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Urban–Rural Comparisons of Biogenic Volatile Organic Compounds and Ground-Level Ozone in Beijing

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Abstract: Ground-level ozone (O_3) pollution has been a severe environmental and health problem for decades. The importance of biogenic volatile organic compounds (BVOCs) in the formation of tropospheric photochemistry O_3 has been highlighted, especially in areas of rapid urbanization. We conducted simultaneous measurements of trace gases, including NO, NO_X, O_3, and BVOCs (i.e., isoprene and α-pinene), in the urban and rural forest areas of Beijing to determine the relationships between them. The results highlight the differences between the urban and rural forest areas of Beijing in terms of ambient air concentrations of BVOCs and O_3, and the interrelationships between BVOCs, NO_X, and ozone were quantified. Moreover, the isoprene concentration was found to be higher in the atmosphere of the urban site than of the rural site, which had higher α-pinene concentrations and higher O_3 concentrations. The NO_X concentration was higher at the urban site than at the rural site, and there was a significant exponential relationship between NO_X and O_3 at the urban site, indicating that the impact of NOx on O_3 at the urban site was greater than that at the rural site. The O_3 concentration increased with rising isoprene and α-pinene in both sites. In the case of substantially increased BVOC concentrations, declining NO_X concentrations strongly promote the formation of O_3. Consideration should be given to planting tree species with low-BVOC emissions, as they are crucial for mitigating O_3 pollution in urban areas. Additionally, the relationships between BVOCs, NO_X, and O_3 should be considered in policymaking related to O_3 control.

Keywords: isoprene; O_3; α-pinene; urban; rural

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Citation: Guo, P.; Su, Y.; Sun, X.; Liu, C.; Cui, B.; Xu, X.; Ouyang, Z.; Wang, X. Urban–Rural Comparisons of Biogenic Volatile Organic Compounds and Ground-Level Ozone in Beijing. *Forests* **2024**, *15*, 508. https://doi.org/10.3390/f15030508

Academic Editors: Giacomo Alessandro Gerosa, Zhaojiang Zuo and Sarathi Weraduwage

Received: 21 January 2024
Revised: 1 March 2024
Accepted: 7 March 2024
Published: 8 March 2024

1. Introduction

As important precursors of tropospheric ozone (O_3) and secondary organic aerosols (SOAs), biogenic volatile organic compounds (BVOCs) represent a substantial amount of the carbon that is fixed by primary producers [1,2]. The BVOCs emitted into the urban atmosphere contribute to the formation of local fine particles and promote an increase in aerosol particle size [3]. The high intensity of BVOC emission in urban green spaces could contribute to atmospheric photochemical processes, resulting in the formation of O_3, with subsequent effects on urban air quality and thus human health [4]. In addition to damaging the human respiratory system [5,6], the increased levels of O_3 in the air could result in decreased crop and timber yields [7,8]. In photochemical reactions with NO_X, BVOCs contribute to O_3 formation in the troposphere [9–11]. The reactions between NO, NO_2, and O_3 are often termed as the triad, representing a null cycle, in which NO_2 serves as the precursor and NO as a sink for O_3, and no net O_3 is produced or removed [6]. In the presence of NOx and sunlight, the degradation reactions of volatile organic compounds lead to the conversion of NO to NO_2 and the formation of O_3 [12]. BVOCs have a greater effect on O_3 formation than do anthropogenic volatile organic compounds (AVOCs), due to their strong reactivity in the atmosphere [13]. As the key BVOCs, isoprene and monoterpenes play pivotal roles in the formation of tropospheric ozone [14,15]. Generally, isoprene has a higher O_3 production potential compared to monoterpenes due to its higher reactivity factor [16] and abundance in the atmosphere [17]. However, the O_3 production potential of monoterpenes can also be significant, especially in regions where there are high emissions from vegetation or under specific atmospheric conditions conducive to O_3 formation.

The impact of biogenic emissions on O_3 formation exhibits a strong spatial pattern. BVOC emissions have distinct impacts on rapid O_3 increments in different regions due to the fact that trends of leaf biomass change differ according to region and vegetation type [18]. Studies on O_3 pollution events in the continental United States have shown that large areas of vegetation with high BVOC emissions can exacerbate O_3 pollution [19]. The differences in processes related to trees that affect tropospheric ozone concentrations along the rural–urban gradient have been highlighted [6]. The O_3 concentrations are more likely to be influenced by BVOC emissions in rural areas than in urban areas [20]. Bao et al. presented a 3D photochemical model of regional O_3 generation that simulates the situation of photochemical occurrence with or without BVOCs and concluded that BVOC emissions in the Kinki suburb of Japan can significantly promote increased O_3 in urban areas [21]. The change in land use and meteorological conditions caused by urbanization in China have increased annual BVOC emissions by 11.4% [22]. Since BVOC emissions vary with tree species and environment, their contribution to total VOCs in the atmosphere of cities is closely related to plant diversity and the local climate conditions. Due to urban expansion in the northeast of the United States, oak forest areas with large isoprene emission potential have decreased, while red maple forest areas with low isoprene emissions have increased, greatly reducing the regional isoprene emissions and significantly decreasing O_3 concentrations in the regional atmosphere [23]. The selection of tree species with low BVOC emissions plays a key role in improving urban air quality [17]. Studies have shown that cities with abundant sunshine and a warm climate are more likely to suffer from poor air quality than those with less sunshine and low temperatures, because light and high temperatures promote BVOC emissions from vegetation and accelerate the chemical reactions resulting in O_3 formation [17].

A large number of studies have illustrated the role of BVOCs in regional air quality. Research shows that the significance of BVOC emissions in ozone formation will increase as NOx levels decline in urban areas [24]. Local O_3 formation depends on the ratio of VOCs to NOx; in urban areas (“VOC-limited” conditions), the decline in NOx emissions causes an increase in VOC-to-NOx ratios, leading to O_3 formation [25]; and it has been found that a large increase in BVOC emissions causes O_3 peak increments of up to 2.0–6.0 ppb in VOC-limited urban areas [26]. Research in a rural area in the Korean Peninsula has shown that the O_3 concentration in the air is very sensitive to NO_X concentration because of the abundance of BVOCs [27]. Ran et al. conducted VOC measurements in suburban areas of Beijing and Tianjin, China, indicating that biogenic isoprene is the second-largest OH sink, and it was concluded that under the action of NO_X, isoprene peroxyradicals play an important role in promoting the generation of O_3 [28]. Geng et al. used 3D regional chemical and migration models combined with an experimental measurement database to evaluate the impact of isoprene on air quality in Shanghai, showing that isoprene and its oxidation products from upwind forests lead to O_3 formation in urban areas of Shanghai [29].

To deal with urban air pollution and improve air quality, the Chinese government has in recent years taken a series of measures to reduce the emissions of CO_2, SO_2, PM_{10}, and $PM_{2.5}$, resulting in some notable improvements. However, pollution from secondary photochemical products, such as O_3, remains severe [30]. BVOC emissions can promote the generation of O_3 in the air. Urban expansion has altered BVOC emissions and their role in atmospheric photochemical reactions in addition to promoting O_3 formation through land use change. The main objective of this study is to explore the differences in BVOC, NO_X, and O_3 in the ambient air between urban and rural sites in Beijing, conduct descriptive and exponential relationship analysis of several (but not all) factors involved in O_3 formation, and analyze the interrelationships between them as well as the main driving factors of O_3 formation. We also provide suggestions for urban ground-level O_3 control in order to improve atmospheric quality.

2. Materials and Methods

2.1. Site Description

Field measurements were conducted at two sites, the Research Center for Eco-environmental Sciences, Chinese Academy of Sciences (RCEES), and Mangshan Forest Park in Beijing, representing the urban and rural forest areas, respectively (Figure 1). The distance between the two sampling sites is approximately 30 km. The urban site is located above the comprehensive scientific research building in RCEES with geographical coordinates 116°20′15″, 40°00′26″ and an altitude of 76 m. The surrounding areas mainly include buildings for teaching, residential areas, and parks. The urban site has a vegetation coverage rate of 50%, covered with broadleaf trees with *Platanus orientalis* L. being the dominant species, with tree age and height averaging about 40 years and 20 m, respectively. There is a northeast–southwest bidirectional four-lane road 150 m to the west of the observation site and an east–west bidirectional two-lane road 200 m to the south, which are used by many vehicles in the morning and evening rush hours on weekdays. The rural site is located in the Mangshan monitoring station with geographical coordinates of (116°16′43″, 40°16′35″), an altitude of about 588 m, and a distance of about 40 km from the center of Beijing. The surrounding background is a national forest park with a vegetation coverage of 96%, and the dominant species are conifers. Ambient samplings of air for the detection of BVOCs were conducted from May to September 2017 for the urban site and August to September 2017 for the rural site. The dates for simultaneous measurements at the urban and rural sites were 8 August 2017, 30 August 2017, 6 September 2017, 12 September 2017, and 18 September 2017. The time used in the current study is Beijing time. Days with calm wind conditions and fine weather were selected for sampling, which was conducted once a week at both sites.

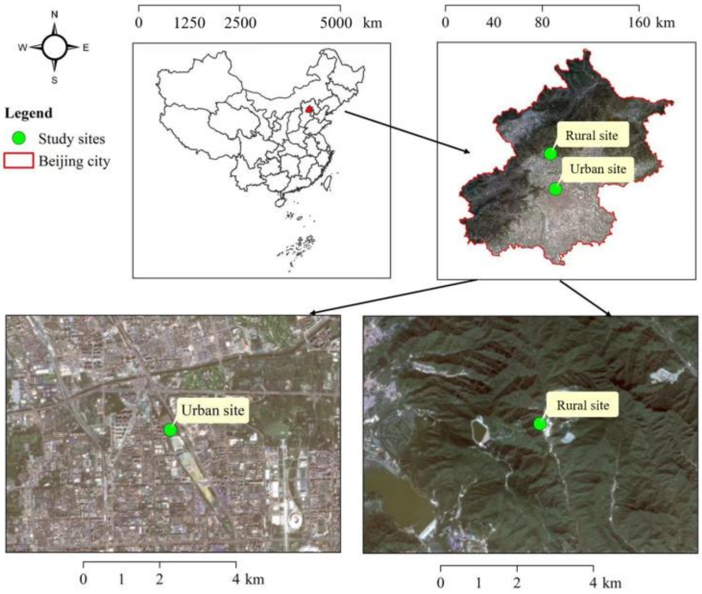

Figure 1. Location of the research sites in Beijing. The urban site and the rural site represent the built-up area and the rural forest, respectively.

The sampling site in the urban area is covered with broadleaf trees with the dominant species *Platanus orientalis* L., which mostly emit isoprene, while the rural site is mainly covered by a coniferous forest with the dominant species *Pinus tabuliformis* Carrière, which mainly emits α-pinene. We assumed isoprene and α-pinene as representative for BVOCs in this research.

Air samples were collected and sampled under calm wind and fine weather conditions, with the ambient temperature ranging between 24.1 and 33.8 °C at the urban site and 20.3~31.5 °C at the rural site, the photosynthetic active radiation (PAR) was 620~933 μmol m^{-2} s^{-1} at the urban site and 608~804 μmol m^{-2} s^{-1} at the rural site, and the wind speed (WS) was 0.01~0.68 m s^{-1} and 0~2.36 m s^{-1}, respectively (Figure 2), which limits the impact of atmospheric transmission. Therefore, the impact of atmospheric transmission during the air sampling period was ignored. All meteorological parameters were measured every 10 min at the meteorological measurement stations using a rainfall sensor (TE525, Texas Electronics Inc., Dallas, TX, USA), temperature and humidity sensor (HMP155, Vaisala, Helsinki, Finland), photosynthetic effective radiation sensor (PQS1, KIPP&ZONEN, OTT HydroMet B.V., Delft, The Netherlands), and wind speed and direction sensor (034B, MetOne, Beckman Coulter Inc., CA, USA).

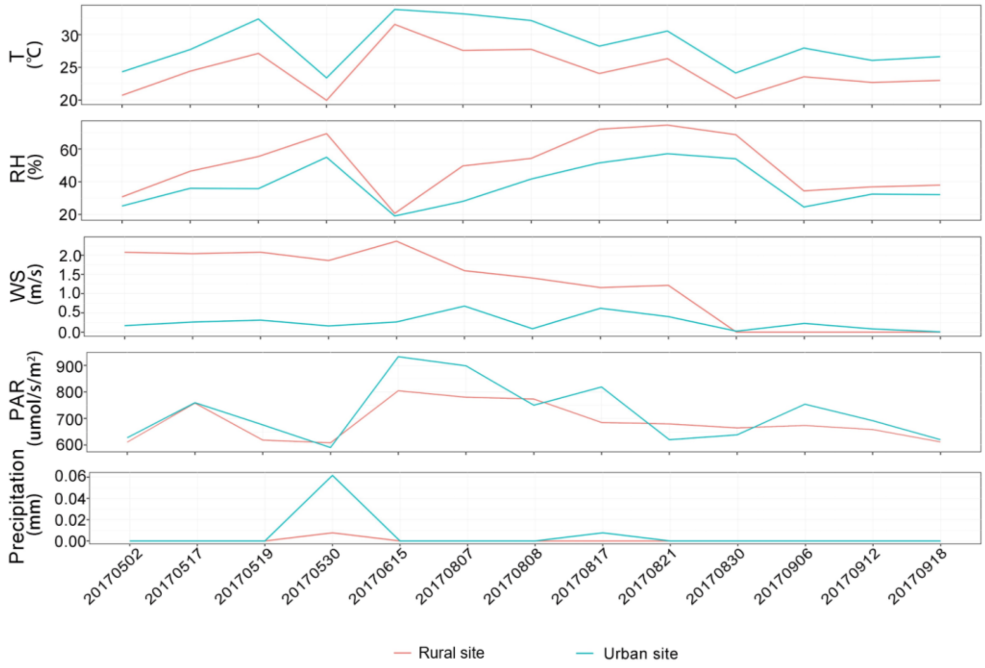

Figure 2. Average value of meteorological parameters during the air sampling periods (T represents temperature with units of °C, RH represents relative humidity (%), WS represents wind speed (m s^{-1}), and PAR represents photosynthetic active radiation (μmol m^{-2} s^{-1})).

2.2. Sample Collection and Analysis

Air samples were collected and concentrated in a ¼″ × 3½″ stainless-steel adsorption tube filled with Tenax GR and Carbograph 5TD (Markes Int., Llanstrisant, UK), preconditioned with purified helium (50 mL min^{-1}) at 300 °C for 10 min, and were stored at approximately 5 °C. The sample flow rate was controlled by an automatic sampling pump (QC-II, Beijing Beilaoke Safety Technology Co., Ltd., Beijing, China) at a flow rate of 200 mL min^{-1} for 30 min. Sampling was conducted every 2 h between 8:00 a.m. and 6:00 p.m. at both urban and rural sites. The collected air samples were immediately sealed with Teflon-coated caps, stored in a portable fridge (4 °C), transported to the laboratory, and kept in the refrigerator until analysis.

An Agilent 7890A GC/5977B Electron Impact Mass Spectrometer (GC–MS) (Agilent Technologies Inc., Santa Clara, CA, USA), in conjunction with a TD-100 thermal desorption system (Markes International Ltd, Wales, UK), was used for the analysis of sorbent cartridge (Tenax GR and Carbograph 5TD, Markes Int., Llanstrisant, UK) sampling. The GC was fitted with an HP-5ms chromatographic column (30 m × 250 μm × 0.25 μm)

(Agilent Technologies, Inc., Santa Clara, CA, USA) and was temperature-programmed with an initial hold step at 35 °C for 2 min, with a subsequent temperature ramping of 5 °C min^{-1} to 160 °C, holding for 3 min; 20 °C min^{-1} to 270 °C, holding for 3 min; and to a final temperature of 300 °C. The detection limit of the GC–MS equipped with the TD-100 thermal desorption system was 6.6 ng for isoprene and 0.9–28.3 ng for monoterpenes.

We employed mixed standard gases containing varying concentrations of isoprene and α-pinene in the adsorption tube (collecting volume A) to establish standard curves. The mixed standard gas of isoprene and α-pinene at 1 ppm was obtained from the National Institute of Metrology (Beijing, China). The standard gas was diluted from 1 ppm to a range of concentrations between 1 and 20 ppb at five dilution levels which were prepared as calibration standards. Calibration of the gas standards was carried out by collecting the diluted gas in the adsorption tube. The target compounds were separated and measured using GC–MS in conjunction with the TD-100 thermal desorption system. The resulting standard curves demonstrated R^2 values exceeding 0.99 for the specified species. Subsequently, we analyzed all target BVOC species within the adsorption tube, which contained a volume of air sample denoted as B, yielding response values. These responses were then applied to the standard curve to calculate the concentration, denoted as C_1. The actual concentration of the target BVOC species in the external atmosphere, denoted as C, was determined using the following formula:

$$C = C_1 \times \frac{A}{B} \tag{1}$$

where C_1 represents the concentration calculated by applying the response value of the target BVOC species in the air sample to the standard curve, A is the volume of standard gas in the adsorption tube used to establish standard curves, and B represents the volume of air sample in the adsorption tube.

An O_3 analyzer was used for O_3 detection and analysis (49i, Thermo Fisher, Waltham, MA, USA), and an NO_X analyzer was used for NO and NO_X detection (42i, Thermo Fisher, Waltham, MA, USA).

2.3. O_3 Formation Potential (OFP) of BVOCs

The O_3 formation potential represents the largest contribution of VOCs to O_3 generation under the best reaction conditions, which is determined by the concentration of VOC species in the atmosphere and the maximum incremental reactivity of VOC species [31]. OFP is the product of the environmental concentration of a VOC compound and its MIR coefficient (O_3 formation coefficient), with a unit of 10^{-9}. The calculation formula is

$$OFP_i = MIR_i \times [VOC]_i \tag{2}$$

where $[VOC]_i$ represents the atmospheric concentration of a VOC compound in units of 10^{-9} and MIR_i is the O_3 formation coefficient of a VOC compound. In this study, the MIR coefficient of Carter's study was adopted [16], and the unit is $\mathrm{cm}^3/(\mathrm{mol\ s})$.

2.4. Statistical Analysis

We analyzed the daily variation and differences in trace gases at the urban and rural sites and applied exponential relationships between the trace gases in the sample sites to assess the main factors that promote O_3 formation. Exponential fitting was conducted to determine the relationships between O_3 and its precursors. We also prepared an iso-concentration map of O_3 under the combined effect of BVOCs and NO_X to evaluate the concentration reaction relationship of BVOCs–NO_X–O_3.

3. Results

3.1. Comparison of Trace Gases in the Urban and Rural Sites

As shown in Figure 3, NO and NO_X were much higher at the urban site than at the rural site, where O_3 was also lower. Compared to the rural site, isoprene was also higher at the urban site although α-pinene was relatively low. The daytime O_3 concentration observed showed higher values at the rural site and reached a peak value in mid-May for both sites. Then, the concentration of O_3 decreased as the rainy season set in, but NO_X, as the precursor of ozone, did not exhibit any similar variation trend. The isoprene concentration showed a similar variation trend as O_3, with higher values in May and lower values in September.

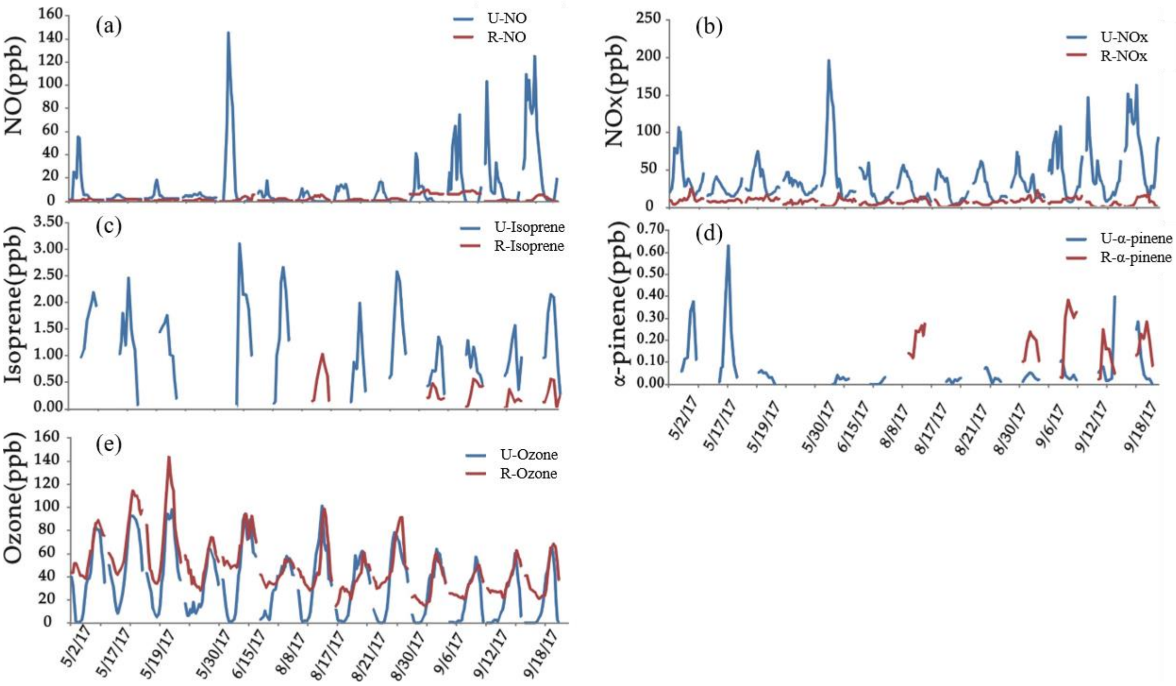

Figure 3. Hourly measured concentrations of NO (**a**), NO_X (**b**), isoprene (**c**), α-pinene (**d**), and ozone (**e**) at the urban and rural sites (U: urban site located in the Research Center for Eco-environmental Sciences, Chinese Academy of Sciences; R: rural site located in Mangshan National Forest Park in Beijing).

Figure 4 shows the variations in NO and NO_X concentrations at the urban and rural sites over the entire day, with the peak value appearing in the morning for the urban site, while there was no significant peak for the rural site, with higher values occurring in the afternoon (Figure 4). As shown in Figure 4a, the urban site NO concentration showed two peaks in the morning around 4:00 a.m. to 9:00 a.m., with the first peak occurring just before the morning rush, around 4:00 a.m. The NO level dropped sharply after 8:00 a.m., reaching nearly zero from 16:00 p.m. to 20:00 p.m., and the NO_X concentration was also lowest at 16:00 p.m. The NO and NO_X concentrations were much lower at the rural site than at the urban site. Moreover, the diurnal variation process was significantly different between the two sites. The levels of NO and NO_X in the air of the rural site were extremely low before 8:00 a.m., and high values tended to occur between 12:00 and 18:00. The hourly averages of NO_X in the air were significantly higher for the urban site than for the rural site (Figure 4, Table 1).

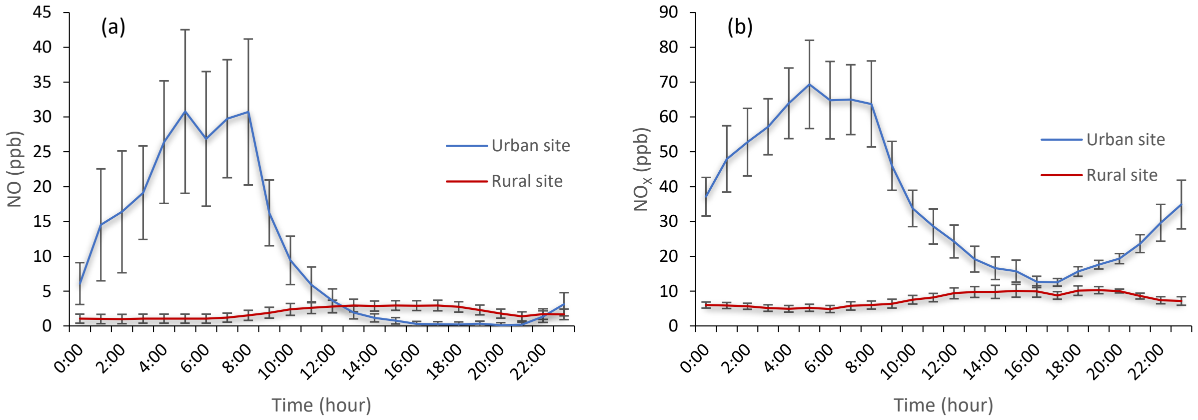

Figure 4. Diurnal variations in the average concentrations of NO (**a**) and NO$_X$ (**b**) in the air at the urban and rural sites.

Table 1. Daily averages of trace gas concentrations and O_3 formation potential (OFP) at the urban and rural sites from May to September of 2017.

Compounds	MIR	Urban Site				Rural Site			
		Mean	Min	Max	OFP	Mean	Min	Max	OFP
Isoprene/ppb	9.1	1.19 ± 0.76	0	3.11	32.75	0.34 ± 0.24	0	1.02	9.29
α-pinene/ppb	3.3	0.07 ± 0.11	0	0.63	1.36	0.19 ± 0.1	0	0.38	3.81
NO/ppb		4.96 ± 10	0.12	61.15		2.66 ± 2.6	0	8.93	
NO$_X$/ppb		23.70 ± 19.23	3.95	97.92		8.94 ± 4.96	0	23.74	
O_3/ppb		48.71 ± 26	3.19	94.26		55.9 ± 28.23	15.3	128.04	

The hourly average concentration of isoprene was significantly higher at the urban site (1.19 ± 0.76 ppb) than at the rural site (0.34 ± 0.24 ppb). The concentration of α-pinene (0.19± 0.1 ppb) was significantly higher at the rural site than at the urban site (0.07 ± 0.11 ppb). The O_3 concentration in the air varied greatly between the urban and rural sites, ranging from 15 to 128 ppb at the rural site with an average value of 55.9 ± 28 ppb during the observation period, which was higher than at the urban site (48.7 ± 26 ppb) (Table 1). The impact of atmospheric transmission during the air sampling period was ignored due to the calm wind and fine weather conditions when the air samples were collected. The OFP of isoprene at the urban site was 32.75, higher than that at the rural site, while the OFP of α-pinene at the urban site was 1.36, lower than that at the rural site.

3.2. Diurnal Variation in BVOCs and O_3

The diurnal variation in the isoprene and α-pinene concentrations at the urban and rural sites is shown in Figure 5. The concentrations of isoprene and α-pinene peaked around 14:00 (Figure 5). The atmospheric isoprene concentration was higher at the urban site than at the rural site, while the α-pinene concentration was higher at the rural site than at the urban site (Figure 5).

The O_3 concentration showed clear diurnal variations during the study period and reached a daily maximum in the late afternoon (Figure 6). The observation of temporal variations showed that there were higher values for O_3 concentration at the rural site than at the urban site for most of the day.

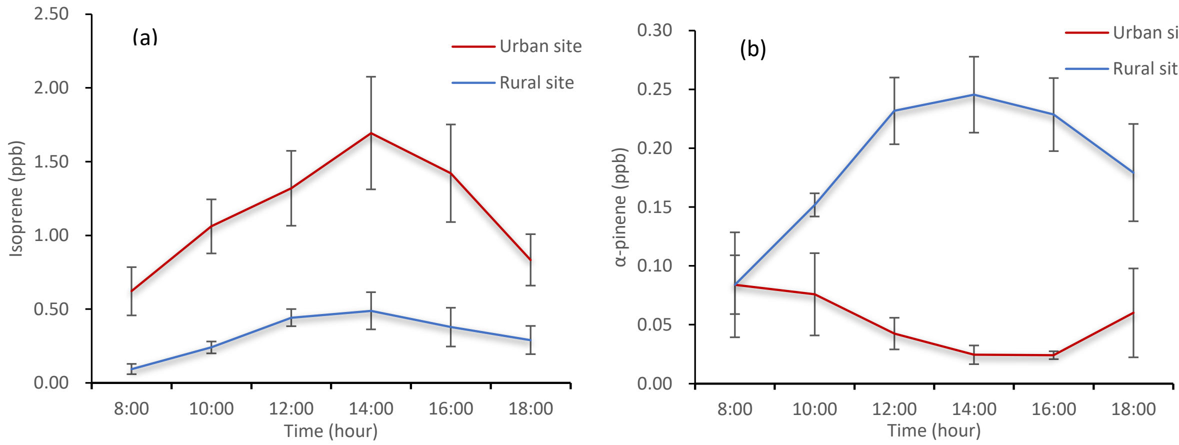

Figure 5. Variations in the average isoprene (**a**) and α-pinene (**b**) concentrations during the daytime.

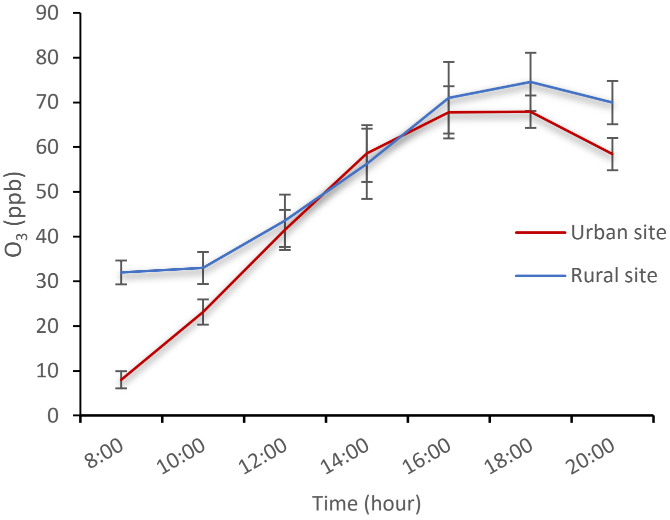

Figure 6. Variations in the average O_3 concentration during the daytime.

3.3. Relationships between BVOCs, NO_X, and O_3

O_3 is a secondary pollutant whose formation depends on the concentration and chemical reactions of precursors such as NO_X and VOCs. Photochemical reactions during the daytime are the basis of changes in O_3 throughout the day. We found that the exponential relationship between the sum of isoprene and α-pinene, and O_3 was relatively weak at the urban site (Figure 7), while the exponential fitting did not converge at the rural site, possibly due to the small amount of data. There was a relatively strong exponential relationship between NO_X and O_3 at the urban site, and the value of R^2 was higher than that at the rural site (Figure 8), indicating that the impact of NO_X on O_3 at the urban site was greater than that at the rural site.

The O_3 concentration was extremely low (0–13 ppb) when $NO_X > 75$ ppb (Figure 9). The high NO_X concentrations at the urban site may be the reason for its O_3 being lower than at the rural site. When the concentration of NO_X was lower than 75 ppb, the O_3 concentration tended to increase as the NO_X concentration decreased and isoprene and α-pinene increased. As soon as the NO_X concentration declined below 20 ppb, the O_3 concentration increased significantly with the increase in isoprene and α-pinene (Figure 9). This also explains, to a certain degree, the O_3 concentration at the rural site being higher than that at the urban site (Figure 6) for most of the day. Under the conditions of increasing BVOCs, a reduction in NO_X strongly promotes the formation of O_3, which means that decreasing NO_X has a negative effect, especially in the case of substantially increased isoprene and α-pinene concentrations.

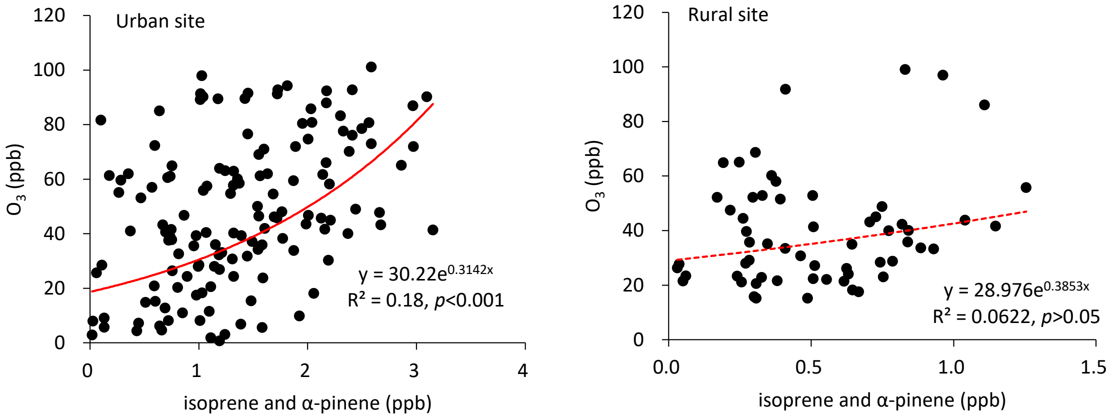

Figure 7. Exponential fitting chart of hourly concentrations of isoprene and α-pinene vs. O_3.

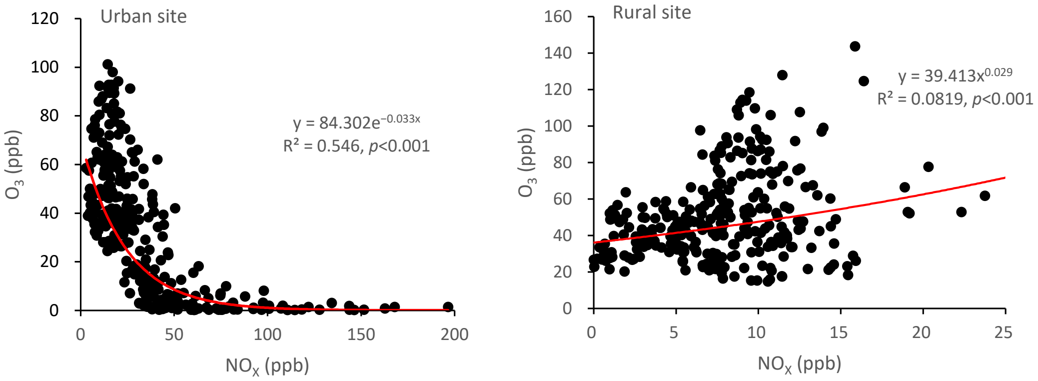

Figure 8. Exponential fitting chart of hourly concentrations of NO_X and O_3.

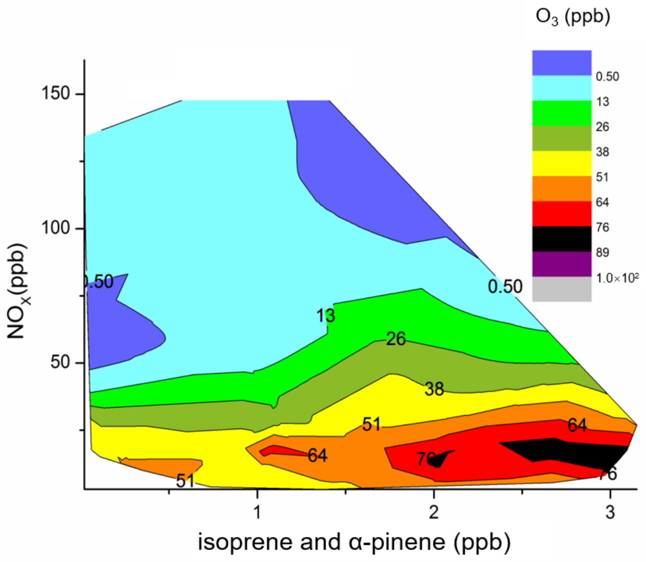

Figure 9. Isoconcentration map showing O_3 concentrations under the combined effect of isoprene and α-pinene and NO_X.

4. Discussion

The differences in BVOCs between the urban site and the rural site mainly resulted from differences in vegetation structure and species composition in Beijing. In the current study, the isoprene concentration was higher at the urban site than at the rural site, where the α-pinene concentration was higher. Isoprene or monoterpenes are the dominant BVOCs emitted from many plant species, and they are the most important plant volatiles [13]. Isoprene emitters are typically found in temperate and tropical forests, while monoterpene emitters are typically found in coniferous forests [32]. The sampling site in the urban area is covered with broadleaf trees, with *Platanus orientalis* L. as the dominant species, which mostly emit isoprene. The rural site is mainly covered by a coniferous forest with the dominant species *Pinus tabuliformis* Carrière, which mainly emits α-pinene. In this study, the OFP of α-pinene was higher at the rural site than in the urban area. Certain trees tend to emit more biogenic volatile organic compounds, which act as precursors for O_3 formation [33]. Due to their four-membered ring structure adjacent to the alkene, α-pinene molecules have strong reactivity in the atmosphere, which promotes the formation of O_3 and secondary organic aerosols.

The O_3 concentration exhibits significant spatial and temporal heterogeneity between the urban and rural sites. In the current study, the values of daytime O_3 concentrations observed in 2017 were higher at the rural site than at the urban site, reaching a peak value in mid-May for both. Regarding the diurnal variation in O_3, high values were often observed in the late afternoon. The diurnal variation in O_3 was related to the abundance of precursors, atmospheric oxidation, and meteorological conditions. Biogenic emissions and meteorological factors were found to be the underlying mechanisms that induce the occurrence of heavy ozone pollution events in the North China Plain, where the daily maximum regional 8 h average O_3 concentration reaches almost 120 ppb [34]. The results of a coupled meteorology/chemistry model suggest that BVOC emissions could increase regional daytime O_3 concentration from 5 to 20 ppb at the Taehwa Research Forest near Seoul, South Korea [35]. The concentration of precursors is one of the important factors affecting the formation of O_3, with NO_X typically being the limiting precursor in ozone production [36]. In the atmosphere, the source rate of global NOx is presently dominated by anthropogenic sources [37]. The contents of NO and NO_2 in the air were significantly higher for the urban site than the rural site in the current study, and the local traffic emissions are a potential factor for NO and NO_2. The higher concentrations of NO and NO_2 were related to the morning rush hour in the urban area. Furthermore, at the rural site, higher contents of NO and NO_2 were observed in the afternoon in this study. Since NO is usually rapidly converted to NO_2 under the oxidation of O_3, the observed peak of NO, if not from anthropogenic emissions, may be from recent emissions, such as a high level of soil NO emissions [38]. Human activities combined with soil NO emissions in the afternoon led to higher NOx and NO concentrations in the rural area. Studies have shown that at low NOx concentrations, O_3 formation is limited by NOx; at moderate NOx levels, the efficient recycling of OH (ROx-NOx cycle) sustains the oxidation of high VOC levels, eventually shifting to a regime where O_3 formation becomes limited by VOCs [16]. Wang et al. found that a high level of VOCs and NO_X emitted during a six-week observation in the northern mountainous area of Beijing in the summer caused an increase in the O_3 concentration in Beijing [39]. Akimoto et al. found that a high level of NO_X emissions in the coastal areas of the Asia–Pacific region was responsible for a significant increase in the regional O_3 concentration [40]. In this study, we observed an exponential relationship between NO_X and O_3 at the urban site, with a higher R^2 value than that at the rural site, indicating that the impact of NOx on O_3 at the urban site was greater than that at the rural site. The high levels of NOx in the city can lead to ozone titration; i.e., NO reacts with O_3 to yield NO_2. Consequently, the NO_2/NO ratio increases while O_3 levels decline. In an earlier microclimate modeling study, a relatively large isoprene-induced O_3 increase was found over the whole modeled area [33]. A box model study conducted in rural background areas such as the Valderejo Natural Park indicated that there were higher O_3 levels with higher isoprene concentrations, especially in NO-saturated atmospheres, and there was a clear relationship between urban layout, proximity to NO_X emitters, tree-species-dependent isoprene emission capacity, and increases in O_3 concentration, rising 500% locally [41]. In our study, we found obviously higher O_3 concentrations during the daytime at the rural site than at the urban site. High O_3 episodes are usually associated with high temperatures, which induce large amounts of BVOC emissions and enhance O_3 chemical production [42].

There are complex interactions between BVOCs, NO_X, and O_3. Photochemical reactions of BVOCs with NO_X result in the formation of O_3 and other atmospheric oxidants, which affect the distribution of hydroxyl radicals (OH) and consequently influence the lifetime of other trace gas species in the troposphere [43]. Theoretically, the O_3 content in the air can be reduced by controlling the concentrations of NO_X and VOCs. In the current study, the O_3 concentration was extremely low (0–13 ppb) when $NO_X > 75$ ppb. When the NO_X concentration was below 20 ppb, the O_3 concentration increased with the increasing BVOCs. At the urban site, O_3 formation was limited by VOCs, as there was sufficient NO_X from vehicular exhausts [44]. Therefore, an effective strategy for mitigating O_3 pollution in urban areas could be obtained by controlling the concentrations of BVOCs in the atmosphere by choosing low-BVOC-emitting tree species for planting. This is consistent with the results of previous studies, which have highlighted the significance of selecting low-emitting tree species for improving urban air quality [45,46].

The negative effect of NOx reduction—i.e., a decrease in NO_x emissions would increase urban O_3 by facilitating the NO titration effect—has received wide recognition in the field of ground-level ozone pollution control [47,48]. In this study, an exponential relationship was found between BVOCs and the O_3 concentration, while there was no significant difference when NO_X exceeded 75 ppb, and the decline in NO_X strongly promotes the formation of O_3, especially in the case of substantially increased BVOC concentrations. Therefore, in the policymaking related to O_3 control, considering only the control of NO_X emissions is insufficient, as the control of BVOC emissions is crucial for O_3 generation. Additionally, the relationships of BVOCs–NO_X–O_3 should also be considered in policymaking.

This study is based on data collected from May to September, which is a relatively short period, and the results may have been influenced by seasonal changes. Therefore, further research over a longer time scale is needed to verify the impact of BVOCs on ozone generation found in this study.

5. Conclusions

This study is focused on the variation in isoprene, α-pinene, and other atmospheric trace gases between urban and rural sites in Beijing. Higher daytime concentrations of isoprene were observed at the urban site compared to the rural site, while the rural site presented higher α-pinene concentrations, and the difference mainly results from differences in the vegetation structure and species composition across these two sites. The observation of temporal variations showed that O_3 concentrations were higher at the rural site than at the urban site for most of the day, which was mainly attributed to the high levels of NO_X at the urban site. The exponential relationship between NO_X and O_3 at the urban site was stronger than that at the rural site, indicating that the impact of NO_X on O_3 at the urban site was greater than that at the rural site. The analysis of the BVOCs–NO_X–O_3 chemical relationships based on observation provides a basis for studies on the influencing factors of O_3 generation in urban areas of Beijing. In addition to controlling NO_X, BVOCs should also be controlled by planting tree species with low potential BVOC emissions, since BVOCs are crucial in O_3 generation, and the relationships between BVOCs, NO_X, and O_3 should be considered in policymaking related to O_3 control.

Author Contributions: Conceptualization, P.G., Z.O. and X.W.; methodology, P.G. and X.W.; software, P.G., C.L., X.X. and B.C.; validation, P.G., X.W. and Y.S.; formal analysis, P.G. and C.L.; investigation, P.G. and X.S.; resources, X.W. and Z.O.; data curation, P.G.; writing—original draft preparation, P.G.; writing—review and editing, P.G. and X.W.; visualization, P.G.; supervision, X.W. and Z.O.; project administration, X.W.; funding acquisition, P.G. and X.W. All authors have read and agreed to the published version of the manuscript.

Funding: This study was supported by the National Natural Science Foundation of China (31600376 and 41571053) and the National Key Research and Development Program of China, sub-project (2022YFF1301103).

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Acknowledgments: Thanks are given to the graduate students of the Research Center for Eco-Environmental Sciences, CAS, who provided fieldwork assistance.

Conflicts of Interest: The authors declare no conflict of interest.

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