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Tempo-spatial variation of emission inventories of speciated volatile organic compounds from on-road vehicles in China

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Abstract

Emission inventories of sixty-nine speciated non-methane volatile organic compounds (NMVOC) from on-road vehicles in China were estimated for the period of 1980–2005, using seven NMVOC emission profiles, which were summarized based on local and international measurements from published literatures dealing with specific vehicle categories running under particular modes.

Results show an exponential growth trend of China's historical emissions of alkanes, alkenes, alkines, aromatics and carbonyls during the period of 1980–2005, increasing from 63.9, 39.3, 6.9, 36.8 and 24.1 thousand tons, respectively, in 1980 to 2781.4, 1244.9, 178.5, 1350.7 and 403.3 thousand tons, respectively, in 2005, which coincided well with China's economic growth. Emission inventories of alkenes, aromatics and carbonyls were gridded at a high resolution of 40 km×40 km for air quality simulation and health risk evaluation, using the geographic information system (GIS) methodology. Spatial distribution of speciated NMVOC emissions shows a clear difference in emission densities between developed eastern and relatively underdeveloped western and inland China. Besides, the appearance and expansion of high-emission areas was another notable characteristic of spatial distribution of speciated NMVOC emissions during the period.

Emission contributions of vehicle categories to speciated NMVOC groups showed annual variation, due to the variance in the provincial emissions and in the relative fractions of the seven emission profiles adopted at the provincial level. Highly reactive and toxic compounds accounted for high proportions of emissions of speciated NMVOC groups. The most abundant compounds were isopentane, pentane and butane from alkanes; ethene, propene, 2-methyl-2-butene and ethyne from alkenes and alkines; benzene, toluene, ethylbenzene, o-xylene, and m,p-xylene (BTEX) and 1,2,4-trimethylbenzene from aromatics and formaldehyde, acetaldehyde, benzaldehyde, acetone and acrolein from carbonyls.

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1 Introduction

Concerns about non-methane volatile organic compounds (NMVOC) have increased due to their crucial role in tropospheric chemistry. Through photochemical reaction with nitrogen oxides in the atmosphere, NMVOC contribute to the production of secondary pollutants such as ozone, peroxyacetyl nitrate (PAN) and secondary organic aerosols (Atkinson, 2000; Odum et al., 1997). Different groups of NMVOC compounds differ significantly in how rapidly they react and the extent to which their reactions contribute to ozone formation. These differences in the effects on ozone formation are referred to as the ozone reactivities of NMVOC (Duffy et al., 1999). Besides, NMVOC are the main inputs to atmospheric chemistry models that study the formation and fate of photochemical oxidants in the atmosphere (Klimont et al., 2002). Therefore, compilation of speciated NMVOC emission inventories is necessary for photochemical modeling calculations and for the design of abatement strategies for ozone and secondary organic aerosols.

Speciated NMVOC profiles of major anthropogenic sources, especially the mobile source, were extensively measured (Duffy et al., 1999; Conner et al., 1995; Kourtidis et al., 1999; Hwa et al., 2002; Batterman et al., 2005; Lough et al., 2005). Recently, major source profiles of NMVOC in China were measured by Liu et al. (2008). These studies obtained fruitful results about the compositional and concentration characteristics of speciated NMVOC groups, together with the important information on the reactivities of specific NMVOC species, which was necessary for evaluating the ozone-formation potentials of NMVOC. Among the major anthropogenic sources of NMVOC emissions, the automobile has been recognized in many countries as a primary contributor: highway vehicle emissions dominated in the USA for the period of 1970–2006, although the contribution of this sector showed a decreasing trend from 48.8% in 1970 to 14.4% in 2007 (USEPA, 2008). Similar situation appeared in UK during the period 1970–2000, with the road transport emissions accounting for 22.5–36.2% of the total emissions. Analysis of the contribution of motor vehicles to ambient hydrocarbon distributions in

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Switzerland concluded that the proportion of VOC from motor traffic amounted to 48–67% (Staehelin et al., 2001). Traffic emission was recently recognized to determine the ambient NMVOC composition in a German city (Niedojadlo et al., 2007). Source apportionment of ambient VOC in Beijing revealed that gasoline-related emissions contributed 52% to the total ambient VOC (Song et al., 2007). Despite the likely dominant contribution of on-road vehicles to NMVOC emissions in China, only limited research on providing China's database of NMVOC emissions was conducted: composition of C_2-C_{10} NMVOC in the urban atmospheres of 43 Chinese cities were measured (Barletta et al., 2005); emission inventories of total NMVOC in China for the years 1990, 1995, 2000, 2010, and 2020 were compiled (Klimont et al., 2002); an Asian emission inventory of anthropogenic emission sources for the period 1980–2020 was developed, which presented Chinese NMVOC emissions in 2000 and for 1980–2003, and the projected NMVOC emissions for 2010 and 2020 (Ohara et al., 2007); the anthropogenic NMVOC emissions in China were estimated for the period of 1980–2005 (Bo et al., 2008), and for the years 1994–1995 (Tonooka et al., 2001). Recently, Wei et al. (2008) compiled a speciated NMVOC emission inventory from major anthropogenic sources in China for the year 2005. However, traffic-related emission inventories of speciated NMVOC were rarely compiled in China, especially for the recently historical emissions, leaving a large information gap. Therefore, for a better understanding of the formation of ozone and other secondary oxidants and for better practices in health risk management and design of control strategies for highly reactive and toxic NMVOC, emission inventories of speciated NMVOC groups from on-road vehicles in China covering the period of 1980–2005 are compiled at the provincial level in this study, and are further allocated to the county level based on differences in local economic development levels and gridded at a high resolution of 40 km×40 km using the geographic information system (GIS) methodology. In particular, temporal variation and spatial distribution of the speciated inventories were discussed, the compositional characteristics of speciated NMVOC groups were identified, and the contributions of various vehicle categories to speciated emissions were evaluated.

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2 Methodology

2.1 Emissions of speciated NMVOC groups

Emissions of speciated vehicular NMVOC groups included speed-dependent hot emissions under thermally stabilized engine and exhaust aftertreatment conditions, the warming-up phase of cold start emissions influenced by ambient temperature and average trip length, and the fuel evaporation emissions. The emissions of each specific NMVOC species were calculated based on the gross NMVOC emissions of specific vehicle category running under particular conditions and the corresponding emission profiles, using Eq. (1), which covered thirty-one provinces/autonomous regions/municipalities on the Chinese mainland, with Hong Kong Special Administrative Region, Macau Special Administrative Region, and Taiwan province excluded.

$$E_s = \sum_{i=1}^{6} (Q_{\text{ext},i} \times P_i) + Q_{\text{eva}} \times P_{\text{eva}} \quad (1)$$

Where: E_s is the emission for each specific NMVOC species in a studied year; $Q_{\text{ext},i}$ are the tailpipe exhaust NMVOC emissions of that year including hot emissions and cold start emissions under a particular condition i, which includes six situations corresponding to each specific vehicle category running under a normal (20 km/h and 40 km/h) mode or a freeway (80 km/h) mode; P_i are the six corresponding profiles of tailpipe exhaust NMVOC emissions for specific vehicle categories running under urban or freeway modes; Q_{eva} is the gasoline evaporation emission and P_{eva} is the emission profile for Q_{eva}.

The tailpipe exhaust and evaporation emissions of each vehicle category at the provincial level from 1980 to 2005 were from the results of Cai and Xie (2007), and the six profiles of tailpipe exhaust emissions including sixty-seven constituents of alkanes, alkenes, alkines, carbonyl compounds and aromatics and the gasoline evaporation emission profile including forty-one constituents were determined based on a wide review of published literatures which reported the NMVOC emission profiles for both

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domestic and abroad on-road vehicles. Thus, the determined emission profiles were representative of the vehicular NMVOC emission profiles for different vehicle types under specific running modes in China.

To determine each P_i and P_{eva}, the NMVOC emission profiles for various vehicle categories under particular running modes were firstly surveyed from available published literatures. Secondly, the relative weight proportions of a specific measured species from all available emission profiles measured with the same vehicle category under similar measurement conditions were used to calculate a mean value using Eq. (2), which represented the relative weight proportion of that species in the emission profile to be determined. Finally, the calculated mean values of all species for the particular emission profile were normalized to be the identified relative weight ratios of various species of that emission profile. As a result, the gasoline evaporation emission profile, and the six profiles for tailpipe exhaust emissions were identified, which included the emission profiles for gasoline vehicles with three-way catalysts (TWC) and without TWC, respectively, running under the normal mode, the emission profiles for diesel vehicles running under normal and freeway modes, respectively, the emission profile for gasoline vehicles running under the freeway mode, and the emission profile for motorcycles.

$$RWP_s = \frac{\sum_{i=1}^{n} RWP_{s_i}}{n} \quad (2)$$

Where: RWP_s is the averaged relative weight proportion of a specific species; RWP_{s_i} is one relative weight proportion of that specific species from surveyed published literatures; and n is the number of surveyed published literatures that reported the relative weight proportion of that specific species.

Tables 1 and 2 show the identified profile of tailpipe exhaust emissions for gasoline vehicles with TWC running under normal mode and gasoline evaporation emission profile. Profiles of tailpipe exhaust emissions for other vehicle categories running under particular modes are provided in the Supplementary Material (see http://www.atmos-chem-phys-discuss.net/9/11051/2009/acpd-9-11051-2009-supplement.zip).

For the period of 2000–2005 when both TWC gasoline vehicles and non-TWC gasoline vehicles were used, since China formulated the regulations that required installing TWC on new gasoline vehicles coming into use after 2000, gasoline vehicles coming into use before 2000 were considered without TWC on them, and all newly-used gasoline vehicles since 2000 were considered with TWC on them. Thus, the identified emission profile for gasoline vehicles with TWC was applied to emissions of all newly-used gasoline vehicles since 2000, and the emission profile for gasoline vehicles without TWC was applied to emissions of all gasoline vehicles used before 2000. Table 3 summarizes the utilization rate of TWC among gasoline vehicles based on the governmental statistical data (NBS, 2006).

2.2 Emission allocation

In order to understand the spatial distribution of NMVOC species, and to aid model simulation and evaluation of the effects of reactive and toxic species on human health and air quality, emissions of alkenes, aromatics and carbonyls in China were gridded at a resolution of 40 km×40 km using Arcgis, a geographic information system (GIS) software. Firstly, provincial emissions were allocated to the county-level emissions, following a top-down approach based on a proxy variable of GDP, using Eq. (3):

$$E_{m,n} = \frac{G_n}{G_m} \times E_m \tag{3}$$

Where: $E_{m,n}$ is the emission in county n of province m; E_m is the emission in province m; G_n and G_m are the GDP in county n and province m, respectively.

Secondly, the latitude and longitude projected map of China was gridded at a resolution of 40 km×40 km using Arcgis, which further calculated the ratios of the areas of each county that fell over various grid cells to the area of that county. Then, the emission of that county were allocated to each covering grid cell based on the calculated ratios. Finally, the emission within a grid cell was the sum of the emissions from the covered areas of various counties.

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3 Results and discussion

3.1 Temporal variation of emissions and emission contributions of vehicle categories from 1980 to 2005

3.1.1 Temporal variation of emissions

Over the past two and half decades, China has experienced fast economic growth, together with a rapid increase of motor vehicle population by 94 times, from 2.1 million in 1980 to 197 million in 2005. Meanwhile, the annual NMVOC emissions in China had increased exponentially by 35 times at an annual average rate of 15%, from 171.1 thousand tons in 1980 to 5958.8 thousand tons in 2005. The direct cause for this emission increase must be ascribed to the substantial growth of vehicle population, increase of the vehicle miles travelled (VMT), and the late execution of more stringent fuel and emission standards in China over the past years.

Multi-year vehicular emissions of sixty-nine NMVOC species, including alkanes, alkenes, alkines, aromatics and carbonyls, are shown in Table 4, which reveals that emissions of all groups experienced exponential increase during the period of 1980–2005: emissions of alkanes, alkenes, alkines, aromatics and carbonyls had increased by about 44, 32, 26, 37 and 17 times, respectively, during the period. Besides, emissions from tailpipe exhaust and emissions from fuel evaporation increased from 143.4 and 27.7 thousand tons, respectively, in 1980 to 4817.7 and 1141.1 thousand tons, respectively, in 2005. Proportion of evaporation emissions grew from 16.2% in 2000 to 19.1% in 2005, showing an increasing trend in recent years. Thus, stricter control of NMVOC emissions from fuel evaporation is required.

Statistical analysis of the relationship between NMVOC emissions and economic growth showed that China's economic growth had a well positive correlation with the tremendous increase of total, total tailpipe exhaust and total evaporation emissions of NMVOC over the period of 1980–2005, with a correlation coefficient of 0.99 between the GDP growth and total NMVOC emission increase, as shown by Fig. 1.

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Figure 1 depicts clearly that economic growth has been a powerful driving force for vehicular NMVOC emissions. With the persistent and rapid growth of income of residents, Chinese people's capabilities and desires of owning a private car have been unprecedentedly strong, which guaranteed the continuous growth of vehicle population in China and thus the enormous increase of vehicular NMVOC emissions.

3.1.2 Annual emission contributions of various vehicle categories

Although light duty vehicles (LDV) and heavy duty vehicles (HDV), and motorcycles were recognized the primary contributors to total NMVOC emissions in the 1980s and for the period of 1990–2005, respectively (Cai and Xie, 2007), contributions of vehicle categories to the emissions of speciated NMVOC groups varied, due to the variance in the gross NMVOC emission quantities and the accordingly adopted emission profiles for different vehicle categories. Contributions of vehicle categories to emissions of speciated NMVOC groups for the period of 1980–2005 are depicted in Fig. 2, to provide the policy-makers with evidences of primary contributors to specific NMVOC groups when designing cost-effective measures for the reduction and control of both total and speciated NMVOC emissions.

Figure 2a shows that contributions of vehicle categories to alkane emissions varied with time. Motorcycles, commonly used in cities in the 1980s and became popular later in rural areas of China, were the primary contributors during the period of 1980–2005, due to their relatively higher emission factors and their huge and ceaselessly growing population. Passenger cars (PC), due to their large and increasing population and poor levels of emission control, were another major contributors. LDV, due to their wide utilization in freight transportation in the 1980s, were also major contributors then. However, their contribution decreased later on, due to their slower increase of population in comparison with other vehicle categories. HDV and buses, due to their relatively small population, contributed less than 1% in the 1980s, about 4–5% in the 1990s and about 3% for the period of 2000–2005. Therefore, motorcycles and PC were responsible for most alkane emissions, altogether accounting for 79%, 90% and

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93%, respectively, in 1985, 1995 and 2005. Besides, provincial differences of vehicle category contribution were significant, mainly due to diverse compositions of provincial vehicle fleet. For example, PC were the primary contributors in Beijing, accounting for 66–81% of alkane emissions during the period of 2000–2005, when motorcycles, however, were the major contributors in Guangdong, responsible for 74–77% of the emissions. Therefore, measures to control and reduce provincial emissions should be established and taken individually according to the specific major contributors in each province.

As shown in Fig. 2b, motorcycles and PC, due to their massive population and high VMT, were the major contributors to alkene and alkine emissions during the period of 1980–2005. In the 1980s, motorcycles contributed 50–59% to the total emissions, followed by PC and LDV, which accounted for 19–23% and 17–20%, respectively. In the 1990s, contribution of HDV mainly burning diesel increased significantly and accounted for about 23–28%, while motorcycles and PC still dominated in the emission share in that period. Due to their huge population and high emission factors, motorcycles continued to dominate in the emission contributions for the period of 2000–2005, followed by HDV and PC, which accounted for 17–20% and 15–17%, respectively. Buses contributed more during this period, due to their growing population stimulated by the increase of demand for public transportation in China's urban areas. Therefore, stringent control on motorcycles and PC is required to reduce the emissions of alkenes and alkines.

Figure 2c illustrates that motorcycles and PC mainly burning gasoline were the dominant contributors to aromatic emissions during the period of 1980–2005, due to their high emission factors of aromatics and much larger populations. This characteristic agreed with the result that gasoline-power vehicles were the main source of aromatic hydrocarbons (Mugica et al., 2003). Moreover, motorcycles were responsible for about 53–61%, 53–57% and 69–74% of aromatic emissions in the 1980s, in the 1990s and during the period of 2000–2005, respectively, showing an increasing trend in their contribution to aromatic emissions, while PC accounted for about 19–23%, 30–32% and

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17–21%, respectively, during the same periods, when LDV contributed about 19–22%, 5–6% and 4–5%, respectively, showing a decreasing trend in their contribution to aromatic emissions. HDV and buses, which mainly burned diesel and had relatively much smaller populations, accounted for only about 1–2% in the 1980s, for about 7–10% in the 1990s and for about 5% during the period of 2000–2005.

Contributions of vehicle categories to carbonyl emissions were significantly different from those to alkane or alkene emissions, since various vehicle categories had remarkably different emission factors for carbonyl compounds and for other speciated NMVOC groups. Figure 2d shows that HDV with higher emission factors for carbonyls were the major contributors during the period of 1990–2005, responsible for about 39%, 32% and 36% of carbonyl emissions in 1995, 2000 and 2005, respectively, when PC, despite their much larger population, accounted for only about 24%, 19% and 18%, respectively, for the same years. Motorcycles, due to their tremendous population, were another major contributors, accounting for about 39–46%, 23–28% and 39–41% in the 1980s, in the 1990s and during the period of 2000–2005, respectively.

3.2 Emissions in 2005

3.2.1 National and provincial emissions of speciated NMVOC groups

The emissions of alkanes, alkenes, alkines, aromatics and carbonyls in 2005 were 2781.4, 1244.9, 178.5, 1350.7 and 403.3 thousand tons, respectively. Alkanes, aromatics and alkenes were the dominant speciated groups, which accounted for 46.7%, 22.7% and 20.9%, respectively.

It appears that China's vehicular NMVOC emission in 2005 was very close to that in the United States for the years of 1990–1994 (5507–5894 thousand tons; USEPA, 2008). There were significant differences, however, in emission densities normalized to population and in emission intensities normalized to gross domestic production (GDP, in current price): emission densities in China and the Unites States in 2005 were about 4.59×10^{-3} and about 1.24×10^{-2} ton per capita, respectively; emission

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intensities in China and the Unites States in 2005 were about 2.66×10^{-3} and about 3.34×10^{-4} ton/10^3 US dollars, respectively. Differences in emission densities revealed that the emission per capita in China in 2005 was only about 37% of that in the USA in the same year, due to the much larger population of China. Emission intensity in China in 2005, however, was about eight times higher than that of the USA in 2005, which revealed that the NMVOC emission per unit of output was much higher in China, mostly due to higher emission factors of vehicles and higher VMT in China.

Emissions of speciated NMVOC groups varied notably among provinces in China, due to remarkable differences in provincial vehicle population and composition. Figure 3, which illustrates the provincial emissions and relative proportions of speciated NMVOC groups in 2005, showed that Guangdong emitted about 823.0 thousand tons of NMVOC and ranked No. 1 among all provinces in 2005, with the emissions of alkanes, alkenes, alkines, aromatics and carbonyls accounting for 454.9, 160.5, 18.0, 149.9 and 39.6 thousand tons, respectively. Guangdong, Shandong, Jiangsu, Henan and Zhejiang, the developed regions constituting 41.0% of the total GDP but covering only 6.9% of the territory, contributed 47.2%, 45.4%, 44.3%, 46.9% and 40.6% of the emissions of alkanes, alkenes, alkines, aromatics and carbonyls, respectively, in 2005. On the contrary, Tibet produced least emissions, with about 3.0, 2.3, 0.4, 2.0 and 1.6 thousand tons of alkanes, alkenes, alkines, aromatics and carbonyls, respectively, in 2005. Only 3.4%, 4.0%, 4.2%, 4.0% and 4.4% of the speciated emissions, respectively, were ascribed to Tibet, Qinghai, Ningxia, Gansu and Xinjiang, five northwestern provinces covering 42.5% of the territory. Annual provincial emissions of speciated NMVOC groups from 1980 to 2005 are provided in the Supplementary Material (see http://www.atmos-chem-phys-discuss.net/9/11051/2009/acpd-9-11051-2009-supplement.zip).

Relative emission proportions of speciated NMVOC groups at the provincial level also varied, as shown by Fig. 3, due to diverse provincial vehicle compositions which resulted in different quantities of gross NMVOC emissions and different proportions of the seven emission profiles adopted at the provincial level. In 2005, provincial ratios of alkane emissions decreased from 57.1% in Hainan, a coastal province in Southern

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China, to 32.1% in Tibet located in Northwestern China, and the provincial emission ratios of alkenes, alkines, aromatics and carbonyls decreased from 24.8% in Tibet, 4.5% in Tibet, 31.2% in Beijing and 17.4% in Tibet, respectively, to 16.0% in Beijing, 1.9% in Guangxi, 17.3% in Hainan, 3.5% in Guangxi, respectively.

3.2.2 Compositional characteristics of national and provincial emissions of speciated NMVOC groups

Knowledge of compositional characteristics of speciated NMVOC groups is necessary for photochemical modeling calculations and for the design of ozone abatement strategies, as well as for the control of the concentrations of toxic air contaminants. Therefore, the compositions of speciated NMVOC groups were decoded, and typical compositional characteristics of the national emissions of speciated groups are represented in Fig. 4, which depicts the proportions of specific constituents among the corresponding groups at the national level in 2005.

Emission fractions of twenty-eight alkanes were estimated, as shown by Fig. 4a. The dominant constituents of alkanes in 2005 were isopentane, pentane, i-pentane and butane, the emissions of which accounted for about 409.9, 388.6, 369.8 and 337.6 thousand tons, respectively, followed by 2-methylpentane, i-butane, 3-methylpentane, hexane, 2,3-dimethylbutane, 2-methylhexane, ethane, 3-methylhexane, heptane, propane and isooctane. The emission of these fifteen abundant constituents was about 2439.5 thousand tons in 2005, accounting for 87.7% of the total alkane emission, and the remaining constituents of 2,2-dimethylbutane, 2-methylheptane, 2,3-dimethylpentane, octane, decane, isobutane, 2,4-dimethylpentane, nonane, methylcyclohexane, cyclohexane, methylcyclopentane and cyclopentane were responsible for only 12.3% of the total.

Alkenes, due to their high photochemical reactivities (Velasco et al., 2007), were crucial for ozone production. Emission fractions of sixteen alkenes and two alkines were estimated, as shown by Fig. 4b. Ethene, propene, 2-methyl-2-butene and ethyne were the most abundant constituents, the emissions of which were about 402.5, 182.1,

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172.0 and 170.2 thousand tons, respectively, accounting for 65.1% of the total. The constituents of trans-2-pentene, trans-2-butene, 1-butene, cis-2-butene, cis-3-heptene, 2-methyl-1-butene, 1-pentene, cis-2-pentene, 1,3-butadiene and 1-hexene were responsible for 33.7% of the total, with isoprene, propyne, 2-methyl-l-butene, 3-methyl-l-butene, cyclopentene and 2-methyl-2-butene giving a minor contribution of 1.2% to the total emissions. High level of highly reactive compounds with large ozone-forming potentials was a distinguishable feature of China's alkene and alkine emissions, since ethene, propene, 1,3-butadiene, trans-2-butene, trans-2-pentene and 1-butene, six highly reactive compounds known to have high absolute and incremental reactivities of ozone production in the polluted atmosphere (Hurley et al., 1998), accounted for as high as 57.6% of the total alkene and alkine emission in 2005. Therefore, it is necessary to promote smarter, more cost-effective NMVOC control measures focusing on the control of compounds with high ozone-forming potentials, rather than merely on the reduction of the mass of NMVOC emitted, to reduce the contributions of NMVOC to troposphere ozone formation.

Aromatic hydrocarbons and their degradation products play an important role in urban air pollution (Jeffries et al., 1995) and they are important precursors for tropospheric ozone formation due to their high reactivities (Hoekman, 1992). Emission fractions of twelve aromatics were estimated. Figure 4c shows that toluene, m,p-xylene, benzene, 1,2,4-trimethylbenzene, o-xylene, m,p-ethyltoluene and ethylbenzene were the dominant constituents, accounting for 91.2% of the total aromatic emissions. The remaining 8.8% of aromatic emissions were ascribed to propylbenzene, 1,3,5-trimethylbenzene, 1,2,3-trimethylbenzene, styrene and o-ethyltoluene. Particularly, benzene, toluene, ethylbenzene, o-xylene, and m,p-xylene (collectively, BTEX), known as hazardous air pollutants, contributed as high as 76.8% to the total emission, which revealed that vehicular aromatic emissions in China were both highly reactive and highly toxic.

Carbonyls, which include aldehydes and ketones, are oxygenated hydrocarbons with high reactivities, and many aldehydes and ketones are themselves toxic and are known

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human carcinogens. Emission fractions of nine carbonyls were estimated. Figure 4d showed that the most abundant constituents were formaldehyde, acetaldehyde, benzaldehyde, acetone and acrolein, responsible for 92.7% of the total carbonyl emission in 2005, while the remaining 7.3% of emissions were ascribed to propionaldehyde, valeraldehyde, butyraldehyde and methylethylketone. High level of highly reactive compounds was a notable characteristic of China's carbonyl emissions, since the low molecular weight constituents of formaldehyde, acetaldehyde and acetone, which have been identified as key photochemical species readily to form photochemical oxidants particularly in rural and remote environments (Martin et al., 1999), contributed as high as 80.7% to the total carbonyl emission.

In sum, high proportion of light molecular weight compounds with high reactivities and toxicity is a remarkable characteristic of China's speciated NMVOC emissions, mainly due to the high emission fractions of the highly reactive ethene, propene and 2-methyl-2-butene from alkenes, toxic formaldehyde, acetaldehyde, benzaldehyde and acrolein from carbonyls, and toxic and highly reactive BTEX, 1,2,4-trimethylbenzene and m,p-ethyltoluene from aromatics.

Emission compositions of speciated NMVOC groups at the provincial level varied to some extent, due to different provincial vehicle compositions. Detailed compositions and the dominant constituents of the provincial emissions of alkanes, alkenes and alkines, aromatics and carbonyls in 2005 were discussed, as illustrated by Fig. 5, to provide evidences for the effective control of local emissions and the reduction of the most abundant and hazardous constituents.

The composition of provincial alkane emissions shown by Fig. 5a revealed that i-pentane, pentane, butane, isopentane and 2-methylpentane were the dominant constituents in each province. Particularly, i-pentane was the most abundant species in almost all provinces except in Beijing, Hubei, Jiangsu Shandong and Xinjiang, where provincial proportions of i-pentane were only 1.2–5.9%, much less than the 9.9–18.7% in other provinces.

Ethene, 2-methyl-2-butene, propene, ethyne, trans-2-butene and trans-2-pentene

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were the dominant constituents of provincial emissions of alkenes and alkines, as shown by Fig. 5b. However, the proportions of specific species varied: provincial proportions of ethene increased from 19.4% in Guangxi to 42.8% in Tibet, while fractions of 2-methyl-2-butene in Beijing and Tibet were only 2.4% and 3.4%, respectively, much less than the average 11.1% in other provinces. The major cause for this discrepancy of emission compositions among provinces was the diverse compositions of provincial vehicle categories that had distinct NMVOC emission profiles.

Toluene, m,p-xylene, benzene, m,p-ethyltoluene and 1,2,4-trimethylbenzene were the dominant species of aromatics in all provinces, as shown by Fig. 5c. Relative proportions of specific aromatic species among provinces showed little variance, and the provincial fractions of BTEX had a minor difference ranging from 72.4% in Chongqing to 81.0% in Henan.

Figure 5d shows that formaldehyde was the most abundant species of carbonyls, and accounted for about 56% in all provinces, followed by acetaldehyde, the provincial fractions of which ranged from 15.1% in Henan to 20.3% in Chongqing.

3.3 Spatial distribution of reactive and toxic species

Emissions of aromatics, alkenes and carbonyls that have an important impact on air quality and human health due to their high atmospheric reactivities and high toxicity, were gridded at a resolution of 40 km×40 km by means of the GIS methodology for the years 1985, 1995 and 2005, as illustrated by Fig. 6, to provide necessary data for air quality simulation and human health risk assessment by atmospheric chemistry and transportation models and exposure models. A significant contrast between the high-emission eastern areas and the low-emission Western Regions is revealed by Fig. 6, which was one notable characteristic of the spatial distribution of China's speciated NMVOC emissions of alkenes, aromatics and carbonyls. Besides, regions with high emissions mainly concentrated in cities, which was in agreement with the fact that vehicles in China concentrated in urban areas. Particularly, the Beijing-Tianjin-Hebei region, the Yangtze River Delta and the Pearl River Delta were the most polluted areas

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located in the prosperous Eastern and Southern Coastal China, while the Northwestern Region, which covers 31.8% of China's territory, generated only about 5–7% of the total emissions during the period of 1980–2005. This characteristic of spatial distribution was fundamentally caused by the unbalanced economic development across China.

Figure 6 illustrates that the emissions of alkenes, aromatics and carbonyls mainly peaked over the large urban areas, and annual variation of the spatial distribution of emissions revealed that the regions of high emission density had been expanding during the period of 1985–2005, resulting in more areas with especially high emission densities, as shown by Fig. 6, which was another typical and important characteristic of spatial distribution of speciated NMVOC emissions in China. From 1985 to 2005, the proportion of gridded areas with alkene emission density higher than 2000 kg/km^2 (kilograms per square kilometer) increased from 0.21% to 6.4%, and the proportions of gridded areas with emission densities of aromatics and carbonyls higher than 1000 kg/km^2 and 500 kg/km^2, respectively, increased from 0.85% and 0.77%, respectively, to 10.1% and 7.6%, respectively. Therefore, emission control and reduction in the developed regions of China must be emphasized while marvelous economic prosperity was achieved there.

Different parts of China are significantly unbalanced in economic development levels and area coverage, based on which China's thirty-one provinces can be grouped into six distinct regions: the Southeastern Region, including the provinces of Guangdong, Guangxi, Hainan, Fujian, Zhejiang, Jiangsu, and Shanghai; the Northeastern Region including the provinces of Heilongjiang, Jilin, and Liaoning; the Northwestern Region including the provinces of Xinjiang, Shaanxi, Gansu, Qinghai, and Ningxia; the Southwestern Region including the provinces of Sichuan, Yunnan, Guizhou, Chongqing, and Tibet; the Northern Region including the provinces of Beijing, Tianjin, Hebei, Shanxi, Neimenggu, Anhui, and Shandong; and the Central Region including the provinces of Henan, Hubei, Hunan, and Jiangxi. Table 5, which summarizes the emission percentages of alkenes, aromatics and carbonyls, as well as the area and GDP percentages of the six regions in 1985, 1995 and 2005, revealed that the emission proportion of

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each region dovetailed well with the corresponding GDP proportion: emission proportion in the Southeastern Region increased significantly with the rapid economic growth during the period of 1985–2005, when emission proportions in the Northeastern and Northwestern Regions decreased with their relatively slow economic growth.

Figure 6 also depicts that the speciated NMVOC emissions in six regions were notably different: the Southeastern, Northern, and Central Regions, which altogether cover 35.2% of China's territory, generated 71.3%, 71.5% and 66.5% of the emissions of alkenes, aromatics and carbonyls, respectively, in 1985. Twenty years later, contributions of these regions to the emissions of alkenes, aromatics and carbonyls increased to 79.3%, 80.7% and 74.4%, respectively. On the contrary, the western provinces of Tibet, Shaanxi, Gansu, Qinghai, Ningxia, and Xinjiang, which altogether cover 44.6% of the territory, contributed only 7.7%, 8.7% and 9.5% to the emissions of the three speciated NMVOC groups, respectively, in 1985, and their contributions decreased to 6.0%, 5.8% and 6.7%, respectively, in 2005. Consequently, high-emission regions became more seriously polluted, with their emission densities and relative emission proportions increasing over the period.

3.4 Uncertainty analysis of speciated NMVOC emissions

Generally, the uncertainty of the estimated emission inventories of speciated NMVOC groups resulted from the uncertainties in the gross NMVOC emissions produced by various vehicle categories and the corresponding emission profiles determined and adopted. We focused the uncertainty analysis on the seven emission profiles determined and used to calculate the emissions of speciated NMVOC groups, and ignored the uncertainty of the gross NMVOC emissions since they were estimated by a reliable methodology using best available raw data of emission factors and activity data (Cai and Xie, 2007). We conducted the uncertainty analysis using Monte Carlo method, of which the principles and procedures were described elsewhere (Bo et al., 2008). It was assumed that the uncertainties of each specific species contained in the emission profiles had lognormal distributions, and the mean values and the standard deviations for

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the lognormal distributions of every specific species were calculated based on available information derived from published literatures that reported the relative weight ratios of specific species. Our main finding was that the 95% confidence interval for the alkane emission in 2005 was about [−16%, +29%], as shown by Fig. 7. Besides, the 95% confidence intervals for the emissions of alkenes, alkines, aromatics and carbonyls in 2005 were [−20%, +34%], [−44%, +84%], [−17%, +22%] and [−20%, +29%], respectively. The results revealed that the uncertainties of speciated NMVOC emissions caused by the adopted emission profiles alone were quite acceptable.

4 Summary and conclusions

Emissions inventories of alkanes, alkenes, alkines, aromatics and carbonyls, five major speciated NMVOC groups, from on-road vehicles were estimated for the period of 1980–2005, using literature-based NMVOC emission profiles for specific vehicle categories running under particular modes. The emission inventories at the provincial level were further allocated to the county level and gridded at a high resolution of 40 km×40 km by means of the GIS methodology, to investigate the characteristics of spatial distribution of emissions, and to provide information for air quality simulation and health risk evaluation by atmospheric chemical and transportation models and exposure models.

Results show that China has experienced an exponential growth of emissions of alkanes, alkenes, alkines, aromatics and carbonyls, which coincided well with China's economic growth. With the persistent and rapid economic growth, the exponentially increasing trend of vehicular emissions continues with the increasing vehicular population stimulated by the expanding demand of owning private cars. Emission contributions of vehicle categories to speciated NMVOC groups showed annual variation, due to the variance in the provincial emissions and in the relative fractions of the seven emission profiles adopted at the provincial level. However, the dominant contributors showed little variance: the primary vehicle categories that contributed most emissions

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of alkanes, alkenes, alkines and aromatics were motorcycles, due to their huge and ceaselessly growing population, followed by passenger cars, while the major contributors to carbonyl emissions were heavy duty vehicles mainly burning diesel, followed by motorcycles and passenger cars. Therefore, these primary contributors, especially motorcycles, should be emphasized in priority when designing control and reduction policies for vehicular speciated NMVOC emissions in China.

Compositional characteristics of emissions are essential for understanding the environmental and health impact of pollutants, as well as for formulating effective control measures. Results show that a high emission proportion of light molecular weight compounds with high reactivities and toxicity is a typical characteristic of China's speciated NMVOC emissions, mainly due to the high emission fractions of the highly reactive ethene, propene and 2-methyl-2-butene from alkenes, toxic formaldehyde, acetaldehyde, benzaldehyde and acrolein from carbonyls, and toxic and highly reactive BTEX, 1,2,4-trimethylbenzene and m,p-ethyltoluene from aromatics.

Spatial distribution of speciated NMVOC emissions shows a clear difference in emission densities between developed eastern and relatively underdeveloped western and inland China. Remarkably high-emission areas mainly concentrated in the Southeastern and Northern Regions, especially, Beijing-Tianjin-Hebei region, the Yangtze River Delta and the Pearl River Delta were the most polluted areas. Moreover, annual variation of the spatial distribution of emissions revealed that the regions of high emission density had been expanding during the period of 1985–2005, resulting in more areas with especially high emission densities, which was another typical and important characteristic of spatial distribution of speciated NMVOC emissions in China.

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Table 1. The identified profile (weight%) of tailpipe exhaust emission for gasoline vehicles with TWC running under the normal mode (55 species), based on a wide literature review.

Species	Schauer et al. (2002)	Duffy et al. (1999)	Liu et al. (2008)	Schmitz et al. (2000)[a]	Schmitz et al. (2000)[b]	Normalized averages
isopentane	3.70	Nd	6.43	6.45	6.34	6.28
2,3-dimethylbutane	0.70	0.50	0.80	3.83	3.85	2.12
ethane	2.54	2.10	5.64	0.85	0.84	2.62
pentane	1.40	4.60	1.31	1.99	1.98	2.47
isooctane	2.68	0.40	0.85	1.99	2.04	1.74
2-methylpentane	2.07	3.40	3.34	1.65	1.67	2.66
butane	0.53	2.70	0.96	1.37	1.32	1.51
isobutane	0.04	Nd	0.64	0.92	0.88	0.68
3-methylpentane	1.23	2.50	2.34	0.97	0.99	1.76
hexane	0.95	2.20	1.08	0.89	0.91	1.32
2,2-dimethylbutane	0.26	Nd	0.10	0.78	0.76	0.52
3-methylhexane	Nd	Nd	0.93	0.70	0.73	0.86
2,4-dimethylpentane	0.96	0.30	0.33	0.56	0.57	0.60
2-methylhexane	0.94	Nd	1.60	0.62	0.65	1.04
heptane	0.60	0.80	0.76	0.59	0.58	0.73
3-methylheptane	Nd	Nd	0.93	0.51	0.57	0.74
2-methylheptane	0.44	Nd	0.66	0.35	0.37	0.50
2,3-dimethylpentane	1.75	Nd	0.48	0.38	0.38	0.82
octane	0.35	0.30	0.35	0.26	0.28	0.34
methylcyclohexane	0.61	0.20	0.42	0.21	0.23	0.36
propane	0.21	0.20	0.36	0.09	0.08	0.21
cyclohexane	0.47	0.10	0.07	0.17	0.18	0.22
nonane	0.14	0.10	0.22	0.09	0.10	0.14
decane	0.10	Nd	0.18	0.03	0.03	0.09
ethene	9.56	7.90	10.22	6.32	6.26	8.82
propene	4.88	4.00	4.84	3.81	3.72	4.65
1,3-butadiene	Nd	0.80	0.96	0.57	0.41	0.75
trans-2-butene	0.72	0.40	0.48	0.45	0.38	0.53
cis-2-butene	0.29	0.30	0.43	0.32	0.27	0.36
trans-2-pentene	0.23	Nd	0.47	0.35	0.33	0.38
1-pentene	0.13	Nd	0.30	0.21	0.20	0.23
1-hexene	0.14	Nd	Nd	0.19	0.19	0.19
cis-2-pentene	0.14	Nd	0.31	0.19	0.18	0.23
isoprene	Nd	Nd	Nd	0.13	0.13	0.14
1-butene	Nd	1.90	2.52	0.00	0.00	1.21
ethyne	4.19	5.40	3.31	4.50	5.52	5.02
propyne	Nd	0.30	0.26	0.00	0.00	0.15
toluene	6.97	13.90	9.60	18.46	19.31	14.95
m,p-xylene	4.68	7.80	4.78	8.20	8.67	7.48
benzene	3.90	9.30	8.69	4.28	4.39	6.70
1,2,4-trimethylbenzene	1.87	0.90	3.60	4.59	4.68	3.43
ethylbenzene	1.37	2.00	1.42	3.79	3.96	2.75
o-xylene	1.77	2.60	2.34	3.28	3.46	2.95
propylbenzene	0.27	0.30	0.50	3.10	3.27	1.63
1,2,3-trimethylbenzene	Nd	Nd	0.90	1.40	1.47	1.38
styrene	Nd	0.20	0.41	0.83	0.77	0.61
formaldehyde	2.84	Nd	Nd	3.17	2.04	2.94
benzaldehyde	0.42	Nd	Nd	1.06	0.94	0.88
acetone	0.39	Nd	Nd	0.12	0.12	0.23
butyraldehyde	Nd	Nd	Nd	0.08	0.05	0.07
propionaldehyde	Nd	Nd	Nd	0.07	0.05	0.07
methylethylketone	Nd	Nd	Nd	0.18	0.14	0.18
valeraldehyde	Nd	Nd	Nd	0.04	0.04	0.05
acrolein	Nd	Nd	Nd	0.25	0.25	0.28
acetaldehyde	Nd	Nd	Nd	0.44	0.38	0.45

[a] referred to the warm phase measurements; [b] referred to the cold start phase measurements; and Nd means not detected.

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Table 2. The identified profile (weight%) of gasoline evaporation emission (41 species), based on a wide literature review.

Species	Na et al. (2004)[a]	Na et al. (2004)[b]	Na et al. (2004)[c]	Nelson et al. (1983)	McLaren et al. (1996)	Wadden et al. (1986)	Conner et al. (1995)	Normalized averages
ethane	0.00	0.00	0.00	0.00	Nd	0.00	0.14	0.02
propane	2.33	1.53	1.40	1.50	Nd	1.80	0.97	1.56
butane	17.34	20.70	19.88	18.70	19.92	19.10	21.80	19.31
i-butane	13.03	10.32	9.73	11.10	5.68	15.20	5.13	9.86
pentane	8.21	8.27	8.42	10.70	12.30	13.10	7.40	9.61
i-pentane	24.38	25.32	25.32	25.40	25.65	35.80	27.90	26.66
2-methylpentane	3.48	4.20	4.45	3.50	3.83	6.30	3.53	4.12
3-methylpentane	2.05	2.58	2.74	2.20	2.20	3.10	1.93	2.36
2,2-dimethylbutane	0.69	0.84	0.87	0.60	0.33	Nd	0.68	0.66
2,3-dimethylbutane	0.82	0.98	1.02	1.10	1.22	Nd	1.49	1.09
hexane	1.56	1.99	2.15	1.90	2.27	3.20	1.20	2.01
2-methylhexane	0.65	1.17	1.31	0.70	Nd	Nd	0.46	0.84
3-methylhexane	0.48	0.89	1.00	0.50	0.47	Nd	0.44	0.62
2,4-dimethylpentane	0.18	0.27	0.27	0.20	Nd	Nd	0.52	0.28
heptane	0.23	0.49	0.46	0.30	0.21	Nd	0.21	0.31
2-methylheptane	0.03	0.07	0.08	Nd	0.05	Nd	0.06	0.06
3-methylheptane	0.04	0.08	0.09	Nd	0.05	Nd	0.01	0.05
octane	0.02	0.05	0.06	0.00	0.03	Nd	0.03	0.03
nonane	0.00	0.00	0.00	0.00	0.00	Nd	0.01	0.00
ethylene	0.00	0.00	0.00	0.00	Nd	Nd	0.01	0.00
propylene	0.00	0.00	0.00	0.00	Nd	Nd	0.13	0.03
1-butene	2.05	1.19	0.92	1.60	Nd	Nd	0.98	1.33
trans-2-butene	5.80	3.06	4.12	3.70	Nd	Nd	1.54	3.58
cis-2-butene	4.49	2.78	2.99	2.90	Nd	Nd	1.38	2.86
1-pentene	1.37	1.39	1.32	0.70	Nd	Nd	1.19	1.17
isoprene	0.00	0.00	0.00	1.50	Nd	Nd	0.07	0.31
trans-2-pentene	2.76	2.83	2.73	Nd	Nd	Nd	2.29	2.61
cis-2-pentene	1.44	1.51	1.46	0.90	Nd	Nd	1.25	1.29
2-methyl-2-butene	3.61	4.08	3.94	2.60	Nd	Nd	2.88	3.37
ethyne	0.00	0.00	0.00	0.00	Nd	Nd	0.01	0.00
cyclopentane	0.62	0.39	0.42	0.60	0.72	Nd	1.49	0.70
methylcyclopentane	0.85	0.94	0.95	0.90	Nd	Nd	0.81	0.88
cyclohexane	0.10	0.08	0.09	0.30	Nd	Nd	0.12	0.14
methylcyclohexane	0.10	0.15	0.15	0.20	0.13	Nd	0.12	0.14
benzene	0.57	0.59	0.51	0.90	0.93	0.90	0.86	0.74
toluene	0.62	0.96	0.93	1.00	1.27	1.00	1.26	0.99
ethylbenzene	0.02	0.04	0.04	0.10	0.07	0.10	0.11	0.07
m,p-xylene	0.06	0.13	0.12	0.20	0.27	0.30	0.32	0.20
o-xylene	0.02	0.05	0.05	0.10	0.08	0.10	0.12	0.07
styrene	0.00	0.00	0.00	0.00	Nd	Nd	0.10	0.02
2,4-trimethylbenzene	0.01	0.05	0.06	0.00	Nd	Nd	0.11	0.05

[a] referred to measurements conducted in Spring; [b] referred to measurements conducted in Summer; [c] referred to measurements conducted in Winter; and Nd means not detected.

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Table 3. Utilization rate of TWC on gasoline vehicles from 2000 to 2005.

Year	2000	2001	2002	2003	2004	2005
Utilization Rate of TWC on Gasoline Vehicles (%)	13.29	25.53	39.5	51.92	60.47	67.65

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Table 4. Emissions (thousand tons) of speciated NMVOC groups (alkanes, alkenes and alkines, aromatics and carbonyls) from 1980 to 2005.

NMVOC Species	1980	1985	1990	1995	2000	2001	2002	2003	2004	2005
propane	0.9	1.8	5.9	16.3	23.2	27.1	29.2	33.5	42.1	45.9
pentane	8.2	17.4	50.9	146.1	208.2	242.7	252.6	290.8	364.1	388.6
octane	0.7	1.6	4.0	11.5	17.0	19.8	20.3	23.6	28.5	30.0
nonane	1.2	2.3	4.0	9.9	14.3	16.2	17.4	19.7	22.5	24.1
methylcyclopentane	0.2	0.5	1.7	4.5	5.7	6.7	7.6	8.5	11.2	12.7
methylcyclohexane	0.6	1.3	3.4	9.8	13.6	15.7	16.1	18.6	22.4	23.9
isopentane	10.9	23.0	59.7	175.1	238.2	273.7	276.0	317.2	379.0	401.9
isooctane	1.1	2.3	6.7	19.3	22.9	26.3	27.4	31.5	36.5	42.0
isobutane	0.3	0.8	2.1	6.5	11.8	14.7	15.6	19.2	24.2	26.2
hexane	2.3	4.8	14.0	40.5	57.4	67.0	69.7	80.7	100.1	107.7
heptane	1.1	2.4	6.6	19.5	28.9	33.9	34.7	40.6	49.9	52.8
ethane	1.9	3.8	9.0	24.7	30.3	35.1	38.0	44.0	50.5	59.2
decane	1.8	3.5	5.3	12.4	17.5	19.7	21.6	24.0	26.7	28.9
cyclopentane	0.2	0.4	1.3	3.4	4.5	5.3	6.0	6.7	8.8	10.0
cyclohexane	0.5	1.0	2.8	8.1	10.8	12.4	12.6	14.4	17.4	18.5
butane	7.0	13.6	45.1	120.7	159.6	186.3	206.3	233.4	301.4	337.6
3-methylpentane	2.4	5.1	15.0	43.1	60.1	70.3	73.7	85.3	105.8	115.1
3-methylhexane	1.4	3.0	8.2	23.8	32.8	38.0	39.0	45.0	54.8	58.8
3-methylheptane	0.7	1.6	4.3	13.2	20.8	24.8	25.5	30.3	37.5	39.9
2-methylpentane	4.2	8.7	24.6	70.0	98.1	114.7	120.8	139.8	173.3	188.7
2-methylhexane	1.5	3.1	8.5	24.9	35.7	41.8	43.4	50.5	62.2	66.8
2-methylheptane	0.5	1.1	2.8	8.6	15.4	18.8	19.6	23.7	29.8	31.4
2,4-dimethylpentane	0.7	1.5	4.2	12.2	14.9	16.9	17.4	19.7	23.3	25.7
2,3-dimethylpentane	1.0	2.1	5.4	15.3	18.5	20.9	21.3	24.1	27.7	30.7
2,3-dimethylbutane	1.4	2.9	8.1	22.8	31.8	38.0	41.3	48.7	59.7	67.8
2,2-dimethylbutane	0.9	1.8	7.2	18.7	23.2	26.1	28.0	31.0	35.8	39.8
i-pentane	7.4	13.9	48.8	126.6	166.0	194.2	220.6	247.8	326.9	369.8
i-butane	2.7	5.1	18.0	46.8	61.4	71.8	81.6	91.7	120.9	136.8
trans-2-pentene	1.4	3.0	8.9	24.9	35.9	42.2	45.1	52.0	66.2	71.7
trans-2-butene	1.6	3.1	9.3	24.9	33.8	39.7	43.9	50.1	64.0	71.7
propene	7.7	15.0	28.3	72.9	98.5	113.5	123.4	141.4	161.6	182.1
isoprene	0.2	0.3	0.9	2.4	3.4	4.1	4.7	5.5	6.9	7.9
ethene	17.5	34.1	61.9	156.7	218.3	251.9	274.6	314.8	360.4	402.5
cyclopentene	0.0	0.0	0.0	0.1	0.1	0.1	0.1	0.1	0.1	0.1
cis-3-heptene	0.7	1.9	4.9	15.6	28.0	33.4	33.4	39.9	50.6	50.7
cis-2-pentene	0.8	1.6	4.6	13.0	18.8	22.2	23.7	27.3	34.7	37.6
cis-2-butene	1.2	2.4	7.3	19.4	26.6	31.2	34.5	39.4	50.6	56.4
3-methyl-l-butene	0.0	0.0	0.0	0.1	0.1	0.1	0.1	0.1	0.2	0.2
2-methyl-l-butene	0.0	0.0	0.1	0.1	0.2	0.2	0.2	0.3	0.3	0.3
2-methyl-2-butene	2.7	6.3	18.4	54.9	90.2	107.2	110.5	129.8	166.1	172.0
2-methyl-1-butene	0.6	1.6	4.3	13.8	24.4	29.1	29.1	34.7	44.0	44.2
2-methyl-2-butene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1-pentene	1.4	2.8	6.1	16.0	22.4	25.8	28.0	31.7	38.6	42.2
1-hexene	0.8	1.6	2.5	5.8	7.9	9.0	10.0	11.2	12.3	13.8
1-butene	1.8	3.7	9.1	24.9	34.9	40.9	44.0	50.9	62.1	68.7
1,3-butadiene	0.8	1.6	3.4	9.1	12.0	14.0	15.1	17.4	20.1	22.9
ethyne	6.6	13.0	27.6	73.7	94.5	108.3	115.6	132.0	151.0	170.6
propyne	0.3	0.5	1.2	3.4	4.5	5.2	5.4	6.2	7.3	7.9
toluene	10.3	21.2	58.6	170.0	220.2	256.9	269.8	314.6	372.9	421.1
styrene	0.6	1.2	3.0	8.0	9.3	10.5	11.2	12.6	14.1	16.4
propylbenzene	1.2	2.3	5.9	16.8	20.2	23.2	24.5	28.3	32.5	37.7
o-xylene	2.3	4.8	12.8	37.0	48.4	56.3	58.7	68.3	80.8	90.4
o-ethyltoluene	0.4	0.7	1.2	2.8	3.8	4.2	4.7	5.2	5.7	6.2
m,p-xylene	6.1	12.7	34.7	100.8	131.5	152.5	158.2	183.5	217.4	241.6
m,p-ethyltoluene	2.8	5.8	11.4	31.3	50.6	59.1	61.1	70.9	85.7	88.4
ethylbenzene	2.0	4.1	11.0	31.8	41.2	48.0	50.3	58.6	69.2	78.0
benzene	6.8	13.5	31.7	86.8	110.2	127.1	135.9	156.2	181.1	206.4
1,3,5-trimethylbenzene	0.4	1.0	2.9	9.3	16.3	19.4	19.4	23.1	29.2	29.5
1,2,4-trimethylbenzene	3.3	6.7	15.9	44.4	57.4	66.3	70.0	80.8	94.1	106.1
1,2,3-trimethylbenzene	0.6	1.2	2.3	6.2	11.0	14.0	16.3	20.2	24.6	28.9
valeraldehyde	0.6	1.1	1.5	3.5	5.1	5.7	6.4	7.1	7.9	8.6
propionaldehyde	0.9	1.7	2.4	5.6	8.0	9.1	10.0	11.2	12.4	13.6
methylethylketone	0.0	0.0	0.1	0.3	0.8	1.1	1.3	1.7	2.1	2.6
formaldehyde	14.1	26.9	48.5	120.1	148.4	163.8	174.9	191.5	208.8	230.9
butyraldehyde	0.5	0.9	1.3	3.0	4.3	4.9	5.5	6.2	6.9	7.6
benzaldehyde	1.2	2.4	5.7	15.4	17.3	19.1	19.8	21.8	24.2	27.5
acrolein	1.0	1.9	3.4	8.4	10.8	12.1	13.1	14.5	16.1	17.9
acetone	1.4	2.6	4.6	11.1	14.2	15.8	17.1	18.8	20.5	22.6
acetaldehyde	4.6	8.7	14.4	34.4	45.3	50.4	54.7	60.2	65.9	72.1
Sum of Alkanes	63.9	130.3	377.5	1054.3	1442.6	1679.1	1783.3	2044.0	2542.9	2781.4
Sum of Alkenes	39.3	78.9	170.1	454.5	655.5	764.6	820.3	946.5	1138.7	1244.9
Sum of Alkines	6.9	13.5	28.8	77.0	99.1	113.5	121.0	138.2	158.3	178.5
Sum of Aromatics	36.8	75.2	191.5	545.1	720.0	837.5	880.1	1022.3	1207.4	1350.7
Sum of Carbonyls	24.1	46.2	81.9	201.9	254.1	281.9	302.6	333.0	384.7	403.3
Total NMVOC Emission	171.1	344.1	849.8	2332.8	3171.2	3676.6	3907.3	4484.1	5412.1	5958.8

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Table 5. Summary of area coverage percentage (%), GDP percentages (%), emission percentages (%) of alkenes, aromatics and carbonyls of the six regions for years 1985, 1995 and 2005.

Region	Area	1985				1995				2005			
		GDP	SG1	SG2	SG3	GDP	SG1	SG2	SG3	GDP	SG1	SG2	SG3
Southeastern	8.2	30.1	28.4	28	22.9	36.7	35.3	31.6	27.4	36.9	40.0	35.8	31.8
Northeastern	8.4	12.7	12.1	11.7	14.3	10.3	8.7	8.7	10.8	9.3	5.8	5.6	8.2
Northwestern	31.8	5.7	7.4	8.3	9.0	4.8	6.1	7.0	8.5	4.6	5.8	5.7	6.4
Southwestern	24.6	8.6	9.3	8.5	10.2	9.3	6.2	5.7	7.9	8.6	9.1	8.0	11.0
Northern	19.3	26.3	28.7	29.6	29.5	24.3	29.9	33.4	31.5	25.8	25.5	29.0	27.4
Central	7.7	16.6	14.2	13.9	14.1	14.6	13.8	13.5	14.0	14.8	13.8	15.9	15.2

SG1: Alkenes; SG2: Aromatics; SG3: Carbonyls.

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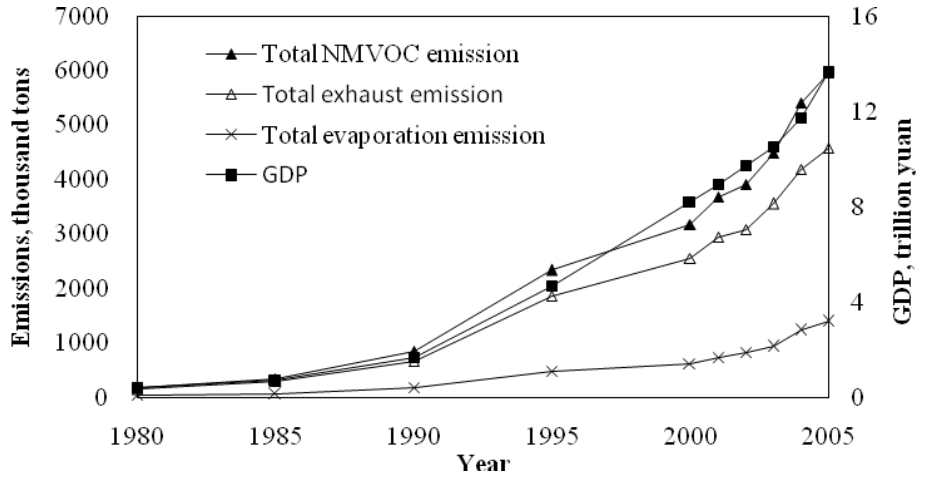

Fig. 1. Exponential increase of vehicular emissions of total NMVOC, including tailpipe exhaust emissions and evaporation emissions from 1980 to 2005, in comparison with China's economic growth during the period.

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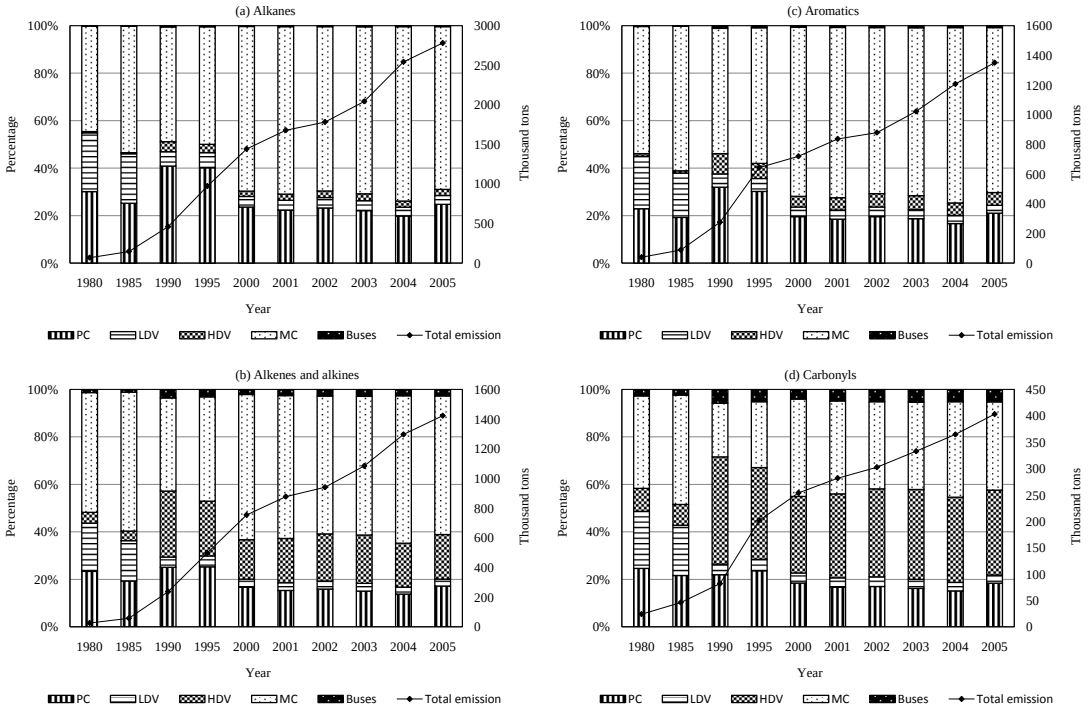

Fig. 2. Annual contributions of vehicle categories to emissions of speciated NMVOC groups (alkanes, alkenes and alkines, aromatics and carbonyls) during the period of 1980–2005. PC: passenger cars; LDV: light duty vehicles; HDV: heavy duty vehicles; MC: motorcycles.

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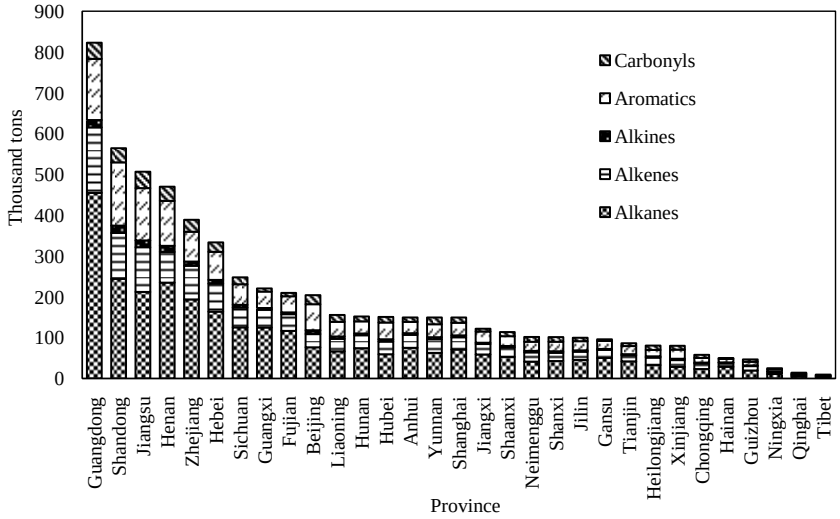

Fig. 3. Provincial emissions and relative proportions of alkanes, alkenes, alkines, aromatics and carbonyls in 2005.

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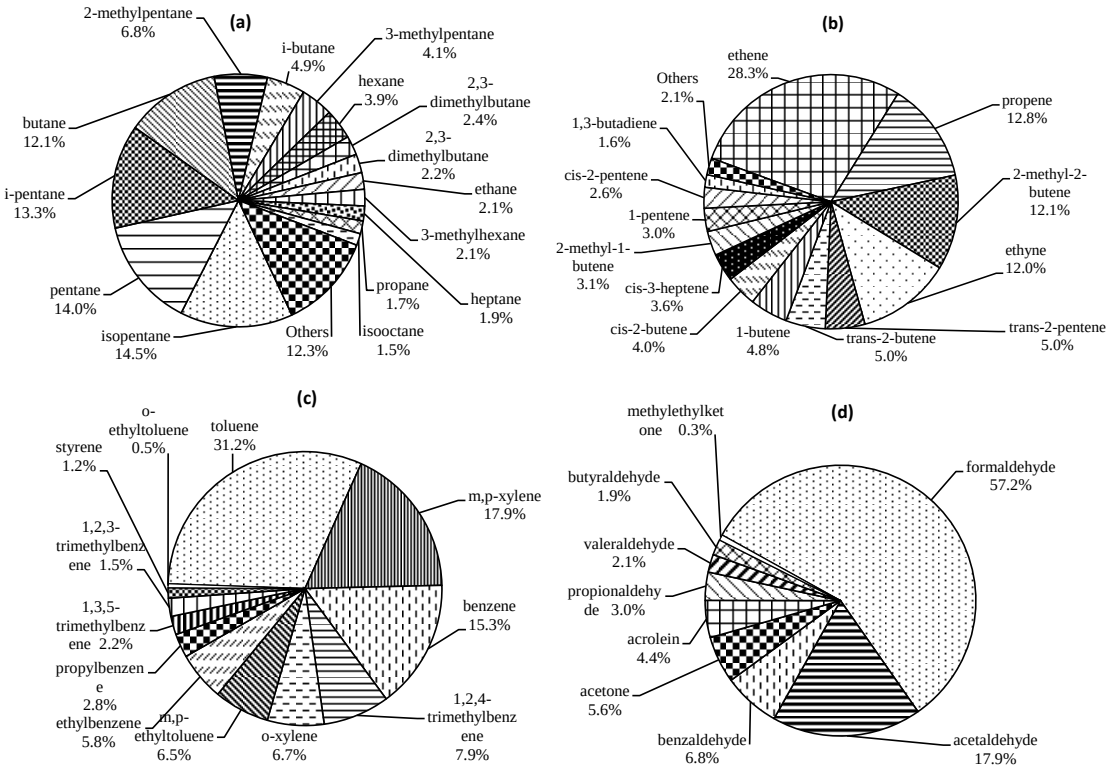

Fig. 4. Emission fractions of specific species within speciated NMVOC groups: **(a)** alkanes; **(b)** alkenes and alkines; **(c)** aromatics; and **(d)** carbonyls for the year 2005, based on the national emissions.

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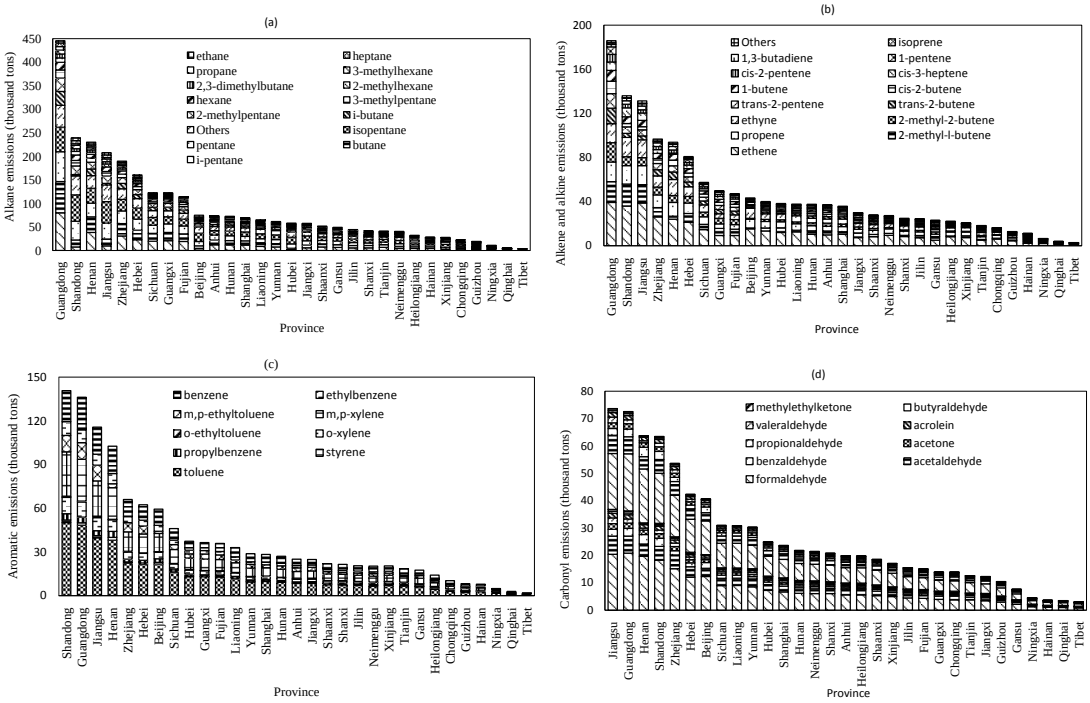

Fig. 5. Provincial emissions and the compositions of **(a)** alkanes, **(b)** alkenes and alkines, **(c)** aromatics and **(d)** carbonyls in 2005.

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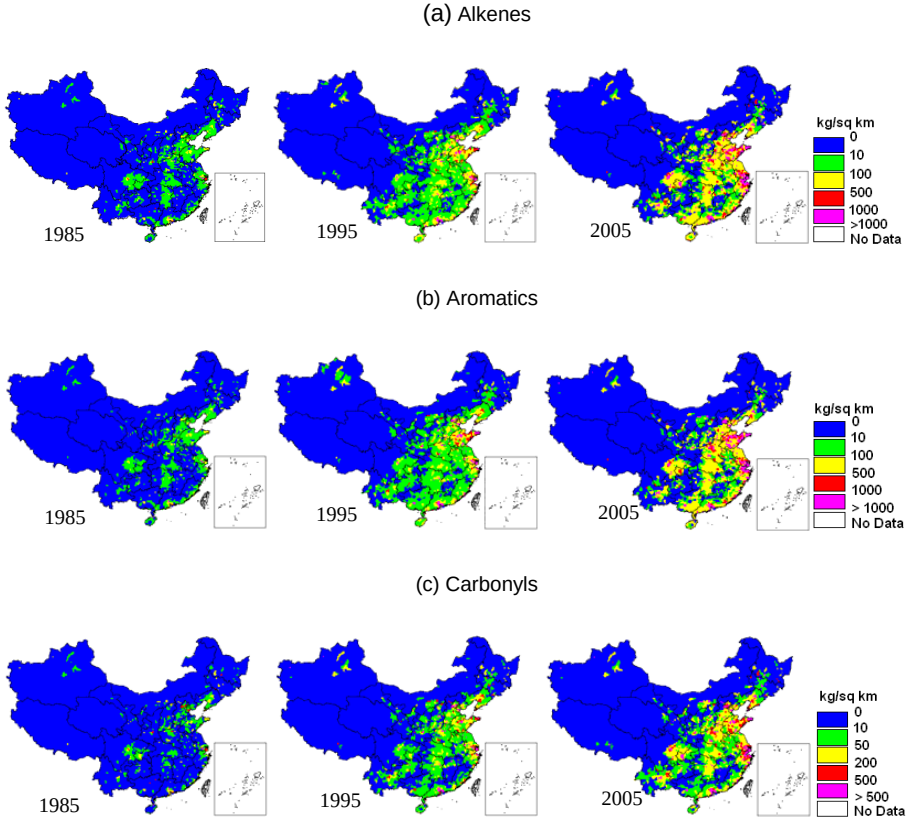

Fig. 6. Spatial distribution of emissions of **(a)** alkenes, **(b)** aromatics and **(c)** carbonyls at a resolution of 40 km×40 km for the years 1985, 1995 and 2005, based on GIS methodology.

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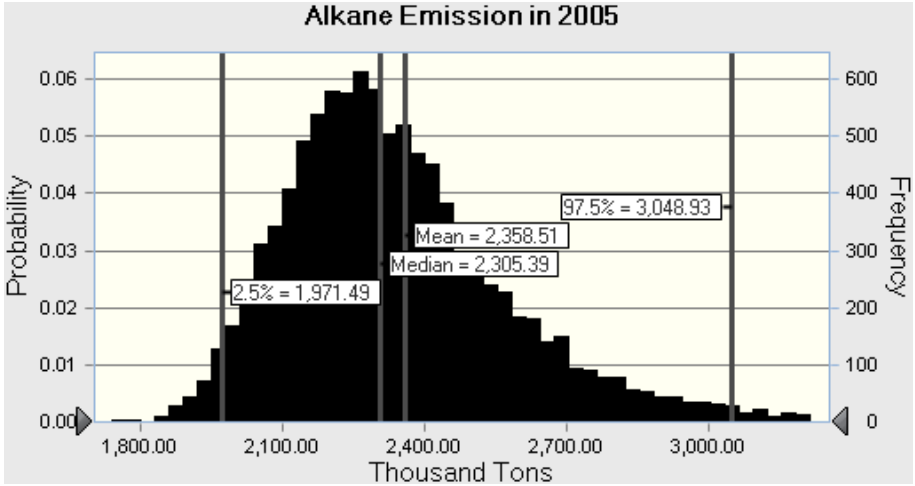

Fig. 7. Probability and frequency distributions of alkane emission in 2005, based on a Monte Carlo simulation.

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