Determination and Characteristic Analysis of Atmospheric Non-Methane Hydrocarbons in a Regional Hub City of North China Plain

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Abstract: Atmospheric non-methane hydrocarbons were measured continuously for one month in east urban area of Jinan in September, 2017. A total of 46 kinds of non-methane hydrocarbons were determined, and studies were performed on their concentration level, diurnal variations, chemical reactivities, and sources as well. The results showed that the total non-methane hydrocarbons concentration was 15.44 ppbv, among them alkanes, alkenes, aromatic hydrocarbons, and acetylene were the major components and their concentration also ranked by this order. The diurnal variation showed bimodal trend and two peaks appeared at 7:00-10:00 and 19:00-21:00, respectively, while the lowest value appeared at 14:00-16:00. Non-vehicle emission sources contributed 86%, 15% and 62.5% to ethylene, methylbenzene and xylene, respectively. Alkenes had higher atmospheric chemical activity and contributed the most to LOH and OFP and the second most contributors were aromatics and alkanes, while the contribution from acetylene was almost zero.

1. Introduction
Non-methane hydrocarbons (NMHCs) play an important role in the atmospheric chemical processes and are important precursors to ozone and secondary organic aerosols (SOA)[1, 2], they can not only affect atmospheric oxidation capacity but also cause harm to human body which include irritations to the eyes and respiratory tract [3]. NMHCs have many types and come from a variety of sources including natural sources and anthropogenic sources; natural sources are mainly plant emissions [4, 5] and anthropogenic sources include vehicle emissions, solvent evaporation, industrial production emissions, biomass burning emissions and etc[6-9]. Wang [10] et al. sampled 56 kinds of VOCs in Shanghai from 2009 to 2010 and analyzed their sources; Li[11] et al. studied the pollution characteristics, ozone formation potential (OFP) and OH- consumption rate (L_{OH}) of 56 kinds of VOCs and 12 kinds of atmospheric carbonyl compounds in Jing-Jin-Ji Region (i.e., Beijing City-Tianjin
City-Hebei Province, it’s the national capital region of China and the largest urbanized region in Northern China). Jinan is the capital city of Shandong Province which ranks among the top three provinces in China in terms of economic volume and is a regional hub city in North China Plain (NCP), and also a main city in the air pollution transmission channel for the Jing-Jin-Ji Region due to severe air pollution in Jinan. In recent years, the ozone problem has become the hot spot for urban air quality management and correspondingly the monitoring and control of VOCs emission have become more and more urgent. To date, some studies have been conducted in Jinan to measure concentrations of VOCs in the downtown area but studies on VOCs in eastern part of urban Jinan are lacking especially on their chemical reactivities and in autumn season when photochemical smog event is easy to occur, and in particular, there is also a large oil refinery locating in the vicinity of eastern urban Jinan.

This study is to determine the concentration and variation trends of NMHCs in eastern urban Jinan in autumn, analyze the sources of some NMHCs and determine their OFP and OH· consumption rate. The measurement and analysis of NMHCs will help to further understand the air pollution status of Jinan and similar cities and therefore facilitate the formulation of control measures for ozone pollution.

2. Material and methods

2.1 Sampling site and time

The sampling site is on the top of a 3-story building in the eastern part of urban Jinan and 17 kilometers away from the city center and 10 meters above the ground. The site is close to the most important main road of urban Jinan running from east to west, which consists of eight lanes in both directions and has a heavy traffic volume, and a large oil refinery in the northwest is 2 kilometers away from this sampling site. The measurement is from September 1 to 30 in 2017 at a time resolution of one hour.

2.2 Instrument

The measurement was performed on an “AirmoOzone” analysis system from Chromatotec Corp. in France. The system consists of 2 set of independent sampling subsystems, which is called Chromatotec CA11000 (low-carbon hydrocarbon analyzer, C2-C6), and Chromatotec CA21022 (high-carbon hydrocarbon analyzer, C6-C12). Ambient air samples were collected by cryogenic capture, then entered GC after thermal desorption, separated by capillary column, and then detected by FID detector. More information about the instrument system can be found in literatures[10, 12]. The “AirmoOzone” system made sampling hourly and data were obtained accordingly for each hour. The meteorological parameters came from the automatic weather station at the same site.

2.3 Data analysis

In this study, two methods were used to analyze the reactivity of NMHCs, one was OH· depletion rate (LOH) and the other was combined with the maximum incremental reactivity (MIR) coefficient to analyze the ozone formation potential (OFP), and the formulas were given respectively:

\[ L_{OH} = [VOC]_i \times K_{i,OH} \]  
\[ OFP = [VOC]_i \times MIR_i \]  

In equation (1), \( L_{OH} \) represents the OH· depletion rate of VOC species \( i \), \([VOC]_i\) is the concentration of some VOC observed in the actual environment, \( K_{i,OH} \) is the rate constant of reaction between \( VOCl \) and OH· radicals at 298 K, \( OFP \) represents the ozone generation potential of VOC species \( i \), \( K_{i,OH} \) and \( MIR_i \) values were derived from literatures[13, 14].

3. Results and discussion

3.1 Weather conditions
The average temperature during the sampling period was 23.5 ± 3.9 degrees Celsius, and average wind speed was 1.8 ± 0.9 m/s, the average humidity was (60 ± 18.3) %, and air pressure was 1025.6 ± 2.4 kPa.

3.2 Pollution characteristics of non-methane hydrocarbons

A total of 46 non-methane hydrocarbons were detected, including 24 alkanes, 9 alkenes, 12 aromatics and acetylene. The average concentrations and standard deviations of these compounds were listed in Table 1. Propane (1.90 ppbv), ethane (1.63 ppbv) and n-butane (1.49 ppbv) were found to be the most abundant species in the alkanes group (Table 1), accounting for 63.65% of the total alkane concentration. Ethylene (3.18 ppbv) had the highest concentration among alkenes, followed by cis-2-butene (1.40 ppbv), these two alkenes accounted for 88.12% of the total alkene concentration. Toluene had the highest concentration of 0.38 ppbv in aromatic hydrocarbons, the concentration of benzene was 0.36 ppb, and m/p-xylene was 0.24 ppb, the above collectively accounted for 63.72% of all the aromatic hydrocarbons. Overall, ethylene was the most abundant NMHC species. Liu [15] et al. have shown that ethylene comes from gasoline vehicle exhausts, coal burning and oil refineries. The ethylene concentration in Jinan was comparable with other city in China (Wuhan [16], 3.3 ppbv) and much higher than Jinan city center[12] (1.73 ppbv) and Xi’an roadside[17] (1.99 ppbv). From the diurnal variations of ethylene in Figure 1, it can be found that ethylene not only peaked in the morning and evening rush hours, but also had a relative high level of concentration in the mid-night and at noon, so it can be proved that measured ethylene was affected by both traffic sources and the nearby oil refineries. Propane is the second most abundant species in NMHCs. Possible sources were the LPG leakage and incomplete combustion of vehicle exhaust[18]. The monitoring site is very close to the main road with large traffic flow, and there is also a gas station about 300 meters to the west. Due to the relatively higher temperature during sampling period, the source of propane may come from incomplete combustion of vehicle exhaust and the LPG leakage as well.

Table 1. Non-methane hydrocarbons concentration and photochemical reaction characteristics

| Group   | Compound   | Mean ± SD (ppbv) | MIR (µg O₃/µg VOCs) | OFP (µg m⁻³) | K₆₆₅ (cm² molecule⁻¹ s⁻¹) | L₄₂⁹ (s⁻¹) |
|---------|------------|------------------|----------------------|--------------|----------------------------|-------------|
| Alkanes | Ethane     | 0.83 ± 0.45      | 0.5                  | 0.44         | 0.9                        | 0.018       |
|         | Ethylene   | 3.18 ± 1.91      | 7.4                  | 24.95        | 8.52                       | 0.666       |
|         | Cis-2-butene| 1.40 ± 1.93      | 10                   | 31.99        | 56.4                       | 1.942       |
|         | Propene    | 0.27 ± 0.32      | 9.4                  | 4.3          | 26.3                       | 0.173       |
|         | Isoprene   | 0.10 ± 0.90      | 9.1                  | 2.64         | 101                        | 0.259       |
|         | 1-Butene   | 0.07 ± 0.11      | 8.9                  | 1.39         | 31.4                       | 0.053       |
|         | Trans-2-butene| 0.05 ± 0.07   | 10                   | 1.19         | 64                         | 0.082       |
|         | Trans-2-pentene| 0.05 ± 0.07  | 8.8                  | 1.21         | 67                         | 0.079       |
|         | Cis-2-pentene| 0.05 ± 0.06     | 8.8                  | 1.26         | 56.4                       | 0.070       |
| Alkenes | 1-Pentene  | 0.03 ± 0.03      | 6.2                  | 0.48         | 31.4                       | 0.021       |
|         | Propane    | 1.90 ± 1.44      | 0.48                 | 1.64         | 1.15                       | 0.054       |
|         | Ethane     | 1.63 ± 0.85      | 0.25                 | 0.5          | 0.26                       | 0.010       |
|         | n-Butane   | 1.49 ± 2.33      | 1.02                 | 3.59         | 2.54                       | 0.093       |
|         | i-Butane   | 0.60 ± 0.81      | 1.21                 | 1.73         | 2.12                       | 0.031       |
| Alkanes | 2-Methylpentane| 0.56 ± 2.15   | 1.5                  | 2.95         | 5.6                        | 0.077       |
|         | i-Pentane  | 0.35 ± 0.65      | 1.38                 | 1.42         | 3.6                        | 0.031       |
|         | Cyclopentane| 0.35 ± 0.39      | 2.4                  | 2.4          | 5.16                       | 0.044       |
|         | n-Hexane   | 0.15 ± 0.22      | 0.98                 | 0.53         | 5.61                       | 0.021       |
|         | Methylcyclohexane| 0.14 ± 0.24  | 1.8                  | 1.01         | 10.4                       | 0.036       |
|         | n-Octane   | 0.11 ± 0.21      | 0.6                  | 0.3          | 8.68                       | 0.023       |
Figure 1 shows the diurnal variation of the concentrations of non-methane hydrocarbons during the monitoring period. The concentrations of NMHCs were basically higher at night and lower at daytime, and showed roughly a bimodal distribution. The NMHCs peak values appeared at 7:00-10:00 and 19:00-21:00. The concentration of NMHCs reached a relative high level at 7:00-10:00 under the influence of direct vehicle emissions, among which alkanes and alkenes were going up most significantly. With the increase of solar radiation with time, VOCs participated in photochemical reactions and were consumed gradually, and the emissions from vehicle exhaust decreased due to the past of rush hour, NMHCs reached the lowest value at 14:00-16:00, and with the arrival of traffic peak in the evening, VOCs from vehicle emissions started to increase, but solar radiation was weakened and VOCs consumption was reduced, together with the falling atmospheric boundary layer, a night peak concentration was formed again. Unlike other cities at home and abroad, the measured ethyne also had a relative high level at 15:00, indicating that ethyne was not only affected by vehicle exhaust emissions, but also was contributed by other sources needed to be determined.
3.3 Diurnal variation of BTEX

Figure 2 shows the diurnal variation diagram of BTEX, they were strongly affected by traffic and reached the highest value during the morning and evening rush hours. With the increase of solar intensity, the concentrations of benzene, toluene and ethylbenzene decreased rapidly at noon, while m/p-xylene concentration decreased much slower after the early peak in the morning compared with the other three species, indicating that m/p-xylene was not only affected by vehicle exhaust emissions, but also affected by industrial emissions or solvent evaporation.
Figure 3. Contribution ratio of non-methane hydrocarbons to L^{OH} and OFP

The sources of BTEX include traffic emissions, industrial emissions and solvent evaporation, which also mean it is difficult to analyze the sources of BTEX. According to the characteristic tracer method proposed by Chang et al. [19], the contribution rate of vehicles and non-vehicle sources to NMHCs was distinguished by the ratios of ethylene to 3-methylpentane, toluene to 3-methylpentane and m/p-xylene to 3-methylpentane [20]. The studies from literatures showed that the average ratios of ethylene/3-methylpentane, toluene/3-methylpentane and m/p-xylene/3-methylpentane in vehicle emissions are 7.5, 5.4 and 1.5. The ratios of ethylene to 3-methylpentane, toluene to 3-methylpentane and m/p-xylene to 3-methylpentane were 54, 6.4 and 4, respectively at this site in Jinan, which were 7.2, 1.18 and 2.67 times higher than those from vehicle emissions. By calculation, 86% of ethylene was contributed by non-vehicle sources, which was verified by Figure 1; only 15% of toluene came from non-vehicle sources and therefore toluene came most from motor vehicles, 62.5% of total m/p-xylene came from non-vehicle sources, as shown in Figure 2.

3.4 Chemical reactivity

Figure 3 shows the contribution ratio of non-methane hydrocarbons to L^{OH} and OFP in eastern urban Jinan. It showed from the figure that the contribution of alkenes to L^{OH} and OFP were more than 50% while accounted for 33% of total non-methane hydrocarbons. Alkanes accounted for almost 50% of total non-methane hydrocarbons, while their contribution to L^{OH} and OFP were less than 20%. Accounting for 12% of total NMHCs, aromatic hydrocarbons contributed to L^{OH} and OFP at 10% and 24% respectively. So the atmospheric chemical activity of alkenes was very high, and the contribution of alkenes to L^{OH} and OFP were the largest, followed by aromatic hydrocarbons. Alkanes, though taking the highest proportion of NMHCs, were not the main contributor of L^{OH} and OFP. The contribution of acetylene was almost zero, which can be ignored.

4. Conclusion

The mixing ratio of Jinan non-methane hydrocarbon was 15.44 ppbv, among which alkanes accounted for 48%, alkenes accounted for 33%, aromatics accounted for 12%, and acetylene accounted for 7%. The diurnal variations of total non-methane hydrocarbons and their components showed a bimodal distribution, the minimum value appeared at 14:00-16:00, while acetylene and ethylene had other pollution sources besides motor vehicle emissions. According to the characteristic tracer method, 86% of ethylene was from non-vehicle resources, 15% of toluene was from non-vehicle resources, and 62.5% of m/p-xylene was from non-vehicle resources. Alkenes in atmospheric non-methane
hydrocarbons contributed most to L\(_{\text{OH}}\) and OFP, followed by aromatic hydrocarbons.

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