

# Major reactive species of ambient volatile organic compounds (VOCs) and their sources in Beijing

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**Abstract** Volatile organic compounds (VOCs) are important precursors of atmospheric chemical processes. As a whole mixture, the ambient VOCs show very strong chemical reactivity. Based on OH radical loss rates in the air, the chemical reactivity of VOCs in Beijing was calculated. The results revealed that alkenes, accounting for only about 15% in the mixing ratio of VOCs, provide nearly 75% of the reactivity of ambient VOCs and the C4 to C5 alkenes were the major reactive species among the alkenes. The study of emission characteristics of various VOCs sources indicated that these alkenes are mainly from vehicle exhaust and gasoline evaporation. The reduction of alkene species in these two sources will be effective in photochemical pollution control in Beijing.

**Keywords:** alkenes, radicals, vehicle exhaust, gasoline evaporation.

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Beijing has been suffering from serious air pollution, and the formation processes are very complex. Besides the primary pollutants emitted directly from industries, traffic and urban area sources, Beijing air quality is more seriously affected by fine particles and photochemical smog formed in secondary reactions<sup>[1]</sup>. In these reactions, VOCs in the air play important roles: the researches on atmospheric aerosols show that organics are the major components in particles, especially fine particles such as PM<sub>2.5</sub><sup>[2]</sup>, while the photochemical smog in urban areas, representing by higher concentrations of O<sub>3</sub>, probably formed through reactions sensitive to ambient VOCs<sup>[3, 4]</sup>. And moreover, some VOCs species at high ambient concentrations are air toxics that have direct impact on human health<sup>[5]</sup>. Therefore, study of atmospheric VOCs is one of the key missions to understand the trend of urban air quality.

Atmospheric VOCs are mixtures of more than 100 species that differ greatly in mixing ratios and chemical reactivity. The differences relate closely with the sources as shown in case studies in various cities: the atmospheric VOCs in Mexico city dominated by species from LPG leakage<sup>[6]</sup> in which alkenes accounted for a minor portion in the mixing ratios of VOCs, but were the major contributor to ambient VOCs reactivity; the continuous high levels of atmospheric O<sub>3</sub> in summer of Huston city depended mainly on reactive VOCs emitted from petrochemical industries<sup>[7]</sup>; while photochemical smog in Atlanta was formed in a VOCs limited chemical regime<sup>[8]</sup> and the reactivity of VOCs was dominated by biogenic isoprene<sup>[8]</sup>.

Technically, there are several approaches to estimate chemical reactivity of ambient VOCs. One is to normalize the reactivity of VOCs species, for example,

calculate the equivalent propene concentrations<sup>[9]</sup>; another is to employ reaction rates of VOCs species with atmospheric radicals, generally the most active OH radicals<sup>[10]</sup>. Maximum incremental reactivity (MIR) is also taken to assess chemical reactivity of VOCs species<sup>[11]</sup>.

As atmospheric VOCs have complex composition and vary with space and time, the effective control strategy can only be formulated after information of speciation and sources of VOCs is obtained. However, the research on atmospheric VOCs is relatively weak in the field of air chemistry in China. This work was performed to analyze the chemical reactivity of VOCs species based on the measurement of ambient VOCs in Beijing, to identify the major VOCs species that influence the air quality and to explore the sources of major reactive VOCs species based on the profiles of main VOCs emission sources.

## 1 Sampling and analysis

Whole air was sampled directly into 3.2-l Fused Silica Lined (FSL) stainless steel canisters (Entech Instrument, Inc.) with a maximum pressure loading of 3 atm. The samples were collected at 6 sites in Beijing from north to south, namely Ming Tomb (MT), Peking University (PKU), Dongcheng district (DC), Dongsi (DS), Xuanwu district (XW) and Tongxian district (TX). All the samples were taken at the top of buildings. The period of sampling was from July 2002 to March 2003 and the diurnal variations of ambient VOCs were done at the PKU site.

Vehicular exhaust, evaporation of gasoline/diesel fuel and LPG, solvent and paintings, and petrochemical industry were the main anthropogenic emission sources of VOCs in Beijing. The samples of mobile sources were taken on two traffic-condensed roads: Haidian bridge and west gate of Tsinghua University. The samples of paintings, solvent and fuels were taken directly from headspace of their evaporations. The emissions of asphalt were sampled at road construction site when asphalt was melted and used to pave the road. Whole air in various oil refineries of Beijing Yanshan Petrochemical Company was sampled to represent the petrochemical emissions.

VOCs analysis was carried out according to the methods of US EPA TO-14 and TO-15<sup>[12,13]</sup>. Whole air samples were pretreated on an Entech concentrator (7100A, SimiValley, CA, USA) at a constant rate manipulated by a mass flow controller (MFC). After removing the water and CO<sub>2</sub> in the samples by the pre-concentrator, VOCs species were separated by Gas Chromatography (Agilent 6890) and quantified by quadruple Mass Spectrum Detector (MSD, Agilent 5973) with a total ion scanning mode. Three internal standards, e.g. chlorobromomethane, 1-4-difluorobenzene and 1-bromo, 3-fluorobenzene were employed for quantification. The calibration of each VOCs specie was performed by linear regression from measurements of 5–7 mixing ratios ranging between  $0.2 \times 10^{-9}$  V/V– $20 \times 10^{-9}$  V/V. The measurement precisions for each VOCs specie were listed in ref. [14]. The GC-MSD system was calibrated by several standard gases from Department of Agriculture, Canada, Entech Incorporation USA and University of California at Irvine, and the deviations of GC-MSD sensitivities for the same VOCs species were within 20%.

## 2 Chemical reactivity of VOCs species

The ambient VOCs in Beijing were a complex mixture with up to 108 VOCs species quantified, including 32 kinds of alkanes, 26 alkene, 20 aromatics, and 18 halogenated alkanes, 9 halogenated alkenes and 3 halogenated aromatics. The mixing ratios and variations of VOCs species in Beijing were described elsewhere<sup>[15]</sup>.

In fact, it would be ineffective to achieve the same reduction of all VOCs species. To identify key species for prior control of ambient VOCs, this work focused on the role of VOCs in atmospheric chemistry instead of their direct toxic effects. So chemical reactivity, in terms of loss rate of OH ( $L_{OH}$ ) due to the reaction with various VOCs species was used<sup>[10]</sup>. Although the ambient concentrations of O<sub>3</sub> are generally much higher than that of OH radicals, the rate constants of O<sub>3</sub> with VOCs are far below those of OH with VOCs. As a consequence, the influence of O<sub>3</sub> on atmospheric life time of VOCs is negligible, so O<sub>3</sub> was not taken into account when calculating the chemical reactivity of

VOCs.

The chemical reactivity of one VOCs species can be expressed as below [10]:

$$L_i^{\text{OH}} = [\text{VOCs}]_i \times K_i^{\text{OH}}, \quad (1)$$

where  $L_i^{\text{OH}}$  is the loss rate of OH radical due to reaction with  $i$  species of VOCs ( $\text{s}^{-1}$ );  $[\text{VOCs}]_i$  is the concentration of  $i$  species of VOCs ( $\text{molecule} \cdot \text{cm}^{-3}$ );  $K_i^{\text{OH}}$  is the rate constant of the reaction of OH radical with  $i$  species of VOCs ( $\text{cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ ).

When a group of VOCs (for example, alkanes, alkenes, aromatics or alkenes with carbon number of 4, etc.) is calculated, the sum of  $L_i^{\text{OH}}$  of every species in the group is used:

$$L^{\text{OH}} = \sum [\text{VOCs}]_i \times K_i^{\text{OH}}. \quad (2)$$

There are abundant literatures on  $K_i^{\text{OH}}$ , the data used in this study were cited from ref. [16].

## 2.1 Chemical reactivity of ambient VOCs in Beijing

The chemical reactivities of alkanes, alkenes and aromatics of total 108 samples were calculated according to eq. (2), and the results were stacked up as shown in Fig. 1. It can be clearly seen that alkenes

were the major contributor of chemical reactivity of ambient VOCs in Beijing. With the VOCs mixing ratio ranged between  $9.8 \times 10^{-9}$  V/V and  $108 \times 10^{-9}$  V/V, alkenes, accounting for only about 15% in VOCs mixing ratios, but contributed (75±7)% of reactivity of total ambient VOCs. In contrast, alkanes took up more than 50% of mixing ratio of VOCs, but only had a sharing of (15±4)% of the reactivity, and the rest (13±4)% reactivity of VOCs was made up by aromatics.

To get an idea on the VOCs reactivity of urban plume, the correlation between reactivity ( $L^{\text{OH}}$ ) and the mixing ratio of VOCs in Beijing was analyzed, and then compared with the results obtained in summer 2004 in New England area of US (around New York and Boston city) (Fig. 2).

As illustrated in Fig. 2, taking VOCs as a whole, the chemical reactivity and mixing ratio of ambient VOCs had a good linear relationship, indicating that the chemical compositions of ambient VOCs from all sites were similar. From the slope of the linear correlation, the rate constant ( $K_{\text{OH}}$ ) of total VOCs with OH radical could be derived, the  $K_{\text{OH}}$  value for Beijing city was about  $11 \times 10^{-12} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ , showing that the chemical reactivity of ambient VOCs was even higher

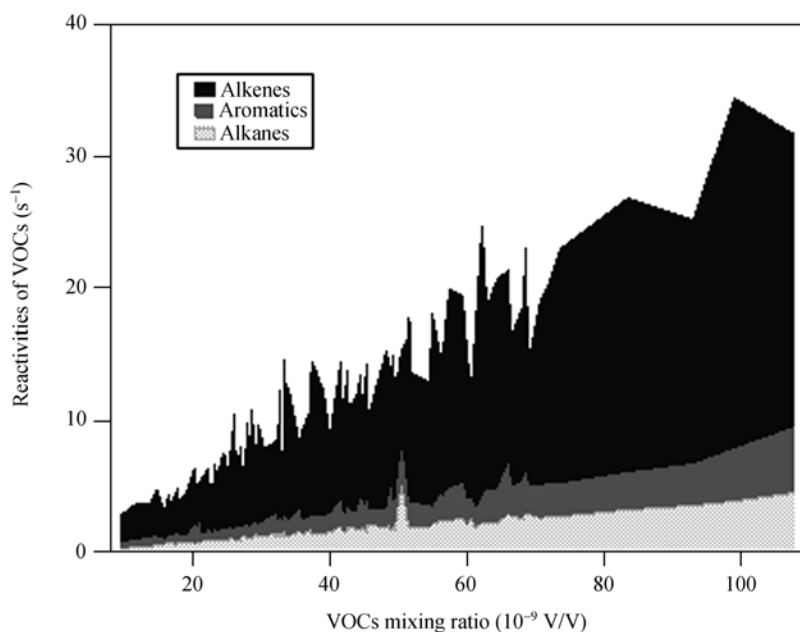


Fig. 1. The aggregated chemical reactivity of atmospheric alkanes, aromatics and alkenes in Beijing.

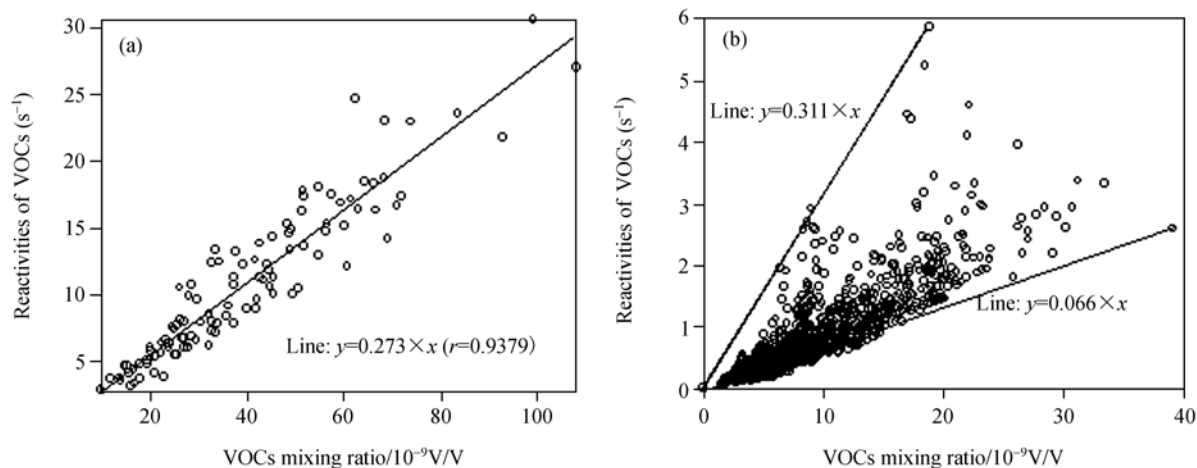


Fig. 2. The correlation between chemical reactivity and mixing ratio of ambient VOCs (a) Beijing city ; (b) New England area, USA.

than that of ethene. Differently, the data measured in New England area were much scattered, the  $K_{OH}$  of ambient VOCs ranged between  $2.7 \times 10^{-12}$  and  $12.6 \times 10^{-12} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$  with an average of  $4.2 \times 10^{-12} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ . The chemical reactivity of ambient VOCs was similar to pentane.

## 2.2 Major reactive VOCs species in Beijing

To further investigate the dominating alkenes species, all of the 26 alkenes were classified by carbon number and the percentage of chemical reactivities of C3 to C8 alkenes in total alkenes reactivities was calculated, as shown in Fig.3 by stacking them up. It should be pointed out that several important tracers, such as propene in C3 group, 1,3-butadiene in C4 group and isoprene in C5 group, were separately presented instead of integrated into the C3, C4 and C5 groups in Fig. 3.

Very similar to Fig.1, from rather clean air mass with only  $9.8 \times 10^{-9}$  V/V of alkenes, to heavily polluted areas where alkene mixing ratio were up to  $108 \times 10^{-9}$  V/V, which was more than one order of magnitude higher, the groups of alkenes had relatively stable sharing in chemical reactivity of alkenes. This meant that though alkenes had short lifetime in the air, the role of groups of alkenes in atmospheric chemistry had distinct similarity at all the sites: down wind, upwind of the city as well as the city center. Furthermore, C4 and C5 alkenes were the most important contributor to

chemical reactivity, the sum of these two groups accounted for about 60% of total alkenes reactivity, 1,3-butadiene alone provided more than 10%. Isoprene was generally considered to be the tracer of biogenic emissions, but actually in urban areas vehicular emission was also a significant isoprene source<sup>[17]</sup>, and this was also proved by the source profile measurement results of this work.

The group of alkenes with 6, 7 and higher carbon numbers had a very low mixing ratio and a big diversity of isomers in the ambient air. So it's difficult to obtain reliable quantification of the whole family of C6-C8 alkenes. From the data that can be quantified so far, these species accounted for more than 30% of the whole alkenes reactivity. Their roles in the Beijing air chemistry were clearly quite essential.

The distribution structure of VOCs chemical reactivity shown in Fig. 3 was found to be quite typical for the city. Measurements of ambient VOCs were performed simultaneously at 5 sites from north to south in Beijing with PKU site used for long-term monitoring. The chemical reactivities of all groups of alkenes and the mixing ratios of total VOCs at all the 6 sites are presented in Fig. 4. It can be seen from Fig. 4 that the mixing ratios and chemical reactivity obtained at the 6 sites are significantly different from each other. However, the relative contribution of different groups of alkenes is very similar, with C4 and C5 alkenes as the major contributor to the chemical reactivity of ambient VOCs at every site.

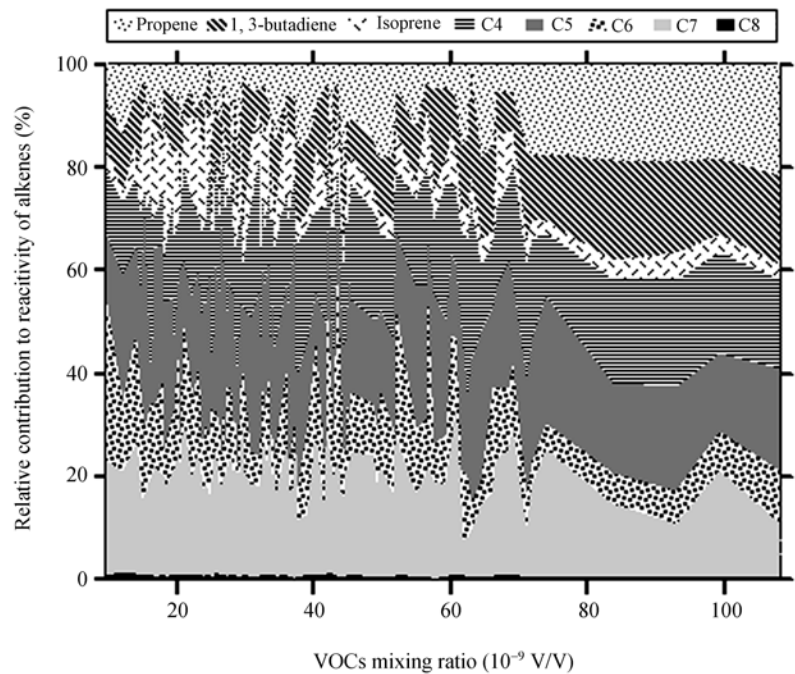


Fig. 3. The percentage of chemical reactivity of different groups of alkenes in the summed reactivity of total alkenes.

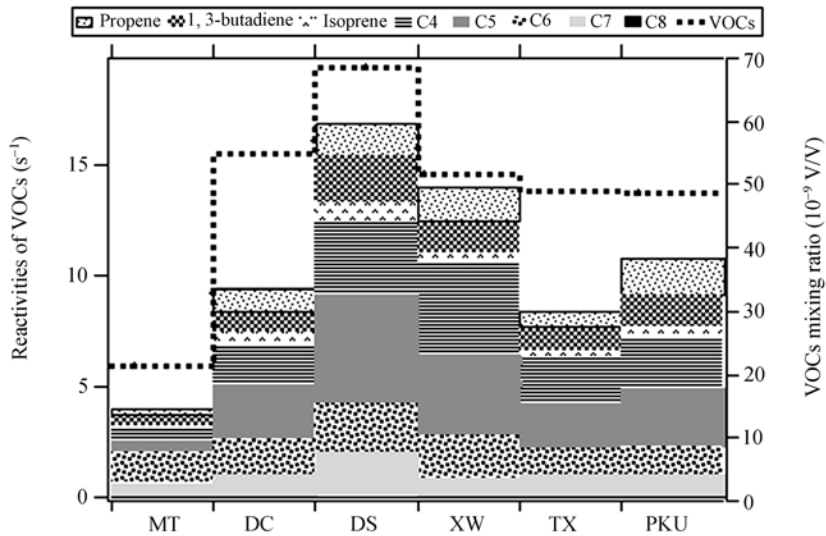


Fig. 4. Comparison of the chemical reactivity of alkenes at the six sampling sites of Beijing city.

Table 1 The relative contribution of different groups of alkenes to the reactivity of total alkenes

| Group            | C3*     | C4*      | C5*      | C6       | C7       | C8      |
|------------------|---------|----------|----------|----------|----------|---------|
| Contribution (%) | 9.2±5.4 | 27.2±7.8 | 31.2±9.0 | 13.5±5.8 | 18.4±5.5 | 0.5±0.2 |

\* Here the results of propene, 1,3-butadiene and isoprene were included in the C3, C4 and C5 alkene groups, respectively.

Also noteworthy, there seemed to be a certain level

of regional background of the chemical reactivity of C6 alkenes. The value obtained at Ming Tomb site, which was considered as a background site for Beijing, was comparable to that obtained at the downtown site (DS). The regional average reactivity of C6 alkenes is more or less the same as the reactivity of alkanes. This phenomenon needs further investigation.

Table 2 The chemical composition of ambient VOCs source profiles in Beijing

|                        |                        |                         |
|------------------------|------------------------|-------------------------|
| <b>Alkanes</b>         | 2,3,4-trimethylpentane | 4-methyl-1-pentene      |
| propane                | 3-methylheptane        | tetrachloroethene       |
| isobutene              | n-octane               |                         |
| n-butane               | n-nonane               | <b>Aromatics</b>        |
| 2,2-dimethylpropane    | n-decane               | benzene                 |
| 2-methylbutane         | undecane               | toluene                 |
| n-pentane              |                        | ethylbenzene            |
| 2,2-dimethylbutane     | <b>Alkenes</b>         | mp-xylene               |
| 2,3-dimethylbutane     | propene                | styrene                 |
| 2-methylpentane        | 1-butene               | o-xylene                |
| 3-methylpentane        | 1,3-butadiene          | isopropylbenzene        |
| n-hexane               | trans-2-butene         | n-propylbenzene         |
| 2,4-dimethylpentane    | cis-2-butene           | 3 or 4-ethyltoluene     |
| cyclohexane            | 1-pentene              | 1,3,5-trimethylbenzene  |
| 2-methylhexane         | 2-methyl-1-butene      | 2-ethyltoluene          |
| 2,3-dimethylpentane    | isoprene               | 1,2,4-trimethylbenzene  |
| 2,2,4-trimethylpentane | cis-2-pentene          | 1,2,3- trimethylbenzene |
| n-heptane              | 2-methyl-2-butene      | 1,3-diehtylbenzene      |
| methylcyclohexane      | cyclopentene           | 1,4- diehtylbenzene     |

### 3 Source identification of reactive VOCs

Till now, numbers of source profiles of VOCs had been established and the target compounds in the profiles have extended from 23 species<sup>[18]</sup> at the early stage to current 55 species<sup>[19]</sup>. In comparison with the existing source profiles, the study of VOCs source profiles in Beijing city was also focused on the same 55 species as listed in Table 2 and the rest species quantified were summed up and referred to as others.

The source profile of VOCs was expressed by the percentage of mass concentration of each VOCs species in the mass concentration of total VOCs in the source emission. The profiles for mobile source, asphalt emission of road construction, leakage of LPG and petrochemical industry were derived from the averages of all the measurement data for each type of sources. The profiles for evaporation of painting, gasoline and diesel fuel were obtained by measuring headspace of their evaporation, and then averaging the measurement data weighted by annual sales of each brand of products. Fig. 5 gives the composition structures of alkanes, alkenes and aromatics in the source profiles measured in this study.

It can be seen from Fig. 5 that the chemical compositions of different VOCs emission sources differ greatly from each other. Aromatics had a very large

sharing in painting evaporation, while the asphalt under high temperature during road pavement mainly emitted alkanes with big carbon numbers (>C6). The major components of LPG were propane and butane and the VOCs emissions from petrochemical industry linked closely with their oil products, i.e. mainly aromatics and alkanes on an average. Alkenes that dominated the chemical reactivity of VOCs in Beijing came mainly from vehicle emissions and gasoline evaporation.

The compositions of alkenes from vehicle emission and gasoline evaporation were compared in Fig. 6. The same grouping of alkenes was adopted so as to make the comparison more compatible with the analysis of VOC reactivity.

It is important to note that the mobile source samples used in this work were the whole air sample taken on the roads. Therefore they were actually a mixture of the vehicular exhaust and gasoline evaporation. From Fig. 6, it can be seen that the composition of alkenes emitted from mobile sources was complicated. Lighter alkenes (<C4) as well as isoprene were mainly from the vehicular exhaust, while the percentages of heavier alkenes (>C4) were larger in gasoline evaporation than that from vehicular exhaust.

From above discussions, we knew that ambient

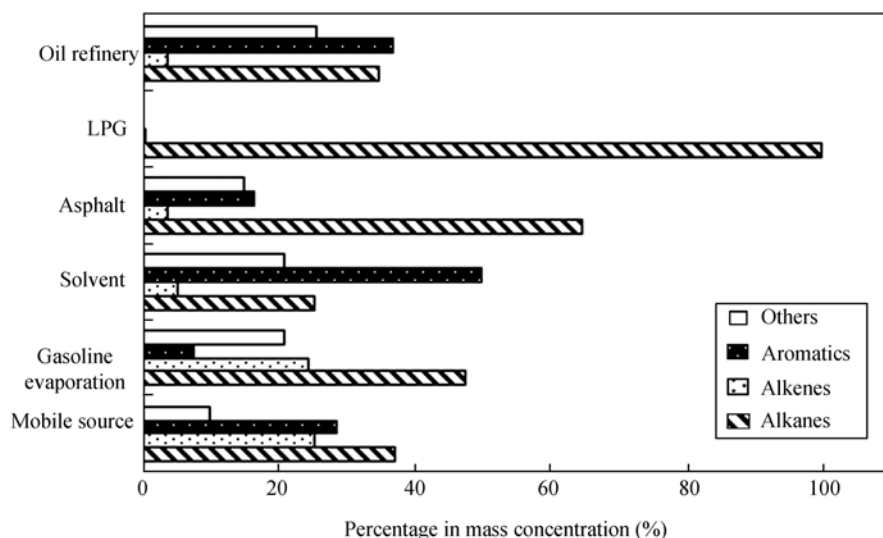


Fig. 5. The chemical composition (in percentage of mass concentration) of main sources of VOCs.

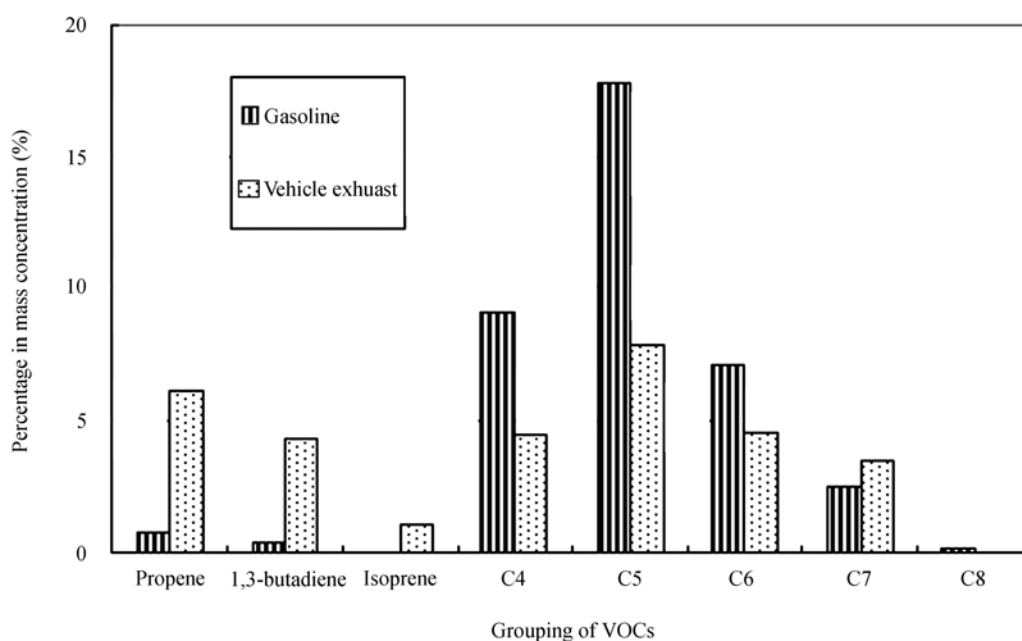


Fig. 6. Comparison of the alkene compositions of emissions from mobile source and gasoline evaporation.

VOCs in Beijing had very strong chemical reactivity, and the major active species were alkenes. The study on source profiles indicated that these alkenes came mainly from mobile sources and gasoline evaporation. Therefore, in the process of rapid increase of vehicle population in Beijing, to achieve control or even reduction of photochemical smog pollution, municipal government needs to set up in-used vehicle emission

control system by focusing on development of three-way catalyst technology. Meanwhile, it is necessary to innovatively adopt as early as possible the most advanced emission standards for new vehicles and to promote the utilization of recycling technology of gasoline evaporation in vehicle. Furthermore, the improvement of fuel quality is also an important way to reduce the vehicular emissions, and the unsaturated

components in fuels need to be reduced by the employment of full hydrogen addition technology in oil refinery industries. And stringent management to control the leakage of fuel in the process of transportation is required as well.

#### 4 Conclusion

The characteristics and sources of ambient VOCs in Beijing city were investigated from the point of their chemical reactivity. The results indicated that the chemical reactivity of VOCs was very strong. The estimated rate constant of total VOCs with OH radical was even higher than that of ethene. Alkenes, only accounting for about 15% in the mixing ratio of total VOCs, contributed about 75% of chemical reactivity. This feature was almost the same in all the 6 sampling sites in Beijing from north to south pathways. Among all the groups of alkenes, the C4 and C5 alkenes were the major contributor to VOCs reactivity in Beijing.

To explore the sources of reactive VOCs species is very important for making appropriate control strategies. However, no effective approaches are available to directly quantify their sources. This work conducted a survey on possible VOCs emission sources in Beijing, and compared the chemical compositions of the obtained source profiles with the reported data. The study showed that atmospheric alkenes in Beijing city were mainly from mobile sources and gasoline evaporation. Thus at the early stage of ambient VOCs control in Beijing, prioritizing the reduction of alkene species will be an effective measure to prevent the aggravation of photochemical smog pollution.

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