutants, their multiple sources, and complex interactions while providing a baseline for future researchers and policymakers. The study can be used as a model to design similar research over different cities in order to evaluate the sources of pollution and to specifically study O₃ sensitivity over the regions in order to combat the rising problem of O₃ pollution across the globe and may also serve as a reference for regional-scale air quality management in future.

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