VOCs pollution characteristics and potential of ozone generation in Kaifeng City

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Abstract: In recent years, the exhausted gas from factories has become an important part of environmental pollution in Kaifeng City. Air samples were collected for 57 kinds of volatile organic compounds (VOCs) and 13 kinds of aldehydes and ketones from the Cancer Hospital of Kaifeng city between May and October 2019. The pollutants were measured by gas chromatography-mass spectrometry (GC-MS) and high-performance liquid chromatography (HPLC) technique. Combined with the 8-hour automatic monitoring data of air ozone automatic monitoring at this sampling site, a total of 31 observations on volatile organic compounds (VOCs) were carried out over between May and October 2019. The results showed that the average concentration of VOCs was in the order of oxygen-containing organic matters > alkanes > olefins > aromatic hydrocarbons > alkynes. Using SPSS26 statistical software, representative key species were selected from VOCs, and correlation analysis was conducted with ozone concentration and meteorological factors. The ozone concentration was significantly correlated with air temperature. Acrolein & propionaldehyde, acetaldehyde, and formaldehyde, had a significant negative correlation with ethylene and ethane. The highest ethylene and ethane concentrations appeared when there was west wind, while toluene showed a significantly high value in the southwest wind. The oxygenated organics had obvious wind direction characteristics and the four kinds of oxygenated organics were rarely affected by the west, northwest and north winds.

1. Introduction
Volatile organic compounds (VOCs), existing widely in the air, refer to organic pollutants with complex compositions. The common VOCs are hydrocarbons, benzene series, alcohols, ketones, aldehydes, phenols, lipids, amines, nitriles, etc. Under light conditions, VOCs can produce photochemical reactions and form photochemical smog, an important precursor of ozone pollution[1]. VOCs have complex sources, various types, and different activities, which makes it challenging to control VOCs. Secondly, due to the complex chemical formation mechanism and the non-linear relationship between ozone and precursors, it is challenging to reduce precursors. Finally, ozone exists for a long time and can "diffuse" for a long distance, thus causing regional pollution.

VOCs and their contribution to ozone pollution are mainly concentrated in large and medium-sized and provincial capital cities, such as Chongqing[2], Shanghai[3], Nanjing[4], Tianjin[5], Shenzhen[6], Zhengzhou[7], etc., and the research results are also different. The VOCs in Chongqing are mainly alkanes and alkenes, while the VOCs in the suburbs are mainly oxygenated VOCs. Controlling the concentration of alkynes and aromatic hydrocarbons can help to control the formation of O₃. The main
sources of VOCs in Shanghai suburbs are vehicle emissions, factory production, fuel combustion, industrial solvent volatilization and natural sources. The prevention and control of VOCs Pollution in Nanjing should focus on petrochemical and surface coating. It was found that the formation of O$_3$ was more sensitive to VOCs in Tianjin. The change of specific species to concentration ratios such as Ethylbenzene / (m, p-xylene) and ethane / acetylene indicated that the aging process of VOCs accompanied the process of O$_3$ pollution. The contribution of toluene, m-xylene, p-xylene, and ethylene to ozone generation ranked the top three among VOCs in Shenzhen. The contribution of VOCs species to OFP was olefin > aromatic hydrocarbon > alkane > alkyne.

Kaifeng is located in the middle and lower reaches of the Yellow River and the south of the North China Plain. It is one of the "2 + 26" cities in Beijing, Tianjin, Hebei, and its surrounding areas. In recent years, ozone pollution has become increasingly prominent. In 2019, the concentration value increased by 9 μ g / m$^3$ compared with that in 2018. There were 86 days with O$_3$-8H as the primary pollutant and reaching the level of mild pollution or above, which increased by 12 days compared with that in 2018. Therefore, it is urgent to study and analyze the characteristics of VOCs Pollution and ozone generation potential in Kaifeng City.

2. Method

2.1. Monitoring point and time periods
The monitoring point was set in Kaifeng Tumor Hospital, which was located in the urban residential administrative office area. It belonged to the shantytowns of the old city of Kaifeng City, with a large population. There was no obvious air pollution emission source and industrial source within 1 km around the site. The site was about 15 m away from the ground. The study period was from May to October, 2019, with a total of 31 days / time.

2.2. Sample collection and analysis method
The specific monitoring factors were 57 kinds of volatile organic compounds (original PAMS substances, namely alkanes, olefins, alkynes, aromatic hydrocarbons) and 13 aldehydes and ketones (original OVOCs substances). Volatile organic compounds (VOCs) were collected in stainless steel tank after inert treatment in inner wall, concentrated in cold trap, separated by gas chromatography and detected by mass spectrometry. Aldehydes and ketones were collected by a sampling tube filled with 2, 4-dinitrophenylhydrazine and detected by high performance liquid chromatography (HPLC), ultraviolet (360 nm) or diode array detector. NOx, O$_3$-8H concentration, wind direction, temperature and other meteorological parameters were monitored by national air automatic monitoring station data of cancer hospital.

2.3. Calculation of ozone formation potential (OFP)
In this study, combined with the analysis results of VOCs, according to the contribution of each VOC$_j$ factor to VOCs concentration and the maximum incremental reaction activity (MIR) of the component, the ozone generation potential of the source was calculated, and then the contribution of various sources to the ozone generation potential was calculated.

$$OFP_i = \sum_{j} [VOC]_{ij} \times \text{MIR}_j$$

$OFP_i$ is the ozone generation potential of the i th source, $[VOC]_{ij}$ is the concentration of species j in the i th source, and $\text{MIR}_j$ is the MIR of species j. MIR values were taken from the study of Cater[8].

3. Results and Discussion

3.1. VOCs Pollution Characteristics
During the monitoring period, the changes of VOCs, O$_3$ and NOx concentrations in the air of monitoring points were shown in figure 1. According to the 31 monitoring results, the daily concentrations of VOCs varied greatly, with the highest concentration of 137.34 nmol / mol and the
lowest concentration of 8.9 nmol / mol. SPSS26 was used to detect the correlation between VOCs and O₃-8H concentrations. The results showed that there was a weak positive correlation between VOCs and O₃-8H (0.308), a strong negative correlation between O₃-8H and NOx (- 0.612). The concentration changes of O₃-8H, NOx and VOCs were shown in figure 1.

![Figure 1. Concentration change during VOCs, ozone and NOx monitoring](image1)

The daily concentration levels of each component in VOCs also varied greatly, as shown in figure 2. However, on the whole, the average concentrations of VOCs were as follows: oxygen-containing organic matter > alkanes > olefins > aromatic hydrocarbons > alkynes. The contribution of five components to VOCs concentration was 46%, 19%, 15%, 14% and 5%, respectively. The results showed that oxygenated organic compounds, alkanes and alkenes were the main concentration components of VOCs, and the sum of the three concentrations accounted for 80%.

![Figure 2. Concentration proportion change of VOCs components during monitoring](image2)
accounted for a large proportion in the 12th (July 6) monitoring. However, olefins gradually increased from the first monitoring (May 1) and reached the peak in the 31st (October 28) monitoring.

The concentration level and contribution percentage of VOCs in the top 20 in the atmosphere were shown in figure 3. The sum of the concentration contribution percentages of the top 20 species was about 80%. The top four species are alkanes, accounting for 31% of the average VOCs. Methylcyclopentane and 2-methylhexane are the two species with the highest average concentration level in VOCs, with the average contribution of 9.20% and 7.74% respectively.

![Figure 3. Top 20 components concentration and proportion of VOCs average concentration contribution](image)

### 3.2. Ozone generation potential analysis

The average OFP of VOCs during the monitoring period was 353.94 μg / m³, of which the OFP of oxygenated organic compounds was the largest, 126.96 μg / m³, accounting for 35.9%, followed by aromatic hydrocarbons and alkanes, accounting for 23.6% and 22.7% respectively. The OFP of alkyne was small, only 1%, as shown in figure 4. Formaldehyde, acetaldehyde and propylene were the top three VOCs species, accounting for 17.7%, 9.31% and 7.41%, respectively. The contribution of the three species to ozone generation was more than one third, as shown in figure 5.
The formation potential of ozone was as follows: oxygen-containing organic matter > aromatic hydrocarbons > alkanes > olefins > alkynes. Oxygen-containing organic compounds, aromatic hydrocarbons, and alkanes accounted for 82.2% of the total, and oxygen-containing organic matters became the most important component of ozone generation.

3.3. Screening of VOCs key species
Some representative key species were selected from 70 aimed species of VOCs. According to the four principles of "species with detection rate greater than 80%", "top 20 species with average concentration ranking", "top 20 species with daily concentration ranking and occurrence frequency"
more than 15 times’ and "species with ozone generation potential contribution greater than 1%", "5 key species" were selected, including acetaldehyde, formaldehyde, propylene, ethylene, acrolein + acetone, as shown in table 1.

Table 1. Screening of VOCs key species

| Number | Detection rate>80% | Top 20 species with average concentration ranking | The daily concentration ranked top 20 and the frequency was > 15 | Species with ozone generation potential contribution greater than 1% | 5 key species |
|--------|------------------|-----------------------------------------------|-------------------------------------------------|-------------------------------------------------|--------------|
| 1      | acetylene        | methylcyclopentane                            | ethane                                         | formaldehyde                                     | acetaldehyde |
| 2      | ethane           | 2-methylhexane                                | propylene                                      | acetaldehyde                                     | formaldehyde |
| 3      | propylene        | 3-methylhexane                                | acetaldehyde                                   | propylene                                        | propylene    |
| 4      | benzene          | N-hexane                                      | formaldehyde                                   | ethylene                                         | ethylene     |
| 5      | acetaldehyde     | formaldehyde                                  | ethylene                                       | M, p-xylene                                      | Acrolein + acetone |
| 6      | formaldehyde     | toluene                                       | Acrolein + acetone                             | toluene                                          |              |
| 7      | ethylene         | acetaldehyde                                  | toluene                                        | methycyclopentane                                |              |
| 8      | Acrolein + acetone | Heptane                                  | Propionaldehyde                               | Acrolein + acetone                               |              |
| 9      | ethane           | 3-methylpentane                               | O-xylene                                       | Propionaldehyde                                  |              |
| 10     | 2,3-dimethylpentane | 3-methylhexane                            | 2-methyl-1,3-butadiene                         | 2-methyl-1,3-butadiene                           |              |
| 11     | ethylene         | 2-methylpentane                               | N-hexane                                       | 2-methylpentane                                  |              |
| 12     | Acrolein + acetone | 3-methylpentane                            | 3-methylpentane                                | 1,2,3-trimethylbenzene                           |              |
| 13     | propylene        | O-xylene                                      | 2,3-dimethylpentane                            | 2,3-dimethylpentane                              |              |
| 14     | Acrolein + acetone | Heptane                                  | 2,3-dimethylpentane                            | Heptane                                         |              |
| 15     | propylene        | 2,3-dimethylpentane                           | 3-methylpentane                                | 3-methylpentane                                  |              |
| 16     | O-xylene         | 1,2,3-trimethylbenzene                        | 1,2,3-trimethylbenzene                         | 1,2,3-trimethylbenzene                           |              |
| 17     | 2-methylpentane  | 2,3-dimethylpentane                           | 2,3-dimethylpentane                            | 2,3-dimethylpentane                              |              |
| 18     | N-octane         | 2,3-dimethylpentane                           | 2,3-dimethylpentane                            | 2,3-dimethylpentane                              |              |
| 19     | 2-methylpentane  | Propionaldehyde                               | Propionaldehyde                               | Propionaldehyde                                 |              |
| 20     | Propionaldehyde  | Propionaldehyde                               | Propionaldehyde                               | Propionaldehyde                                 |              |

3.4. Analysis of ozone formation conditions

It can be seen from table 2 that ozone concentration was significantly correlated with air temperature, acrolein + propionaldehyde and acetaldehyde at 0.01 level, significant correlation with formaldehyde in 0.05 level, and significant negative correlation with ethylene in 0.05 level. Air temperature, acrolein + propionaldehyde, acetaldehyde and formaldehyde were likely to be the main conditions for the formation of ozone, while ethylene might be the main consumption of ozone.

Table 2. Correlation test of VOCs key species with ozone concentration and temperature change

| propylene       | acetaldehyde | formaldehyde | Acrolein + acetone | ethylene | air temperature | ozone |
|-----------------|--------------|--------------|--------------------|----------|----------------|-------|
| propylene       | .1           | -.230        | -.302              | -.053    | .586**         | .085  |
| acetaldehyde    | -.230        | 1            | .772**             | -.357    | .436*          | .513**|
| formaldehyde    | .772**       | 1            | .387               | -.283    | .494**         | .445* |
| Acrolein + acetone | .053        | .664**       | .387               | 1        | -.316          | .558**|
| ethylene        | .586**       | -.357        | -.283              | -.316    | 1              | -.350 |
| air temperature | .085         | .436*        | .494**             | .558**   | -.350          | .789**|
| ozone           | .003         | .513**       | .445*              | .558**   | -.460*         | 1     |

** At 0.01 level (double tail), the correlation was significant.
* At 0.01 level (double tail), the correlation was significant.

In the correlation test of VOCs key species, it was found that there was obvious correlation between some related species. There was a significant correlation between ethylene and propylene, acetaldehyde, acrolein + acetone and propionaldehyde. Maybe because they came from the same
related industry. Ethylene and propylene were widely used as chemical intermediates or sources and filling stations. Acetaldehyde, acrolein + acetone and propionaldehyde might come from plate processing and anticorrosion.

During the monitoring period, with the change of wind direction, the concentration of VOCs key species showed certain change characteristics, as shown in figure 6 and figure 7. When the wind direction was westerly, the concentrations of ethylene and propylene were the highest, which indicated that there might be emission sources of the two species with high pollution in the west of the monitoring point. There were high values of three kinds of oxygen-containing organic compounds in the direction of East, Southeast and south wind, indicating that there were pollution sources of oxygen-containing organic matters from northeast to southwest of the monitoring point.

4. Conclusions
Based on the analysis of the pollution characteristics of VOCs and the potential of ozone generation in Kaifeng City, the conclusions were as follows:

- The average concentrations of VOCs in Kaifeng City were as follows: oxygenated organics > alkanes > olefins > aromatic hydrocarbons > alkynes. Ozone generation at monitoring sites was sensitive to VOCs concentrations.
Oxygen containing organic compounds, alkanes and alkenes were the main concentration components of VOCs, which might reflect the characteristics of pollution in Kaifeng City due to its industrial structure, urban planning, geographical and climatic conditions.

The ozone generation potential of VOCs in Kaifeng was as follows: oxygenated organics > aromatic hydrocarbons > alkanes > alkenes > alkynes. Formaldehyde, acetaldehyde and propylene were the top three species in the OFP.

The key species of VOCs in Kaifeng City were acetaldehyde, formaldehyde, propylene, ethylene, acrolein + acetone, etc. Ethylene might be the main consumption of ozone. When the wind direction was westerly, the concentration of ethylene and ethane was the highest, and toluene was obviously high when the wind direction was southwest. The oxygen-containing organic compounds have obvious wind direction characteristics, and the four kinds of oxygen-containing organic compounds were rarely affected by the west, northwest and north winds.

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