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Variations, sources, and effects on ozone formation of VOCs during ozone episodes in 13 cities in China

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In recent years, ozone (O_3) pollution has worsened in China and contributes frequently to air pollution problems. To support the implementation of coordinated control for ozone and fine particulate matter, it is essential to study the chemical compositions and sources of volatile organic compounds (VOCs), which are the crucial precursor of both ozone and fine particulate matter. In this study, 117 volatile organic compounds were monitored in 13 cities in Beijing-Tianjin-Hebei Urban Agglomeration and Fenwei plain. Concentrations of total volatile organic compounds ranged from 42 to 279 μg/m^3 during the monitoring episode. In all 13 cities, alkanes, halogenated hydrocarbons, aromatics and oxygenated volatile organic compounds (OVOCs) were the dominant volatile organic compounds. Contributions of alkanes, halogenated hydrocarbons, aromatics and oxygenated volatile organic compounds to total ozone formation potential (OFP) were 21.7%–32.6%, 21.0%–27.9%, 24.3%–50.8% and 28.6%–52.3%, respectively. Furthermore, the results of source apportionment by positive matrix factorization (PMF) model indicated that solvent usage, gasoline evaporation, vehicle emissions, petrochemical industry and combustion were essential volatile organic compounds sources in 13 cities. Moreover, the sensitivity of ozone production was studied using an Empirical Kinetic Modeling Approach (EKMA) model, and it was found that ozone formation was volatile organic compounds limited in all 13 cities.

KEYWORDS

VOCs, Beijing-Tianjin-Hebei urban agglomeration, Fenwei plain, PMF, EKMA, OFP

Highlights

- VOCs showed significant temporal and spatial variations in 13 cities.
- VOCs were mainly composed of alkanes, halogenated hydrocarbons, aromatics and OVOCs in all 13 cities.

- Aromatics and OVOCs contribute the most to the OFP.
- Solvent usage, gasoline evaporation, vehicle emissions, petrochemical industry and combustion were essential VOC sources in 13 cities.
- Ozone formation was VOCs-limited in all 13 cities.

1 Introduction

After the declaration of Ambient Air Quality Standards (Ministry of Environmental Protection of the People's Republic of China, 2012) in 2012 and the implementation of the Air Pollution Prevention and Control Action Plan (https://www.mee.gov.cn/zcwj/gwywj/201811/t20181129_676555.shtml) in 2013, pollution of PM_{10} and $PM_{2.5}$ have been efficiently controlled. The average annual concentrations in all regions of China demonstrated a significant downward trend (e.g., Ni and Zhu, 2021; Song et al., 2021; Fu et al., 2022; Yu et al., 2022). In contrast, in the last decades, ozone (O_3) concentration keep up the upward trend, and ozone has become a priority pollutant, particularly in summer and autumn in China (e.g., Zhang et al., 2021; Jia et al., 2022; Lin and Guo, 2022). As essential precursors for both ozone and fine particulate matter, the increasing emission of Volatile Organic Compounds (VOCs) was inferred as one of the main causes of high ozone pollution in China (e.g., Yang et al., 2016). Therefore, studying the variations, concentrations, sources of VOCs, and their impact on ozone formation is of great importance.

In China, there are many researches on atmospheric volatile organic compounds in various urban areas. For example, Ding and Jing (2016) monitored 52 kinds of VOCs during summer and the main components of VOCs in Tangshan City were alkanes and aromatic hydrocarbons, alkenes were the most sensitive components of ozone formation potential (OFP) of VOCs. Xu et al. (2020) conducted online monitoring of VOCs in urban Chengdu from June to September 2019. The monitoring results showed that alkanes and halogenated hydrocarbons were the main components of VOCs. Aromatics contributed most to total OFP (42.7%), followed by alkenes (27.4%). Zhao et al. (2021) analyzed the pollution characteristics of atmospheric VOCs in summer and autumn in Liaocheng City. The component content was alkanes > alkynes > aromatics, and the influence of OFP was aromatics > alkynes > alkanes; In particular, toluene had the highest OFP contribution rate. In a similar research, conducted in 2019, Deng et al. (2021) carried out online monitoring of 56 kinds of VOCs in Shishan Town, Foshan City, and the main components of VOCs were alkanes (56.5%) and aromatics (30.1%), and O_3 generation was in the VOCs control area. Aromatics contributed the most to the total OFP (54.6%). Qi et al. (2022) found that the atmospheric VOCs pollution in Zhengzhou during the summer of 2019 and 2020 was dominated by alkanes, aromatics and alkenes, and the total OFP of VOCs were 224.9 and 243.6 μg/m^3, respectively. Another study by Su et al. (2022) assessed the characteristics, compositions, OFP, sources, and health risks of 57 kinds of VOCs during summer 2019 in Taizhou. The result showed that alkanes accounted for the largest proportion of VOCs, and the compound contributing largest (5.5 μg/m^3) to total OFP was ethylene. In general, the composition of VOCs pollutants in China mainly comes from alkanes, aromatics and alkenes, and they are also the main OFP substances. However, most of the research focused on an individual city, while the studies of VOCs on city clusters were limited.

Due to the distribution of China's industrial structure, the north is dominated by heavy industries, while the south is dominated by light industries. Northern China cities suffered from severe air pollution. The average annual mass concentrations of air pollutants were about 4.95%–32.74% higher than those in southern China (e.g., Dong et al., 2020). Particularly, the Beijing-Tianjin-Hebei area (BTH), one of the most air-polluted regions in China, has also been threatened by high ozone pollution in the summertime (e.g., Li, 2018; Lu et al., 2020; http://www.huanjing100.com/p-11368.html).

In order to study the VOCs pollution in Northern China, 13 urban points were set up in the BTH region and Fenwei Plain, including Baoding, Xingtai, Langfang, Tangshan, Anyang, Xinxiang, Jiaozuo, Luoyang, Hebi, Jincheng, Linfen, Yuncheng and Xi'an. The sites span four provinces and basically cover the key industrial cities in the BTH region and Fenwei Plain. We monitored atmospheric concentrations of 117 VOCs, including aldehydes and ketones, halogenated hydrocarbons, alkanes, aromatics, alkenes, OVOCs, alkyne and organic sulfur. Then, the variations, compositions, photochemical properties and sources of VOCs in 13 cities were analyzed. Moreover, the sensitivity of ozone production was analyzed using the EKMA model. This study comprehensively analyzed the characteristics of VOCs pollution in the BTH region, which is of great significance to the development of ozone pollution control strategies in China.

2 Experiments and methods

2.1 Sampling

Ambient air samples were collected in 13 cities from 1 April to 30 September 2020. The locations of 13 sites were illustrated in Figure 1.

117 kinds of VOCs collected were list in Supplementary Table S1. According to the standard method HJ 683-2014(Ministry of Environmental Protection of the People's Republic of China, 2014), 13 aldehydes and ketones were collected with an air sampler (KC-6D, Qingdao Laoshan Electronic Instrument Factory Co. Ltd., China) through cartridges coated with acidified 2,4-Dinitrophenylhydrazine (DNPH) (TupLabs, China) at a flow rate of .5 L/min. A

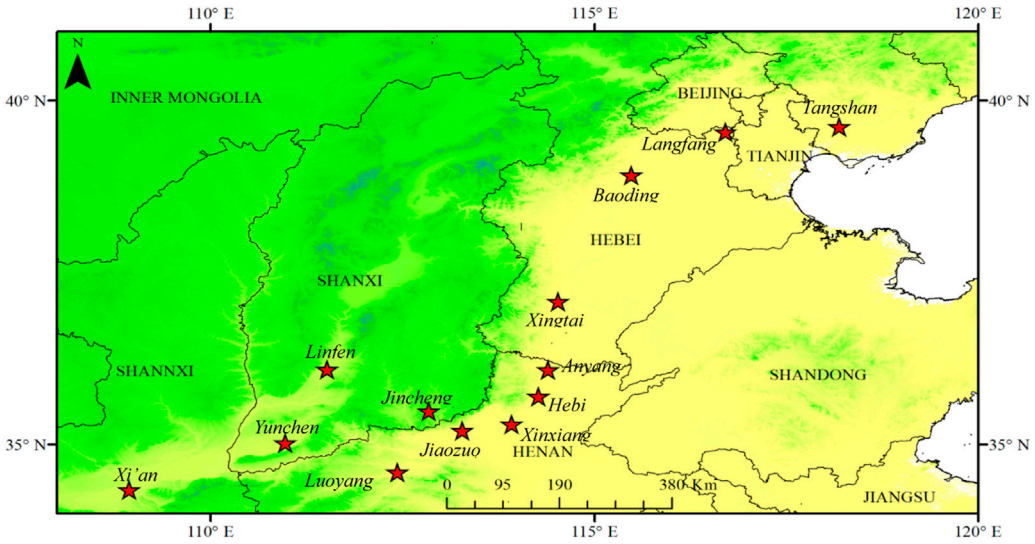

FIGURE 1
The locations of sampling sites in 13 cities.

denuder filled with potassium iodide (KI) was connected to the upstream of the cartridge to eliminate ozone interference. The sampling was from 12:00 p.m. to 15:00 p.m.

The other 104 VOCs were collected for 24 h sample with 3.2 L stainless steel canisters (ENTECH, United States) by connecting to a 24 h constant flow controller, according to the standard method HJ 759-2015 (Ministry of Environmental Protection of the People's Republic of China, 2015).

After sampling, cartridges and canisters were re-sealed and taken to the analysis laboratory. The cartridges were analyzed within 1 week, and the canisters were analyzed in 2 weeks.

2.2 Analysis

Cartridges were analyzed using high-performance liquid chromatography (HPLC) system according to the standard method (HJ 683-2014). 13 aldehydes and ketones were eluted from cartridges with acetonitrile, and analyzed using an HPLC system (Ultimate 3000, Thermo Fisher Scientific Inc., United States). An external standard method with correlation coefficient of calibration curve ≥.995 was used for quantitation. For each batch of samples 10% parallel samples were added and the relative deviation of ≤25% between samples and parallel samples was required.

Detailed analytical method for the other 104 VOCs are reported in the previous study (e.g., Zhang et al., 2019). Briefly, 104 VOCs collected in canisters were quantified by a double column multi dean switching QP2010 Ultra Gas chromatography-Mass spectrometry system (Shimadzu, Japan) coupled with sorbent assisted electronically controlled cryo-focusing unit (CIA-Kori-UNITY, MARKES, United Kingdom). Ethane, ethylene, acetylene, propane, and propylene were measured by flame ionization detector (FID) with external standard method. And mass spectrometry (MS) was used to quantify the other 99 VOCs with an internal standard method. The correlation coefficient of calibration curve ≥.990, and the peak area of internal standard varied below 40%. 10% replicates were added in each sample batch. The duplicate samples showed the bias was less than 30%.

Concentrations of trace gases (such as NO_X, O_3 and CO) were monitored by the national ambient air urban monitoring stations in 13 cities and could be obtained from the China National Environmental Monitoring Centre (http://www.cnemc.cn/). Meteorological data could be obtained from the China Meteorological Data Service Centre (http://data.cma.cn).

2.3 OFP calculation

OFP has been widely used to evaluate the relative ozone-forming capability of VOCs (e.g., Zou et al., 2017). OFP of each VOCs could be calculated using the following equation:

$$OFP_i = MIR_i \times [VOC]_i$$

Where MIR_i represents the maximum incremental reactivity (e.g., Cater, 2010), and $[VOC]_i$ is the mass concentration of the VOC species *i*. Halogenated hydrocarbons in the atmosphere have little effect on ozone formation, so they are usually neglected in the calculation of OFP.

2.4 Source apportionment

VOCs sources are critical to develop control measures for VOCs emission. Ratios of different species of VOCs have been applied to roughly identify sources of VOCs (e.g., Barletta B. et al., 2005; Zhang et al., 2013). However, ratios of different species could only be used to identify a few certain sources and could not provide quantitative contribution of different sources. In this case, receptor models have been applied to identify and quantify VOCs sources, such as principal component analysis (PCA) (e.g., Wang et al., 2019), chemical mass balance (CMB) model (e.g., Liu et al., 2008a) and PMF model (e.g., Zhang et al., 2013). Considering the usage of CMB requires well-known profiles of emission sources, which are hard to obtain in most cases, PMF model has been extensively applied for source apportionment of VOCs in different cities or regions of China, such as Shanghai (e.g., Lin et al., 2019), Guangzhou (e.g., Zhang et al., 2013), Chengdu (e.g., Xu et al., 2020), Zhengzhou (e.g., Qi et al., 2022), Nanjing (e.g., Fan et al., 2021), and Chongqing (e.g., Li et al., 2018). In most of the studies, 19–34 species were selected for PMF analysis, and solutions with 4–8 factors were recognized as the optimum results. Solvent usage, vehicle exhaust, petrochemical industry, LPG/LNG leakage, industrial processes and biogenic emission were frequently identified as main sources of VOCs, although the source profiles of these sources varied among different cities.

The PMF model developed by EPA was a powerful tool to resolve and quantify VOC emission sources. The detailed description of PMF model could be found elsewhere (e.g., Paatero and Tapper, 1994; Paatero, 1997). The study applied PMF 5.0 with a multiple linear engine version 2 (ME-2) to analyze the VOCs sources in 13 cities simultaneously. In order to minimize the uncertainty induced by chemical losses of various VOCs, species with high concentrations or long lifetime were selected preferentially as input for PMF analysis. However, tracers of emission sources were also served as PMF input in order to identify the resolved factor. Accordingly, 21 species (ethylene, acetylene, ethane, propylene, propane, isobutane, n-butane, cis-2-butene, trans-2-butene, isopentane, n-pentane, 2-methylpentane, 3-methylpentane, n-hexane, benzene, n-heptane, toluene, m/p-xylene, ethylbenzene, styrene and o-xylene) in 13 cities were input into the PMF model simultaneously. The PMF solutions were calculated with 3-6 factors, and a solution with five factors were recognized as the most optimum result.

2.5 EKMA model

In urban atmosphere, ozone is formed through photochemical reactions of VOCs and nitrogen oxides (NOx). In order to provide information for development of ozone control strategies, it is essential to study the sensitivity of ozone formation with VOCs and NO_X. Several methods have been applied to investigate the ozone-VOCs-NO_X sensitivity in different studies, such as VOCs/NO_X (e.g., Sillman and He, 2001), HCNO/NO_2 (e.g., Li et al., 2021), air quality model and observation-based model (OBM) (e.g., Lin et al., 2020; Fan et al., 2021). However, the methods such as VOCs/NO_X and HCNO/NO_2 highly simplified the relationship of ozone and its precursors and were only used to preliminarily estimate the ozone formation sensitivity. Ozone formation sensitivity analysis with air quality model requires emission inventories, which could induce large uncertainties and bias to the analysis result. In OBM, the relative incremental reactivity (RIR) could be calculated, which is useful and quantitative parameter to describe the influence of VOCs/NOx to ozone formation. Besides, an isopleth diagram for ozone net production potential could be plotted based on OBM, namely, Empirical Kinetic Modeling Approach (EKMA), which is intuitive to identity whether ozone formation is VOCs or NO_X limited (e.g., Jiang et al., 2018; Fan et al., 2021).

Observation-based model (OBM) and Empirical Kinetic Modeling Approach (EKMA) is widely used to evaluate the relationship between ozone and its precursors by conducting a series of scene simulation experiments (e.g., Santos et al., 2021). Detailed introduction of OBM could be found elsewhere (e.g., Cardelino and Chameides, 1995). In this study, the EKMA isopleth diagrams were obtained with an OBM coupled with a Master Chemical Mechanism (MCMv3.3.1) (e.g., Sauders et al., 2003; Rickard et al., 2015). Decreased or increased concentrations of VOCs and NOx were applied as the model input. At the same time, the averaged photolysis frequencies, temperature, pressure, and the averaged daytime values of other trace gases (i.e., SO_2, CO, and NOx) were used as constraints. The campaign averaged NOx, and VOCs speciation was selected as the base case. The ozone production rate was calculated along with scaling the concentration of NOx and VOCs from 10% to 300% compared with their base values. By interpolating the results, a smooth contour diagram was obtained, showing the relationship between the daily maximum ozone production rate and relative changes of in NOx and VOCs.

3 Results and discussion

3.1 Temporal and spatial variations of total VOCs

The total volatile organic compounds (TVOCs) were obtained by total concentrations of all 117 VOCs to characterize the pollution degree of VOCs in different cities. Figure 2 shows the variations of daily TVOCs in 13 cities during the whole sampling period.

The result demonstrated the significant daily variation of TVOCs concentration in all 13 cities. The highest TVOCs concentration (279 μg/m^3) was found on June 27 in Hebi city, while the lowest TVOCs concentration (42 μg/m^3) was observed

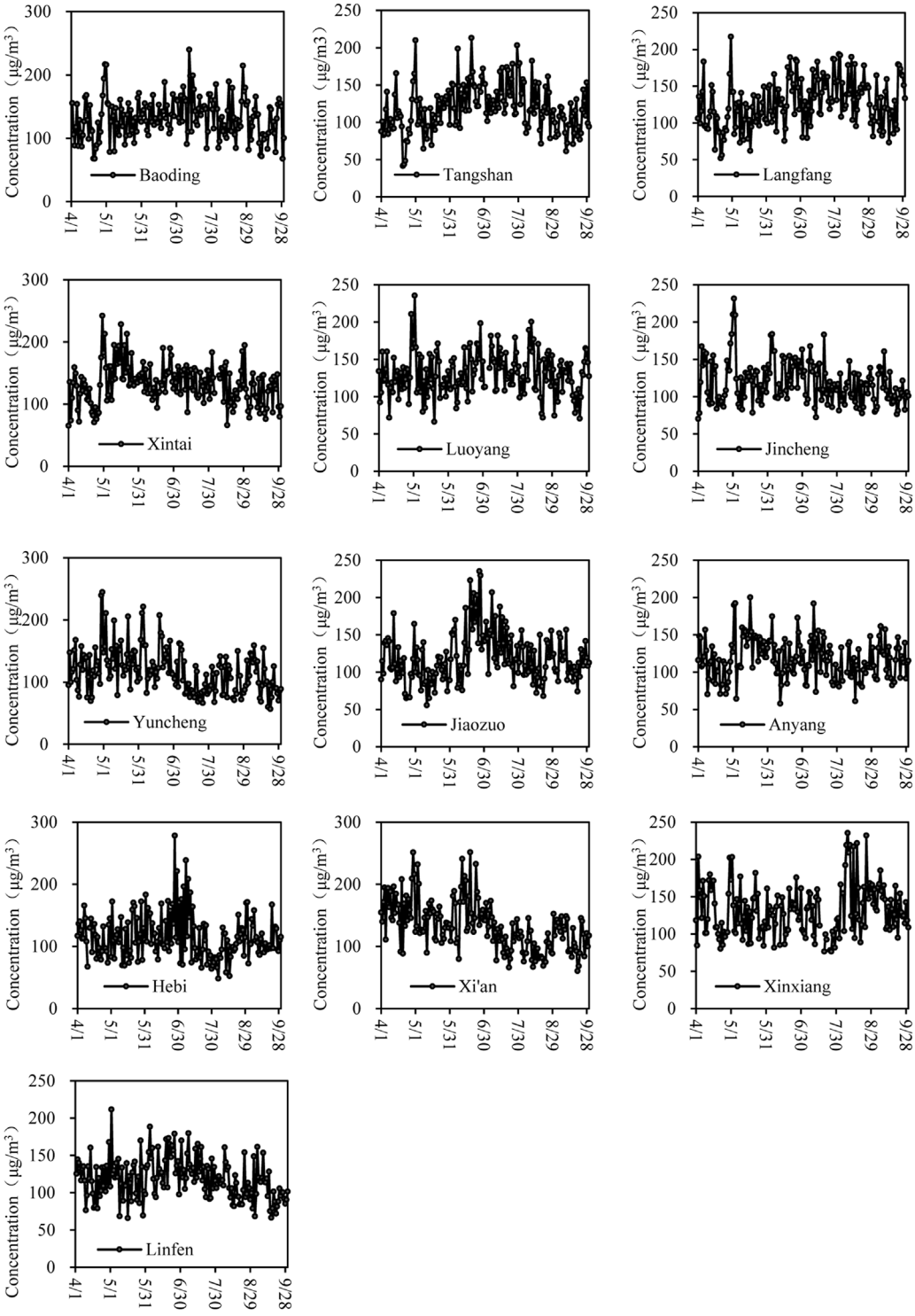

FIGURE 2
Daily variations of TVOC in 13 cities.

on 20 April in Tangshan city. Notably, higher spikes in TVOCs concentration (TVOCs>200 μg/m^3) were occasionally found in each city. The TVOCs concentration approximately increased from April to June or July, then decreased. However, the temporal trend of TVOCs varied among different cities. The highest monthly average TVOCs concentration was possibly

found in June and July, when the high temperature could bring high VOC emissions from certain sources, such as solvent usage. However, for Xingtai and Anyang, the monthly average TVOCs concentration was highest in May. In Langfang and Xinxiang, VOCs pollution was most severe in August. In Xi'an, the monthly average TVOCs concentration reached 166 μg/m^3 in April, higher than any other month. In most cities, the lowest monthly average TVOCs concentration could be noticed in April, May, August, and September, except in Yuncheng, where the monthly average TVOCs concentration was lowest in July. The different pattern of VOC temporal variation can be partly attributed to geographical locations and meteorological factors. Except for Xi'an, Yuncheng, Jincheng and Linfen, the other nine cities are scattered in North China Plain, where air pollutants are easy to transport and become even among cities, but the four cities mentioned above are surrounded by mountains such as Taihang, Lvliang and Qinling Mountain, which is not good for atmospheric diffusion.

Xi'an suffered the most severe VOCs pollution during the whole sampling period compared to the other 12 cities. The average concentration of TVOCs over the entire sampling period was lowest in Hebi. From April to September, the most VOCs polluted city in each month was Xi'an, Xingtai, Baoding, Luoyang, Xinxiang, and Langfang. In contrast, the lowest monthly average concentration of TVOCs was found in Hebi, Anyang, Jiaozuo, Jincheng, Yuncheng, Linfen and Tangshan. The VOCs pollution level may correlate to the city's size of economy or industrial emissions, among 13 cities Xi'an ranks 1 in terms of Gross Domestic Product (GDP) of RMB 1,069 billion, while Hebi ranks last with GDP of RMB 106.5 billion in 2021 (National Bureau of Statics, 2022, 2022-02).

The results showed that TVOCs showed significant temporal and spatial variations in 13 cities during the sampling period. The abundances of VOCs in atmosphere could be influenced by many crucial factors, such as temperature, wind speed, photochemical reaction, and differences in local emission sources. Thus, continuous monitoring is needed in each city to further study the reasons causing the temporal and spatial variations of VOCs.

3.2 Compositions of VOCs

Concentrations of different VOCs groups in each city are listed in Table 1. In this study, the monitored 117 VOCs in 13 cities in the BTH region were divided into alkanes, alkenes, alkynes, aromatics, OVOCs, halogenated hydrocarbons, and organic sulfur by species, Their concentrations in the 13 cities were 26.0 ± 10.1–41.3 ± 12.9, 3.33 ± 1.66–6.52 ± 2.26, .57 ± .36–1.29 ± .72, 17.8 ± 10.6–38.3 ± 15.9, 22.0 ± 7.75–36.2 ± 13.1, 25.0 ± 4.77–36.5 ± 8.21, and 1.40 ± 1.36–2.74 ± 2.43 μg/m^3, respectively.

Compared with the VOCs studies in other areas of China, most of which monitored about 50 species of VOCs, this study monitored more species simultaneously, and this could explain the higher TVOC in this study. Alkanes in 13 cities were lower than Handan, comparable to Chengdu, Zhengzhou, and higher Beijing and Tianjin. Alkanes, alkenes and alkynes in 13 cities were close to the other cities in China. However, it is worth noting that the total concentrations of aromatics in 13 cities were higher than most of the other studies. The 13 cities monitored in this study have developed industries and dense population, and the higher concentration of aromatics might be a result of larger local emission. Considering aromatics are toxic and harmful substances, more monitoring research focusing on aromatics should be carried out in the future.

Figure 3 shows the percentages of measured VOCs groups to the TVOCs. The results show that alkanes, halogenated hydrocarbons, aromatics and OVOCs were the main groups of VOCs. Alkanes contributed 21.7%–32.6% to the TVOCs, mainly including ethane, propane, isopentane, etc. During the entire sampling period, concentrations of alkanes were highest in Langfang, Tangshan, Xi'an and Yuncheng. Alkanes also exhibited the second-highest concentration in the other six cities. Halogenated hydrocarbons accounted for 21.0%–27.9% of TVOCs in 13 cities, mainly including chloromethane, dichloromethane, difluorodichloromethane, etc. They were the main VOCs in Baoding, Xingtai, Anyang, Jiaozuo, Hebi and Jincheng. Aromatics accounted for 13.5%–29.3% of TVOCs, mainly including toluene, m/p-xylene, etc., which was the largest group in Luoyang and Linfen. OVOCs, accounted for 18.1%–27.4% of TVOCs in 13 cities. The main components of OVOCs include formaldehyde, acetone, acetaldehyde, isopropyl alcohol, etc. OVOCs was the dominant group in Xinxiang and was the second highest group in Anyang.

The contributions of alkenes to TVOCs were much lower than OVOCs, alkanes, aromatics, and halogenated hydrocarbons, which could be attributed to their high reactivities in the atmosphere. During the whole sampling period, alkenes contributed less than 5.5% to TVOCs in all 13 cities. Alkyne accounted for less than 1.2% in 13 cities. Organic sulfur accounted for 2.3% of the TVOCs in Jiaozuo and Hebi. In other cities, contributions of organic sulfur to TVOCs were less than 2%.

The top 10 VOC species were listed in Supplementary Table S2, which accounted for over 50% of TVOC in all 13 cities. Ethane, isopentane, chloromethane, toluene, ethylbenzene, m/p-xylene, formaldehyde and acetone were most abundant in all 13 cities.

3.3 OFP of VOCs

During the entire sampling period, the total OFP of Luoyang, Baoding, Linfen, Xingtai, Xi'an, Anyang, Xinxiang, Tangshan, Yuncheng, Langfang, Jincheng, Hebi and Jiaozuo were 384, 346, 342, 340, 326, 319, 316, 315, 310, 299, 292, 277, and 269 μg/m^3, arranged in descending order. The contributions of different VOCs groups to the total OFP in each city are listed in Table 2.

TABLE 1 Concentrations of different VOCs species in 13 cities and other cities of China (μg/m³).

City	Period	Alkanes	Alkenes	Alkynes	Aromatics	OVOCs	Halogenated hydrocarbons	Organic sulfur	TVOC	Reference
Beijing	2017.4–2017.5	13.6 ± 8.96	1.85 ± 1.16	.51 ± .49	8.80 ± 3.11	—	—	—	24.7 ± 17.2	Zhang et al. (2020)
	2017.7–2017.8	16.0 ± 7.43	3.18 ± 2.55	.90 ± .55	12.5 ± 7.69	—	—	—	32.5 ± 17.4	
Tianjin	2019.6–2019.8	20.3–29.9	4.93–7.31	.90–1.95	6.10–8.95	—	—	—	32.9–41.7	Wang et al. (2021)
Chengdu	2019.6–2019.9	33.24	6.43	2.87	15.96	25.13	26.17	2.86	112.66	Xu et al. (2020)
Zhengzhou	2019.6–2019.8	36.7	7.55	2.04	19.4	—	—	—	65.7	Qi et al. (2022)
	2020.6–2020.8	39.1	10.2	1.06	20.7	—	—	—	71.0	
Handan	2017.10.1–31	53.4 ± 36.0	16.9 ± 10.0	≈3.7	28.2 ± 21.8	—	—	—	102.2 ± 45.8	Wang et al. (2019)
Taiyuan	2019.8	—	—	—	—	27 ± 8.9	—	—		Chang et al. (2022)
Baoding	2020.4–2020.9	28.9 ± 9.54	3.53 ± 1.53	.62 ± .42	33.1 ± 14.4	27.6 ± 8.06	36.4 ± 8.97	2.09 ± 1.97	132 ± 32.1	This study
Xingtai		28.7 ± 8.10	4.43 ± 1.80	.72 ± .44	35.7 ± 18.5	23.9 ± 8.50	36.5 ± 8.21	2.05 ± 2.06	132 ± 32.0	
Langfang		41.3 ± 12.9	3.40 ± 1.52	.57 ± .36	26.7 ± 12.5	23.3 ± 8.27	30.0 ± 7.43	1.67 ± 2.07	127 ± 32.1	
Tangshan		31.2 ± 10.3	4.61 ± 1.81	.87 ± .57	30.1 ± 13.6	22.0 ± 7.75	28.8 ± 6.64	2.05 ± 1.76	120 ± 31.2	
Anyang		26.0 ± 10.1	3.41 ± 1.51	.78 ± .50	24.7 ± 11.3	29.6 ± 9.45	31.1 ± 7.07	2.02 ± 1.75	118 ± 26.8	
Xinxiang		35.9 ± 15.8	3.82 ± 1.65	1.03 ± .62	17.8 ± 10.6	36.2 ± 13.1	34.9 ± 6.99	2.35 ± 2.17	132 ± 33.9	
Jiaozuo		31.1 ± 13.1	3.33 ± 1.66	1.29 ± .72	20.3 ± 13.7	27.8 ± 9.23	33.1 ± 7.14	2.74 ± 2.43	120 ± 33.2	
Luoyang		29.0 ± 9.71	4.28 ± 1.61	.89 ± .55	38.3 ± 15.9	27.4 ± 8.04	28.9 ± 6.21	2.01 ± 1.41	130 ± 28.5	
Hebi		29.0 ± 13.3	3.60 ± 1.82	.84 ± .58	18.9 ± 14.0	28.2 ± 9.41	32.2 ± 6.99	2.62 ± 1.83	115 ± 35.6	
Jincheng		31.0 ± 10.3	3.90 ± 1.80	1.10 ± .64	24.5 ± 12.1	25.5 ± 8.59	31.7 ± 6.43	1.40 ± 1.36	119 ± 28.1	
Linfen		30.4 ± 9.73	6.52 ± 2.26	.88 ± .46	30.4 ± 14.0	24.2 ± 6.17	25.0 ± 4.77	1.57 ± 1.54	119 ± 27.1	
Yuncheng		29.8 ± 14.1	4.05 ± 2.31	.72 ± .43	25.9 ± 16.2	28.3 ± 8.79	27.5 ± 5.17	1.77 ± 2.11	118 ± 35.4	
Xi'an		36.2 ± 13.7	4.09 ± 1.83	.77 ± .45	31.8 ± 18.7	26.5 ± 7.43	31.8 ± 7.04	1.83 ± 1.83	133 ± 39.3	

Aromatics and OVOCs contributed majorly to total OFP. Aromatics accounted for 24.3%–50.8% of total OFP in 13 cities. Aromatics contributed highest to total OFP in Baoding, Xingtai, Langfang, Tangshan, Luoyang, Linfen, Yuncheng, and Xi'an and demonstrated the second-highest contribution to total OFP in Anyang, Xinxiang, Jiaozuo, Hebi and Jincheng. OVOCs accounted for 28.6%–52.3% of the total OFP in 13 cities, and made largest contribution in Anyang, Xinxiang, Jiaozuo, Hebi and Jincheng . Alkenes, with relatively strong reactivities in the atmosphere, contributed 9.9%–18.0% to total OFP in 13 cities. A

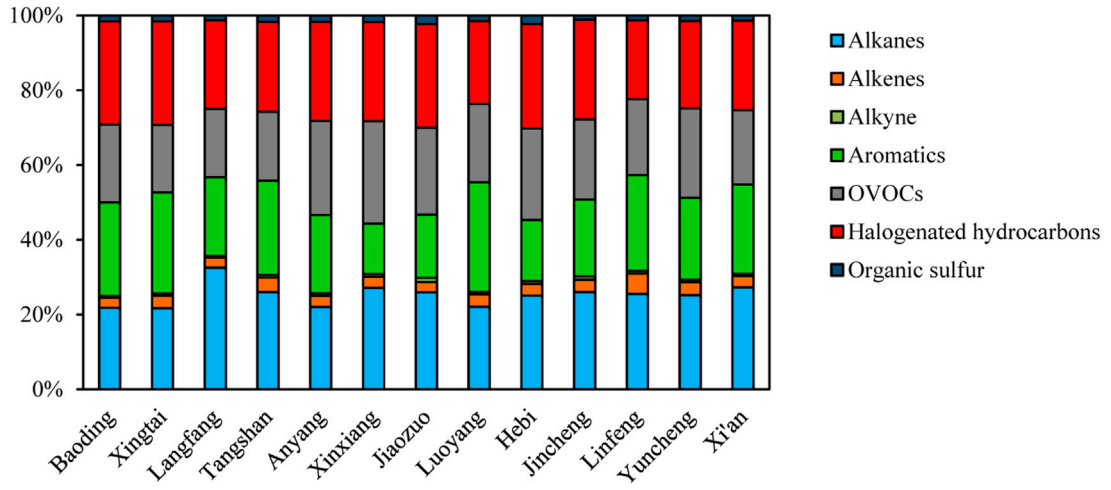

FIGURE 3
Contributions of different VOCs groups to TVOC from April to September 2020.

TABLE 2 Contributions of different VOCs groups to total OFP during the whole sampling period (%).

City	Alkanes	Alkenes	Alkyne	Aromatics	OVOCs
Baoding	8.0	9.9	0.2	47.1	34.9
Xingtai	7.9	12.6	0.2	50.8	28.6
Langfang	13.6	10.9	0.2	39.5	35.8
Tangshan	9.2	13.7	0.3	44.8	32.1
Anyang	8.0	10.1	0.2	37.1	44.6
Xinxiang	11.5	11.5	0.3	24.3	52.3
Jiaozuo	12.0	11.8	0.5	31.8	44.0
Luoyang	7.5	10.6	0.2	49.4	32.4
Hebi	10.6	12.2	0.3	31.6	45.3
Jincheng	11.1	12.9	0.4	36.6	39.0
Linfen	8.3	18.0	0.2	39.2	34.2
Yuncheng	9.4	12.6	0.2	39.5	38.2
Xi ‘an	11.3	12.1	0.2	42.9	33.5

slightly lower contributions to total OFP was demonstrated by alkanes, which were 7.5%–13.6% in different cities. In most cities, the contribution of alkanes to total OFP was lower than aromatics, OVOCs and alkenes. Notably, alkyne contributed less than .5% to the total OFP in all 13 cities.

The top 10 species that contributed most to the total OFP in 13 cities are listed in Supplementary Table S3. Formaldehyde, acetaldehyde, m/p-xylene, o-xylene, and toluene were probably key species for ozone formation in all 13 cities. The top 10 species accounted for about 80% of the total OFP in all 13 cities, which should be given priority over all other VOCs in the control of VOC emissions and O_3 pollution.

3.4 Source apportionment

The profiles of five resolved factors are shown in Figure 4.

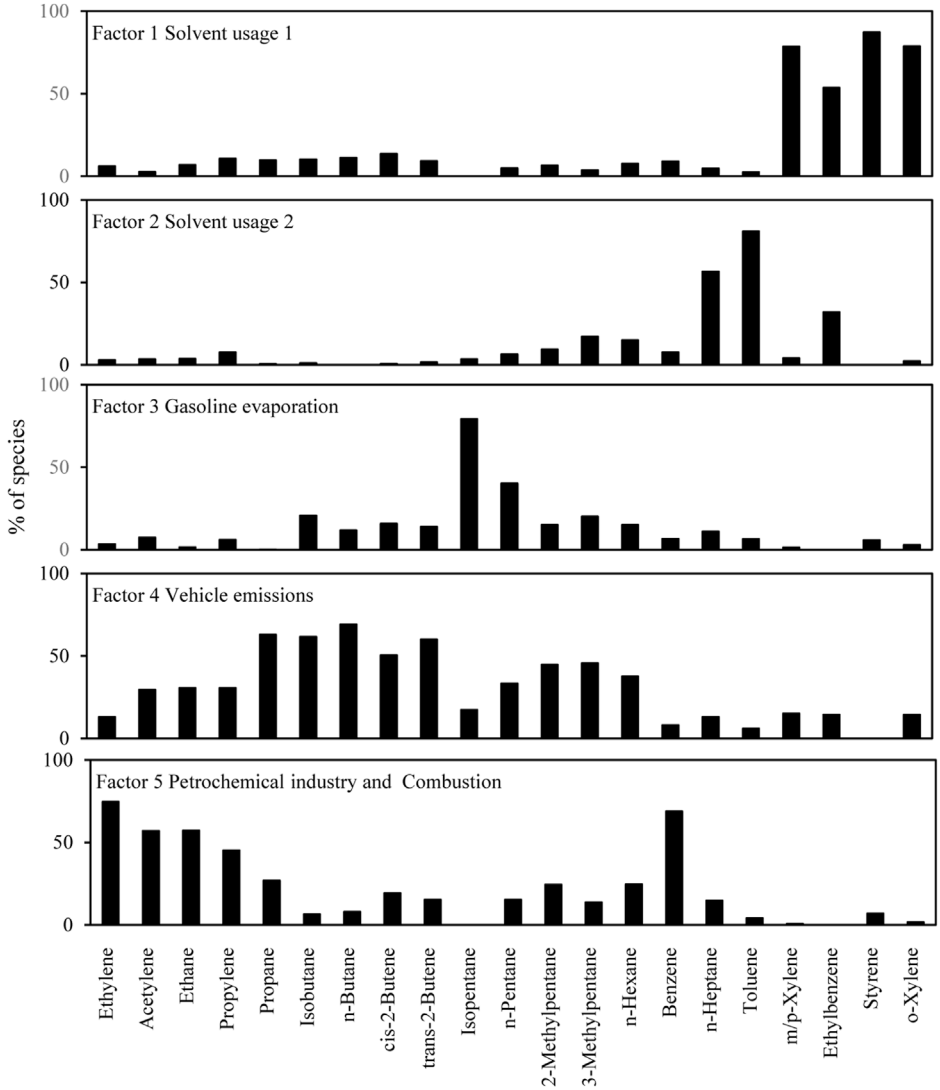

FIGURE 4
Profiles of factors resolved by PMF model for 13 cities.

Factor 1 was characterized by high levels of m/p-xylene, o-xylene, ethylbenzene and styrene, which are predominantly emitted from solvent usage (e.g., Liu et al., 2008b; Cai et al., 2010; Wang et al., 2013). Therefore factor 1 was assigned to solvent usage.

Factor 2 was distinguished by high loading of toluene, n-heptane, and moderate loading of ethylbenzene. Toluene and ethylbenzene are associated with several sources, such as vehicle emissions (e.g., Wang et al., 2018) and solvent usage (e.g., Wang et al., 2013). N-heptane is one of the main components of gasoline and widely used as solvent in industries (e.g., He et al., 2002; Chan et al., 2006). Considering the lack of markers of combustion (such as acetylene) (e.g., Barletta M. et al., 2005) and gasoline evaporation (isopentane and n-pentane) (e.g., Wang et al., 2013; Zheng et al., 2018) in this factor, factor 2 was more likely to be a profile for solvent usage in industries.

Factor 3 was rich in isopentane and n-pentane, which are markers of gasoline evaporation (e.g., Cai and Xie, 2009). 11.7%–20.6% of isobutane, n-butane, 2-methylpentane and 3-methylpentane were also found in factor 3, which were all associated with vehicle emission (e.g., Araizaga et al., 2013; Cheng et al., 2017). Therefore factor 3 was recognized as gasoline evaporation.

Factor 4 explained high abundances of vehicle emission markers, such as, cis-2-butene, trans-2-butene, 2-methylpentane and 3-methylpentane (e.g., Sigsby et al., 1987; Jorquera and Rappenglück, 2004; Araizaga et al., 2013). Meanwhile, factor 4 was also characterized by isobutane,

TABLE 3 Contributions of different sources to total selected VOCs in 13 cities.

	Solvent use 1	Solvent use 2	Gasoline evaporation	Vehicle emissions	Petrochemical industry and combustion
Baoding	25.1%	16.3%	6.4%	38.4%	13.9%
Xingtai	27.2%	15.5%	12.9%	23.2%	21.3%
Langfang	8.9%	23.2%	3.3%	52.8%	11.7%
Tangshan	36.5%	12.8%	5.7%	22.4%	22.6%
Anyang	5.6%	55.9%	14.3%	10.7%	13.5%
Xinxiang	12.5%	12.8%	32.6%	20.8%	21.3%
Jiaozuo	10.4%	28.8%	27.5%	20.3%	13.0%
Luoyang	34.2%	25.1%	13.7%	14.7%	12.4%
Hebi	20.9%	14.9%	23.8%	23.3%	17.1%
Jincheng	14.0%	33.6%	12.9%	23.2%	16.3%
Linfen	24.7%	15.5%	17.1%	8.9%	33.7%
Yuncheng	16.4%	19.9%	15.6%	33.0%	15.1%
Xi'an	9.6%	36.7%	17.0%	24.7%	11.9%

n-butane, isopentane and n-pentane, which are main components of gasoline (e.g., Araizaga et al., 2013; Cheng et al., 2017). Consequently, we identified factor 4 as vehicle emissions.

High percentages of propylene, propane, and ethane were found in factor 5, which were the most abundant species in the petrochemical plant (e.g., Mo et al., 2015). Besides, 68.8% of benzene was also observed in factor 5, which was also an important specie emitted from petroleum refining (e.g., Rao et al., 2007). However, 57.1% of acetylene, a combustion marker, was also found in factor 5 (e.g., Barletta B. et al., 2005). Coal was one of the most common fuels used in China, especially in North China Plain, and it was suggested that coal burning was possibly the main combustion sources of VOCs. It was also found that acetylene, ethene were associated with biomass burning (e.g., Andreae and Merlet, 2001). Therefore factor 5 was recognized as a mixed source of petrochemical industry and combustion.

The relative contributions of each source to total selected VOCs as input of PMF analysis were listed in Table 3. For most cities solvent use (solvent use 1 and solvent use 2) accounted for the largest proportion of total selected VOCs. In Luoyang, one of the oldest industrial bases and new industrialized city of China, the contribution of solvent use to total selected VOCs exceed 50%. Sources related to traffic (gasoline evaporation and vehicle emissions) contributed 25.0%–56.2% to total selected VOCs, indicating the significant influence of traffic to urban atmosphere. In Langfang the contribution of vehicle emissions to total selected VOCs was higher than 50%. Samples of Langfang were collected in Hebei University of Technology, which was located next to a highway between Tianjin and Xiong'an, So the site was likely to be mainly influenced by the highway traffic. Petrochemical industry and combustion accounted for 11.7%–33.7% of total selected VOCs. Compared with other cities, contribution of petrochemical industry and combustion to total selected VOCs was highest in Linfen, which was a heavy industrial city based on coal resource. The PMF results provide preliminary analysis of VOCs sources in 13 cities. However, it should be noted that source profiles in reality might be varied among different cities, and uncertainties could be induced to the PMF result performed for 13 cities simultaneously.

3.5 Analysis of VOCs/NOx limitation for ozone formation

The EKMA model has been widely used as a powerful tool to study ozone formation sensitivities to NOx and VOCs (e.g., Santos et al., 2021). Isopleth diagrams of ozone formation (EKMA curve) constructed by the OBM model for 13 cities are illustrated in Figure 5. The ridge line (black line) in each graph was given by OBM model and was calculated from the maxima of each isopleth line. The red dot represented the measured values of VOCs and NO_X. With the ridge line each diagram is divided into two regions. In the top left region, the isopleths were oriented vertically, and ozone formation was relatively more sensitive to VOCs, meaning that a change in VOCs concentration could lead to a significant increase or decrease in ozone concentration. In contrast, ozone formation is NOx-limited in the lower right region. It was observed that for

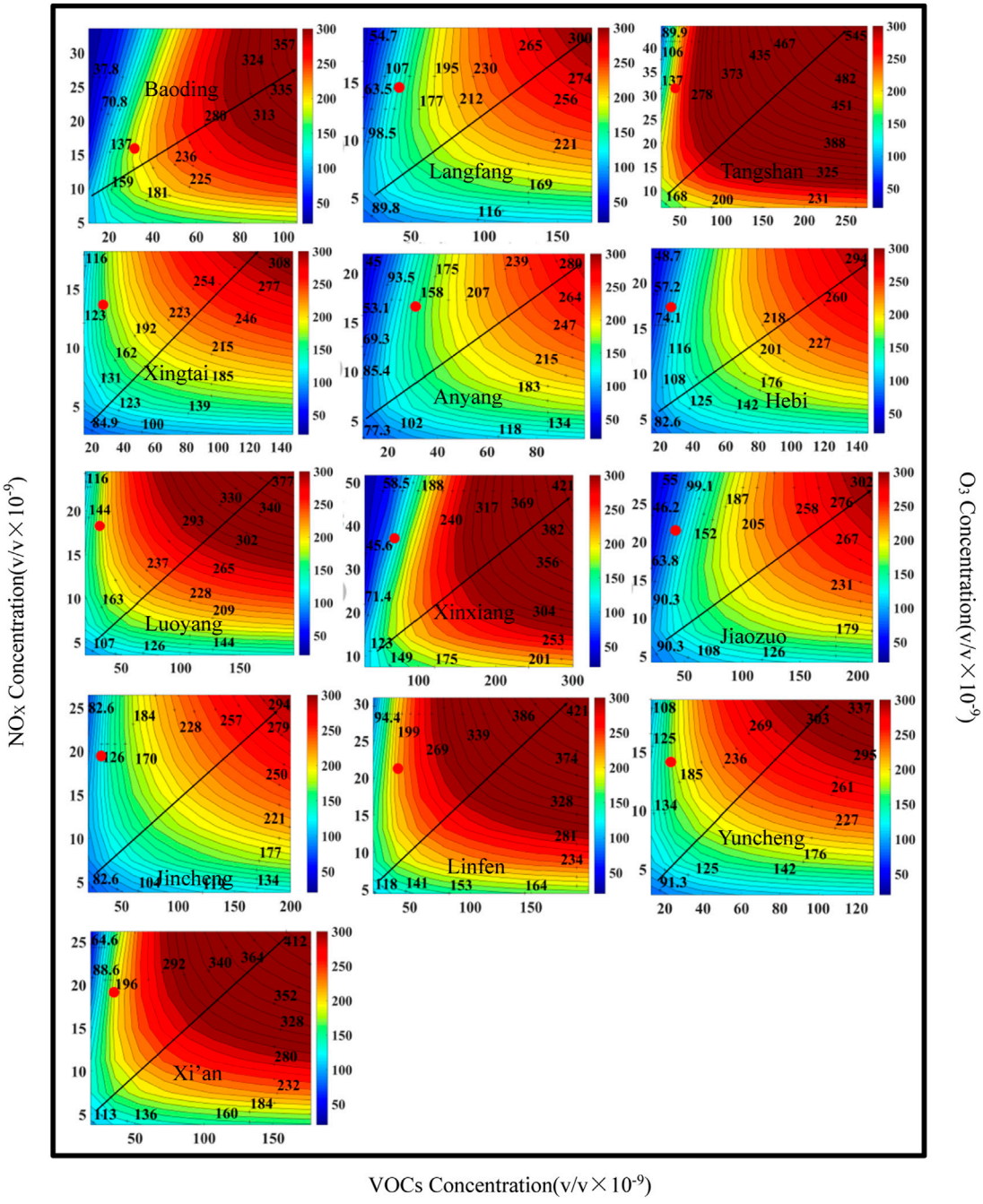

FIGURE 5
Isopleth diagram of ozone formation for 13 cities.

all 13 cities, the red dots were always located in the VOCs-limited region, indicating the reduction of VOCs in 13 cities was efficient to control ozone pollution. The VOCs/NOx ratio of the ridge line represents the optimal emission reduction ratio of VOCs and NOx to most efficiently control ozone pollution. The VOCs/NOx ratios of the ridge line were 9:1, 11:1, 5:1, 10:1, 8:1, 8:1, 8:1, 7:1, 10:1, 11:1, 7:1, 9:1 and 7:1 for Baoding, Langfang, Tangshan, Xingtai, Anyang, Hebi, Luoyang, Xinxiang, Jiaozuo, Jincheng, Linfen, Yuncheng and Xi'an, respectively. Cities with high ridge line VOCs/NO_X ratios should take more strict control strategies of VOCs to improve ozone pollution.

It was found that ozone formation in urban atmosphere was widely VOCs-limited in BTH regions, Yangtze River Delta (YRD), Pearl River Delta (PRD), and Sichuan Basin (SCB)

(e.g., Jiang et al., 2018; Fan et al., 2021), which were consistent with 13 cities in this study. However, it was also found the sensitivity of ozone formation in urban atmosphere varied with time and might be NO_X-limited in certain pollution episodes (e.g., Zheng et al., 2022). Ozone sensitivity analysis based on long-term and online measurement should be carried out to provide a scientific basis for developing refined ozone control policies.

4 Conclusion

Ambient air samples were collected in 13 cities from 1 April to 30 September 2020, and were analyzed for 117 kinds of VOCs. The concentrations of total VOCs in 13 cities showed significant temporal and spatial variations. In particular, alkanes, halogenated hydrocarbons, aromatics and OVOCs were the dominant groups of VOCs in 13 cities, which accounted for 21.7%–32.6%, 21.0%–27.9%, 13.5%–29.3% and 18.1%–27.4% of TVOCs, respectively. Aromatics, OVOCs, alkenes, alkanes, and alkyne contributed 24.3%–50.8%, 28.6%–52.3%, 9.9%–18.0%, 7.5%–13.6% and .2%–.5% to total OFP in 13 cities, respectively. Notably, formaldehyde, acetaldehyde, m/p-xylene, o-xylene, and toluene were the main ozone formation species. The results of the PMF model indicated that solvent usage, gasoline evaporation, vehicle emission, petrochemical industry and combustion were key sources of VOCs for 13 cities. Furthermore, ozone formation sensitivities to NO_x and VOCs were studied using the EKMA model, which demonstrated that ozone formation in all 13 cities was limited by VOCs, indicating the importance of emission reduction of VOCs for ozone pollution control.

Data availability statement

The original contributions presented in the study are included in the article/Supplementary Material, further inquiries can be directed to the corresponding author.

Author contributions

DS and ZD contributed equally to this work and should be considered as co-first authors; SL is correspondence author. SL and TZ designed the research. GC and KT performed the sampling, DS, XZ and ZY performed the experiments. ZL contributes analysis on EKMA model. DS and ZD analyzed the VOCs result and wrote the manuscript. SL reviewed and edited the manuscript. All authors have read and agreed to the published version of the manuscript.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Publisher's note

Supplementary material

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fenvs.2022.1084592/full#supplementary-material

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