



Characteristics and ozone formation potentials of volatile organic compounds in a heavy industrial urban agglomeration of Northeast China

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Abstract

Understanding the pollution levels, potential sources, and chemical reactivity of atmospheric volatile organic compounds (VOCs), the key precursors of ozone (O₃) and fine particulate matter (PM_{2.5}), is important for emission control and air pollution abatement. This study presents a systematic VOCs analysis in a less studied heavy industrial urban agglomeration located in Northeast China. Using a cruising platform, we conducted real-time monitoring of VOC concentrations and components at Changchun (CC), Jilin (JL), Siping (SP), and Liaoyuan (LY) in Jilin Province. During the observation period, the average VOC concentrations at CC, JL, SP, and LY were 63.38 ± 127.03 , 260.39 ± 855.76 , 18.06 ± 17.17 , and 10.12 ± 17.48 $\mu\text{g}/\text{m}^3$, respectively. Halocarbons were predominant with a high percentage of contribution (22.4–31.1%) to the total observed VOCs for all cities. Combined with 2020-based anthropogenic VOCs emission inventory of Jilin Province, we concluded that industrial processes had the largest contribution to VOCs concentration in CC, whereas petrochemical emission was the major source of VOCs in JL. The assessment of atmospheric photochemical reactivity indicates the dominant role of aromatics and alkenes in O₃ formation potential (OFP). As the second-most abundant species in CC and JL, aromatics contributed over 50% of the OFPs. Alkenes played a dominant role in O₃ formation in SP and LY, accounting for nearly half of the total OFPs. Considering the VOC emission characteristics and OFP results, we suggest that reducing aromatics emissions, particularly benzene, toluene, ethylbenzene, and xylene, should be given higher priority to mitigate O₃ pollution and prevent health risks. Moreover, industrial-related, and petrochemical sources are crucial in the evolution of O₃ pollution, which should be incorporated into heavy industrial urban air quality management and targeted control of O₃ pollution in Northeast China.

Keywords VOCs · Mobile monitoring · Emission inventory · Industrial · O₃ formation

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Introduction

Concurrent with rapid economic growth and urbanization in China, most Chinese cities suffered from severe air pollution characterized by high fine particle matter (PM_{2.5}) concentrations. In response to this environmental issue, China implemented the Air Pollution Prevention and Control Action Plan, and a 33% decline in PM_{2.5} concentrations was successfully achieved from 2013 to 2017 (Huang et al. 2022; Zhang et al. 2019). However, a gap remains compared with the PM_{2.5} concentration of 35 µg/m³ specified by the National Ambient Air Quality Standard (Ding et al. 2022). In addition, ozone (O₃) pollution has recently become an increasingly prominent problem, the annual average of the 90th percentile of daily maximum eight-hour average O₃ concentration (MDA8) in 337 Chinese cities increased 20.3% from 123 µg/m³ in 2015 to 148 µg/m³ in 2019 (Lu et al. 2018; Ministry of Ecology and Environment of the People's Republic of China 2016, 2020; Wang et al. 2020). To tackle this problem, collaborative reduction of both PM_{2.5} and O₃ is required for further improvement in air quality.

Atmospheric volatile organic compounds (VOCs) play a vital role in air quality and human health (Shao et al. 2009). It is well-known that the photochemical reaction between VOCs and nitrogen oxides (NO_x) is the major source of O₃ in the troposphere (Seinfeld et al. 2006). Moreover, VOCs are key precursors to the formation of secondary organic aerosol (SOA), which is an important organic component of PM_{2.5} (Huang et al. 2014). Therefore, a comprehensive investigation of VOC emission characteristics and an in-depth exploration of the secondary transformation potential of VOCs will provide useful knowledge for PM_{2.5} and O₃ collaborative control. In addition, some VOC species pose direct harm to human health. For instance, benzene, toluene, ethylbenzene, and xylene (BTEX) are considered as human carcinogens. Long-term exposure to these substances can cause various severe diseases (Chen et al. 2018; Masih et al. 2016). Given the health risks of specific VOCs, clarify the chemical composition and source profiles of anthropogenic VOCs is of great significance.

Apart from the characteristics and sources of VOCs, it is also important to evaluate the influence of different VOC species on O₃ production. The ability of VOCs to generate O₃ depends greatly on their chemical reactivity (Ran et al. 2009). Currently, hydroxyl radical (OH) reactivity method and ozone formation potential (OFP) estimation have been widely applied to investigate the chemical reactivity and the relative contribution of individual VOCs to O₃ pollution, especially in highly industrialized regions such as North China Plain (NCP), Yangtze River Delta (YRD) and Pearl River Delta (PRD) (He et al. 2019; Liu et al. 2020a; Ou et al. 2015; Xu et al. 2017). These reactivity-based approaches

provide technical support for the prevention of O₃ pollution. However, research on VOC characteristics, emissions and their contributions to O₃ formation in the heavy industrial urban agglomerations in Northeast China is extremely limited.

Jilin Province is a major agricultural province in the center of northeastern China. Large-scale crop production leads to a huge amount of straw, which is basically disposed of by open burning. Moreover, due to its cold and snowy climate, Jilin province experiences a prolonged heating season lasting nearly six months, resulting in a high demand for coal consumption. Consequently, air pollution from extensive straw and fuel combustion is a frequent issue (Chen et al. 2017, 2022; Li et al. 2020; Lu et al. 2021). Jilin Province is also a typical representative of old industrial bases in China, characterized by an unbalanced industrial structure and uneven distribution. Recently, owing to the industrial transformation and upgrading processes, many new and high-tech industries have emerged in Jilin Province. Industrial emissions are recognized as the primary anthropogenic source of VOCs in China (Li et al. 2019). However, the most recent research on Jilin Province dates back more than a decade (Barletta et al. 2005; Liu et al. 2000; Xue et al. 2011). Therefore, there is an urgent need to update our understanding of pollution levels, spatiotemporal characteristics, source contributions, and chemical reactivity of VOCs in Jilin Province.

In this study, a comprehensive mobile VOC monitoring was conducted in the Central Urban Agglomerations of Jilin Province (JCUA) during the period from 13 to 25 November, 2020. As the most economically dynamic and densely populated region in Jilin Province, this city cluster has over 60% of the industrial enterprises and produces 73% of the gross domestic product (GDP), which is a reasonable representative of the urban ambient atmosphere of Jilin Province. In addition, a high-resolution emission inventory of anthropogenic VOCs was developed to help understand and analyze the pollution status. The objectives of this study are (1) to determine the characteristics and sources of VOCs in JCUA; (2) to investigate the spatiotemporal variation of VOCs in Changchun, the capital of Jilin province; (3) to assess the O₃ formation potentials (OFPs) and reveal major contributors that leads to O₃ pollution; and (4) to develop effective strategies towards controlling and mitigating VOC emissions.

Methodology

Sampling sites and time

The mobile observation was conducted in the Central Urban Agglomerations of Jilin Province (JCUA), which is located in northeastern China with longitudes ranging from 124°36' E to 126°55' E and latitudes ranging from 42°90' N to 43°84' N (Fig. 1). JCUA is a cluster of four cities including Changchun (CC), Jilin (JL), Siping (SP), and Liaoyuan (LY). Changchun, capital city of Jilin Province, takes automobiles as its pillar industry and promotes the development of new technology industries such as biopharmaceuticals and optoelectronics. Jilin City has intensive chemical and petrochemical industries. Siping and Liaoyuan are dominated by traditional agriculture but fewer industry activities.

To further investigate the spatial distribution of VOCs between different functional areas, four sites in CC were selected based on their distinctive industrial structure and social activities. Automobile Economic and Technology Development Zone (AETD), as implied by its name, is a cluster of automobile and related industries located in the southwestern part of CC. Unlike AETD, representative of old industry, North Lake Technology Development Zone (NLTD) mainly specializes in the business of new energy, novel materials, biomedicines, and high-end equipment manufacturing, which is in the northeastern suburbs of the city. In contrast, Chaoyang District (CYD) is a central business district located in the central residential area, and Nong'an County (NAC) is a representative agricultural

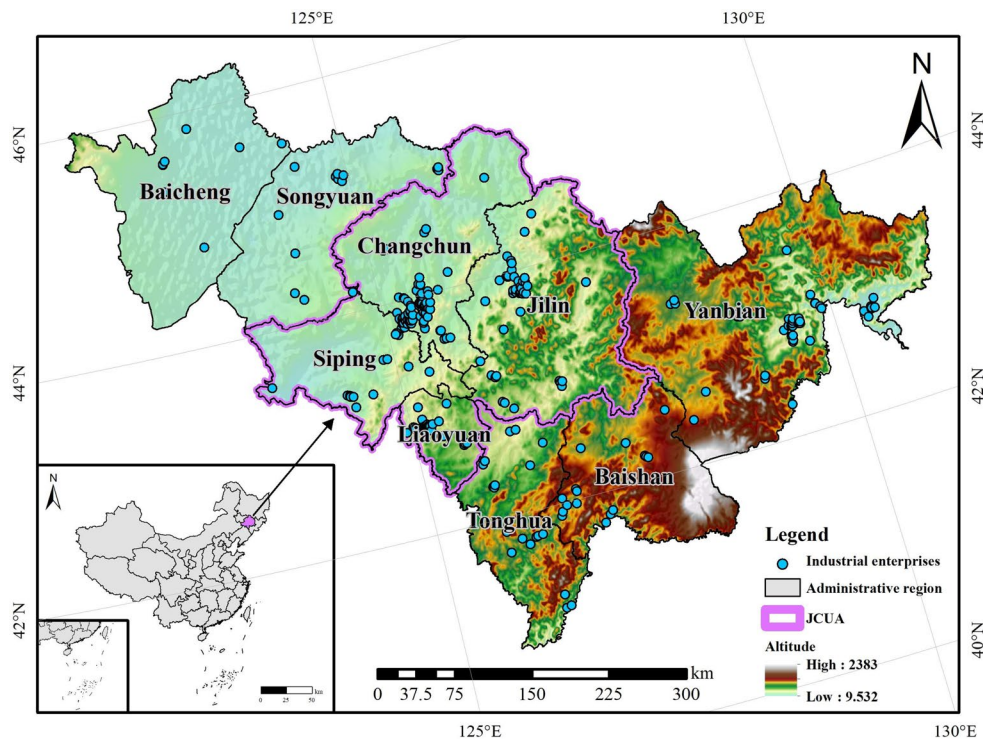
county located in a rural area. Accurate geographical locations of these four areas are presented in Fig. S1. In general, JCUA is an ideal region to investigate the impact of VOCs on local and regional air pollution.

The sampling periods in CC, JL, SP, and LY were 12–15, 16–17, 22–23, and 24–25 November 2020 respectively, covering all major areas within each city. The whole sampling period was in heating season, with temperature varying between -9.0 and 12.4 °C, and relative humidity in the range of 61.2–74.7%. The specific monitoring area, time, and meteorological parameters of each day, the daily average concentrations of total VOCs, trace gases, and particulate matter during the sample period are summarized in detail in Table S1.

Mobile monitoring and instrumentation

Mobile monitoring is an efficient tool for fine and extensive data acquisition in a wide range of study regions. Recently, mobile sampling methods are increasingly used in building spatial maps of pollutant concentrations, and quantifying on-road or chemical industrial park pollutions (Huang et al. 2022; Li et al. 2016; Wen et al. 2019; Zhou et al. 2021). Compared to fixed site measurements, mobile monitoring offers pollution profiles at a high spatial resolution and enables the determination of specific source impacts. In this study, on-road measurements were performed by a specialized vehicle that was equipped with a series of online instruments, a meteorological sensor, a global positioning system (GPS) receiver, and an uninterrupted power supply

Fig. 1 Geographic location and topography of Jilin Province. The blue circles indicate industrial enterprises and the solid violet lines frame the scope of JCUA



(UPS) that supported all the equipment operations (Liang et al. 2020). To comprehensively investigate the VOC pollution profile in JCUA, the vehicle cruised along the arterial roads of each city at a speed ranging from 20 to 30 km/h. The air inlet is positioned at least 0.2 m above the roof of the vehicle to avoid interference from vehicle exhausts. The observation time as well as the precise locations (longitude and latitude) were simultaneously recorded.

VOCs concentrations were measured online using a commercial single photon ionization time-of-flight mass spectrometer (SPI-MS 2000, Guangzhou Hexin Instrument Co., Ltd., China). SPI-TOF-MS was widely used in the real-time monitoring of VOCs due to its high sensitivity and high accuracy (Gao et al. 2013; Liu et al. 2020b; Zhao et al. 2020). The SPI-MS 2000 used in this mobile navigation consists of three main components: the membrane inlet system, ionization system, and mass spectrometry system. Gas samples are first passed through the polydimethylsiloxane membrane (PDMS), and then enter the ionization system. A soft ionization of the gas is carried out by a vacuum ultraviolet light with an energy of 10.6 eV. Subsequently, the ions are transmitted into the vertical acceleration reflective time-of-flight mass analyzer, allowing for qualitative and quantitative analysis of different species. Finally, the electrical signal is gathered by the data acquisition system and stored in the computer.

In this study, 56 VOCs with relatively accurate quantification were sorted into eight classes based on their functional groups: alkanes, alkenes, halocarbons, oxygenated VOCs (OVOCs), amines, aromatics, sulfides, and others (due to the presence of indistinguishable isomers, e.g., acetone and butane). The mass concentrations of O₃, NO_x, SO₂, CO, PM_{1.0}, PM_{2.5}, and PM₁₀ were measured by a portable detector (Sniffer 4D, Shenzhen Soarability Technology Co., Ltd., China). Temperature and relative humidity were simultaneously recorded.

Quality control/quality assurance

The VOC data acquisition during the cruise observation followed rigorous quality assurance and quality control (QA/QC) procedures. Calibration was performed at five different concentrations by the standard gases including Photochemical Assessment Monitoring Stations (PAMS), TO-14, and organic sulfur compounds mixtures. The method detection limits (MDLs), correlation coefficients (R²), and calibration standard curves of each identified VOC are presented in Table S2. Calibration was conducted every other day to ensure the stability and accuracy of the system, and the relative standard deviation (RSD) for all measured compounds was lower than 10%.

Emission inventory

The emission inventory of anthropogenic VOCs in JCUA was developed using the bottom-up method based on the local annual activities in 2020 and source-specific emission factors. With reference to *Technical Manual for the Compilation of City-level Air pollutants Emission Inventory*, local emission characteristic, and previous lectures (Simayi et al. 2020; Yin et al. 2015), the sources of emissions were classified into seven major categories, including fossil fuel combustion, industrial process, traffic exhaust, solvent utilization, biomass burning, storage and transportation, as well as other sources (cooking). Activity data were obtained through environmental statistics, city-level statistical yearbooks, field investigation, department requests, remote sensing feature extraction and Point of Information (POI) searches. Details of the calculation methodologies for emission estimation were explained in our previous study (Zhang et al. 2021).

Chemical reactivity of VOCs

The OH loss rate (L_{OH}) and ozone formation potential (OFP) were calculated to explore the chemical reactivities of individual VOC compounds. Ozone formation potential (OFP) is extensively adopted to identify the relative importance of VOC species to O₃ formation. In this study, the OFP of different VOC species was estimated by the maximum incremental reactivity (MIR) coefficient method via Eq. (1):

$$\text{OFP}_i = [\text{VOC}]_i \times \text{MIR}_i \quad (1)$$

where OFP_{*i*} represents the ozone formation potential of individual VOC *i*, [VOC]_{*i*} is the average concentration of VOC *i*, and MIR_{*i*} is the O₃ formation coefficient for individual VOC *i*, which is defined by Carter (Carter 2010). It should be noted that species with isomers were excluded from the OFP analysis due to significant differences in MIR values.

L_{OH} is generally used to characterize the chemical reactivity of VOC species and is calculated by the following equation:

$$L_{\text{OH},i} = [\text{VOC}]_i \times k_{\text{OH},i} \quad (2)$$

where L_{OH,*i*} is the OH radical loss rate of VOC *i* (s⁻¹), [VOC]_{*i*} is the concentration of VOC *i* (molecule⁻¹·cm³), and k_{OH,*i*} is the rate constant of OH radicals with individual VOC *i* (molecule⁻¹·cm³·s⁻¹), which is originated from a previous study on reactions of VOCs with OH radicals (Atkinson and Arey 2003).

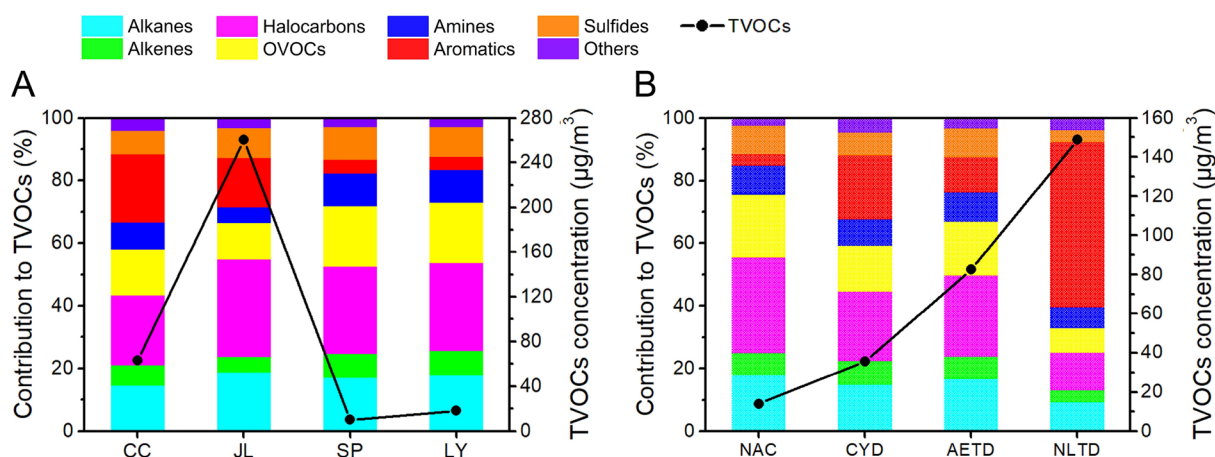


Fig. 2 Contributions of different VOC groups and average TVOC concentrations (black dots) (A) at each site in JCUA and (B) at NAC, CYD, AETD and NLTD

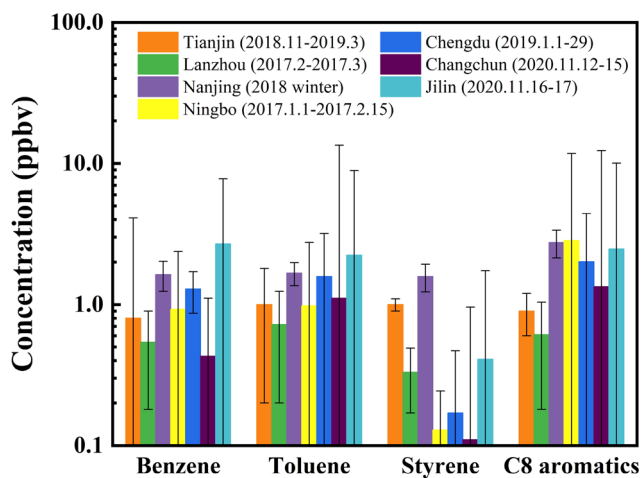


Fig. 3 Comparison of aromatics mixing ratios in JCUA and other cities in China (The unit of VOC species in this study was transformed into ppbv instead of $\mu\text{g}/\text{m}^3$). Tianjin (Gu et al. 2020), Lanzhou (Zhou et al. 2019), Nanjing (Mozaffar et al. 2021), Ningbo (Yang et al. 2023), Chengdu (Xiong et al. 2021)

Results and discussion

Characteristics of VOCs at JCUA

The average concentrations and standard deviations of 56 VOC species measured at JCUA were summarized in Table S2. JL was the most polluted region, with a total VOC (TVOC) concentration of $260.39 \pm 855.76 \mu\text{g}/\text{m}^3$, followed by CC ($63.38 \pm 127.03 \mu\text{g}/\text{m}^3$), LY ($10.12 \pm 17.48 \mu\text{g}/\text{m}^3$), and SP ($18.06 \pm 17.17 \mu\text{g}/\text{m}^3$). It can be seen in Fig. 2A that halocarbons were dominant at JCUA, accounting for 22.4–31.1% of the TVOC concentration at four cities. The concentrations of different VOC classes were similar at SP and LY, where the contributions of different VOC groups to TVOCs were in the order of halocarbons (27.9% and

28.0%), OVOCs (19.3%), alkanes (17.0% and 18.0%), amines (10.5%), sulfides (10.5% and 9.5%), alkenes (7.8% and 7.6%), aromatics (4.3% and 4.2%), and others (2.8%). Varied from the pollution pattern in SP and LY, relatively higher concentrations of aromatics were observed at CC and JL. The aromatics VOC group was the second-largest contributor to TVOCs in CC and JL after halocarbons, accounting for 21.9% and 15.9% of the TVOCs, respectively. The high TVOCs level and high proportion of aromatics imply the great influence of anthropogenic sources on VOC emissions in CC and JL, as compared to SP and LY (Simayi et al. 2020).

Higher concentrations of aromatics are considered to result from stronger primary emissions from industrial processes and vehicle exhaust (Dumanoglu et al. 2014; Lyu et al. 2020; Yang et al. 2023). Figure 3 compares the mixing ratios of aromatics in CC and JL with those of other cities in China during winter seasons. CC exhibits the lowest levels of benzene and styrene among all cities. However, toluene and C8 aromatics (xylene and ethyl benzene) were the most abundant components, accounting for up to 76.7% of the total aromatic concentration in CC. The concentrations of toluene and C8 aromatics are higher than those recorded in Tianjin (Gu et al. 2020) and Lanzhou (Zhou et al. 2019), two of the largest industrial cities. This result may be attributable to the use of solvents, as toluene and C8 aromatics are frequently connected to painting, printing, solvent evaporation, and are also closely related to industrial processes (Yuan et al. 2010). JL is the most important chemical-producing city in Jilin Province, industrial and petrochemical emissions seem to have a substantial impact on the regional air quality in JL (Fang et al. 2020; Shang et al. 2022). The levels of aromatics in JL are relatively high compared to other cities, although the impact of traffic sources is minimal. In particular, the concentrations of benzene (2.69 ± 5.09 ppbv) and

toluene (2.24 ± 6.67 ppbv) are 1.7 and 1.3 times higher than those measured in an industrial area in Nanjing (Mozaffar et al. 2021), respectively. Benzene and toluene are widely used as solvents for organic compounds, cleaning equipment, and other industrial processes (Ling et al. 2011; Liu et al. 2008). The highest level of these two species suggested the relative serious VOC pollution from industrial emissions in JL. Since BTEX and styrene are all listed as hazardous air pollutants by the US Environmental Protection Agency due to their mutagenic and carcinogenic effects on human health, proper rules and standards should be formulated for reducing the emission of these pollutants in JUCA.

The spatial variations in VOC emissions in CC are shown in Fig. 2B and Table S4. As expected, VOCs pollution in NAC was the lowest (13.91 ± 7.97 $\mu\text{g}/\text{m}^3$) because of the little influence of industrial activities in this region. Therefore, NAC could be regarded as a background area of CC. NLTD exhibited the highest concentration of VOCs at 148.76 ± 352.23 $\mu\text{g}/\text{m}^3$, followed by AETD and CYD with concentrations of 82.54 ± 80.72 and 35.53 ± 37.23 $\mu\text{g}/\text{m}^3$, respectively. Different features of VOCs distributions could be recognized between different functional areas. Specifically, concentrations of all VOC groups were higher in industrial areas (AETD and NLTD) with numerous factories, followed by urban area (CYD) with dynamic human activities than that in rural area (NAC), which is consistent with the results of previous studies (Li et al. 2018; Luo et al. 2020; Simayi et al. 2020). Aromatics concentration was the highest at NLTD among the four areas, even account for 52.5% of the VOCs concentration. In contrast, a different pollution profile was observed at AETD, where halocarbons were the dominant VOC group and the concentration of OVOCs was also relatively higher than that in NLTD. This distinct observation in two development zones indicates the great impact of industry type and process on VOC emission characteristics. The local source profiles of VOCs in Changchun city showed that aromatics are the dominant pollutants in automobile manufacturing, wood processing and furniture manufacturing, packaging and printing industries (Shang et al. 2022). AETD of CC has gathered automobile manufacturing, machinery manufacturing, and packaging industries, which are significant sources of local halocarbons and OVOCs. Since the concentrations of aromatics and halocarbons are important to assess human risk (Na et al. 2001), aromatics at NLTD and halocarbons at AETD deserve more attention to achieve VOCs abatement in CC. The observation suggests the necessary to formulate targeted plans for the prevention and control of VOCs pollution in different areas of the city.

VOCs emission inventory

In this research, as the mobile campaign was conducted along the main roads in the urban area during the winter season, biogenic VOCs play a minor role in the total VOC emissions. Establishing a high-resolution anthropogenic VOCs emission inventory and comparing it with our measurement can provide comprehensive insights in the characteristics, spatiotemporal variations and source structures of local VOC emissions. The county-level emission inventory of anthropogenic VOCs in Jilin Province in 2020 was depicted in Fig. 4. As can be seen, the spatial distribution of VOCs measured during the mobile navigation is highly correlated to that of emission inventory. Among all the cities, the highest VOC emission was observed in Jilin city (248.90 kt), followed by Tonghua (129.01 kt), Changchun (112.51 kt), Siping (99.81 kt), and Liaoyuan (53.75 kt). The other cities in the province had relatively low VOC emissions due to their smaller population and industries. JUCA was the dominant emission area, contributing 71.14% of the VOC emissions in Jilin Province, as a result of the significant concentration of industrial enterprises in this region (Fig. 1).

The contribution of anthropogenic sources to VOC emissions in Jilin Province in 2020 are summarized in Fig. 5. The estimated total emissions in Jilin Province were 723.88 kt, with industrial processes being the largest contributor, accounting for up to 70.6% of total emissions. Emissions from biomass burning were also noticeable and made 17.9% contribution to anthropogenic VOCs. Traffic exhaust, stationary fossil fuel combustion, solvent utilization, storage and transportation, and cooking accounted for 4.6%, 3.5%, 2.7%, 0.5%, and 0.1% of the total emissions, respectively. Among industrial processes, petrochemical and related industries were responsible for the majority of VOC emissions, accounting for 65.9% of the total. These findings are consistent with the mobile observation that the VOC emissions within JUCA are dominated by industrial processes.

OFF and L_{OH} of VOCs

The OFF of measured VOCs at CC, JL, SP, and LY were 137.61, 396.07, 13.21 and 23.72 $\mu\text{g}/\text{m}^3$, respectively. The OFFs in CC and JL were one order of magnitude higher than those in SP and LY, suggesting a serious photochemical pollution caused by high levels of VOCs in CC and JL. As shown in Fig. 6A and Table S5, the contribution of different VOC classes to OFFs in SP and LY was highly similar. Alkenes played a dominant role in O_3 formation and accounted for half of the total OFFs in SP and LY, followed by OVOCs accounting for 13.7% and 13.1% of OFFs in SP and LY, respectively. Halocarbons made relatively small contribution to O_3 formation, though they displayed the

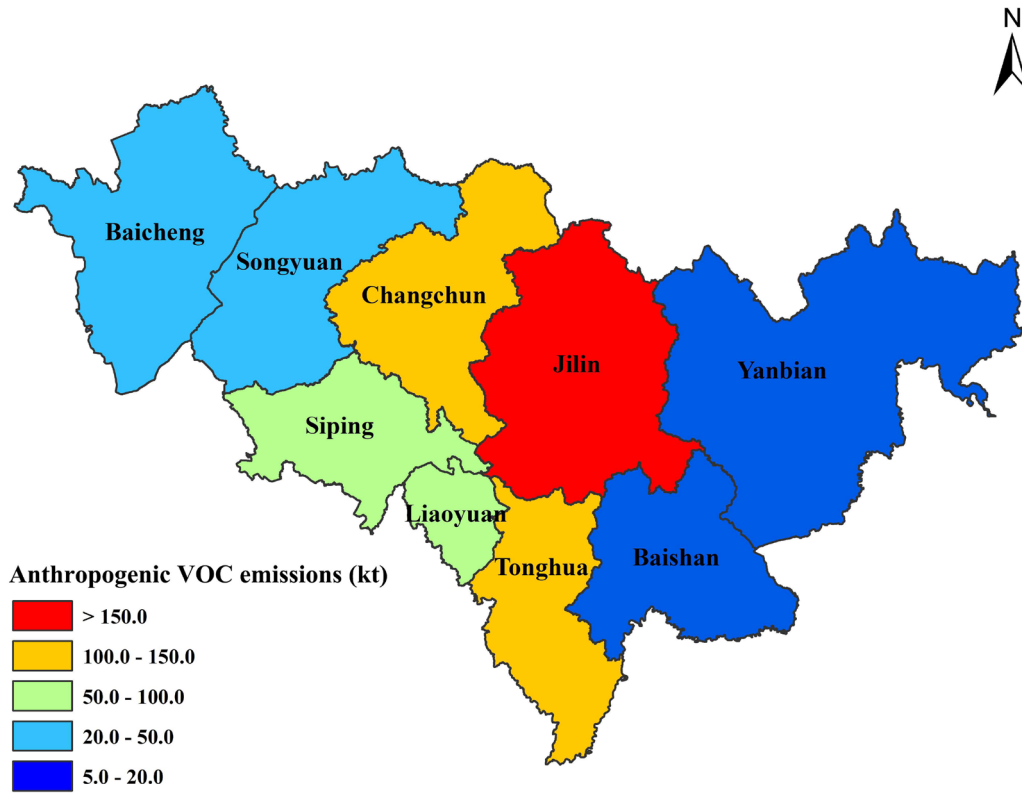
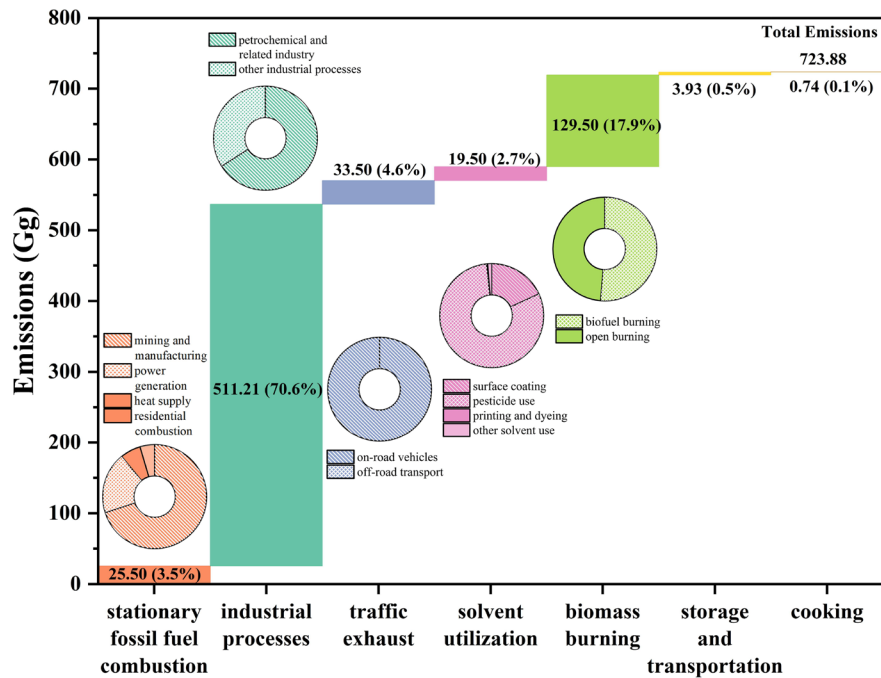


Fig. 4 Spatial variation of anthropogenic VOC emissions in Jilin Province for the year of 2020

Fig. 5 Source contributions of anthropogenic VOCs in Jilin Province for the year of 2020



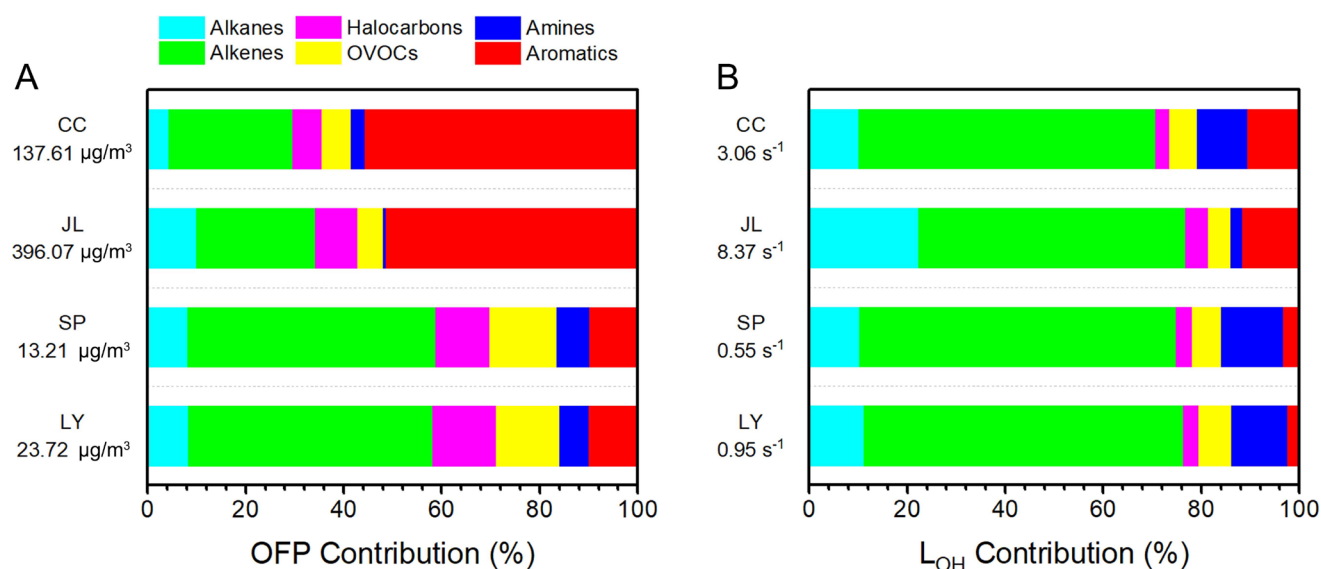


Fig. 6 Contributions of six VOC groups to (A) OFP and (B) L_{OH} at different sites in JCUA

largest TVOC occupation. The top 10 VOC species contributing the most to OFP along with their contributions to VOCs are shown in Fig. 7. Butene was the largest contributor to OFPs in both SP (14.8%) and LY (14.2%), which was likely released from organic raw chemicals manufacturing (Guo et al. 2007). The contribution of VOC classes to OFPs in CC and JL showed obvious variation compared to that in SP and LY. Owing to the relatively high proportion in TVOCs, aromatics significantly affected the O_3 formation at CC and JL, accounting for half of the OFPs (55.6% and 51.3%, respectively). C8 aromatics were the largest-contributing species to OFPs in CC and JL, with contributions of 34.4% and 22.6%, respectively (Fig. 7A and B). Additionally, toluene and trimethyl benzene were also important contributing aromatic species, making up 7.1–17.0% of the OFP. Alkenes were the second-largest contributing VOC class, making up 25.4% and 24.4% of the OFP in CC and JL, respectively. It was observed that species with large emissions may not have the same great impact on O_3 production. For instance, nonane was the second-largest contributor to VOC emission in JL, whose mixing ratio (6.8%) was the sum of C8 aromatics (4.4%) and trimethyl benzene (2.4%). However, its low reactivity in photochemical reaction and secondary transformation resulted in a relatively lower OFP.

As shown in Fig. 6B, the calculated L_{OH} in four cities were 3.06 s^{-1} (CC), 8.37 s^{-1} (JL), 0.55 s^{-1} (SP), and 0.95 s^{-1} (LY). The OH reactivity of VOCs came mainly from alkenes, with the highest contribution ranging from 54.46 to 65.18% in JCUA (Table S6). Regarding the high-contributing species, a consistent trend was observed, where all alkene species including butene, pentene, isoprene, 1,3-butadiene, and cyclohexene were the greatest contributors to L_{OH} in JCUA. These species were also among the

top 10 VOCs contributing the most to OFP. In general, due to the high chemical reactivity and contribution to O_3 formation, controlling the emissions of aromatics and alkenes preferentially would be effective in reducing O_3 pollution in JCUA.

Comparisons of air pollutants

Fig. 8 shows the average concentrations of O_3 and NO_x at JCUA during the navigation detection. Whereas the concentration of O_3 precursors (VOCs and NO_x) was relatively low in LY, the highest O_3 level was observed there. Indeed, the level of O_3 were influenced by a combination of factors, including the emission strength of precursors, photochemical reaction processes, and meteorological conditions (Hui et al. 2020; Liu et al. 2020a). The relatively elevated levels of O_3 in LY were suspected to be caused by favorable meteorological conditions facilitated both the photochemical reactions and the accumulation of pollutants to a certain extent. In contrast to the result in LY, a high concentration of NO_x was observed in SP but without a significant increase in of O_3 concentration. It has been demonstrated that VOCs and NO_x have a nonlinear relationship with O_3 formation (Atkinson 2000). A low concentration of NO_x can promote the formation of O_3 , whereas O_3 will be titrated by NO under high- NO_x conditions (Wang et al. 2017). The concentration of O_3 and NO_x varied widely in CC at $0\text{--}170.40 \text{ µg/m}^3$ and $0\text{--}97.80 \text{ µg/m}^3$, respectively. These bigger fluctuations in gaseous pollutants concentration suggests large spatial variations of air quality and pollution characteristic in the city, which was also demonstrated by Fig. 2B. Furthermore, despite the highest VOCs concentration, O_3 levels were comparatively low in JL. Therefore, due to the complicated

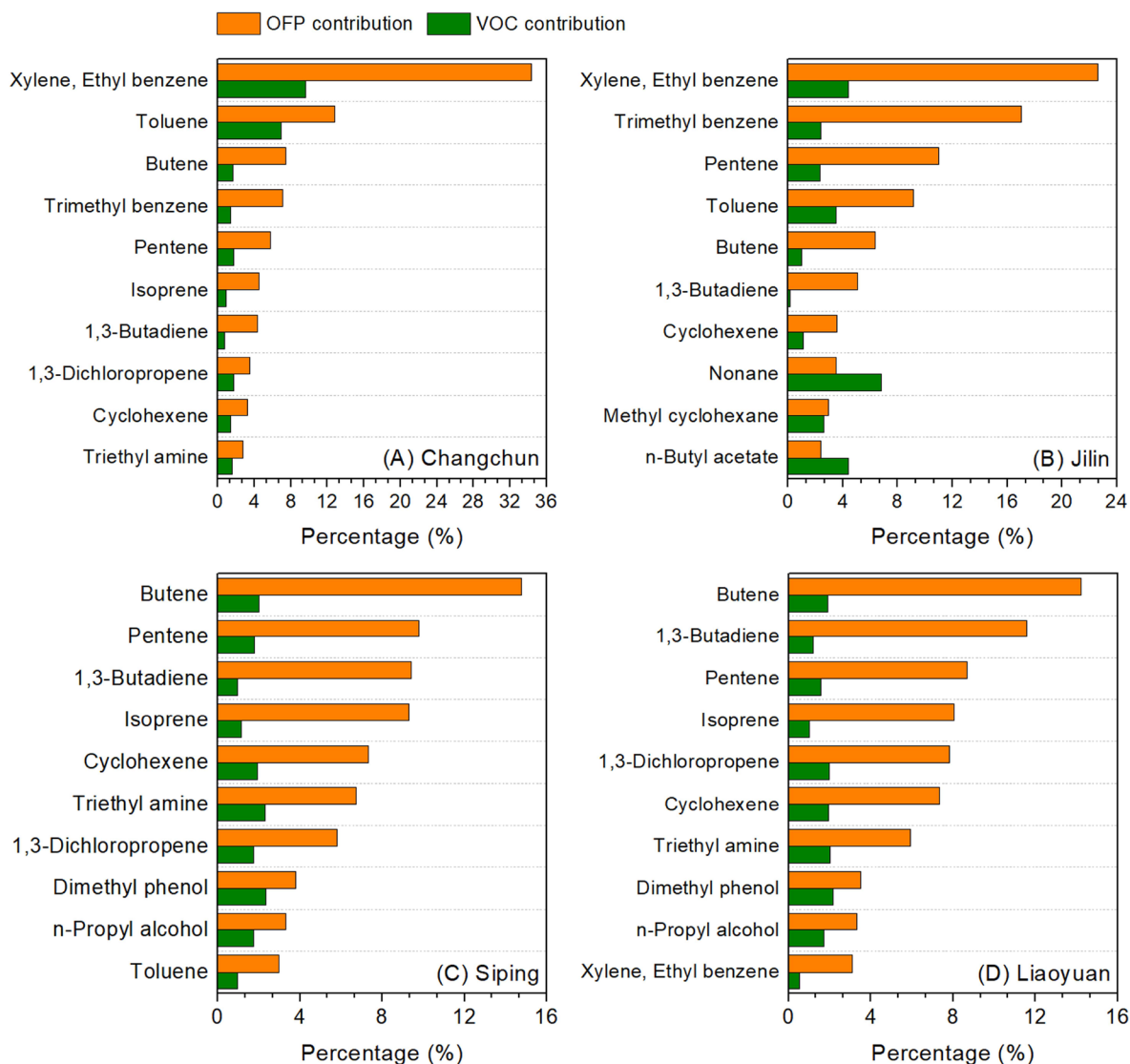
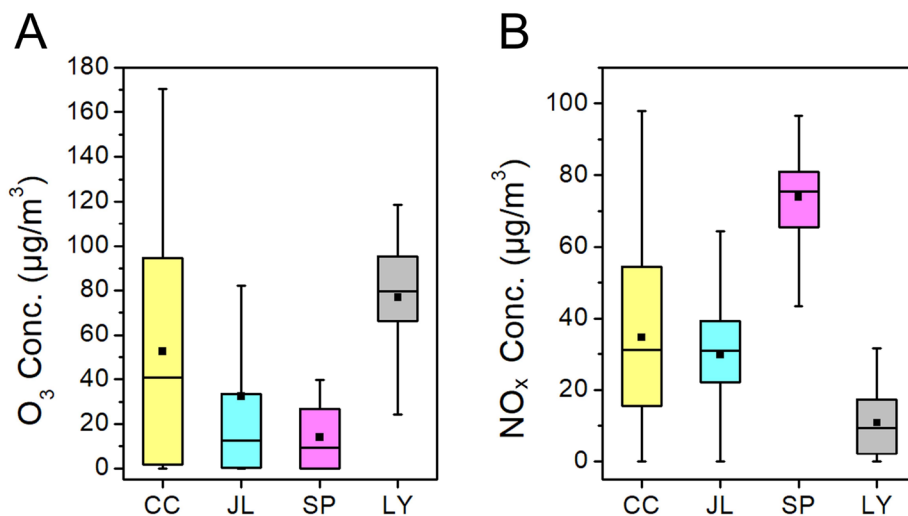


Fig. 7 Key contributing species to OFP and VOCs emissions in JCUA

Fig. 8 Concentration distributions of (A) O₃ and (B) NO_x at each site in JCUA. The line in the box represents the median, and the solid squares represent the arithmetic average. The whiskers and the box represent the 5–95th percentiles and the 25–75th percentiles, respectively



chemistry between NO_x and VOCs, it is a pivotal task to identify the O_3 formation regime in future research for science-based regulation of O_3 pollution

Conclusion

This study presents the pollution profile of VOCs in JCUA, a heavily industrialized urban agglomeration in Northeast China, by focusing on the concentration levels, compositions, and sources of ambient VOCs and their chemical reactivity for O_3 formation. Unlike other air pollution hotspots in China, halocarbons were the most abundant VOC group in JCUA. Additionally, a relatively high proportion of aromatics was observed in CC and JL compared to that in SP and LY. The monitoring results indicated that high concentrations of aromatics were mainly occurred in the industrial areas of CC. Petrochemical emissions were identified as the leading cause of high VOC levels in JL. In terms of the chemical reactivity of VOCs, aromatics and alkenes contributed the most in JCUA.

Based on the observational data and emission inventory, more attention should be paid to industrial-related and petrochemical emissions when considering VOC control strategies in JCUA. It is highly recommended to prioritize the control of aromatics, especially BTEX, that come from solvent utilization during industrial processes due to their large emissions, high contributions to O_3 formation, and adverse effects on human health. Furthermore, owing to the different emission characteristics and source structures of VOCs in different areas, targeted real-time measures should be conducted in specific areas of the city to provide local source profiles for the refined prevention and control of regional VOC pollution.

It is worth mentioning that the results above represent the characteristics of VOC pollution during wintertime in JCUA, based on mobile monitoring for only two weeks. Moreover, due to the lack of synchronous meteorological data and gaseous pollutants concentrations during this cruise observation, as well as the lack of long-term real-time monitoring at stationary sites in this region, it may cause uncertainty for a thorough understanding of the spatiotemporal variations and abatement mechanisms of VOCs. Therefore, multi-technical approach for high time-resolution observation and analysis of VOC emissions is urgently needed in future research.

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Data availability All data generated or analyzed during this study are included in this published article and its supplementary information files. Any of the sections are relevant to manuscript and applicable for the section.

Declarations

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