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Pollution Characteristics of Ambient Volatile Organic Compounds During Ozone Episode in Tangshan

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Abstract: Analysis of ambient air samples for 117 volatile organic compounds (VOCs) was performed from April to September 2020 in Tangshan City using preconcentration-GC/MS and high-performance liquid chromatography methods. During sampling, daily average concentration of total VOCs (TVOC) varied from 42 $\mu g/m^3$ to 213 $\mu g/m^3$. Contributions of alkanes, OVOCs, aromatics and halogenated hydrocarbons to TVOC were 32%, 28.7%, 18.4%, and 11.0%, respectively, and formaldehyde, propane, acetone, aldehyde, toluene, ethylene, m/p-xylene, n-butane and chloromethane were the dominate species of VOCs in Tangshan City. Results of source apportionment showed that vehicle emissions, combustion, gasoline evaporation and solvent usage were 4 important sources of VOCs in Tangshan. Aromatics contributed 48.7% to total ozone formation potential (OFP), followed by OVOCs, alkenes and alkanes, contributing 26.6%, 14.9% and 9.4% to total OFP, respectively. Arranged in descending order, the 10 species contributing most to total OFP were m/p-xylene, formaldehyde, toluene, acetaldehyde, ethylene, o-xylene, ethylbenzene, propylene, 1-butene and isopentane, and their contributions to total OFP were 19.1%, 17.3%, 11.5%, 7.7%, 7.6%, 7.6%, 3.5%, 2.0%, 2.0% and 1.5%, respectively. The sensitivity of ozone (O_3) production was studied with an empirical kinetic modeling approach (EKMA) model. It was found that ozone formation in Tangshan City was under VOC-limited conditions, indicating the importance of emission reduction of VOCs to ozone pollution control.

Keywords: Volatile Organic Compounds (VOCs), Source Apportionment, Ozone Formation Potential (OFP), Empirical Kinetics Modeling Approach (EKMA)

1. Introduction

Tangshan is located in the east of Hebei Province, and is the central city of the Beijing-Tianjin-Hebei (BTH) industrial base. It is one of the largest industrial cities in China, and its four pillars resource-based industries are steel, cement, ceramics and coal, which once accounted for 80% of Tangshan's total economy. The booming industrialization also caused increasing air pollution problems [1-3]. In the end of 2017, the former Ministry of Environmental Protection issued the Monitoring Plan for Ambient Volatile Organic Compounds (VOCs) of Key Regions in 2018. According to the plan, VOCs should be monitored in heavy polluted regions, such as cities in BTH, Yangtze River delta and Pearl

River delta areas. Tangshan was one of the listed cities that were required to carry out VOC monitoring [4].

VOCs, according to the definition of the World Health Organization (WHO), refer to organic compounds with a boiling point of 50–250°C. VOCs include a variety of chemicals, and could be roughly divided into several groups, such as alkanes, alkenes, alkynes, aromatics, halogenated hydrocarbons, oxygenated volatile organic compounds (OVOCs), esters, aldehydes, ketones and the others [5, 6]. In recent years, researches on VOCs have been gained a lot of interest for the adverse effect on human health and the key role VOCs played in photochemical reactions. As key precursors for both ozone and $PM_{2.5}$, The increasing emission of VOCs is suspected to be the main reason of growing ozone pollution in summer and autumn [7-10].

In this study, 117 kinds of ambient VOCs in Tangshan were manually monitored from April to September 2020. Temporal variations, compositions, and primary sources of VOCs were studied. The ozone formation potential (OFP) was calculated based on the concentrations and maximum incremental reactivity (MIR) of each volatile organic compound. Moreover, the sensitivity of O_3 production was studied with EKMA model.

2. Experiments

2.1. Sampling

Ambient VOCs samples collection was conducted on the rooftop of Research Center of Kailuan Group, Lunan District, No. 8 Zengsheng East Street, Tangshan. Samples were collected every day from April 1 to September 30, 2020, when the ozone pollution was more severe than the other months of the year.

13 aldehydes and ketones were collected and analyzed according to the standard method HJ 683-2014 [11]. Briefly, the samples were collected with acidified 2, 4-dinitrophenylhydrazine (DNPH) coated cartridges (TupLabs, China) by an air sampler (KC-6D, Qingdao Laoshan Electronic Instrument Factory Co. Ltd., China). The sampling began at 12:00 pm and lasted for 3 hours.

The other 104 VOCs, including 29 kinds of alkanes, 11 kinds of alkenes, 18 kinds of aromatics, 9 kinds of OVOCs, 35 kinds of halogenated hydrocarbon, acetylene, and carbon disulfide, were collected with 3.2 L stainless steel canisters (ENTECH, USA), according to the standard method HJ 759-2014 [12]. Before sampling, the canisters were cleaned and evacuated to <10 Pa. With the help of a flow controller, the canisters could be filled with air at a constant flow rate. The sampling began at 9:00 each day and lasted for about 24 hours.

2.2. Analysis

Cartridges were eluted with acetonitrile and further detected for 13 aldehydes and ketones using an Ultimate 3000 HPLC system (Thermo Fisher Scientific Inc, USA). External standards were used to identify and quantify the aldehydes and

ketones. The linearities of standard curves (R) of 13 aldehydes and ketones were greater than 0.995 [10].

The other 104 VOCs were quantified using a double column multi dean switching gas chromatography-mass spectrometry/flame ionization detector (GC-MS/FID) system coupled with a sorbent-assisted electronically controlled cryo-focusing unit (CIA-Kori-UNITY, MARKERS, UK) [13, 14]. The cryo-focusing unit was used for VOCs enrichment and desorption. The operating temperature of the cold trap was minus 30 to 300°C. An analysis system of QP2010Ultra Gas chromatography (Shimadzu, Japan) with InterCap-624MS quartz capillary column (60 m×0.32 mm×1.8 µm) and TC-BOND (Na_2SO_4) PLOT column (25 m×0.32 mm×5.0 µm) were used to separate the VOCs. The FID and MS were employed for C_2-C_3 and C_4-C_{12} components detection, respectively. The correlation coefficients (R) of the standard curves of 104 VOCs were no less than 0.997. Detailed description could be found in our previous study [13].

3. Results and Discussion

3.1. Concentrations and Compositions of VOCs

Temporal variations of daily total VOCs (TVOC) are illustrated in Figure 1. Daily TVOC varied from 42 µg/m³ to 213 µg/m³. Roughly, TVOC increased gradually from April to June, decreased from July to September, and then slightly raised again at the end of September. High spikes of daily TVOC could be observed in each month. For example, on April 4 and May 1, the concentrations of TVOC were as high as 166 µg/m³ and 210 µg/m³, respectively.

Figure 2 shows the percentages of measured groups of VOCs in the TVOC. During whole sampling period, alkanes were the most abundant components, contributing 32.0% to TVOC, while OVOC, aromatics, and halogenated hydrocarbons contributed 28.7%, 18.4%, and 11.1% to TVOC, respectively. From April to September, monthly contributions of aromatics and OVOCs to TVOC increased first, highest in June or July, and then decreased gradually. The peak contribution of aromatics to TVOC on summer was probably caused by intense emission with high temperature, while more OVOCs were likely generated through photochemical reactions in summer. Concentrations of alkanes increased slightly in summer, but the contribution of alkanes to TVOC in summer decreased. Monthly contributions of alkenes and acetylene were lowest in June and July. Halogenated hydrocarbons were relatively unreactive in atmosphere, and their contributions to TVOC varied from 10.0% to 12.1%. Concentrations and monthly contributions of carbon disulfide to TVOC both kept increasing from April to September, indicating growing emission of carbon disulfide from combustion of sulfur-containing fossil fuels.

In terms of single component, the 10 most abundant components in Tangshan were formaldehyde, ethane, propane, acetone, acetaldehyde, toluene, ethylene, *m*/p-xylene, n-butane, and chloromethane during the whole sampling period.
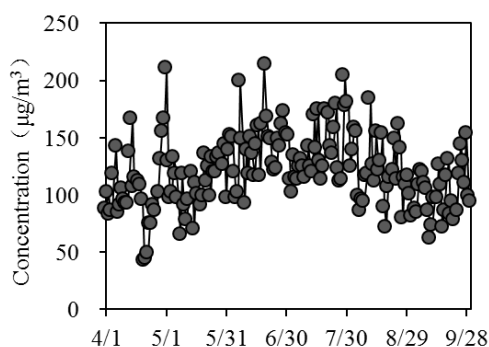
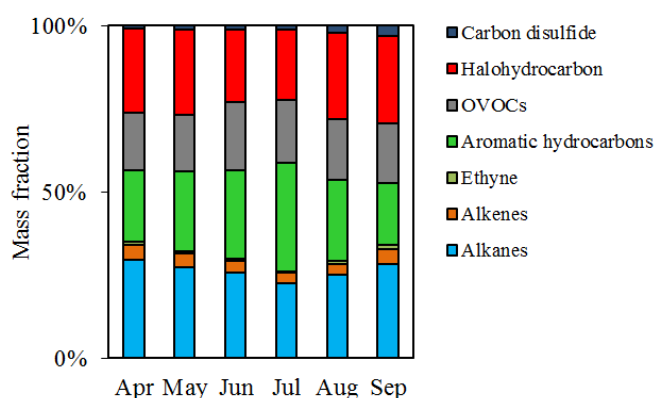***Figure 1.*** *Time variations of daily TVOC in Tangshan.*

Figure 2. *Monthly compositions of VOCs in Tangshan.*

3.2. Source Apportionment

The positive matrix factorization model (PMF 5.0) developed by EPA was employed to identify and quantify sources of VOCs in Tangshan. Measurement results of 23 species were input into PMF model. Solutions with 3 to 6 factors were calculated by PMF. A result with 3 factors was recognized as the most optimum solution for this study. Results of PMF source apportionment are shown in figure 3.

Factor 1 exhibited high loadings of 2-methylpentane, benzene, toluene, and moderate loading of isobutane, n-butane, isopentane, n-pentane. 2-methylpentane, isobutane and n-butane are associated with vehicle exhaust, while isopentane and n-pentane are typical markers for gasoline and diesel fuel evaporation. Benzene and toluene are products of vehicle exhausted emissions [15, 16]. Therefore Factor 1 was assigned to vehicle emissions. High percentages of tracers for combustion, such as ethylene, acetylene, propylene and benzene were found in Factor 2. On the other hand, Factor 2 was also characterized by high percentages of isobutane, n-butane, isopentane and n-pentane, which are markers for gasoline and diesel fuel evaporation [17]. Therefore Factor 2 was identified as a mixed source of combustion and gasoline evaporation. Factor 3 explained most of m/p-xylene, styrene, ethylbenzene and o-xylene, which are all profoundly emitted from solvent usage [18, 19]. Therefore Factor 3 was identified as solvent usage.
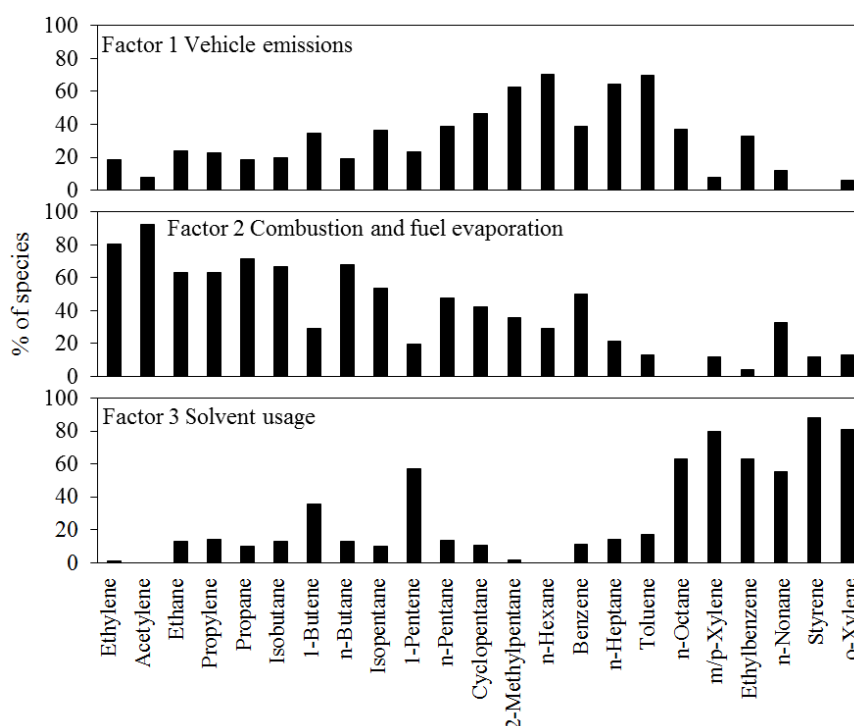

Figure 3. *Results of PMF source apportionment.*

3.3. Ozone Formation Potential (OFP)

OFP is used to evaluate the relative contributions of different VOCs to ozone formation. Total OFP of VOCs in atmosphere depends on concentrations and maximum incremental reactivities (MIR) of different VOCs. The MIR applied in this study is listed in table 1.

Table 1. *MIR of different VOCs (g O^3/g VOC).*

Name	MIR	Name	MIR	Name	MIR
Ethylene	8.88	n-Hexane	1.14	n-Propylbenzene	1.96
Ethyne	0.95	2,4-Dimethylpentane	1.46	1-ethyl-2-methylbenzene	5.54
Ethane	0.26	Methylcyclopentane	2.05	1-ethyl-3-methylbenzene	7.39
Propylene	11.57	Benzene	0.69	1,3,5-Trimethylbenzene	11.75
Propane	0.46	Cyclohexane	1.14	p-Ethyltoluene	4.39
Isobutane	1.18	2-Methylhexane	1.09	Decane	0.59
n-Butene	9.57	2,3-Dimethylpentane	1.25	1,2,4-Trimethylbenzene	8.83
n-Butane	1.08	3-Methylhexane	1.5	1,2,3-Trimethylbenzene	11.94
cis-2-Butene	14.26	2,2,4-Trimethylpentane	1.2	1,3-Diethylbenzene	7.08
trans-2-Butene	15.2	n-Heptane	0.97	p-Diethyl benzene	5.43
Isopentane	1.36	Methylcyclohexane	1.56	Undecane	0.52
1-pentene	7.07	2,3,4-Trimethylpentane	0.95	Dodecane	0.47
n-Pentane	1.22	2-Methylheptane	0.97	1,3-Butadiene	10.9
trans-2-Pentene	10.47	Toluene	3.93	Formaldehyde	7.2
2-methyl-1,3-butadiene	10.48	3-Methylheptane	1.12	Acetaldehyde	5.5
cis-2-Pentene	10.28	n-Octane	0.8	Acrolein	7.45
2,2-Dimethylbutane	1.11	m-Xylene, p-Xylene	7.8	Acetone	0.56
Cyclopentane	2.24	Ethylbenzene	2.96	Propionaldehyde	6.5
2,3-Dimethylbutane	0.9	Nonane	0.68	MethylEthylKetone	1.48
2-Methylpentane	1.4	Styrene	1.66	Butyraldehyde	5.28
3-Methylpentane	1.69	o-Xylene	7.58	N-Hexanal	3.79
1-Hexene	5.35	Isopropylbenzene	2.45		

OFP of different VOCs could be calculated according to the formula [20, 21],

$$OFP_i = [VOCs]_i \times MIR_i \qquad (1)$$

Where $[VOCs]_i$ represents the concentration of each VOCs. OFP of different VOCs groups are shown in Figure 4. During the whole sampling period, total OFP of all VOCs were 286 μg/m^3. Aromatics, OVOCs, alkenes, alkanes and ethyne accounted 48.7%, 26.6%, 14.9%, 9.4% and 0.3% of total OFP, respectively. It was found that OFP of alkanes, alkenes, aromatics, and OVOCs were all highest in summer (June or July), caused by the increased concentrations of these species. However, OFP of acetylene dropped significantly in summer. Arranged in descending order, the 10 species contributing most to total OFP were m/p-xylene, formaldehyde, toluene, acetaldehyde, ethylene, o-xylene, ethylbenzene, propylene, 1-butene and isopentane, and their contributions to total OFP were 19.1%, 17.3%, 11.5%, 7.7%, 7.6%, 7.6%, 3.5%, 2.0%, 2.0% and 1.5%, respectively.
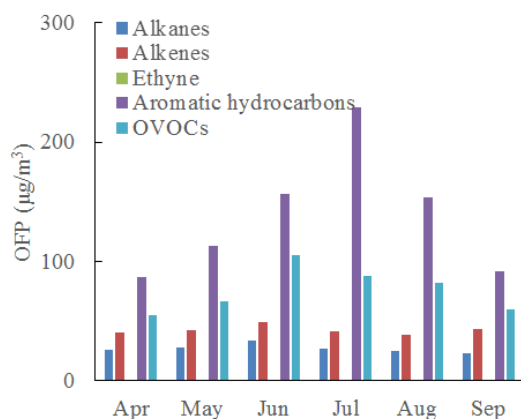
3.4. Analysis of VOCs/NO$_x$ Limitation for Ozone Formation

The EKMA model was an effective tool to determine whether ozone formation was under VOCs or NO$_x$ limited conditions [22]. The Isopleth diagram of ozone formation potential under different concentrations of VOCs and NO$_x$ of Tangshan was constructed by the EKMA model, as illustrated in Figure 5. The ridge line (black line connected with each turning point of each isopleth line) divided the diagram into two parts. In the lower right part of the diagram, changes of VOCs concentrations have little effect on ozone formation, while the reduction of NOx will lead to a significant decrease of ozone. In this case, ozone formation is limited by NOx. In contrast, in the higher left part of the diagram, changes of VOCs concentrations could lead to a significant increase or decrease of ozone concentrations, indicating that the ozone formation is under VOCs-limited conditions. The VOCs/NO$_x$ ratio of the ridge line represents the optimal emission reduction ratio of VOCs and NO$_x$ for ozone pollution control.

Figure 4. *OFP values of a different kind of VOCs in Tangshan.*
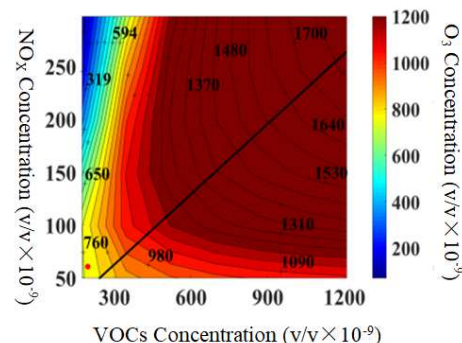

Figure 5. *Isopleth diagram of ozone formation in Tangshan.*

As seen in Figure 5, the VOCs/NOx ratio of the ridge line is 5:1. The red dot in Figure 5 shows the average concentrations of VOCs and NO$_x$ during sampling in Tangshan, with a VOCs/NOx ratio of

about 1.6:1, indicating that ozone formation was limited by VOCs. Attention should be paid on the emission reduction of VOCs with higher OFP to efficiently control the ozone formation.

4. Conclusion

Ambient VOCs were collected and analyzed during high ozone episode (from April to September 2020) in Tangshan. The results indicated that: (1) VOCs in Tangshan were mainly composed of alkanes, aromatics, OVOCs and halogenated hydrocarbons, concentrations of TVOC varied in the range of 42-213 $\mu g/m^3$; (2) vehicle emissions, combustion, gasoline evaporation and solvent usage were recognized as the 4 main sources of VOCs in Tangshan; (3) Among the 117 VOCs, aromatics contributed 48.7% to the total OFP in Tangshan, suggesting the importance of aromatics emission reduction to ozone control; (4) According to the results of EKMA model, VOCs play a dominant role in the formation of ozone during the observation period, and the control of VOCs emission should be intensified.

Acknowledgements

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