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The Hong Kong Polytechnic University
Department of Civil and Structural Engineering

**Characterization and Speciation of Non-methane Hydrocarbons
(NMHCs) and Their Implications on the
Atmosphere of South China**

By

Jianhui TANG

Supervisor: Dr. Lo-Yin CHAN

A thesis submitted in partial fulfillment of the requirements for the
Degree of Doctor of Philosophy

January 2007



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CERTIFICATE OF ORIGINALITY

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TO MY FAMILY

Abstract of Thesis Entitled

**Characterization and Speciation of Non-methane Hydrocarbons (NMHCs) and
Their Implications on the Atmosphere of South China**

Submitted by **Jianhui TANG**

For the degree of Doctor of Philosophy

South China has experienced rapid economic growth, fast industrialization and urbanization in the last two-three decades. The excessive uses of resources, dramatic changes of land use pattern and rapid increases of motor vehicles and industries have resulted in severe degradation of air quality both in the urban and rural areas of the region.

Non-methane hydrocarbons (NMHCs) are among the most important constituents in the atmosphere. They play crucial roles in atmospheric chemistry and the formation of tropospheric ozone and other secondary pollutants. This thesis investigates the characterization and speciation of NMHCs in the fast changing South China region with an aim to assess their implications on its atmosphere.

A large pool of ambient and source NMHC data was obtained for the first time in various environments of South China, extending from less developed Yunnan and Hainan Provinces to more developed Guangdong and Zhejiang Provinces. Evolution of the characteristic NMHC profiles in representative atmospheric environments in South China through this study will greatly enhance our knowledge in these important ozone precursors. The source and source regions of these C₂-C₁₀ NMHC species were assessed through comparison of the profiles and characteristic ratios of NMHC

species in ambient and source samples. Tools such as backward air trajectory and satellite images are utilized.

Analysis of characteristic spectra in these regions unveiled that there were complex characteristics of NMHCs involving different extents of contributions from urban vehicular and industrial emissions, local biofuel combustion and biogenic emissions, and biomass burning emissions. At the developed sites, such as Guangzhou in PRD and Lin'an in YRD, vehicular and industrial emissions were the major contributors. However, in rural and remote areas such as at Jiangfeng Mountain on Hainan Island and Tengchong Mountain in southwest of China, long-range transports of biomass burning pollution from the SE Asia subcontinent in addition to contributions from in situ biogenic and other local anthropogenic emissions from South China, are important sources of NMHCs in spring.

More in depth studies were conducted in the urban sites of Guangzhou and at the rural site of Dinghu Mountain during 2001 to 2005. The increase in concentration of NMHCs from vehicular and industrial emissions such as ethyne and toluene were more noticeable on Dinghu Mountain than in Guangzhou. The latter even showed decrease levels of toluene, which was contrary to the increase of industrial activities in this region. This was due to the streamlining of urban traffic, upgrading of road networks not only in the urban area but throughout the whole of Guangdong Province, the implementation of stringent emission standards for vehicles as well as polluting industries especially in the urban cities, the relocation of polluting industries from urban to the less developed parts of the PRD and the significant increase in vehicular traffic in the rural areas. We had found for the first time significant increase of

propane levels in the urban air of Guangzhou, due to the introduction of LPG-fueled buses and taxis. The signatures of LPG influence were also found in Sanya of Hainan Province, where LPG was used as a fuel in Taxis.

The results of this study imply that there are complex emission sources of air pollutant which discharge into the atmosphere from the fast changing urban and rural environments in South China. Hence we observed the rapid changes of NMHC emission patterns. As such, much more research efforts are needed to better understand the impacts of these changes on the atmospheric environment and air quality in this region.

Publications:

1. **Tang, J. H.**, L. Y. Chan, C. Y. Chan, Y.S. Li, C.C. Chang, S.C. Liu, and Y.D. Li, 2007. NMHCs in the transported and local air masses at a clean remote site on Hainan Island, South China. *Journal of Geophysical Research - Atmosphere*, in press.
2. **Tang, J. H.**, L. Y. Chan, C. Y. Chan, Y.S. Li, C.C. Chang, S.C. Liu, D. Wu, and Y.D. Li, 2007. Characteristics and diurnal variations of NMHCs in urban, suburban, and rural sites of the Pearl River Delta and a remote site in South China. *Atmospheric Environment*, in revision.
3. Chan, C. Y., Y. S. Li, **J. H. Tang**, Y. K. Leung, M. C. Wu, L. Y. Chan, C. C. Chang, and S. C. Liu, 2007. An analysis on abnormally low ozone in the upper troposphere over subtropical East Asia in spring 2004. *Atmospheric Environment*, 41, 3556-3564.
4. Chan, C. Y., **J. H. Tang**, Y. S. Li, and L. Y. Chan, 2006. Mixing ratios and sources of halocarbons in urban, semi-urban and rural sites of the Pearl River Delta, South China. *Atmospheric Environment*, 40, 7331-7345.
5. **Tang, J. H.**, C. Y. Chan, X. M. Wang, L. Y. Chan, G. Y. Sheng and J. M. Fu, 2005. Volatile organic compounds in a multi-storey shopping mall in Guangzhou, South China. *Atmospheric Environment*, 39, 7374-7378.

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Chapter 1

Introduction

1.1 Overview

China has experienced rapid economic growth since the implementation of a reform and open-door policy in 1978. It has now become one of the world's fastest growing economies and most important manufacturing centers in the world. Accompanying with population increases and such dramatic economic development, China consumes an increasing amount of resources and energy as results of urbanization, industrialization, and mobilization as indicated by the continuous growth of gross domestic product (GDP), population, energy consumption and vehicle number from 1978 to 2004 (National Bureau Statistics of China, 2005) (Figure 1.1). China is the biggest producer and consumer of coal, with 25% of the world's total, and China overtook Japan to become the second-largest consumer of petroleum after the United States in 2003 (Liu and Diamond, 2005). As a result, it has experienced widespread deterioration of air quality and degradation in atmospheric environment in many regions, especially in the well-developed zones such as the Beijing mega city, the Yangtze River Delta (YRD) and Pearl River Delta (PRD).

According to Liu and Diamond (2005), three out of four city dwellers in China lived below national air quality standard. In the 342 cities of various sizes, the percentage of cities that had good air quality, light pollution and heavy pollution in 2004 was about 39%, 41% and 20%, respectively (SEPAC, 2005). In 2005, among the 522 cities monitored, there were 55 cities that did not meet the

Chinese standard class III air quality standard. Indeed, some large cities have been ranked as the most polluted cities in the world (SEPAC, 2006).

Non-methane hydrocarbons (NMHCs) are vital constituents in the atmosphere. Some hydrocarbons such as benzene are toxic to human. They play crucial roles in atmospheric chemistry and contribute to about 40% of the total global net photochemical ozone production (Houweling et al., 1998). They react with hydroxyl radical (OH) to produce many oxygenic compounds, and result in the formation of ozone and other secondary air pollutants in the atmosphere, which impose serious health threat to human in elevated concentrations. In Hong Kong, ozone levels were reported to have increased two-folds in the urban area from 1980s to 2000 (Chan et al., 2003). Chan et al. (2003) derived that the background ozone of South China has been increasing in a rate of 1.5% per year over the same period. This ozone increase has resulted in frequent occurrence of high concentration episodes (Chan and Chan, 2000; Lee Y. et al., 2002; Huang et al., 2006, Luo et al., 2000; Wang H. et al., 2006; Wang Z. et al., 2006). Wang H. et al. (2005) estimated that the enhanced ozone levels had resulted in 20-30% lost of winter wheat yields in the YRD. Ozone is found to be significantly associated with total and cardiovascular mortality in the cold season in Shanghai (Zhang et al., 2006) and childhood asthma hospital admission in Hong Kong (Lee S. L. et al., 2006).

NMHCs have various emission sources ranging from vehicular emissions, biofuel combustion, biomass burning, solvent evaporation, industrial emissions, biogenic emissions and others (Singh and Zimmerman, 1992). A study in a rural

site of the YRD showed that vehicular emissions, biofuel combustion, biomass burning and industrial emissions were the major contributors to NMHCs and other trace gases (Guo et al., 2004a). While in another rural site of Hong Kong, vehicular emission from the Hong Kong urban area and industrial emission from the Pearl River Delta (PRD) were the major contributors (Guo et al., 2006). A study on NMHCs in industrial, industrial-urban, and industrial-suburban atmospheres of the PRD showed that industrial emissions greatly influence the ambient levels of NMHCs (Chan L. Y. et al., 2006). However, existed NMHC data in China are very limited and sparse, and this had jeopardized the understanding of the mechanism of ozone formation and other related air pollution problems.

South China is the most developed and prosperous region of China. It includes two most urbanized and industrialized regions of China: the YRD and the PRD. The YRD and PRD account for 30.8% of the national GDP in 2004 (ISIC, 2005). Recently, the concept of the Pan-Pearl River Delta (PPRD) has been proposed to integrate and reinforce the cooperation among the nine provinces in South China plus Hong Kong and Macau Special Administrative Regions to further boost the industrial and urban development in South China. The PPRD accounts for 21% of area, 35% of population, and 40% of GDP of the nation (Yeung, 2005). With such ongoing fast increase of economy, anthropogenic emissions of air pollutants will further increase. It is therefore urgent need to assess the impact of anthropogenic emissions from human activities on the overall atmospheric quality in this region.

In the past years, Dr. L. Y. Chan and his group had conducted several research projects on the study of ozone and its precursor-volatile organic compounds (VOCs) in the PRD region in collaboration with professor Donald Blake's group at University of California, Irvine (UCI), Dr. Wang Xin-Ming at Guangzhou Institute of Geochemistry (GIG), Chinese Academy of Sciences and Dr. Zou Shi-Chun at Zhongshan University. Extensive canister samplings had been carried out in various sites of China, and Professor Blake's group was responsible for the NMHC sample analysis. In late summer 2000, a wide range of VOCs were measured throughout five target cities in the PRD region of South China to study the effects of rapid industrialization on the VOCs profile in the PRD (Chan L. Y. et al., 2006; Chan and Chu, 2007). Later, in January and February, 2001, 158 canister samples were collected at 43 Chinese cities to study the distribution of VOCs and their major sources (Barletta et al., 2005, 2006). All of these early projects were funded by the Research Grants Council (RGC) of Hong Kong Special Administrative Region (HKSAR).

With an increasing concern on the deteriorating air quality in the PRD and South China, additional data were extracted from more recent field studies which the author had involved. Other than those obtained from the author's own PhD research project titled: *“Characterization and Speciation of Non-methane Hydrocarbons (NMHCs) and Their Implications on the Atmosphere of South China”*, the other involved projects are: RGC funded projects *“Emission Characteristics of Volatile Organic Sources in the Pearl River Delta of South China and its Implications on Domestic Air Pollution and Chemical Outflow to the Pacific”* and *“Implications of Volatile Organic Emissions from Pearl River*

Delta Cities of South China including Hong Kong”, and The Hong Kong Polytechnic University (HKPU) and RGC funded projects titled “*TAPTO-China (Transport of Air Pollutants and Tropospheric Ozone over China), 2004*” and “*TAPTO-China,2005*”.

My contributions in these research projects are:

1. collection of ambient canister samples in Liwan, Guangzhou and Dinghu Mountain in March 2001, when I was a graduate student at Guangzhou Institute of Geochemistry, Chinese Academy of Sciences;
2. set up an observatory station at Jianfeng Mountain, Hainan Province in April and May 2004 to collect canister samples and make measurement of other trace gases;
3. further more, I was involved in the preparation and coordination of VOC sampling and the aftermath data analysis in the referred research projects.

1.2 Aim and Objectives

The aims of this study are to characterize the NMHC species profile in various urban, rural, and relatively remote areas of South China, especially in the PRD and YRD and to assess their implications for air pollution on atmospheric environment and regional air quality in South China.

The objectives are:

1. To collect air samples in various roadside, urban, rural and remote sites of South China, especially the YRD and PRD in order to build up a systematic dataset of NMHCs.

2. To identify the major sources of NMHCs in representative atmospheres of South China.
3. To assess the contributions of various emission sources on the ambient NMHC levels in South China.
4. To identify representative source signatures and fingerprints in air masses transported from different source regions in South China.
5. To assess the effects of local and/or regional emissions and/or long-range transport on the NMHC profiles in urban, suburban, rural, and remote sites of South China.
6. To assess the impacts of human activities on the modification of NMHC profile in the PRD within four-year period (2001-2005).

The outcome of this study will enable us to know more about the NMHC chemistry and the source to receptor characteristics in the atmosphere of South China. Such scientific information will be useful in air pollution modeling studies and is urgently needed to enable the authorities to formulate a feasible air pollution control strategy, which helps to protect the health of residents and prevent the continuous deterioration of air quality.

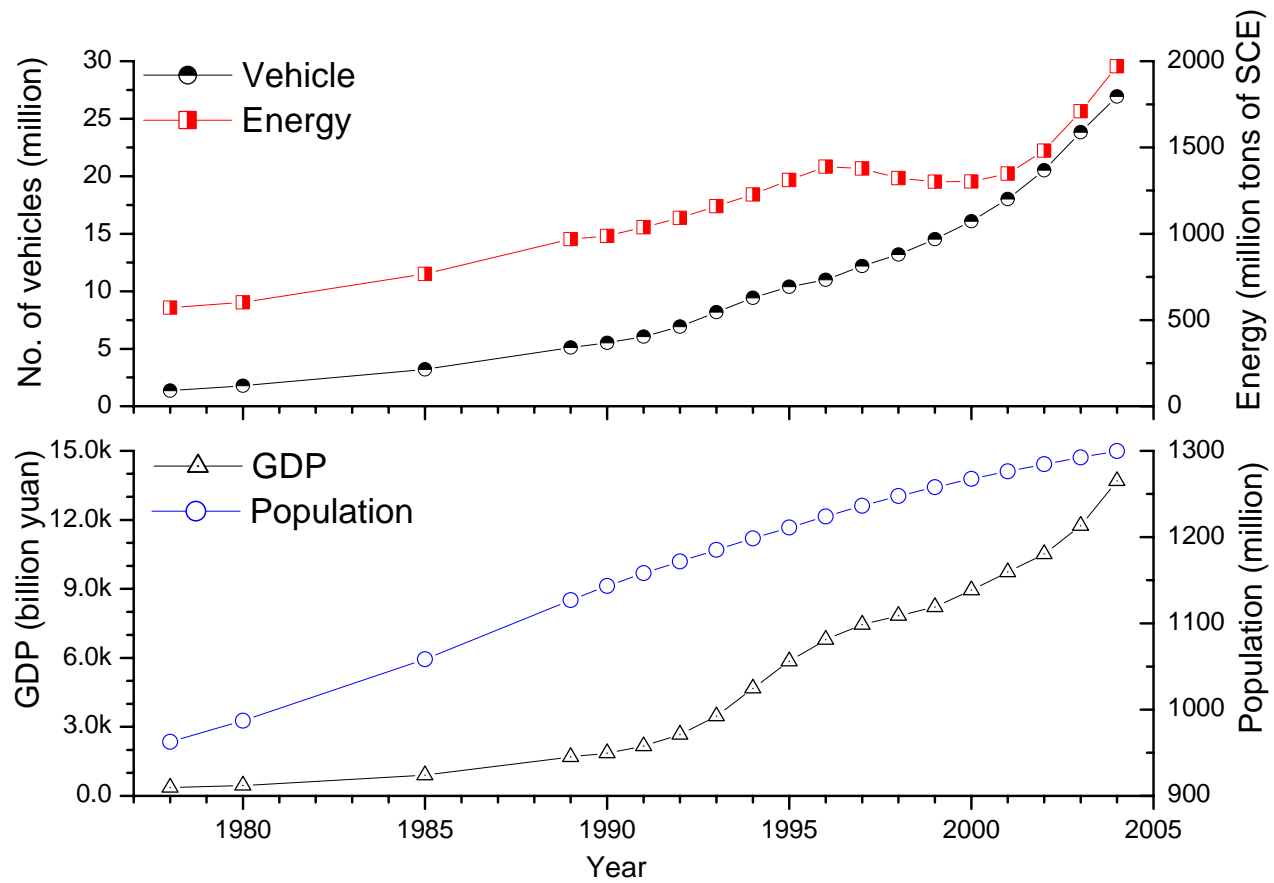


Figure 1.1 Increases of GDP, population, vehicle and energy consumption in China from 1978 to 2004

(Source: National Bureau Statistics of China, 2005)

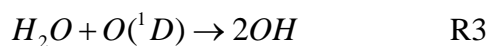
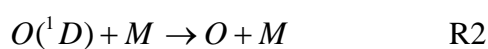
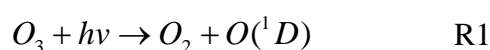
Chapter 2

Literature Review

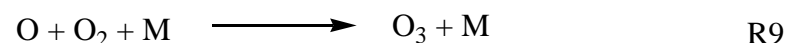
2.1 The role NMHCs in the troposphere

A large variety of NMHCs are found in the atmosphere and there are in excess of 10^3 NMHC species that are emitted to the atmosphere from anthropogenic and biogenic sources (Singh and Zimmerman, 1992). NMHCs play an important role in tropospheric photochemistry through their reactions with hydroxyl radical (OH), ozone and nitrogen oxides. Oxidation of NMHCs produces a variety of oxygenated intermediates including aldehydes, ketones, dicarbonyls, alcohols, phenols, peroxides, organic acids, organic nitrates and ozone, and ultimately leads to the formation of CO and CO₂ (Houweling et al., 1998; Atkinson, 2000; Poisson et al., 2000).

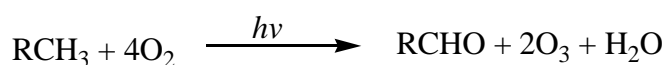
NMHCs and nitrogen oxides (NO_x) are the most important precursors. Under favorite meteorological conditions, they will produce ozone through a series of photochemical reactions (Jacob, 1999). These reactions are initiated by production of OH radical,



and are propagated by reaction of OH with hydrocarbons. Using RCH₃ (where R represents an alkyl group or a hydrogen atom) as a simplified notation for hydrocarbons, their photochemical reactions initiated by OH are shown as following:



The net reaction of R4-R9 is



Houweling et al. (1998) used the global Tracer Model 3 (TM3) to investigate the impact of NMHCs on tropospheric chemistry. It was found that the contribution of NMHCs to global net photochemical ozone production is estimated at about 40%, leading to a 17% increase of the tropospheric ozone column.

OH radical is depleted over the continents owing to reaction with NMHCs, especially in the regions with strong biogenic emissions. Although NMHCs significantly influence the global OH distribution, their effects on total tropospheric OH content seem to be marginal (Houweling et al., 1998). Isoprene is a major sink for OH near the surface over land in the tropics and at mid-latitudes in summer. It was found that OH was depleted by more than a factor of 2 when the levels of isoprene were over about 250 parts per trillion by volume (pptv). When the levels of isoprene are above 500 pptv, photolysis of products of isoprene oxidation is the dominant source of OH (Spivakovsky et al., 2000). Using a global three-dimensional chemistry-transport model, Poisson et al. (2000) investigated the impacts of natural and anthropogenic NMHCs on tropospheric chemistry. Oxidation of NMHCs causes an increase of surface O₃ concentrations by up to 50-60% over the continents, and by up to 40% in

the marine boundary layer. Oxidation of NMHCs also reduces OH concentrations by 20-60% in the NMHC source regions but increases by 10 -20% in the remote oceanic boundary layer due to the elevation in NO_x and O₃ concentrations. Oxidation of NMHCs adds about 45% to the photochemical source and tropospheric abundance of CO (Poisson et al., 2000).

2.1.1 Ozone formation of NMHCs

As discussed in the above sections, oxidation of NMHCs results in ozone formation in the presence of NO_x and sunlight. However, different hydrocarbons react at different rates in the atmosphere, and then exhibit differences in reactivity with respect to the formation of ozone. To assess the contributions of individual hydrocarbons to the ozone production, several methods of ranking NMHCs were established.

Chameides et al. (1992) had proposed the following equation to compare the reactivity of individual hydrocarbon in relation to ozone formation:

$$\text{Propy} - \text{Equiv}(J) = C_J \frac{K_{OH}(J)}{K_{OH}(C_3H_6)}$$

Where propy-equiv(*J*) is a measure of species *J* on an OH reactivity based scale, normalized to the reactivity of propylene; C_{*J*} is the concentration of species *J* in the atmosphere in parts per billion by carbon atom (ppbC); k_{OH}(*J*) is the rate constant between species *J* and OH radical; and k_{OH}(C₃H₆) is the rate constant between C₃H₆ and OH radical. This method accounts for a hydrocarbon's rate of reaction as well as its atmospheric concentration, and provides a good measure of hydrocarbon reactivity related to ozone formation. However, the photochemical formation of ozone is

influenced by many factors besides the reactivity of hydrocarbon, such as the NO_x concentration, solar radiation intensity and meteorological conditions.

Cater and Atkinson (1989) investigated the influence of various NMHCs on the increment of daily maximum ozone concentrations and proposed to use “Incremental Reactivity” to quantify ozone impacts of hydrocarbons. Later, Cater (1994) studied the ozone formation of hydrocarbons under various NO_x conditions in model scenarios representing different urban areas. Incremental Reactivity is defined as the amount of ozone formed per unit amount of hydrocarbons added to, or subtracted from, a given air mass:

$$\text{Incremental Reactivity} = \Delta[\text{O}_3]/\Delta[\text{hydrocarbon emitted}]$$

where $\Delta[\text{O}_3]$ is the change in the amount of ozone formed as a result of the change in the amount of hydrocarbon emitted ($\Delta[\text{hydrocarbon emitted}]$). Maximum Incremental Reactivity (MIR) scenario is the one under this case the NO_x inputs are adjusted to yield the highest ozone formation in the airshed. MIR is a good indicator for comparing the ozone formation potential (OFP) of individual hydrocarbons. The following equation was used to calculate the contribution of ozone formation by each hydrocarbon under optimal conditions:

$$\text{Ozone Formation Potential } (j) = \text{concentration } (j) \times \text{MIR coefficient}(j)$$

Where Ozone Formation Potential (j) is the OFP of species j ; concentration (j) is the concentration of species j in the atmosphere, and MIR coefficients are taken from Carter (1994).

Derwent et al. (1996) used the concept of photochemical ozone creation potential (POCP) to quantify the contribution of hydrocarbons to the model calculated ozone

formation. The POCP_j for a particular hydrocarbon, *j*, was defined in the following equation:

$$\text{POCP}_j = \frac{\text{ozone increment with the } j\text{th hydrocarbon}}{\text{ozone increment with ethene}} \times 100$$

Later, using a Master Chemical Mechanism model, Derwent et al. (1998) investigated the POCP_j value for a variety of hydrocarbon under conditions appropriate to the polluted boundary over northwest Europe. Table 2.1 shows the OH rate constant, MIR value and POCP value of selected hydrocarbons. Generally, reactive hydrocarbons, such as alkenes, show high MIR and POCP values. Xiao and Zhu (2003) examined the variations of POCP under different NMHC/NO_x ratios in the situations of China. It has found that the POCP values of NMHC species decrease with NMHC/NO_x ratio increasing, but the POCP values of low reactivity species change little.

2.1.2 Aerosol formation of NMHCs

Atmospheric aerosols originate from the condensation of gases, especially for fine particles (less than 1 μm in radius), and from the action of the wind on the Earth's surface (Jacob, 1999). Hydrocarbons are important precursors of aerosols. The oxidation of NMHCs produces a variety of oxygenated hydrocarbons as discussed in sections above. These species finally transfer to the particulate phase through the process of nucleation, and condensation or coagulation in the atmosphere. Compounds identified in the ambient aerosol include *n*-alkanes, *n*-alkanoic acids, *n*-alkanals, aliphatic dicarboxylic acids, diterpenoid acids, retene, aromatic polycarboxylic acids, polycyclic aromatic hydrocarbons, and *iso*- and *anteiso*-alkanes (Seinfeld and Pandis, 2006). It has been experimentally shown that oxidation of various hydrocarbons can produce secondary organic aerosol (SOA), such as alkenes (Forstner et al., 1997), aromatic hydrocarbons (Kleindienst et al., 1999, 2004; Alfarra et al., 2006; Na et al.,

2006), 1,3- butadiene (Angove et al., 2006), isoprene (Claeys et al., 2004; Böge et al., 2006), and monoterpenes (Koch et al., 2000; Alfara et al., 2006). Odum et al. (1997) investigated the atmospheric aerosol-forming potential of whole gasoline vapor, and found that the major contributor is the aromatic fraction of the fuel. The total amount of SOA produced from the photooxidation of whole gasoline vapor can be represented as the sum of the contributions of individual aromatic molecular constituents of the fuel (Odum et al., 1997).

The ability of a given hydrocarbon to produce secondary organic aerosol depends on three factors: (a) the volatility of its oxidation products; (b) its atmospheric abundance; (c) its chemical reactivity (Seinfeld and Pandis, 2006). It has been found that temperature is one of the most important factors in SOA formation. The SOA yield at 283 K was approximated twice than that at 303 K and high SOA yield was observed under the low temperature (Takekawa et al., 2003). Using 3-D Lagrangian Chemistry Transport Model, Derwent et al. (2003) found that the global mean surface concentration of terpene aerosol is 538 ng m^{-3} . This value is much higher in tropical regions than others, and a maximum up to or exceeds 6000 ng m^{-3} is found over the tropical areas of South America (Derwent et al., 2003). Andreae and Crutzen (1997) estimated 30 to 270 Tg yr^{-1} of SOA production from the biogenic organic compounds. Later, this value was estimated to be among 13-24 Tg yr^{-1} with an average of 18.5 Tg yr^{-1} by Griffin et al. (1999). Tsigaridis and Kanakidou (2003) estimated that the global annual SOA production from biogenic volatile organic compounds (VOCs) might range from 2.5 to 44.5 Tg of organic matter per year and from anthropogenic VOCs range from 0.05 to 2.62 Tg of organic matter per year.

2.1.3 Health effects of NMHCs

Both the NMHCs themselves and their photochemical products (such as ozone) aroused increasing concerns for their health effects to people exposed. In the 1990 Amendments to the Federal Clean Air Act of U.S.A., 189 species are defined as hazardous air pollutants (HAPs), of which benzene, 1, 3- butadiene, cumene, ethyl benzene, hexane, styrene, toluene, and xylenes are NMHCs (USEPA, <http://www.epa.gov/oar/caa/caaa.txt>). These compounds are known or suspected to cause cancer or other serious health effects, and are regulated to release into the atmosphere by the United States Environmental Protection Agency (USEPA).

Based on the epidemiological evidence, benzene was considered as a human carcinogen (group 1) by the International Agency for Research on Cancer (IARC, 1987). Increased incidence of leukemia has been observed in humans occupationally exposed to benzene, and benzene has been classified as a Group A, know human carcinogen, by USEPA (USEPA, 2000a, <http://www.epa.gov/ttn/atw/hlthef/benzene.html>). A large epidemiological study demonstrated a consistent association between 1, 3-butadiene exposure and occurrence of leukemia. It has been classified as a Group B2, probable human carcinogen, by USEPA. However, USEPA is now reevaluating the cancer classification of 1, 3-butadinene based on recently available human data (USEPA, 2000b, <http://www.epa.gov/ttn/atw/hlthef/butadien.html>). Based on the sufficient evidence from experimental animal data and limited evidence for carcinogenicity from human data, 1, 3-butadiene also has been classified as probably carcinogenic to humans (group 2A) by the IARC (IARC, 1992).

2.2 Distribution of NMHCs in the troposphere

Non-methane hydrocarbons are ubiquitous in the troposphere, from the upper troposphere to the planetary boundary layer, and from the urban roadside, to urban background, to rural and to remote maritime background sites. The atmospheric abundances of NMHCs range from below the detection limits (several pptv) to the ppbv level and higher (even to ppmv levels) (Singh and Zimmerman, 1992).

2.2.1 Spatial distribution of NMHCs

The latitude and vertical distributions of NMHCs have been well investigated by both surface and aircraft measurements. Several common features are found (Singh and Zimmerman, 1992):

- Mixing ratios of many hydrocarbons are high in the Northern Hemisphere and decrease toward the equator with relatively constant values in the Southern Hemisphere.
- Alkenes, which have very short lifetimes, are relatively uniformly distributed in the marine boundary layer.
- Superimposed on the latitudinal cycles are the seasonal cycles of NMHCs.
- Relative high mixing ratios of NMHCs are found near the ground and lower mixing ratios aloft.

Several large campaigns sponsored by National Aeronautics and Space Administration (NASA) of U.S.A. investigated the vertical and latitude distribution of NMHCs over the Western Pacific ocean, such as the Pacific Exploratory Mission-West expedition phase A and phase B (PEM-West A and PEM-West B) and the Transport and Chemical Evolution Over the Pacific (TRACE-P) (Blake et al., 1996a,

1997, 2003). Using the data collected during the campaign PEM-West B, Singh et al. (2001) investigated the spatial distributions of the sum of C₂-C₈ NMHCs (Σ NMHCs) and oxygenated organic species (Σ Ox-org) over tropical Pacific Ocean (30°N to 30°S). The mixing ratios of Σ NMHCs are much higher in the Northern Hemisphere than in the Southern Hemisphere, and the decrease trends of Σ NMHCs from the lower altitude to the higher altitude are also more significant in the Northern Hemisphere than in the Southern Hemisphere (Figure 2.1 and Figure 2.2). During a cruise survey in clean maritime boundary layer air at latitudes between 53°N and 81°N, Hopkins et al. (2002) found that the levels of anthropogenic hydrocarbons (for example, benzene) decreased with increasing latitude until very lower background levels were reached. In the maritime boundary layer air at latitude between 45°S and 77°S, a relatively regular decrease of levels of ethane and propane were also observed (Gros et al., 1998).

2.2.2 Urban environments

NMHCs have been measurement in a variety of urban atmospheres in many countries in recent decades. Table 2.2 shows average mixing ratios of selected hydrocarbons in different cities. A study about the NMHCs at 11 urban background site of United Kingdom shown that urban background hydrocarbon air quality was heavily influenced by motor vehicles, and motor vehicle exhaust, gasoline evaporation, natural gas leakage, petrol station forecourt evaporation, and industrial emission were the major sources of hydrocarbons (Derwent et al., 2000). A study about 54 VOCs in 13 urban locations of United States found that aromatic hydrocarbons (benzene, toluene, xylenes, and ethylbenzene) were the most common species and emissions from motor vehicle were their preliminary sources (Mohamed et al., 2002). Ethane, ethyne and ethene are always the most abundant hydrocarbons in the urban

atmospheres (Table 2.2). Ethyne and ethene are products of incomplete combustion from fossil fuel and biofuel, and their major sources in urban area are from vehicular emissions. In some cities, propane and n-butane are among the most abundant hydrocarbons due to the leakage from LPG (Blake and Rowland, 1995). Watson et al. (2001) reviewed the sources apportionment results using chemical mass balance (CMB) receptor model in more than 20 urban areas, and found that gasoline vehicle exhaust, liquid gasoline, and gasoline evaporation contributed up to 50% or more of the ambient volatile organic compounds (VOCs) in many of those studies.

A study in Hong Kong indicates that 39% and 48% of the total NMHCs mass concentrations measured at two urban sites Central & Western (CW) and Tsuen Wan (TW) were originated from vehicle emissions, respectively. 32% and 36% of the total NMHCs mass concentrations measured were emitted from the use of solvent and 11% and 19% were attributed to the LPG or natural gas leakage, respectively (Guo et al., 2004b). A recently study in Hong Kong shows that vehicle emissions made a significant contribution to ambient non-methane hydrocarbons in urban areas ($65\pm 36\%$, average \pm standard deviation) and in sub-urban areas ($50\pm 28\%$ and $53\pm 41\%$) (Guo et al., 2007). In the capital of China, Beijing, the contribution to the total hydrocarbons by vehicle exhaust was estimated to be about 58%, and by painting operations, gasoline evaporation, and liquefied petroleum gas (LPG) were 12%, 11% and 6%, respectively (Liu et al., 2005).

2.2.3 Rural environments

The mixing ratios of anthropogenic NMHCs are generally lower in rural and remote environments than those at urban areas. Table 2.2 shows average mixing ratios of

selected hydrocarbons in various rural sites. At three national parks in rural southeast United States, isoprene, propane, isopentane, and ethane were all among the top 10 most abundant hydrocarbons (Kang et al., 2001). Isoprene was emitted by biogenic emissions, and others were produced mainly by fossil fuel combustion and industrial processes. The high levels of propene found at Mammoth Cave and Great Smoky Mountains National Parks in 1997 were attributed to the emission from liquid petroleum gas (Kang et al., 2001). At rural site near the metropolis Hong Kong, the mixing ratios of NMHCs at Tai O are more influenced by traffic and industrial emissions from urban areas (Wang T. et al., 2005). At a high altitude rural site of Greece, the mixing ratio of the determined hydrocarbons were generally lower than those measured in southeastern US and western France, but higher than those measure in more remote regions (Moschonas and Glavas, 2000).

2.2.4 Remote environments

In the remote sites, the most abundant hydrocarbons are always the two hydrocarbons with relative long lifetime in atmosphere: ethane and ethyne. In some circumstances, the mixing ratios of isoprene are relative high due to the local biogenic emission. At a remote boreal site in Canada, the seasonal trends of C₂-C₅ hydrocarbons were investigated (Jobson et al., 1994). Concentrations of biogenic hydrocarbon isoprene showed maximum values in July to August. In contrast, alkanes and acetylene displayed a summer minimum (July to August) and a winter maximum (January to February), well matched with the seasonal patterns of OH radical abundance in the atmosphere. The major source of acetylene and C₂-C₅ alkanes is long-range transport of urban plume to this remote site (Jobson et al., 1994). At the remote site of Mauna Loa Observatory, Hawaii, higher mixing ratios of most NMHCs in January through

April and much lower mixing ratio in mid-May through October were also observed (Greenberg et al., 1996).

2.2.5 NMHCs studies in mainland China

While measurements of NMHCs in the other countries or regions are quite well documented, measurements in mainland China are still sparse and relatively limited. Only in recent years, several field measurements of NMHCs were carried out in some urban and rural areas (Shao et al., 1994a, b; Xu et al., 1996; Kuang et al., 2003; Guo et al., 2004a; Barletta et al., 2005). Table 2.4 shows the average mixing ratios of selected hydrocarbons in Mainland China at various sites.

Shao et al. (1994a, b) investigated the characteristics of NMHCs in different microenvironments at Beijing, and traffic emissions together with petrochemical industry emissions were attributed the major sources. Xu et al. (1996) reported the characteristics of NMHCs obtained at three World Meteorological Organization (WMO) Global Atmosphere Watch stations in China, i.e. Waliguan Baseline Station, Longfengshan Background Station, and Lin'an Background Station. Results showed that alkanes and alkenes with less than 6 carbon atoms were the majority of NMHCs. The correlations between the levels of NMHCs and surface ozone maxima at three stations were explored. The ozone maxima were influenced by reactive hydrocarbons, i.e., isoprene and pinenes at Longfengshan station, and by total alkenes at Lin'an station (Xu et al., 1996). Later, study at Lin'an station shown that a combination of vehicular emissions and biofuel burning was the dominant sources (about 70%) of carbons monoxide and volatile organic compounds, and biomass burning (about 10%), industrial solvent emissions (about 10%), gasoline evaporation and solvent emissions

(about 7%) were also the contributing sources (Guo et al., 2004a). Barletta et al. (2005) investigated the characteristics of NMHCs in 43 Chinese cities. The major sources of NMHCs were from combustions or gasoline evaporation. Traffic related emissions are the major sources of NMHCs in some cities, while coal/biofuel combustions are the major sources in other cities. In a suburban site of Lhasa, Southwest China, the total concentrations of hydrocarbons in June 1998 (166.8 ppbC) are about two times higher than in September (60.2 ppbC), and aromatic hydrocarbons is the most abundant hydrocarbon group (Yu et al., 2001). The combustions of biofuel and biomass are the major sources of NMHCs. Biogenic emissions are also important sources of NMHC. However, vehicular emissions contribute less to ambient NMHC levels in Lhasa compared with other parts of China (Yu et al., 2001). A study at PRD stated that the average mixing ratios of TNMHCs ranged from 0.02 to 0.61 ppmv, and the highest levels of TNMHC and aromatic hydrocarbons were found at summer time (July and August), while the highest monthly average mixing ratios of saturated alkanes and alkenes were found in winter and spring (Wang B. G. et al., 2004).

In urban areas, aromatic hydrocarbons (mainly benzene, toluene, ethylbenzene and xylenes, abbreviated as BTEX) showed very high levels (Liu et al., 2000; Wang X. M. et al., 2002). Table 2.5 compares the mixing ratios of BTEX in various Chinese cities. Compared with other cities in Table 2.2, Chinese cities exhibited very high levels of BTEX. High levels of BTEX were also reported in the urban areas of Hong Kong (Lee S. C. et al., 2002). This may partly due to the high content of aromatic fractions in gasoline in Asia compared with other countries in America and Europe.

2.3 Sources of NMHCs in the atmosphere

NMHCs are emitted both from anthropogenic sources and biogenic sources. It was estimated that the global annual VOC flux is 1150 teragram of Carbon (Tg C, 1 Tg = 10^{12} g = 10^6 t), of which 44 % isoprene, 11% monoterpenes, and 22.5% of other VOCs (Guenther et al., 1995). In China, the biogenic emission of VOCs was estimated to be 21 Tg C (Klinger et al., 2002). Poisson et al. (2000) summarized the sources of NMHCs from both biogenic and anthropogenic sources in recent studies (Table 2.6). Biogenic emissions are major sources of light hydrocarbons. Streets and Waldhoff (1999) examined the emissions of carbon-containing greenhouse gases from biofuel combustion in Asian countries in 1990. The emissions of NMHCs from combustion of fuelwood, crop residue, and animal waste were 658.2, 1608.4 and 224.7 gigagrams of carbon (Gg C, 1 Gg = 10^9 g = 1000 t) in China in 1990, which accounted for 33.8%, 66.4% and 9.9% of the total of Asia, respectively (Streets and Waldhoff, 1999). Klimont et al. (2002) investigated the inventory of NMHCs from different sources of China, and combustion of biofuel was found to be the major source. Table 2.7 shows the speciation of NMHC emission in China in the year 2000. Stationary combustion and transport are the two dominant sources for most of hydrocarbons. The total emissions of alkanes, alkenes, ethyne and aromatics were estimated to be 4939, 3540, 914 and 3500 Gg, respectively, in China in 2000 by Klimont et al. (2002), which very closed to those estimated by Streets et al. (2003b). In that study, the emissions of alkanes, alkenes, ethyne, and aromatics in China in 2000 were estimated to be 5067, 3629, 892, and 3435 Gg, which account for about 36.4%, 31.9%, 37.3%, and 38.0% of the Asia total, respectively (Streets et al., 2003b).

Biomass burning is also a major source of NMHCs in the atmospheric. A study on the emission of carbons from forest fire in China between 1950 and 2000 found that the emissions of NMHCs from forest fire was about 0.113 Tg with a range from 0.05 to 0.19 Tg (Lü et al., 2006). This value was steady since 1980 because of the application of fire suppression in China.

Table 2.1 Ozone formation potentials of selected hydrocarbons.

Hydrocarbon	Rate Constant With OH ^a	MIR Value ^b	POCP Value ^c
ethane	0.248	0.25	12.3
propane	1.09	0.48	17.6
i-butane	2.12	1.21	30.7
n-butane	2.36	1.02	35.2
i-pentane	3.6	1.38	40.5
n-pentane	3.80	1.04	39.5
n-hexane	5.2	0.98	48.2
n-heptane	6.76	0.81	49.4
n-octane	8.11	0.60	45.3
ethene	8.52	7.4	100.0
propene	26.3	9.4	112.3
isoprene	100	9.1	109.2
ethyne	0.9 ^d	0.50	8.5
benzene	1.22	0.42	21.8
toluene	5.63	2.7	63.7
ethylbenzene	7.0	2.7	73.0
m-xylene	23.1	8.2	110.8
p-xylene	14.3	6.6	101.0
o-xylene	13.6	6.5	105.3

a: Atkinson and Arey, 2003, (unit: $\times 10^{-12}$ cm³/molecular s).

b: Carter, 1994, (g O₃/ g hydrocarbons).

c: Derwent et al., 1998.

d: Finlayson-Pitts and Pitts, 2000.

Table 2.2 Average mixing ratios of selected hydrocarbons in various urban sites (unit: ppbv).

City	Sydney ^a	Los Angeles ^b	Boston ^b	Porto Alegre ^c	Saxony ^d	Birmingham ^e	London ^e	Edinburgh ^e	Helsinki ^f	39 U.S. Cities ^g	20 U.S. Cities ^h
Periods	Sept 79-Jun 80	Oct 95	Aug-Sept 95	96-97	Apr 95	Jan-Dec. 94	Jan-Dec. 94	Jan-Dec. 94	Feb 04	84-85	99-03
ethane	7.5	10.1	4.1	3.2	3.4	5.4	3.4	3.8	3.2	11.7	0.70-19.79
propane	5.9	9.2	1.8	1.8	1.9	3.2	1.6	2.6	1.8	7.8	0.41-12.40
i-butane	4.7	7.2	3.2	0.9	0.6	1.8	2.4	1.6	0.9	3.7	0.10-1.71
n-butane	7.5	4.1	1.2	1.8	1.2	3.9	3.2	2.8	1.8	10.1	0.18-5.06
i-pentane	9.0	2.5	1.1	1.5	0.8	2.4	2.0	1.6	1.5	9.1	0.38-1.50
n-pentane	5.0	3.1	1.3	0.6	0.5	0.7	0.7	0.8	0.6	4.4	0.13-1.18
n-hexane	2.1			0.1	0.2	0.2	0.2	0.3	0.1		0.08-0.25
ethene	12.5	7.5	3.4	1.7	4.3	3.0	3.1	1.9	1.7	10.7	0.41-1.65
propene	7.4	2.0	1.0	0.3	0.8	1.9	1.4	1.0	0.3	2.6	0.08-0.46
isoprene		0.1	0.3	0.0	0.0	0.2	0.2	0.1	0.0	0.0	0.14-1.81
ethyne	10.1	8.7	2.8	1.5	3.0	4.8	2.5	2.8	1.5	6.5	0.39-1.49
benzene	2.6	1.6	0.8	0.6	1.0	1.1	1.1	0.7	0.6	2.1	0.09-0.29
toluene	8.9	4.7	2.7	0.7	1.1	2.5	2.0	1.8	0.7	4.8	0.14-1.96
ethylbenzene	1.3	0.7	0.6	0.1		1.4	0.6	0.8	0.1	0.7	0.03-0.78
m/p-xylene	3.9	2.5	1.1	0.4		1.7	0.9	1.2	0.4	2.3	0.06-1.01
o-xylene	1.5	0.9	0.4	0.2		0.9	0.5	0.5	0.2	0.9	0.03-0.41

a. Nelson and Qulgey, 1982; b. Calvert et al., 2002; c. Grosjean et al., 1998; d. Gnauk and Rolle, 1998; e. Dollard et al., 1995;

f. Hellén et al., 2006; g. Median mixing ratio, Seila et al., 1989; h. Doezema, 2004.

Table 2.3 Average mixing ratios of selected hydrocarbons in various rural sites (unit: ppbv).

Location	Kejimkujik ^a	Lac la Flamme ^a	Egbert ^a	Saturna ^a	Schauinsland ^b	Mediterranean ^c	Kentucky ^d	Tennessee ^d	Virginia ^d	Five ^e	Tai O ^f
	Canada	Canada	Canada	Canada	Germany	Greece	USA	USA	USA	France	Hong Kong
Period	Apr 1991	Apr 1991	Apr 1991	Jun 1991	1989-1994	Jun-Sept 96	Jun-Sept 97	Jun-Aug 97	Jun-Aug 97	1999-2000	2001-2002
ethane	2.40	2.60	2.65	1.33	2.21		3.66	3.32	4.16	3.96	2.22
propane	0.95	1.04	1.19	0.26	0.90	0.64	2.99	2.36	6.42	1.8	2.14
isobutane	0.19	0.20	0.24	0.06	0.27	0.07	1.91	0.98	1.83	0.87	0.85
n-butane	0.34	0.38	0.6	0.17	0.46	0.11	0.92	1.27	3.32	1.61	1.74
isopentane	0.20	0.14	0.27	0.09	0.33	0.09	1.66	4.05	2.74	1.43	0.85
n-pentane	0.2	0.03	0.05	0.05	0.12	0.04	0.95	1.76	1.53	0.54	0.48
ethene	0.15	0.20	0.33	0.31	0.47		0.43	0.68	0.70	2.72	1.77
propene	0.06	0.04	0.08	0.06	0.09	0.06	3.79	4.31	0.42	0.67	0.24
isoprene	0.20	0.03	0.05	0.05		0.78	11.74	18.38	10.08	0.05	0.37
ethyne	0.71	0.74	0.91	0.31	0.58	0.40	0.52	0.95	0.57	1.54	2.94
benzene						0.08	0.63	0.8	0.97	0.78	0.92
toluene						0.16	1.28	1.68	3.83	2.32	6.01
ethylbenzene						0.05	0.23	0.38	0.79	0.26	0.93
m/p-xylene						0.18	0.73	0.91	2.11	0.71	1.02
o-xylene						0.06	0.55	0.55	1.20	0.18	0.40

a. Botternheim and Shepherd, 1995; b. Klemp D., 1997;

c. Moschonas and Glavas, 2000; d. Kang et al., 2001;

e. Borbon et al., 2002; f. Wang T. et al., 2005.

Table 2.4 Average mixing ratios of selected hydrocarbons in various sites of Mainland China (unit: ppbv).

Location	Dinghu Mountain ^a	Lin'an ^b	Lin'an ^b	Dinghu Mountain ^c	Baiyun Mountain ^c	Heshan ^c	Liuxihe ^c	43 Chinese cities ^d
Period	Jun-Aug 96	Autumn, 99	Spring, 01	N.A.	N.A.	N.A.	N.A.	Jan-Feb 2001
ethane	1.27	3.35	3.11	2.33	1.2	1.36	1.98	3.7-17.0
propane	2.66	1.59	1.2	0.57	1.69	0.18	0.66	1.5-20.8
i-butane	1.34	0.49	0.39	0.25	0.61	0.05	0.21	0.4-4.6
n-butane	2.76	0.59	0.43	0.36	0.99	0.11	0.42	0.6-14.5
i-pentane	0.82	0.19	0.33	0.42	0.68	0.08	0.36	0.3-18.8
n-pentane	0.17	0.17	0.13	0.14	0.28	0.09	0.19	0.2-7.7
ethene	1.41	3.07	1.61	1.47	2.23	0.92	1.89	2.1-34.8
propene	0.41	0.54	0.28	0.47	0.63	0.28	0.61	0.2-8.2
isoprene	0.67	0.11	0.072					0.04-1.7
ethyne	0.88	2.6	2.39	2.07	3.23	0.8	1.83	2.9-58.3
benzene	0.87	1.33	0.8	0.61	1.55	0.36	0.43	0.7-10.4
toluene	0.6	2.54	1.5	0.44	3.29	5.43	1.05	0.4-11.2
ethylbenzene	0.03	0.19	0.19	0.05	0.36	0.04	0.2	0.1-2.7
m/p-xylene	0.06	0.32	0.49	0.09	0.7	0.06	0.47	0.4-15.3
o-xylene	0.05	0.11	0.19	0.08	0.26	0.02	0.47	0.1-6.9

a. Bai et al., 2001; b. Guo et al., 2004a; c. Kuang et al., 2004; d. Barletta et al., 2005.

N.A. = not available.

Table 2.5 Average mixing ratios of BTEX in various cities of mainland China (unit: ppbv).

City	Sampling period	Benzene	Toluene	Ethylbenzene	m/p-Xylene	o-Xylene	References
Guangzhou	Jul. 1996	10.5	16.7	3.6	8.8	4.2	Wang et al., 1999
Maoming	Apr. 1998	3.8	2.6	0.7	1.2	0.9	Liu G. et al., 2000
Changchun	Sept 97-Jul 98	13.6	21.9	3.3	4.2*		Liu C. et al., 2000
Beijing	Nov. 2001	24.4	18.0	2.8	6.4	3.4	Lu et al., 2003
Hanzhou	Oct.2001	11.0	24.5	4.0	6.9	1.0	Luo et al., 2003
Nanjing	Feb-Nov. 2001	2.8	2.8	0.8	0.6	1.2	Hang et al., 2004
Beijing	Dec.02 & Apr.03	2.3	3.4	0.5	0.9	0.3	Zhang et al., 2004
Nanning	Oct. 2003	14.7	43.0	4.3	12.7	4.8	He et al., 2005
Shanghai	Dec. 2004	4.5	15.0	3.7	5.6	2.0	Zhang et al., 2006

* The sum of m/p-xylene and o-xylene

Table 2.6 Annual natural and anthropogenic emissions of NMHCs in the world.

(Tg-C/year)	C ₂ H ₆	C ₃ H ₈	C ₂ H ₄	C ₃ H ₆	C ₅ H ₈	C ₄ H ₁₀
Biogenic sources						
Soils	0.3	0.2	3.2	0.9		0.1
Vegetation	1.6	1.6	11.8	7.7	353	63.1
Oceans	1.5	1.4	8.3	6.4		4.4
Sub-tatal biogenic	3.4	3.3	22.1	15		67.6
Anthropogenic sources:						
Biomass burning	2.9	0.8	7.7	2.6		3.3
Urban areas	4	4.7	4.7	2.1		70
Sub-tatal anthropogenic	6.3	5.5	12.4	4.8		73.3
Total	9.7	8.8	34.5	19.7	353	140.9

Source: Poisson et al., 2000, references therein.

Table 2.7 Speciation of NMHC emission in China^a in the year 2000 (unit: Gg).

Chemical	Stationary combustion	Extraction and processing	Chemical industry	Solvent use	Paint use	Transport	Waste disposal	Miscellaneous	Total	Percent of total
ethane	626	63	1	3	0	85	99	39	915	7.1
Propane	177	142	7	8	0	263	28	9	634	4.9
Butanes	103	142	7	79	0	543	7	9	890	6.9
Other alkanes	208	394	6	135	370	1327	19	39	2498	19.4
Ethene	973	0	23	0	0	416	199	121	1732	13.4
Propene	371	10	8	0	0	171	74	10	643	5.0
Other alkenes	669	27	5	10	3	316	125	10	1165	9.0
Acetylene	553	0	48	0	0	220	88	5	914	7.1
Benzene	483	8	0	2	0	73	90	67	722	5.6
Toluene	239	23	0	83	530	286	35	6	1202	9.3
Other aromatics	427	61	10	109	126	797	46	0	1576	12.2
Total	4829	870	115	429	1029	4497	810	315	12891	100.0

a. Including Hong Kong but excluding Taiwan, China (Source: Klimont et al., 2002)

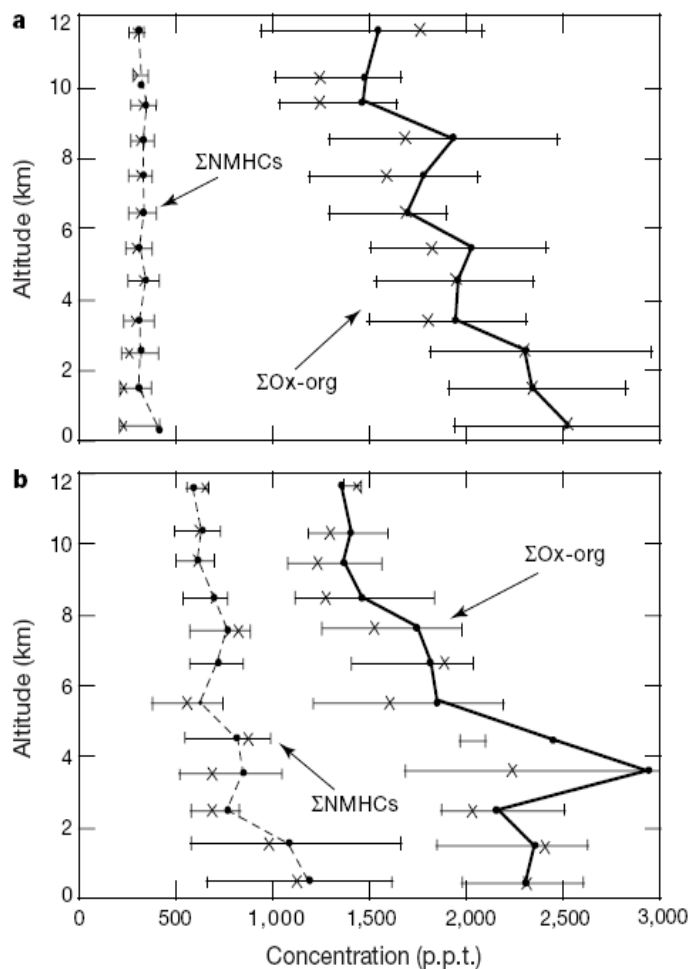


Figure 2.1 Distribution of total oxygenated organics ($\Sigma\text{Ox-org}$) and total C2-C8 NMHCs (ΣNMHCs) in the remote troposphere of the Pacific. Data were collected from the South Hemisphere (**a**: 3-30°S, 165°E-100°W) and the Northern Hemisphere (**b**: 0-30°N; 170-120°W). Mean (filled circles), median (crosses) and 25 and 75 percentile (error bars) value are shown (Source: Singh et al., 2001).

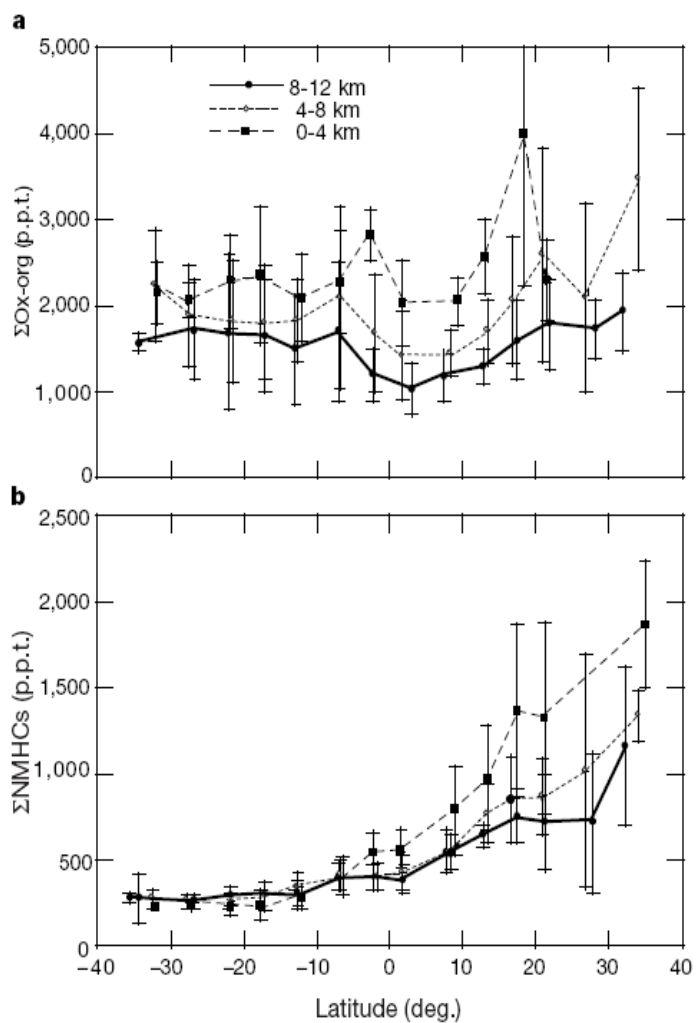


Figure 2.2 Latitudinal distribution of total oxygenated organics ($\Sigma\text{Ox-org}$) and total C2-C8 NMHCs (ΣNMHCs) over the Pacific. Latitudes south of the Equator are shown as negative values. The data are divided into three altitude bands representing the lower (0-4 km), middle (4-8 km) and upper (8-12 km) troposphere (Source: Singh et al., 2001).

Chapter 3

Methodology

3.1 Overview

In this study, various representative sites in South China were carefully selected for field study. Table 3.1 summarized the field sampling information at these sites. In March 2001, ambient air samples were collected at a rural site of PRD: Dinghu Mountain and an urban site in Guangzhou: Liwan District. In April and May 2004, three rural sites in different regions of South China were selected to collect ambient air sample: Lin'an (LA) in the Yangtze River Delta, Tengchong Mountain (TM) in the border of Southwest China, and Jianfeng Mountain (JM) in Hainan Island. Additional urban samples were collected at Sanya (about 120 km to JM) and Tengchong City (about 10 km to TM) to study impacts of local emissions on the NMHC levels at these rural/remote sites. Later, in autumn and early winter, air samples were also collected at JM to compare the characteristics of NMHCs transported from different source regions. In April of 2005, air samples were taken during April 7-13, and 16-18, 2005 at urban (Guangzhou), suburban (Panyu) and rural sites (Dinghu Mountain) of the PRD, and at a clean remote site of South China (Jianfeng Mountain). Additional roadside samples were collected at Guangzhou (GZ) and Qingxi (a small town in Dongguan with dense industrial factories) to establish the source signatures of NMHCs.

3.2 Sampling

Pre-cleaned and pre-evacuated 2-L electropolished stainless steel canisters are used to collect air samples. Parts of these canisters were provided by Professor Donald

Blake's group at the University of California, Irvine (UCI), while the other canisters are provided by the Research Center for Environmental Changes (RCEC), Academia Sinca, Taiwan (Table 3.1). The samples collected using the canisters from the UCI were returned to the UCI for chemical analysis, while the samples collected by the canisters from RCEC were returned to the RCEC for chemical analysis. The canisters in the RCEC were bought from UCI, and they have the same configuration.

The manufacture and preparation of canisters in the UCI were found in works by Chen (1996), Sive (1998) and Doezema (2004). Before sampling, each canister was flushed with high purity helium (in order to remove residue from the previous sample in the canister) three times and then evacuated to 1×10^{-2} torr. Samples were collected in the field by slowly opening the canister valve to let the ambient air sucked in. Sampling collection time were approximately a minute, allowing for a well integrated sample. In the RCEC, high purity of nitrogen gas was used to purge the canister. From April 2004, a controlling device was attached on the inlet of canister to restrict the sampling flow. The initial sampling flow rate was about 35 ml/min, and decreased gradually with the decrease of pressure in the canister. About one-hour integrated air masses were collected.

3.3 Chemical analysis

After sampling, the canisters were sealed and returned to UCI or RCEC for subsequent chromatographic analysis. The determination consists of a selective pre-concentration of NMHCs followed by chromatographic separation of individual NMHCs on a high-resolution column and sensed by detector. The detail of analytical procedures for NMHCs at UCI can be found in the works by Sive (1998), Colman

(2001), and Doezema (2004). Here we describe it briefly. Figure 3.1 shows the diagram of analytic system in UCI (Doezema, 2004). A 1316 cm³ (at STP) air sample in the canister were concentrated on a glass bead filled loop immersed in liquid nitrogen. The condensed sample was warmed and flushed into a helium carrier flow. This sample flow was split into five streams reproducibly, and introduced to gas chromatography (GC) systems. Each stream was separated by an individual chromatographic column and sensed by a single detector. Two GC columns (DB-1 and DB-5/RTX-1701) connected to flame ionization detectors (FID) and another column (DB-5MS) connected with mass selective detector (MSD) were responsible for the separation and quantification of NMHCs. The detection limit of this system for individual hydrocarbon is 3 parts per trillion by volume (pptv).

At the RCEC, an automated GC/MS/FID system (Varian 3800 and Saturn 2200) system was used to separate and quantify of NMHCs (Figure 3.2). To encompass NMHCs of a wide range of volatility within each analysis, the system uses dual-columns and dual-detectors to simultaneously analyze both low and high-boiling compounds with each injection. The PLOT column connected to a FID was responsible for separation and detection of C₂–C₄ compounds, and the DB-1 column was connected to the MS for separation and detection of MTBE and C₄–C₁₀ compounds. Each aliquot of 190 ml from the canisters was drawn to the cryogenic trap packed with fine glass beads cooled at –170 °C for preconcentration. During injection, the trap was resistively heated up to 80 °C within seconds, and a stream of high purity He flushed the trapped hydrocarbons onto the columns. The oven temperature was initially held at –50 °C for 3.1 min, then ramped to –10 °C at 20 °C/min, to 120 °C at 5 °C/min, to 180 °C at 20 °C/min, and held at 180 °C for 21.5

min. The precision of the system was examined by repeatedly injecting a standard mixture made from Scott Marrin Company. In general, the precision for the C₂–C₁₀ NMHCs were usually lower than 3%. The detection limit for individual hydrocarbon is 15 pptv (Chang et al., 2003).

3.4. Variations of NMHCs in canister

It was found that reactive hydrocarbons, such as isoprene, could react with O₃ quickly in the atmosphere, thus underestimated the mixing ratios of these compounds and overestimated the mixing ratios the reaction products in the sampled air. To evaluate the hydrocarbons lost or production in the canister during transportation and storage, two parallel canister samples (A and B) were collected simultaneously near the carpark of the Institute of Earth Science at 14:25, 16th Jun. 2004. The other recorded parameters are: ozone (80.2 ppbv), NO_x (10.8 ppbv) and temperature (25 ~ 30 °C). An aliquot of 190 ml air mass was drawn to analyze the concentrations of hydrocarbons using the same method and procedure for the real samples at 0.1, 1, 3, 24, 48, 72 hours in sample A and 2,120, 168, 336, 504, 672 hours in sample B after sampling. The decay curves of some common hydrocarbons in the ambient air are shown in Figure 3.3. The changes of these hydrocarbons were in the range of ± 15%. For most hydrocarbons, the changes were in the range of ± 5%.

3.5. Data comparison between two laboratories

In this study, air samples were analyzed by two laboratories. To test the consistency of data from the two labs, a comparison study was carried out. Eight canisters filled with identical contents of gas mixture were prepared by the RCEC. Four canisters were

sent to UCI for analysis, and four were left in the RCEC for analysis, using their own analytical procedure and calibration methods.

Table 3.2 shows the comparison results. Both labs show high analytical precisions (very low value of RSD). The differences (based on the UCI result) between the two labs are under 20% for most hydrocarbons. Large differences were also found for some hydrocarbons due to the lower mixing ratios. In the section where data from both labs were used, the data from UCI were used as a benchmark, to make the data from the two laboratories comparable.

Table 3.1 Summary of the sampling information.

Sampling period	Type	No. of samples	Location	Analyzer
Feb. 2000	Tunnel	2	Guangzhou	UCI*
Feb. 2000	Roadside	2	Guangzhou	UCI
Aug. 2000	Roadside	2	Guangzhou	UCI
Mar. 2001	Ambient	39	Dinghu Mountain	UCI
Mar. 2001	Ambient	43	Guangzhou	UCI
Apr.- May 2004	Ambient	91	Jianfeng Mountain	UCI
Apr.- May 2004	Ambient	84	Tengchong Mountain	RCEC**
Apr.- May 2004	Ambient	83	Lin'an	RCEC
Apr. 2004	Ambient	6	Sanya	RCEC
Apr. 2004	Ambient	12	Tengchong City	RCEC
Sept.- Dec.2005	Ambient	77	Jianfeng Mountain	UCI
Jan. 2005	Roadside	3	Qinxi	UCI
Apr. 2005	Ambient	52	Jianfeng Mountain	RCEC
Apr. 2005	Ambient	30	Dinghu Mountain	RCEC
Apr. 2005	Ambient	33	Panyu	RCEC
Apr. 2005	Ambient	28	Guangzhou	RCEC
Sept. 2005	Roadside	6	Guangzhou	UCI

*UCI: University of California, Irvine;

**RCEC: The Research Center for Environmental Changes, Academia Sinica, Taiwan

Table 3.2 Comparison results between UCI and RCEC.

Hydrocarbon	RCEC			UCI			Difference*	Factor**
	Mean	S.D.	RSD (%)	Mean	S.D.	RSD		
ethane	5.642	0.048	0.8%	5.384	0.016	0.3%	-4.81%	0.95
propane	3.438	0.033	1.0%	3.124	0.013	0.4%	-10.03%	0.91
isobutane	0.837	0.021	2.5%	0.810	0.006	0.7%	-3.41%	0.97
n-butane	3.170	0.027	0.9%	2.529	0.007	0.3%	-25.35%	0.80
isopentane	3.699	0.022	0.6%	4.364	0.008	0.2%	15.24%	1.18
n-pentane	1.584	0.027	1.7%	1.708	0.005	0.3%	7.27%	1.08
2,2-dimethylbutane	0.204	0.006	3.0%	0.269	0.005	1.9%	24.16%	1.32
cyclopentane	0.185	0.005	2.6%	0.166	0.003	1.7%	-11.27%	0.90
2-methylpentane	1.353	0.031	2.3%	1.702	0.020	1.2%	20.52%	1.26
3-methylpentane	0.917	0.018	1.9%	0.999	0.006	0.6%	8.20%	1.09
n-hexane	0.860	0.026	3.1%	1.089	0.006	0.5%	21.05%	1.27
cyclohexane	0.363	0.017	4.7%	0.416	0.003	0.8%	12.82%	1.15
2-methylhexane	0.602	0.013	2.2%	0.742	0.005	0.6%	18.87%	1.23
2,3-dimethylpentane	0.480	0.008	1.6%	0.537	0.003	0.6%	10.72%	1.12
3-methylhexane	0.586	0.010	1.6%	0.747	0.017	2.2%	21.53%	1.27
2,2,4-trimethylpentane	0.591	0.007	1.1%	0.816	0.007	0.9%	27.54%	1.38
n-heptane	0.316	0.007	2.2%	0.355	0.005	1.5%	11.08%	1.12
methylcyclohexane	0.255	0.004	1.5%	0.187	0.003	1.8%	-36.28%	0.73
2,3,4-trimethylpentane	0.221	0.005	2.3%	0.274	0.004	1.6%	19.32%	1.24
2-methylheptane	0.163	0.003	1.6%	0.223	0.005	2.2%	26.85%	1.37
3-methylheptane	0.169	0.007	3.9%	0.179	0.003	1.7%	5.88%	1.06
n-octane	0.118	0.004	3.2%	0.141	0.001	0.9%	16.00%	1.19
n-nonane	0.044	0.002	3.9%	0.085	0.002	1.8%	48.96%	1.96
ethene	33.987	0.100	0.3%	33.201	0.107	0.3%	-2.37%	0.98
propene	8.550	0.050	0.6%	10.018	0.034	0.3%	14.65%	1.17
trans-2-butene	0.582	0.007	1.3%	0.581	0.003	0.5%	-0.30%	1.00
1-butene	1.340	0.025	1.9%	1.221	0.006	0.5%	-9.83%	0.91
isobutene	5.128	0.027	0.5%	5.805	0.022	0.4%	11.67%	1.13
cis-2-butene	0.577	0.012	2.0%	0.570	0.002	0.4%	-1.15%	0.99
3-methyl-1-butene	0.122	0.003	2.3%	0.118	0.003	2.2%	-3.67%	0.96
1-pentene	0.171	0.003	1.9%	0.127	0.001	0.6%	-34.78%	0.74
isoprene	0.029	0.001	4.4%	0.026	0.000	0.0%	-10.52%	0.90
trans-2-pentene	0.269	0.003	1.3%	0.248	0.001	0.5%	-8.88%	0.92
cis-2-pentene	0.136	0.004	3.0%	0.137	0.002	1.6%	0.97%	1.01
2-methyl-2-butene	0.253	0.006	2.5%	0.262	0.003	1.0%	3.23%	1.03
cyclopentene	0.103	0.003	2.6%	BDL***				
2-methyl-1-pentene	0.085	0.004	4.7%	0.308	0.002	0.6%	72.45%	3.63

(Continued)

ethyne	22.269	0.139	0.6%	19.967	0.006	0.4%	-11.53%	0.90
benzene	2.776	0.030	1.1%	3.133	0.011	0.3%	11.39%	1.13
toluene	5.206	0.046	0.9%	5.925	0.009	0.4%	12.13%	1.14
styrene	0.025	0.001	3.5%	BDL				
ethylbenzene	0.986	0.007	0.7%	0.921	0.007	1.6%	-7.03%	0.93
m/p-xylene	2.941	0.037	1.3%	3.363	0.013	0.4%	12.54%	1.14
o-xylene	1.093	0.011	1.0%	1.214	0.010	0.7%	9.95%	1.11
isopropylbenzene	0.075	0.001	1.5%	0.050	0.015	2.6%	-51.76%	0.66
n-propylbenzene	0.130	0.001	0.9%	0.134	0.009	2.3%	3.38%	1.03
1,3,5-trimethylbenzene	0.196	0.003	1.6%	0.199	0.016	1.4%	1.73%	1.02
1,2,4-trimethylbenzene	0.620	0.004	0.7%	0.716	0.007	1.4%	13.43%	1.16

* Difference: (UCI data – RCEC data)/ UCI data

** Factor: RCEC data/UCI data

*** BDL: below detection limit

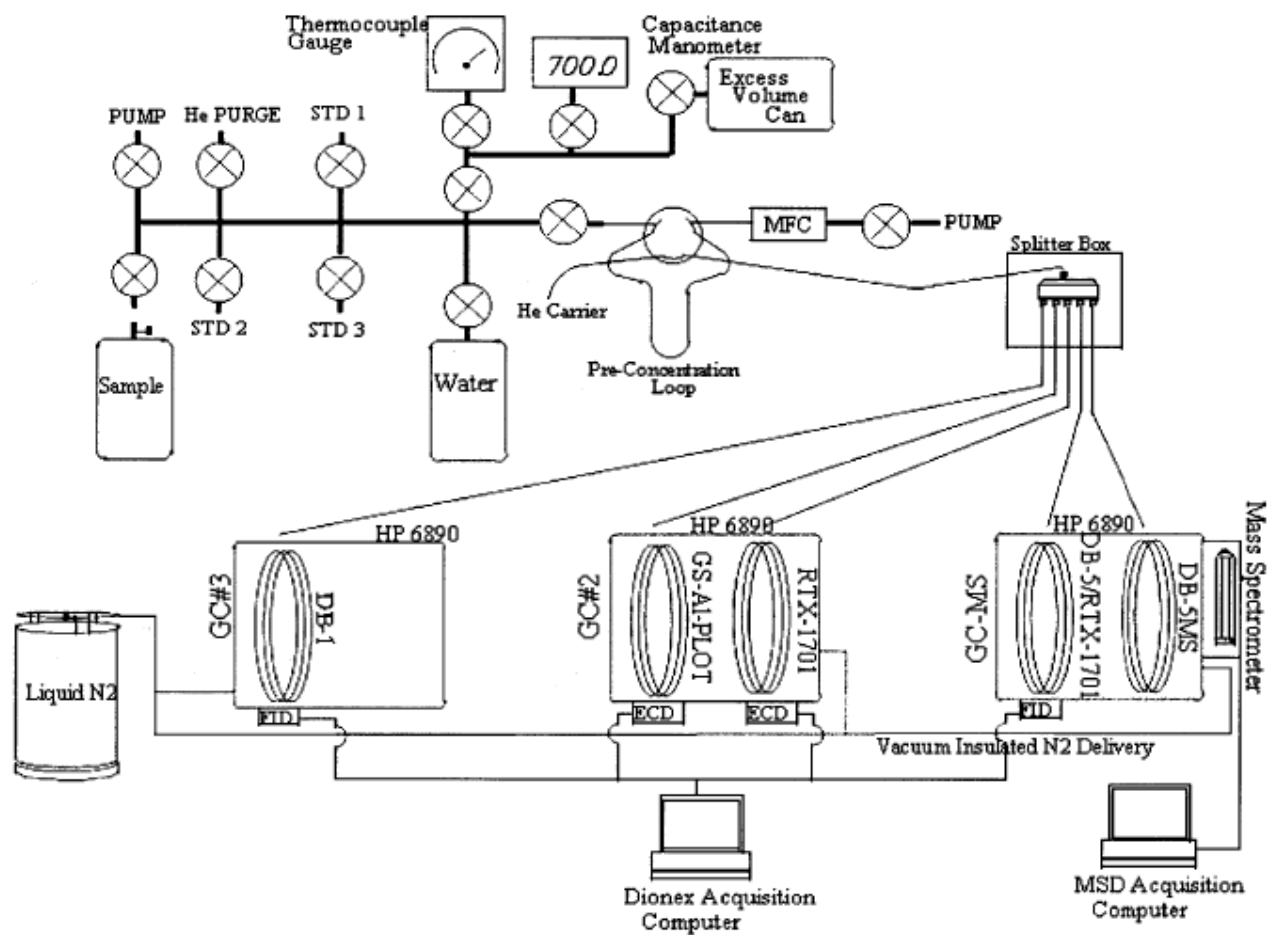


Figure 3.1 Diagram showing the analytic system at UCI (Source: Doezema, 2004).

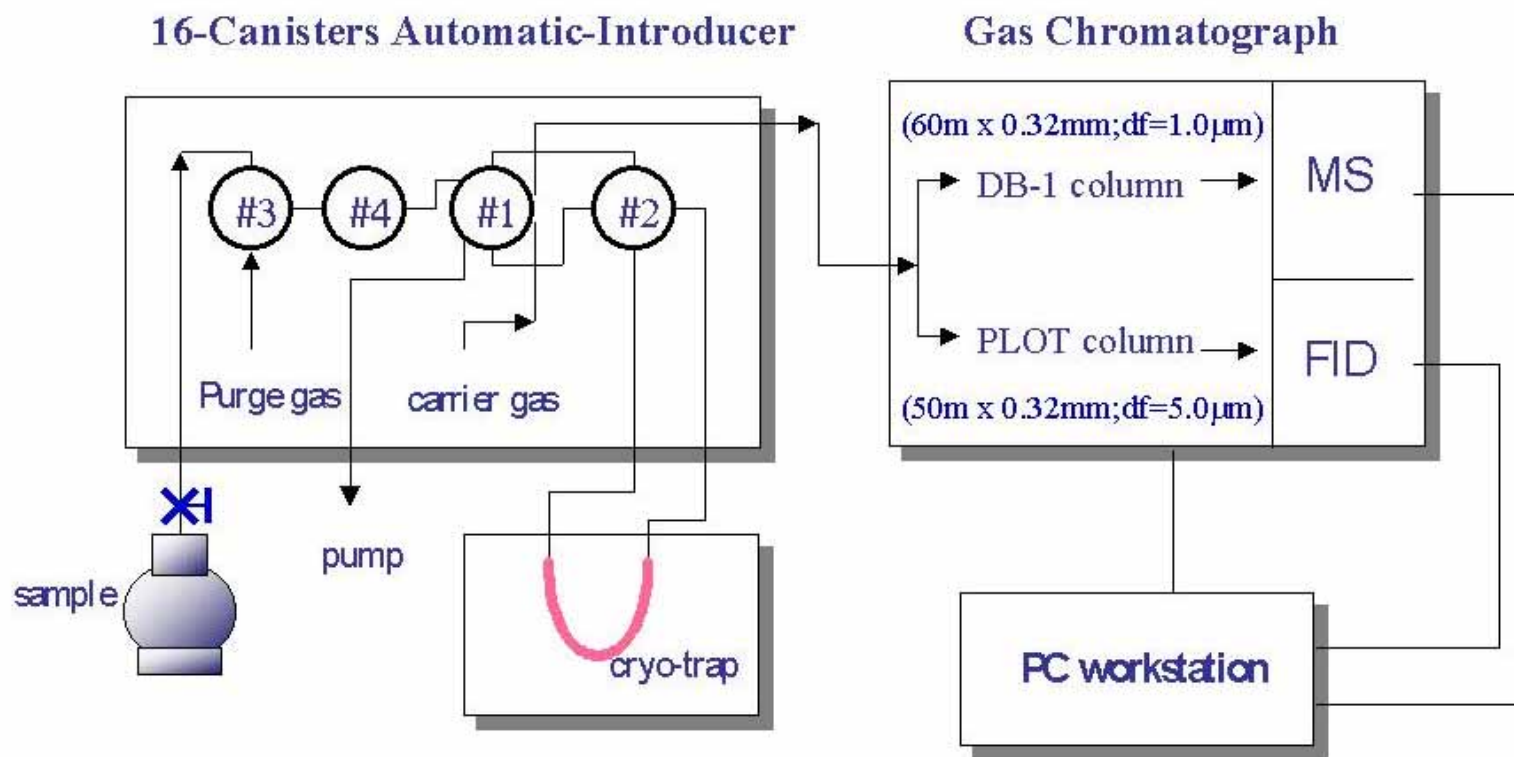


Figure 3.2 Diagram showing analytic system at RCEC.

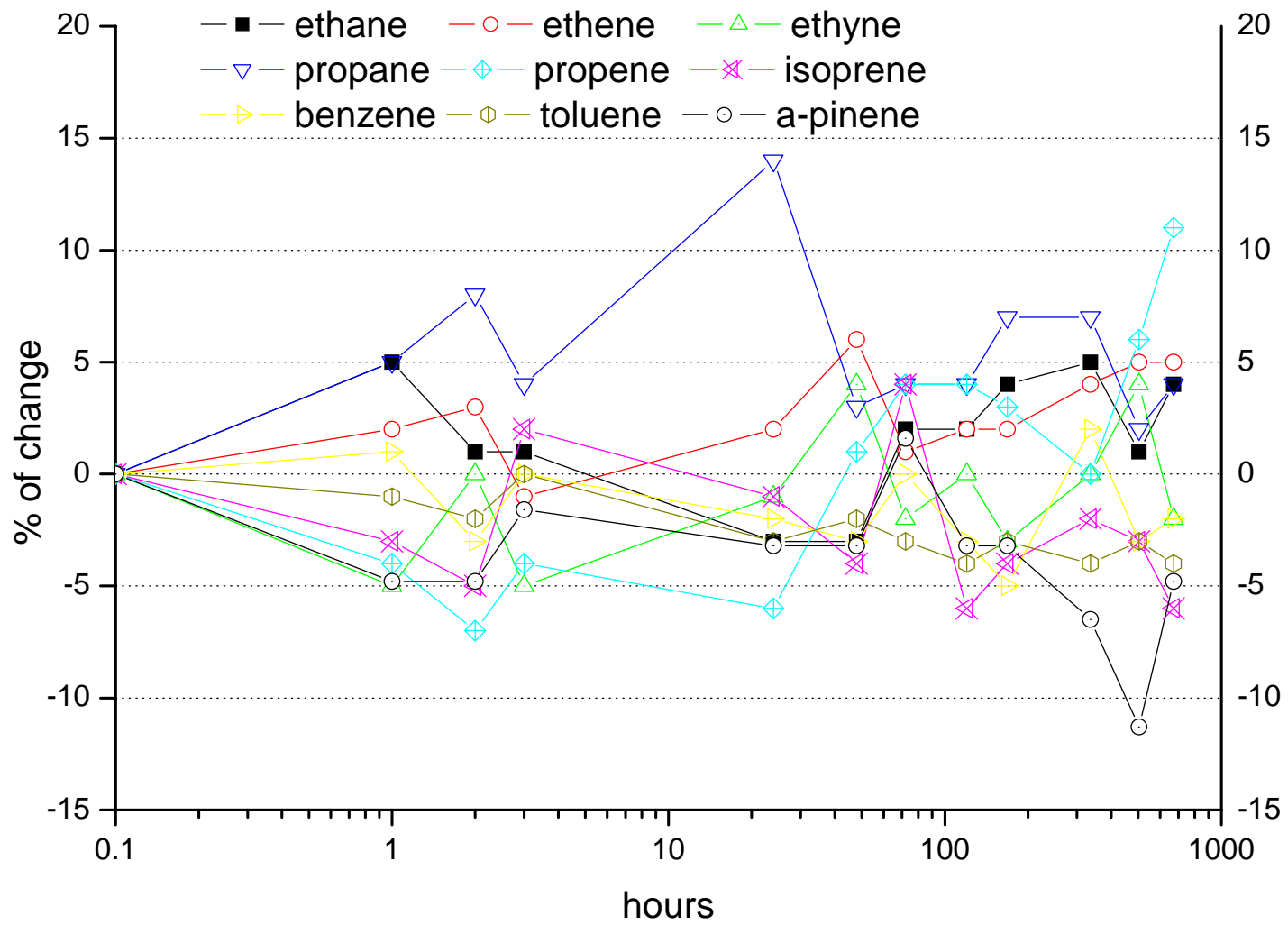


Figure 3.3 Percent changes of selected hydrocarbons versus time in canister.

Chapter 4

NMHCs in the long-range transported and local air masses at Jianfeng Mountain

4.1 Introduction

This chapter compares the NMHC data collected in spring (April 10 to May 21) and Autumn (September 1 to December 4) of 2004 at Jianfeng Mountain. Jianfeng Mountain is situated at the southwest of Hainan Island, South China. It is about 120 km to Sanya, the second largest city of Hainan province, to the northeast, and 315 km to Haikou, the capital city of Hainan province, to the southeast. This sampling site is surrounded by tropical rainforest with a total area of 475 km². There are several hills around the sampling sites with elevation above 1000 meters above the sea level (asl). The details about this site can also be found at Tang et al. (2007). Figure 4.1 shows the geographic location of Jianfeng Mountain and Figure 4.2 shows a picture about the surrounding of sampling sites. It is a remote site located in a tropical rainforest and there are only a few inhabitants lived nearby. The nearest town is located at the foot of the mountain about 10 km away. The sampling site locates at the top of the mountain with elevation about 820 m asl. The canister samples collected in spring were analyzed by the Research Center for Environmental Changes (RCEC), Academic Taiwan, and the samples collected in autumn were analyzed by the University of California, Irvine. To facilitate comparison of NMHC data sets analyzed by the two laboratories, the UCI scale was used. Each individual hydrocarbon data from the RCEC was adjusted by multiplying a conversion factor in Table 3.2.

4.2 Result and Discussion

4.2.1. General characteristics of NMHCs in Spring and Autumn

The average concentrations of selected C₂-C₇ hydrocarbons for the two seasons are shown in Table 4.1. The hydrocarbons listed in Table 4.1 accounted for about 90 % of the total mixing ratio of measured C₂-C₁₀ hydrocarbons (Σ NMHC). In this study, only samples collected at 11:00 – 15:00 were included in the dataset for a fair comparison with other studies. Table 4.1 also shows the OH reaction rate constant (Atkinson and Arey, 2003) and lifetime of these hydrocarbons in the atmosphere based on an annual global mean OH concentration of 1.16×10^6 molecules cm⁻³ (Spivakovsky et al., 2000). Ethane, ethyne and isoprene are the three most abundant hydrocarbons in this site in both seasons. Ethane and ethyne can be originated from various sources, among which incomplete combustion, such as burnings of fossil fuel, biomass/biofuel including agricultural residues and coal, are the major sources (Choi et al., 2003). They have relatively long atmospheric lifetimes in the troposphere (Table 4.1). Thus, they can be transported to remote areas far away from the source regions. They are also reported to be the two dominant hydrocarbons in most rural and remote sites (Saito et al., 2000; Sharma et al., 2000 and Wang T. et al., 2003, 2004). Isoprene is a major biogenic hydrocarbon (Guenther et al., 1995). Due to the very short lifetime in the atmosphere (Table 4.1), its major source is local vegetation emission. The dominance of the two long-lived species based on mixing ratios in this remote site-Jianfeng Mountain indicates that the major sources of NMHCs in this site are from long-range transport of pollutants. The mixing ratios of some hydrocarbons show large variations. This can be attributed to the fact that the sampling site is a remote clean site and there were differences in the accumulation, dilution, and the residence

time of hydrocarbons during the long-range transport from the source regions while traveling different pathways.

Compared to the rural sites of Japan, the USA and other rural sites of China in the higher latitudes, most hydrocarbons showed lower concentrations in Jianfeng Mountain except for those measured in Autumn at Happo, Japan (Table 4.1). Happo is a mountainous site in the center of Japan Islands, and is free of local anthropogenic emission (Sharma et al., 2000). The mixing ratios of most hydrocarbons in Jianfeng Mountain were higher in Autumn but lower in Spring than those in Happo. This phenomenon illustrates that Jianfeng Mountain was affected by the long-range transport of pollutants from the upwind urban and industrial region of SE China in Autumn. Otherwise, the mixing ratios in Happo should be higher since the latitude of Happo is higher than Jianfeng Mountain, and thus the lifetimes of hydrocarbons in Happo should be longer due to the low level of OH radical (Sharma, et al., 2000). Hok Tsui is a relatively clean site in Hong Kong, but it is still affected by short range transport from the nearby urban area (about 10 km), especially in Spring under the prevailing east-northeast flow (Wang et al., 2003). The concentrations of most hydrocarbons, such as ethane, ethyne, propane and toluene, were several times higher in Hok Tsui than in Jianfeng Mountain in Spring (Table 4.1). Lin'an is a rural site in the Yangtze River Delta region, one of the most industrialized and urbanized region in China (Guo et al., 2004a). Almost all species, such as toluene, ethene and benzene, showed concentrations several times higher at the Lin'an site than at Jianfeng Mountain in Autumn (Table 4.1). Hence, the low NMHC concentrations in Jianfeng Mountain area, especially when it is not affected by transported air masses, suggest that this site is not significantly impacted by local anthropogenic pollution. Therefore,

it is an appropriate site for the assessment of the impact of long-range transport of air pollutants from various source regions.

4.2.2 Local emission and diurnal variation of isoprene

Local emission from the tropical rain forest is the major source of isoprene. Figure 4.3 shows the diurnal variations of isoprene in April, May and November. Isoprene showed a strong diurnal cycle in these three months. The diurnal variation of isoprene in November is different from those in April and May. In November, the peak hour occurred at 11:00-12:00. While in April and May, it occurred at 14:00-15:00. The diurnal biogenic emission of isoprene is affected mostly by sunlight and temperature (Kesselmeier and Staudt, 1999). Unfortunately, we had not recorded the light intensity and temperature during the sampling periods. So we can only offer an argument for this phenomenon. After sunrise, both radiation intensity and temperature increase, and the biogenic emission of isoprene is activated. It reaches its full strength near 14:00 in Spring. As the reactions of isoprene with OH radical and ozone are temperature dependent also, and the level of OH and ozone increase with available radiation, the photochemical destruction of isoprene increases with the increase of radiation. The isoprene level is thus reduced and starts to fall. In Autumn (October and November) of South China, strong sunlight and photochemical reaction are commonly found in the afternoon (Wang T. et al., 2001) and isoprene is destructed by photochemical reactions at a faster rate from noon onwards. Hence, isoprene concentration started to fall at a fast rate after noon.

The average mixing ratios of isoprene at the four rural sites of Southeast United States were in the same order as those in Jianfeng Mountain (Table 4.1), whereas in four

rural sites of Canada, the levels of isoprene (0.01 – 0.20 ppbv in October and November) were much lower than at Jianfeng Mountain (Bottenheim and Shepherd, 1995). At a remote tropical forest site in central Amazonia, levels of isoprene (between 4 and 8 ppbv in March and April) were much higher than at Jianfeng Mountain (Kesselmeier et al., 2000), and at the boundary layer of tropical forests of Surinam in South America, the mean average mixing ratios of isoprene were 2.6 ppbv (in March 1998), which were also much higher than that at Jianfeng Mountain (Crutzen et al., 2000). In another tropical forest site of Southwest China, the levels of isoprene (about 1.5-3.5 ppbv between 12:00-20:00 in July) were also higher than that at Jianfeng Mountain. There are several factors that affect biogenic isoprene emission, such as plant species and vegetation types, available photosynthetic active radiation (PAR), atmospheric temperature, water stress and phenology (Kesselmeier and Staudt, 1999). Without details information about these parameters, we are not able to tell the causes of the differences in isoprene levels. Also, the levels of isoprene in Spring were nearly 60% higher than in Autumn at this site, the exact causes of this phenomenon are unclear, and further study is needed to unveil the relevant controlling forces.

Alpha-pinene was also an important biogenic hydrocarbon. However, its mixing ratio measured in this study was very low (with a mean of 0.06 ppbv in Spring and 0.03 ppbv in Autumn and early winter, respectively) compared to the levels of isoprene. It may be that there is a lack of pinenes-emitter species in this region. Another study on the emission of VOC from tropical forest vegetation of Southwest China showed that only a few species emit monoterpene (Geron et al., 2006).

4.2.3. Characteristics of long-range transport air masses

Mixing ratios of ethane, ethyne, and propane observed during PEM-West B (February – March 1994) were on average a factor of 2 larger than those observed during PEM-West A (September – October 1991) (Talbot et al., 1997). They were attributed to the difference in prevalent winds during the two experimental periods. Air masses from the Asian Continent contained higher concentrations of hydrocarbons than those from the Pacific. In addition, it was also affected by the longer lifetimes of NMHCs at the lower latitude ($<25^{\circ}\text{N}$) than at the higher latitude ($>25^{\circ}\text{N}$). In this study, most hydrocarbons show higher concentrations in Autumn than in Spring, in particular ethane, ethyne, propane and benzene (Table 4.1). The differences of NMHC levels between the two seasons were more like the situation at the lower latitude of Western Pacific regions observed by Blake et al. (1997). They are associated with the change of wind direction. In Autumn, the prevailing winds are northeastern, and the air masses passed over SE China, which is the most industrialized and urbanized region in China. While in Spring, the prevailing winds are southwestern, and the air masses passed over SE Asia. This region is less developed than SE China, and active biomass burning are commonly found in Spring time due to the slash-and-burn agriculture activities.

Figure 4.4 compares the average concentration of these anthropogenic hydrocarbons together with their standard deviation in different months. For a fair comparison, only samples collected between 11:00-15:00 were shown. Generally, most hydrocarbons had the highest concentrations in December, and lowest in May. This trend coincided with another study in a rural site of South China where NMHCs show a maximum in Autumn-winter and a minimum in summer (Wang T. et al., 2005).

Backward air mass trajectory analysis is a useful tool to determine the possible transport pathways of air masses. Using the NOAA HYSPLIT model (Rolph, 2003), 5-day backward trajectories of the sampled air masses reaching Jianfeng Mountain were calculated. According to the origin of the transport pathways of the air masses, the trajectories were classified into four major categories (Figure 4.5).

Coast of East Asia (CEA): Air masses originated from the boundary layer of mainland China and East Asia, and had passed over the coast of southeast China. They experienced a descending motion during the transport to Jianfeng Mountain. The air masses are affected by the fresh or aged plume from the continental urban/industrial area. Most Autumn samples (from September 24 to December 4) are categorized to this type.

Southeast Asia (SEA): Air masses originated near the surface of Indian Ocean or South China Sea and had passed over the SE Asian continent. They experienced an ascending motion during their transport to Jianfeng Mountain. These air masses are impacted by the emissions from the SE Asian continent. This happened during the periods of April 14, 18 – 19, May 12 – 14 and September 1 – 7.

Western Pacific (WP): Air masses originated from the boundary layer of the Western Pacific and passed over the tropical and subtropical regions of northwestern Pacific. They experienced a descending motion during their transport to the sampling sites. The samples collected during May 15 – 20 belong to this type.

South China Sea (SCS): Air masses originated from the surface of the South China Sea, and had experienced an ascending motion. The samples collected during April 16 – 17 and April 20 – 24 are under this category.

In each season, there are several samples with very low concentration of anthropogenic species. Backward trajectory analysis indicates that the air masses in these samples originated from the lower troposphere of the South China Sea and the Western Pacific. We classified these samples as Spring and Autumn background samples respectively.

Table 4.2 summarizes the average concentrations together with standard deviations of selected hydrocarbons in different groups of trajectories in the two seasons. From Table 4.2, we can see that air masses from CEA in Autumn had the highest concentration of most hydrocarbons (such as ethane, ethyne, propane and ethene), compared with those from the other regions. The air masses of CEA group had to pass over large areas of the East Asian coast including highly urbanized and industrialized regions of the Yangtze River Delta, Central-eastern China, Taiwan and the Pearl River Delta of SE China. They had picked up industrial/urban pollutants from these regions and hence contained the highest concentrations of most long-lived NMHCs. But due to the long journey, hydrocarbons (for example, propene) with short lifetimes in the atmosphere showed very low concentration in these air masses. Two typical enhancements with obviously higher concentrations of ethane, ethene, ethyne and benzene were captured from October 18 to 21 and from November 26-28.

The air masses from SEA in Spring are influenced by biomass burning emissions in SE Asia. This is demonstrated by the higher concentrations of ethane, ethyne and propane in SEA than in SCS from the ocean. This was also confirmed by the fact that although SEA air masses passed over SE Asia both in Spring and Autumn, air masses in Autumn contained lower concentration of ethane, ethene, propane and ethyne than those in Spring because Spring is the biomass burning season in SE Asia. The burning activities are believed to emit huge amounts of pollutants including NMHCs, which were transported to downwind regions of the South China Sea and Hainan Island following the prevailing winds. Thus high concentrations of NMHCs were observed in the air masses from this region. During April 18 – 20, enhanced levels of ethane, propane, ethyne, and ethene were detected even at night. This phenomenon may indicate that the pollutants were elevated on a regional scale.

We also noted that the concentrations of many species including propane, isobutene, n-butane, ethane, propene, ethyne and benzene had the lowest concentrations in the air mass from WP in Spring. This reflects the fact that there are no significant man-made sources of air pollutants over the Pacific region.

Table 4.3 compared the average concentrations of selected hydrocarbons during the observed enhanced days to the background samples in the same seasons. Most hydrocarbons showed several times higher concentration in these enhanced days than in the background days. However, the composition of hydrocarbons in these enhancements varied remarkably. This reflects the source characteristics.

Figure 4.6 shows the backward trajectory of April 18 with the air masses passed through most of SE Asia following the South wind and the fire count map on April 16-18 for the SE Asian region. The fire counts were detected by MODIS (Moderate Resolution Imaging Spectroradiometer) on the NASA satellites and the integrated data are available at the website of the University of Maryland (<http://maps.geog.umd.edu/products.asp>). One fire point in the map represents an active fire in a 1×1 km pixel. On these days, the air masses passed through the regions of Vietnam, Cambodia, and Laos and to a lesser extent eastern Thailand, where active biomass burning occurred. Ethane, ethyne, ethene and propane are the dominant hydrocarbons which contributed to 65% of the total NMHCs. n-Butane and propane are the most enhanced hydrocarbons in biomass burning plume compared to the Spring background samples. These species are the characteristic hydrocarbons in the biomass burning plume (Woo et al., 2003).

Figure 4.7 shows the backward trajectory on October 19 with the air masses trespassing the East and SE China following the ENE to NE wind and the fire count map during October 16-18. The air masses passed through the boundary layer of SE China. In this period, the burning of crop residues after harvest is one of the most important NMHC sources in rural China (Streets et al., 2003a, b). High concentrations of ethane and ethyne were found on these days (Table 4.3). High ethane is associated with biomass/biofuel burning, but the high ethyne concentration is influenced by additional contribution from vehicular exhaust, as ethyne is a major component of vehicular exhaust. Although ethene is a major pollutant both in the biomass burning and vehicular emission, its concentration is lower compared to that of ethane and ethyne. This is due to the long journey from the source region to the sampling site

compared to the short lifetime of ethene in the atmosphere. The lifetime of toluene is as short as ethene in the atmosphere, the average concentration of toluene (0.20 ± 0.13 ppbv) is found to be nearly three times higher than that of the April enhancement (0.07 ± 0.02 ppbv) which mainly due to biomass burning emission transport. It demonstrates the contribution of anthropogenic emission of toluene in SE China.

In the November enhancement, the highest concentration of propane (1.08 ± 0.07 ppbv) and ethene (1.06 ± 0.44 ppbv) was detected. Figure 4.8 shows the backward trajectory on November 26 with the air masses trespassed the East and South China coast following the NE wind. The fire count map during November 24 – 26 is also shown. This is the typical air mass pathway during the November enhancement. In these days, air masses passed through the boundary layer of the coast of Eastern China, and the Pearl River Delta (PRD), which are major industrial source regions. The higher level of ethene (1.06 ± 0.44 ppbv) in the November enhancement compared to that in October enhancement (0.61 ± 0.19 ppbv) indicates the contribution of urban vehicular emission from PRD urban cities. Due to the short lifetime of ethene, such high concentrations typically can not survive during long-range transport from a remote source region. So they are likely originated from local or regional sources. However, concentrations of even shorter-lived propene, which is co-emitted with ethene from vehicle exhausts, were low (0.07 ppbv) on the days that ethene was high. This indicates that regional rather than local or remote emissions dominated ethene levels at the sampling site during this period.

4.2.4 Characteristic ratios of long-range transport air masses

In this section, we further examine source signature ratios which are presented in Table 4.3. Both ethane and propane are mostly emitted from anthropogenic sources. Fossil fuel combustion, biomass burning, nature gas and liquefied petroleum gas (LPG) are the major sources of ethane, while nature gas, LPG and biomass burning are the major sources of propane (Choi et al., 2003). The concentration ratio of ethane to propane is widely used to investigate the emission characteristics of various source regions and the relative age of the air mass (Talbot et al., 1997; Carmichael et al. 2003; Russo et al., 2003; Wang T. et al. 2003, 2005). The ratio of ethane/propane (C_2H_6/C_3H_8) was estimated to be 2.1 in China and 3.8 in SE Asia based on the anthropogenic emission inventory (Russo et al., 2003). Carmichael et al. (2003) reported the C_2H_6/C_3H_8 ratio of 8 in the SE Asian biomass burning plumes, 2.3 in biofuel combustion exhaust and 0.5 in traffic affected air. They also reported a ratio of 1 to 6 during the TRACE-P campaign. Wang et al. (2003, 2005) found a C_2H_6/C_3H_8 ratio of 2.6-2.7 in the air mass from local urban region and mainland China, 3.1 from the coast of mainland China in Hok Tsui, 2.7 in Lin'an (a rural site in Eastern China) and 1.6 in Tai O (a rural site of Hong Kong). In this study, the C_2H_6/C_3H_8 ratio was 4.6 ± 0.8 in the April enhancement (April 17 – 18), 3.4 ± 0.3 in the October enhancement and 2.2 ± 0.1 in the November enhancement. The highest ratio of C_2H_6/C_3H_8 (4.6) in air masses from SE Asia is associated with biomass burning emission. In addition, the increasing use of LPG in vehicles and domestic use in the more developed regions (e.g. PRD) results in the lowering of the C_2H_6/C_3H_8 ratio. A low ratio (1.6) was observed in Tai O as its air is more impacted by the fresh plume from the Hong Kong urban region. We also observed lower ratios in the air masses

during the October enhancement and November enhancement periods when air masses passed through east coastal China, especially through the PRD region.

Carmichael et al. (2003) found that the observed propane/benzene ratios during the TRACE-P period matched well with the calculated ratios based on the emission inventory in China. Propane and benzene have close atmospheric lifetime against OH (9.2 and 8.2 days, respectively, Table 1). In the absence of mixing with other air masses from different sources, the ratio of benzene to propane remains unchanged after emission. Thus, the ratio may reflect the source signatures. The April and October propane/benzene ratios (Table 3) fall within the observed ratios (<1.6) for SE Asia reported by Carmichael (2003). It is also close to the ratios found in the other two rural sites of China: Linan (1.4) and Tai O (1.4) (Wang et al., 2005). In the November enhancement, the C_3H_8/C_6H_6 ratio lies within the observation in Southeast China (1.6 – 2.0) during the TRACE-P campaign (Carmichael et al., 2003).

One major source of ethyne is incomplete fossil fuel combustion, such as vehicle exhaust. It is the dominant species in roadside samples in PRD region (Chan L. Y. et al., 2006). The ethane/ethyne ratio thus reflects the degree of urban vehicular contribution to the air masses. In the October and November enhancements, the ratios were 1.2 ± 0.1 and 1.1 ± 0.2 , respectively, compared to 2.0 ± 0.4 in the April enhancement. In the outflow from South China which passed through the Hong Kong urban region, the value was 0.8 at Tai O, Hong Kong (Wang T. et al., 2005). The low value of this ratio indicates the contribution of ethyne from urban vehicular emission.

4.3 Conclusion

This study investigated the impacts of air masses transported from long-range/region (e.g. coastal China emission) on the NMHC profile at a remote tropical forest site in Hainan Island, South China, and they were compared with the impact of local emissions. Jianfeng Mountain is a good site for assessing the impacts of long-range transport of industrial/urban air pollutants in South China as well as biomass burning pollutants in SE Asia as there are very limited local anthropogenic sources of hydrocarbons. In the two seasons, NMHCs show different patterns. In Spring, biomass burning emission in SE Asia contributed significantly to the NMHC concentration under the prevailing southwest wind. In the biomass burning plumes, high mixing ratios of ethane, ethyne, propane and ethene were observed and compared to the ratios from background air masses. In Autumn, the long-range transport of anthropogenic pollutants from SE China was the major source. Pollutant sources are fossil fuel combustion, LPG leakage, industrial solvent evaporation and vehicular emission. The high level of toluene in October and November enhancements reflect the contribution from industrial solvent use. The high levels of ethane and ethyne in the October enhancement are attributed to Autumn harvesting biomass burning in addition to industrial and urban source emission, while the high levels of ethene in November enhancement is attributed to picking-up of vehicular emission when traveling through the PRD urban region. Apart from long-range pollutants transported to this site, the sampling location was relatively free of short-range/local anthropogenic emissions. Isoprene is the most abundant hydrocarbon emitted from local biogenic sources which showed strong diurnal variations in Spring and Autumn. However, the levels of isoprene in this site are lower than other tropical forest sites, and the exact reasons need to be further explored.

The high C_2H_6/C_3H_8 ratios observed for SE Asia air masses was indicative of a large contribution from biomass burning emissions. A C_3H_8/C_6H_6 ratio of around 1.8 in the November air masses from coast of East Asia reflects the impact of fuel combustion in the South China region, while the low C_2H_6/C_2H_2 ratio reflects the contribution from the urban vehicle exhaust. These ratios are good indicators of source region characteristics.

Table 4.1 Average mixing ratios (mean \pm S.D.) of selected species in Jianfeng Mountain and comparison with other rural sites (unit: ppbv).

	Jianfeng Mountain ^a		Ala- bama ^b	Missi- ssipi ^b	Geor- gia ^b	North Carolina ^b	Chichi- jima ^c	Happo ^d		Lin'an ^e		Hok Tsui ^f	K _{OH} ^g	Lifetime ^h (days)
	Spring (n=34*)	Autumn (n=48)	Autumn	Autumn	Autumn	Autumn	Winter	Spring	Autumn	Autumn	Spring	Spring		
ethane	0.81 \pm 0.34	1.43 \pm 0.65	1.56	1.64	1.21	1.26	1.58	1.74	0.95	3.35	3.11	2.37	0.248	40.2
propane	0.15 \pm 0.10	0.46 \pm 0.28	1.41	1.36	1.36	1.26	0.54	0.61	0.49	1.59	1.2	0.81	1.09	9.2
isobutane	0.06 \pm 0.13	0.11 \pm 0.08	0.26	0.28	0.24	0.24	0.1	0.13	0.11	0.49	0.39	0.22	2.12	4.7
n-butane	0.10 \pm 0.19	0.16 \pm 0.12	0.55	0.57	0.60	0.71	0.17	0.22	0.19	0.59	0.43	0.33	2.36	4.2
isopentane	0.21 \pm 0.18	0.17 \pm 0.12	0.31	0.31	0.54	0.58	0.08	0.11	0.09	0.19	0.33		3.6	3.2
n-pentane	0.15 \pm 0.07	0.09 \pm 0.06	0.21	0.19	0.35	0.23	0.05	0.08	0.07	0.17	0.13	0.09	3.80	3.0
ethene	0.33 \pm 0.17	0.48 \pm 0.38	0.44	0.54	0.53	0.84	0.17	0.21	0.23	3.07	1.61	0.50	8.52	1.2
propene	0.12 \pm 0.04	0.16 \pm 0.46	0.22	0.29	0.27	0.23				0.54	0.28	0.06	26.3	0.4
isoprene	0.77 \pm 0.47	0.50 \pm 0.33	0.53	0.53	0.35	0.49	0.08						100	0.1
ethyne	0.34 \pm 0.19	1.05 \pm 0.67	0.53	0.62	0.58	0.67	0.45	0.7	0.36	2.6	2.39	1.40	0.88	11.3
benzene	0.15 \pm 0.08	0.29 \pm 0.17	0.15	0.13	0.16	2.13	0.12			1.33	0.8	0.49	1.22	8.2
toluene	0.16 \pm 0.13	0.22 \pm 0.26	0.15	0.13	0.31	0.32	0.78			2.54	1.5	0.54	5.63	1.8

a. Spring & Autumn: data collected at 11:00-15:00. *Number of samples.

b. Hagerman et al., 1997. Samples were collected at 12:00-13:00 local time, 1993. Unit transforms from ppbC.

c. Kato et al., 2001. Samples were collected at 4:00, 7:00, 13:00 and 18:00 local time, 1999.

d. Sharma et al., 2000. Samples were collected in spring, 1998-1999.

e. Guo et al., 2004a. Samples were collected at noon between October-November 1999 and March-June 2001.

f. Wang T. et al., 2003. Samples were collected at 12:00-13:00, March – April, 2001.

g. Atkinson and Arey, 2003 (unit: $\times 10^{12}$ cm³ molecule⁻¹ s⁻¹ at 298K).

h. Based on global annual mean OH = 1.16 x 10⁶ molecules cm⁻³, Spivakovsky et al., 2000.

Table 4.2 Average mixing ratios together with standard deviations of selected species in different trajectory groups (unit: ppbv)*.

	Spring			Autumn	
	WP (n=8)**	SEA (n=10)	SCS (n=13)	CEA (n=39)	SEA (n=5)
ethane	0.59 ± 0.09	1.00 ± 0.36	0.69 ± 0.16	1.63 ± 0.59	0.63 ± 0.18
propane	0.10 ± 0.03	0.19 ± 0.10	0.12 ± 0.08	0.54 ± 0.27	0.16 ± 0.06
isobutane	0.03 ± 0.01	0.04 ± 0.02	0.09 ± 0.21	0.13 ± 0.08	0.04 ± 0.03
n-butane	0.05 ± 0.02	0.06 ± 0.03	0.15 ± 0.31	0.19 ± 0.12	0.07 ± 0.03
isopentane	0.27 ± 0.07	0.16 ± 0.07	0.12 ± 0.05	0.18 ± 0.11	0.18 ± 0.18
n-pentane	0.17 ± 0.05	0.14 ± 0.05	0.11 ± 0.02	0.10 ± 0.06	0.05 ± 0.03
ethene	0.26 ± 0.11	0.33 ± 0.16	0.37 ± 0.22	0.48 ± 0.28	0.26 ± 0.11
propene	0.10 ± 0.02	0.10 ± 0.03	0.14 ± 0.05	0.08 ± 0.05	0.18 ± 0.10
isoprene	0.81 ± 0.17	0.54 ± 0.40	0.99 ± 0.59	0.51 ± 0.34	0.36 ± 0.24
ethyne	0.21 ± 0.07	0.41 ± 0.21	0.30 ± 0.09	1.23 ± 0.64	0.31 ± 0.09
benzene	0.10 ± 0.02	0.18 ± 0.09	0.12 ± 0.03	0.33 ± 0.16	0.12 ± 0.04
toluene	0.13 ± 0.02	0.13 ± 0.04	0.16 ± 0.20	0.23 ± 0.26	0.22 ± 0.10
ΣNMHC***	3.29 ± 0.42	3.57 ± 0.74	3.93 ± 1.06	6.18 ± 2.45	5.03 ± 3.95

*Data for the samples collected from 11:00-15:00. **Numbers of samples.

*** ΣNMHC: The sum is the total mixing ratio of all hydrocarbons measured and quantified.

Table 4.3 Comparison of the average mixing ratios of selected species in enhanced days with the background average mixing ratios (unit: ppbv for hydrocarbons and volume/volume for hydrocarbon ratios).

	Spring background (n=2)	April 18-19 (n=6)	Autumn background (n=2)	Oct. 18-21 (n=6)	Nov. 26-28 (n=3)
ethane	0.45 ± 0.02	1.33 ± 0.13	1.00 ± 0.10	2.57 ± 0.33	2.44 ± 0.14
propane	0.05 ± 0.02	0.28 ± 0.05	0.25 ± 0.01	0.74 ± 0.08	1.08 ± 0.07
isobutane	0.01 ± 0.01	0.06 ± 0.04	0.04 ± 0.01	0.17 ± 0.04	0.28 ± 0.03
n-butane	0.02 ± 0.01	0.15 ± 0.20	0.06 ± 0.02	0.24 ± 0.03	0.43 ± 0.04
isopentane	0.25 ± 0.05	0.14 ± 0.09	0.05 ± 0.02	0.19 ± 0.06	0.26 ± 0.13
n-pentane	0.16 ± 0.04	0.13 ± 0.05	0.03 ± 0.01	0.12 ± 0.03	0.19 ± 0.04
ethene	0.15 ± 0.01	0.47 ± 0.19	0.23 ± 0.01	0.61 ± 0.19	1.06 ± 0.44
propene	0.09 ± 0.02	0.13 ± 0.04	0.03 ± 0.00	0.11 ± 0.04	0.07 ± 0.05
isoprene	0.08 ± 0.08	0.20 ± 0.15	0.09 ± 0.02	0.79 ± 0.34	0.22 ± 0.17
ethyne	0.06 ± 0.02	0.64 ± 0.12	0.49 ± 0.06	2.25 ± 0.44	2.19 ± 0.39
benzene	0.06 ± 0.01	0.25 ± 0.03	0.16 ± 0.03	0.56 ± 0.09	0.60 ± 0.15
toluene	0.08 ± 0.02	0.12 ± 0.04	0.05 ± 0.03	0.20 ± 0.13	0.61 ± 0.51
ΣNMHC *	1.67 ± 0.13	4.34 ± 0.57	2.61 ± 0.05	9.18 ± 1.39	10.58 ± 2.46
C ₂ H ₆ /C ₃ H ₈	10 ± 6	4.9 ± 0.9	4.1 ± 0.6	3.4 ± 0.3	2.2 ± 0.1
C ₂ H ₆ /C ₂ H ₂	8.7 ± 3.3	2.1 ± 0.4	2.1 ± 0.1	1.2 ± 0.1	1.1 ± 0.2
C ₃ H ₈ /C ₆ H ₆	0.7 ± 0.2	1.1 ± 0.2	1.6 ± 0.2	1.3 ± 0.1	1.8 ± 0.3

* ΣNMHC: The sum is the total mixing ratio of all hydrocarbons measured and quantified.



Figure 4.1 Map showing the sampling site- Jianfeng Mountain.



Figure 4.2 Photo showing the sampling site at Jianfeng Mountain.

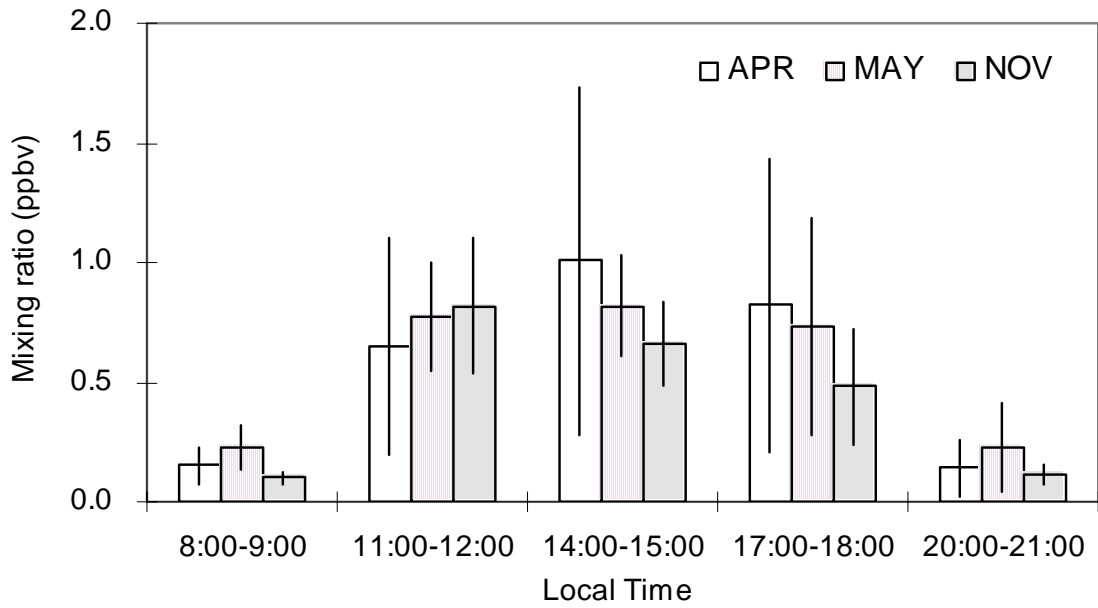


Figure 4.3 Diurnal variations of isoprene in the three intensive study periods.

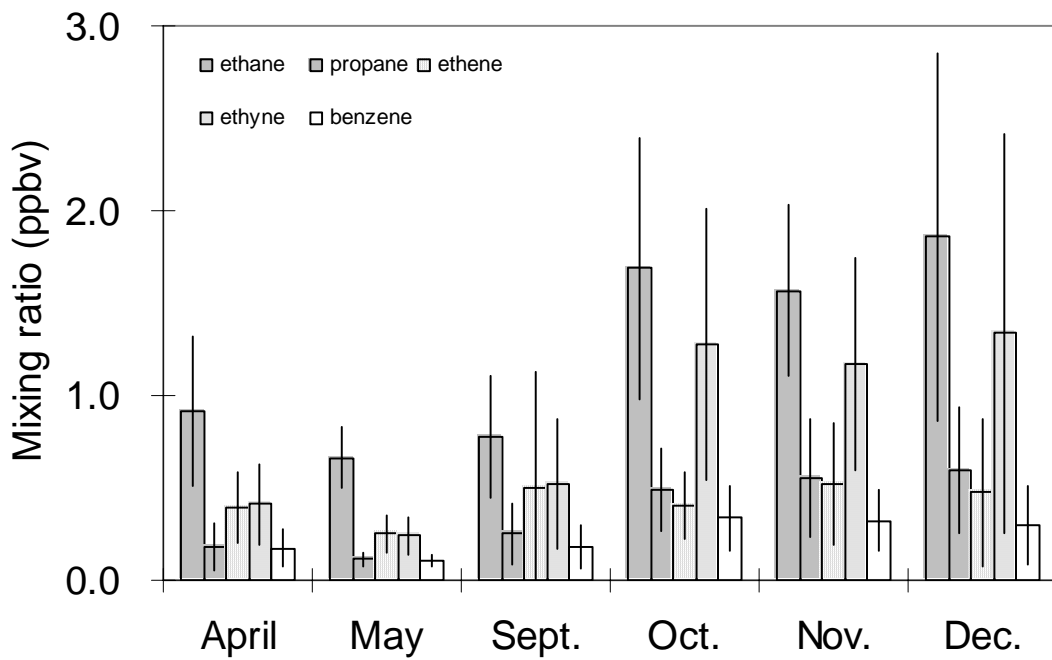


Figure 4.4 Average concentrations together with standard deviation of selected hydrocarbons in different months. Samples were collected from 11:00-15:00.

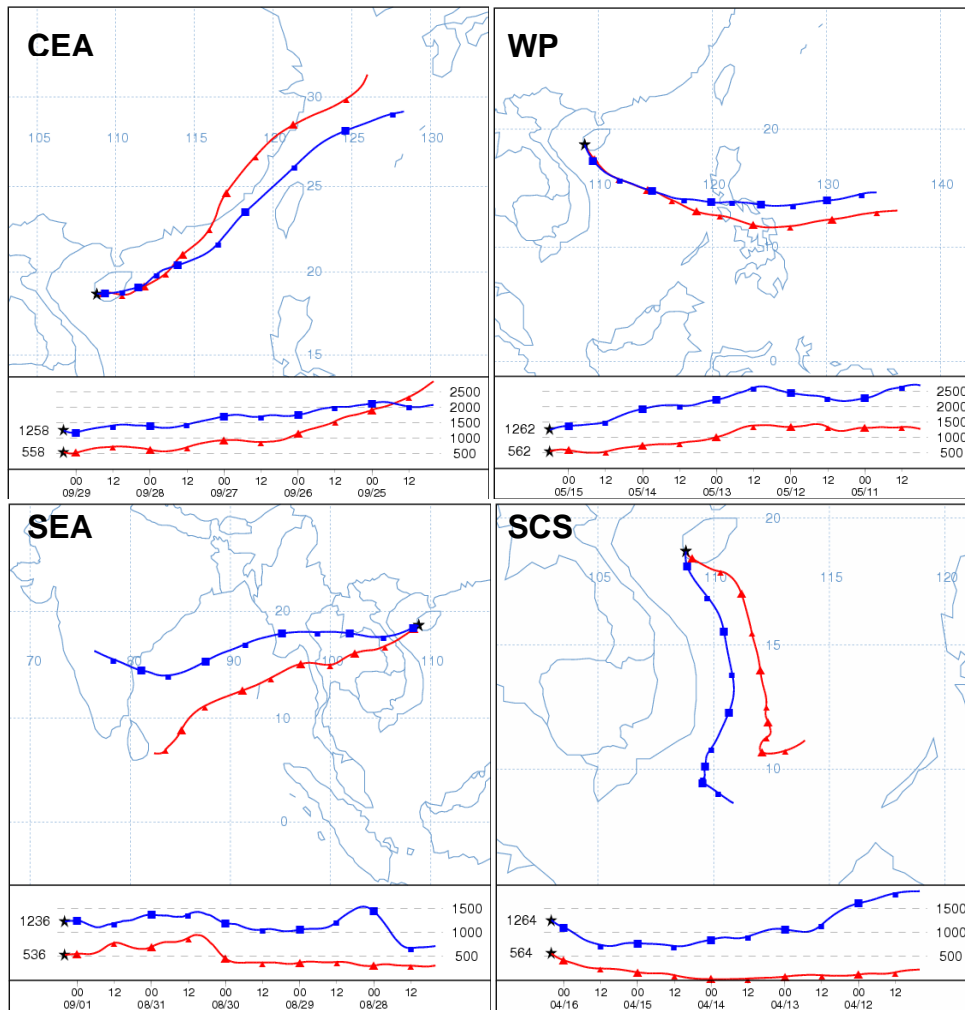


Figure 4.5 Representative back air trajectories in different trajectory groups.

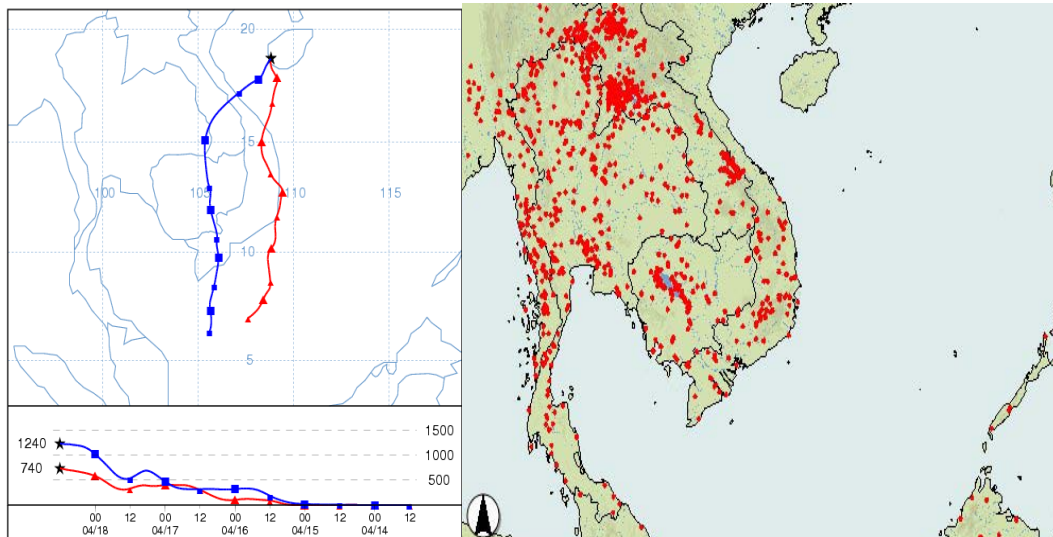


Figure 4.6 Back air trajectory on April 18 and fire count map on April 16-18, 2004.

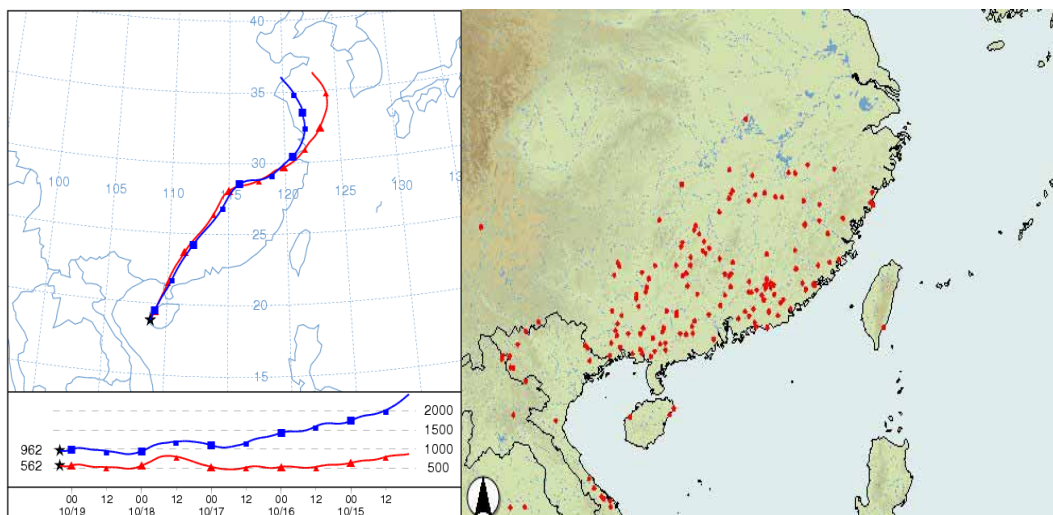


Figure 4.7 Back air trajectory on Oct. 19 and fire count map on Oct. 16-18, 2004.

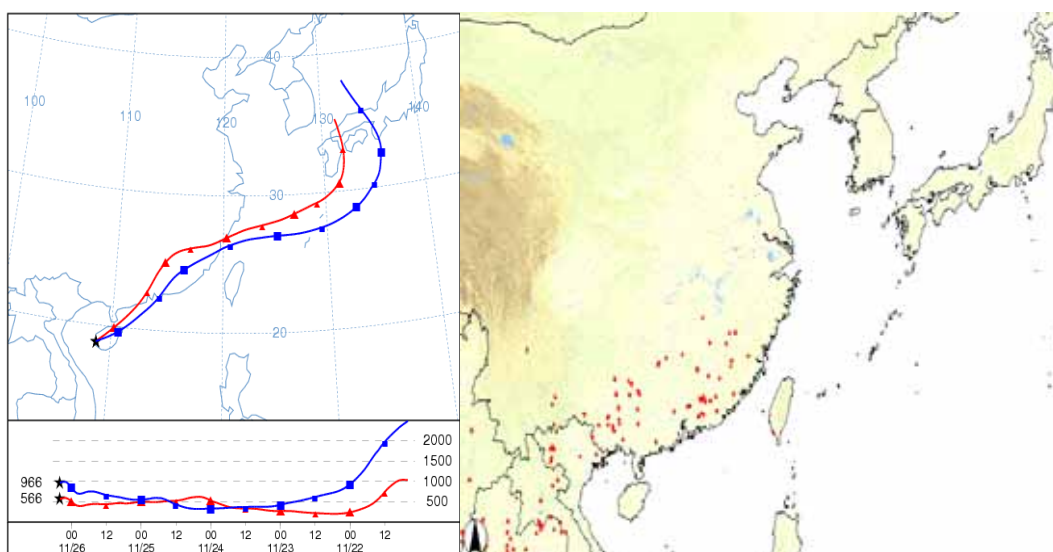


Figure 4.8 Back air trajectory on Nov. 26 and fire count map on Nov. 24-26, 2004..

Chapter 5

Characteristics of NMHCs at three rural and remote sites of South China in spring 2004

5.1 Introduction

This chapter analyzes results of the NMHC data collected at three rural remote sites of South China in April and May 2004: Jianfeng Mountain (JM) at the Southwest coast of Hainan Island, Tengchong Mountain (TM) at the western border of Yunnan Province, and Lin'an (LA) at Zhejiang Province. Additional NMHC data collected at Tengchong City (about 10 km to TM in the south direction) and Sanya (about 120 km to JM to the southeast direction) were also evaluated. Figure 5.1 shows the geographic locations and Table 5.1 describes the characteristics of the sampling sites. The sampling periods in the three rural remote sites were during 2 April to 24 May, while at Tengchong County, it was during 18 to 24 May and at Sanya on 24 April.

5.2. Sampling site description

5.2.1 Lin'an (LA)

Lin'an is a rural remote site located at the Yangtze River Delta. The sampling site is located in the Baseline Air Pollution Monitoring Station of China at Lin'an. The general surroundings of Linan monitoring station include the Lin'an County, 10km to the south; Hangzhou, the provincial capital, 53 km to the east; and the metropolitan Shanghai, 210 km to the northeast. To the west are less developed and less populous mountainous regions. Near the station, several small villages are within 2 km range. The elevation of the sampling site is about 130m asl. The detail information about this site can also be found at Cheung et al. (2001) and Wang T. et al. (2004).

5.2.2 Tengchong Mountain (TM)

Tengchong Mountain is a rural remote site at the east border of Yunnan province. It is located about 60 km to the east of the Myanmar border and 750 km to the west of Kunming, the capital of Yunnan Province. The closest town, Tengchong County is about 10 km to the South. There are small villages surrounding the sampling site. The details about this site can also be found at Chan C.Y. et al. (2006).

5.2.3 Jianfeng Mountain (JM)

Jianfeng Mountain is situated at the southwest of Hainan Island, south China. The detail information about this sampling site was introduced in Chapter 4, and can also be found in found at Tang et al. (2007).

5.3 Features of total and dominant NMHC species

56 Photochemical Assessment Monitoring Stations (PAMS) target compounds are identified and quantified. The mixing ratios of some hydrocarbons are very low and some are below the detection limit in the three rural remote sites. Here we only present the common and representative species found in the three rural remote sites. The statistics of selected hydrocarbons at the five sites are shown in Table 5.2. Selective NMHC data at JM has been discussed in detail in chapter 4 of this dissertation. Here we show the entire data for comparison. The total mixing ratio of all measured hydrocarbons (Σ NMHC) is also shown in Table 5.2. The listed C₂-C₇ hydrocarbons accounted for approximately 90% and 80% of the Σ NMHC in rural remote sites and urban sites respectively. The mixing ratios of Σ NMHC followed the order: JM<TM<LA<SY<TC. Ethane, ethyne, ethene, propane and benzene were among the top 10 most abundant compounds, although the order differed at each site.

Among the three rural remote sites, JM shows the highest levels of isoprene but the lowest levels of other hydrocarbons, while LA shows the highest levels of most hydrocarbons except for isoprene. The contributions of hydrocarbons to the Σ NMHC are shown in Figure 5.2. The profiles of NMHCs in the three rural remote sites and the two urban sites varied remarkably. Ethane, ethene and ethyne were among the top 5 contributors to the Σ NMHC at all sites. But there are other distinguishing features. At JM, isoprene were the second largest contributor (14.8%) after ethane (23.4%), while at LA, toluene is the largest contributor (15.9%) as well as ethane. At SY, propane (11.0%) was the largest contributor to the Σ NMHC, and n-butane (8.7%) was the fourth contributor after ethyne (9.4%) and ethane (9.0%). The percentages of hydrocarbons to the Σ NMHC between TM and TC were very similar except for ethane, whose percentage shown about two times higher at TM (25.3%) than at TC (9.8%).

5.4 Sources of hydrocarbons at different sites

5.4.1 Industrial emission

JM locates in the remote tropical rainforest with very few inhabitants lived nearby, while TM and LA are surrounding by small villages and locates close to their capital cities. TM is about 10 km to Tengchong County and LA is about 10 km to Lin'an County. It is expected that TM and LA are more impacted by local anthropogenic emissions and should have higher levels of anthropogenic hydrocarbons.

Table 5.3 shows some statistical data for the three rural regions. Most of the inhabitants are lived in rural remote areas in the three regions (83% at JM region, 92% at TM region and 87% at LA region, Table 5.3) compared to the 58% of the nation's population lived in rural region of China in 2004 (National Bureau of Statistics of China, 2005). These three regions represent typical rural remote area of China, but

they also show some differences with each other. JM is under the administration of Ledong County. Agriculture is the pillar sector of economy and industry contributes little to local economy in this county (Table 5.3). The major sources of NMHCs at JM were long-range transport from remote sources regions, except for isoprene, whose major sources is local biogenic emissions (Tang et al., 2007). LA site is neighboring the YRD region. The industrial enterprises and their contributions to the GDP are at least one order of magnitude larger at LA than at the other two regions (Table 5.3). This was demonstrated by the much higher levels of toluene at LA than at other two sites.

Figure 5.3 shows the correlations of several hydrocarbons versus toluene. Toluene correlated well with ethylbenzene ($R^2 = 0.74$), m/p-xylene ($R^2 = 0.69$) and o-xylene ($R^2 = 0.82$), but correlated poorly with i-pentane, ethyne, and benzene. It indicates that toluene, ethylbenzene, m,p-xylene, and o-xylene (TEX) shared common sources, i. e. industrial emissions. The poor correlation of toluene with i-pentane and ethyne implies that gasoline evaporation and vehicular exhausts contribute less to the high levels of toluene. The wind rose of toluene at LA demonstrates that air masses from southwestern and south directions contain abundant toluene (up to 16 ppbv) (Figure 5.4). LA County (with a population of about 150,000 in 20 km² area) is about 10 km away from the sampling site to the south direction, so industrial emission from LA County was expected to be the major source of TEX.

5.4.2 Combustion sources

The major sources of ethyne in the atmosphere are combustion processes, such as biomass burning, fossil fuel combustion (Choi et al., 2003). In urban area, its major

source is vehicular emission and it is commonly used as a tracer for vehicular emissions (Henry et al., 1994; Barletta et al., 2005; Lee et al., 2006). While in the rural regions of China, biofuel combustion may be its major sources. It was estimated that 45% of ethyne and ethane and 50% ethene were attributed to biofuel combustion in East Asia (Streets et al., 2003b). The average mixing ratios of hydrocarbons to ethyne was calculated to explore the possible sources signatures of NMHCs at different sites (Figure 5.5). The data collected from March to June 2001 by Guo et al. (2004a) at the same site LA were compared with our LA data. The hydrocarbon/ethyne ratios matched very well in this study with the study by Guo et al. (2004a) except for an increase in toluene/ethyne ratio. It indicates that the source profiles of NMHCs are similar between 2001 and 2005, except for increasing emission strengths of toluene from industrial sources. In the study of 2001 at LA, about 70 % of emissions for the total volatile organic compounds were attributed to a combination of vehicular emissions and biofuel burning, and about 7% to gasoline evaporation and solvent emissions (Guo et al., 2004a). In this study, the combustion of fossil fuel and biofuel are still the major sources for NMHCs, but industrial emission plays a more important role in 2005 than 2001.

TM is a site affected more by local emissions than JM and less by industrial emissions than LA as there are very few industrial enterprises (Table 5.3). This was also demonstrated by about three times higher ethene and ethyne mixing ratios at TM than at JM, but about one order of magnitude lower toluene mixing ratios at TM than at LA (Table 5.2). The profile of hydrocarbon/ethyne ratios at TM is very similar to that at TC, except for a higher ethane/ethyne ratio at TM (1.8) than at TC (0.56) (Figure 5.5). It indicates that the sources profile of NMHCs at TM is similar to that at TC. The high

ethane/ethyne ratio at TM may due to the additional source of ethane at TM and the longer atmospheric lifetime of ethane than ethyne. Biogas was widely used in TM region (Li et al., 2005) and this is a major additional ethane source. Ethene and ethyne are mainly from combustion sources, such as burnings of fossil fuel, biomass/biofuel including agricultural residues and coal (Choi et al., 2003). These two species accounted for about 35% and 40% of the Σ NMHC at TM and TC, respectively. In China, it has been reported that biomass accounts for about two-thirds of the total energy used by rural households (Jiang and O'Neill, 2004). As a less developed province in China, the major energy sources in rural households are firewood (41%), coal (38%) and straw (12%) in Yunnan Province (Li et al., 2005). So, biofuel combustion by peasant households in TM region plays very important roles on the high levels of ethene and ethyne. There is only one highway from TC to TM, and only a few vehicles were running on this mountainous and remote region. So, vehicular emission is not an important contributor to the levels of NMHCs.

TC is a small town with a population of about 44,000 in 14 km², while SY is the second largest city in Hainan Province with a population of 140,000 in 37 km². The hydrocarbon/ethyne patterns between TC and SY are significantly different. The ratios of propane/ethyne, n-butane/ethyne, isobutene/ethyne, i-pentane/ethyne, and toluene/ethyne are several times higher at SY than at TC. Taxis in SY were promoted to use liquefied petroleum gas (LPG) as fuel. Several large LPG stations were set up in urban area like in Mexico City (Blake and Rowland, 1995). It is likely LPG leakage contributes to the high levels of propane, n-butane, and i-butane in SY. There were also more industries in SY than TC, and this resulted in the higher levels of toluene in SY than in TC.

5.4.3 Biomass burning emissions

In the period of May 6 - 10, 2004, at the same sampling site Tengchong Mountain, Chan et al. (2006) reported that enhanced levels of ozone, carbon monoxide (CO), particulate matters and total reactive nitrogen (NO_y) were found in the air masses from Southeast (SE) Asian subcontinent where active biomass burnings occurred. At Jianfeng Mountain, biomass burning emissions in SE Asia in April 2004 were found to be a contributor to the high levels of ethene and ethyne (Tang et al., 2007). This was also discussed in Chapter 4. At this chapter, the impacts of biomass burning in the neighboring SE Asian subcontinent on TM were investigated with the help of backward air trajectory analysis and satellite images of fire count.

Figure 5.6 shows the variations of selected hydrocarbons and the daily rainfall during the measurement periods at TM and Figure 5.7 shows those at JM. On April 8 and 17, several samples with high levels of ethene and ethyne together with other hydrocarbons were captured although it is rainy days. Backward air trajectory on these days calculated by the National Oceanic and Atmospheric Administration (NOAA) HYSPLIT Model (Rolph, 2003) was used to determine the possible source region of air masses. Fire count map (<http://maps.geog.umd.edu/products.asp>) of SE Asia was also used to identify the biomass burning activities in SE Asia region. Figure 5.8 shows the 5-day backward trajectory on April 17 at TM and JM and fire count map during April 12-16 in SE Asia. There are several fire activities occurred immediate TM sites, but intensive burning activities were found on the west border regions of Burma. At the low boundary lay of TM (altitude < 300 m), the weather condition on April 17 was stagnant and air masses were originated from surface of immediate TM region (Figure 5.8). Figure 5.9 compares the average mixing ratios of selected

hydrocarbons in the enhancements of April, April with and without enhanced samples, and May. It clearly shows that the mixing ratios of most hydrocarbons especially isopentane, ethene and ethyne are about three to six times higher in the enhanced samples than those in April without enhanced samples and May. The average mixing ratios of most hydrocarbons in April are very close to those in May when excluded the enhanced samples. However, when included those enhanced samples, they elevated the average mixing ratios of isopentane, ethene and ethyne in April compared in May.

Figure 5.10 shows the hydrocarbon/ethyne ratios in the enhanced samples of TM and JM (18-19 April) and the ambient samples in TC. At the enhanced samples of JM, the levels hydrocarbons were strongly influenced by the biomass burning emissions in the Southeast Asia as discussed in Chapter 4. The profiles of hydrocarbon/ethyne in the enhanced samples of TM matched well with that TC expect for higher isopentane/ethyne and ethane/ethyne ratios at the enhanced TM samples. This indicates that in these enhanced samples, local biofuel combustion plus gasoline evaporation may be the major sources.

The major air masses pathways in April are originated from the Bay of Bengal and traveled across Burma like that on April 17. While in May, they major originated from the southwest of China. Figure 5.11 shows the typical pathways of air masses, and Figure 5.12 shows the fire count maps during sampling periods in April and May, respectively. At April, intensive biomass burning activities were detected at SE Asia subcontinent, while at May, less were detected. However, in the pathways of air masses approached to TM, there were very limited biomass burning activities (Figure 5.11 and Figure 5.12). So, biomasses burning emission in Southeast Asia contributed

less to the levels of hydrocarbons at TM, although they significantly increased the levels of most hydrocarbons at JM. Local biofuel combustions are the major sources of NMHCs at TM.

5.4.4 Biogenic emissions

Isoprene and α -pinene were identified and quantified in this study. The two species are major components of biogenic emission in the atmosphere (Guenther et al., 1995). Compared with isoprene, the levels of α -pinene were relatively low. Among the three rural remote sites, JM shows the highest isoprene levels, while TC shows the lowest, and LA shows the highest α -pinene levels. Figure 5.13 shows the diurnal variations of isoprene at the three rural remote sites. The higher levels of isoprene at midday than at morning and evening indicate that there are strong local sources at JM and LA. Emission from local vegetation is expected to be the major source at JM and LA. While at TM, the levels of isoprene are very lower compared with other two sites. It indicates that there are very limited isoprene-emitting vegetations.

5.5. Hydrocarbon reactivities with hydroxyl radical

Photochemical reactions of NMHCs are mainly initiated by the OH radical, and the mechanism of ozone formation for each hydrocarbon varies greatly. To estimate the reactivity of individual hydrocarbons, propylene-equivalent concentration method proposed by Chameides (1992) were used. The detail of this method is discussed in chapter 2.

Using the method, the contributions of individual hydrocarbons to the total propylene-equivalent concentrations were calculated (Table 5.4). Isoprene is the largest

contributor to the propylene-equivalent concentration at JM and LA, but the second largest at TM after ethene. The second contributor to propylene-equivalent concentration at JM is ethene, while at LA it is toluene. The major group contributor to propylene-equivalent concentration is biogenic compounds (isoprene and α -pinene) (62%) at JM and alkenes (61%) at TM. While at LA, biogenics and alkenes each account for about one third. At the urban sites, ethene (15.5%) and propene (8.7%) were the major contributors to ozone formation at TC, while at SY, isoprene (21.4%) was the dominant contributor and ethene (6.1%) was the second largest contributor.

5.6 Conclusion

Among the three rural remote sites, LA shows the highest levels for most hydrocarbons, and JM shows the lowest levels except for isoprene. Ethane, ethene, and ethyne are the most abundant anthropogenic hydrocarbons at the three sites. The source profiles of NMHCs at three rural remote sites varied largely. Combustions of fossil fuel and biofuel are the major sources at LA, and industrial emission also played an important role for the higher levels of toluene, ethylbenzene and xylenes. While at JM, long-range transport was the major sources of most hydrocarbons. Air masses from SE Asian biomass burning region elevated the mixing ratios of most hydrocarbons at JM, but they contributed less to the levels of NMHCs at TM. Local biofuel combustion was the major source of TM and TC. Local biogenic emissions were the major sources for isoprene and α -pinene at JF and LA. However, the emission strength is negligible at TM. Biogenic hydrocarbons are the major contributors to ozone formation at JM and SY. While at TC and TM, the major contributors are alkenes from local biofuel combustion. At LA, biogenic hydrocarbons and alkenes each account about one third of ozone formation.

Table 5.1 Characteristics of the sampling sites.

Site	Abbr.	Location	Altitude*	Sampling period	Site description
Jianfeng Mountain	JM	18°40' N, 108°49' E	820	April 9-24, May 12-21, 2004	Remote site, in a tropical rain forest site
Tengchong Mountain	TM	24°57' N, 98°29' E	1960	April 8-17, May 18-24, 2004	Rural site, in mountainous area with small villages around
Lin'an	LA	30°30'N, 119°75' E	130	April 2 - May 20, 2004	Rural site, in mountainous area with small villages around
Tengchong County	TC	25°01' N, 98°30' E	1660	May 18 - 24, 2004	Urban site, at rooftop of a 5-story building in urban center
Sanya	SY	18°14' N, 109°30' E	20	April 24, 2004	Urban site, at rooftop of a 5-story building in urban center

*unit: m, above sea level.

Table 5.2 Statistics of selected hydrocarbons at the five sites.

hydrocarbon	JM (n=91) ¹					TM (n=85)					LA (n=83)					TC (n=12)					SY (n=6)				
	Mean	SD	Median	Min	Max	Mean	SD	Median	Min	Max	Mean	SD	Median	Min	Max	Mean	SD	Median	Min	Max	Mean	SD	Median	Min	Max
ethane	0.86	0.45	0.74	0.38	3.20	1.43	0.34	1.40	0.71	2.26	2.63	0.81	2.50	1.29	8.32	2.31	0.86	2.00	1.36	3.76	0.86	0.16	0.85	0.65	1.14
propane	0.17	0.16	0.13	0.02	1.26	0.25	0.08	0.22	0.07	0.44	1.31	1.01	1.06	0.37	7.98	0.73	0.42	0.56	0.36	1.72	2.15	0.69	2.15	1.22	2.97
isobutane	0.05	0.09	0.03	BDL ²	0.80	0.04	0.04	0.03	BDL	0.27	0.51	0.46	0.37	0.08	2.85	0.54	0.39	0.40	0.17	1.59	0.97	0.32	0.96	0.58	1.40
n-butane	0.10	0.18	0.06	0.02	1.46	0.07	0.05	0.06	0.02	0.30	0.73	0.77	0.52	BDL	5.31	0.48	0.26	0.42	0.17	0.97	1.71	0.65	1.61	0.99	2.75
isopentane	0.20	0.18	0.16	BDL	1.22	0.24	0.45	0.13	0.03	3.32	0.46	0.28	0.38	BDL	1.33	1.15	0.56	1.08	0.54	2.36	1.15	0.34	1.13	0.69	1.64
n-pentane	0.15	0.15	0.12	0.06	1.44	0.15	0.15	0.12	0.06	1.33	0.29	0.24	0.25	0.09	2.02	0.49	0.20	0.49	0.27	0.89	0.65	0.21	0.63	0.38	0.96
ethene	0.38	0.32	0.32	0.14	2.14	1.03	0.70	0.79	0.33	3.50	1.73	1.17	1.52	0.37	8.45	4.73	3.12	3.16	1.23	9.74	1.76	0.77	1.67	0.76	3.00
propene	0.11	0.08	0.10	0.05	0.77	0.20	0.11	0.16	0.09	0.65	0.33	0.27	0.29	0.09	2.11	0.86	0.56	0.56	0.22	1.89	0.47	0.18	0.45	0.23	0.76
isoprene	0.55	0.52	0.32	0.02	2.19	0.08	0.16	0.06	BDL	1.32	0.40	0.39	0.27	0.02	1.88	0.13	0.06	0.10	0.06	0.25	0.53	0.41	0.54	0.04	1.07
alpha-pinene	0.05	0.03	0.05	BDL	0.12	0.06	0.04	0.04	0.02	0.18	0.17	0.12	0.14	0.01	0.74	0.13	0.10	0.10	0.05	0.40	0.04	0.00	0.04	0.04	0.05
ethyne	0.39	0.35	0.31	0.04	2.97	0.94	0.64	0.78	0.05	4.01	2.18	0.93	1.90	0.79	4.54	4.35	2.19	3.55	1.42	7.45	1.84	0.67	1.89	0.85	2.83
benzene	0.13	0.09	0.11	0.05	0.79	0.27	0.13	0.24	BDL	0.89	0.75	0.37	0.67	0.24	2.41	1.13	0.59	0.92	0.45	2.12	0.53	0.21	0.49	0.25	0.89
toluene	0.17	0.44	0.09	0.05	4.16	0.23	0.36	0.14	0.05	3.06	2.64	3.00	1.90	0.22	16.07	1.08	0.78	0.85	0.37	2.86	1.29	0.39	1.21	0.88	1.88
ethylbenzene	0.02	0.02	0.02	BDL	0.12	0.05	0.10	0.02	BDL	0.73	0.33	0.26	0.27	0.03	1.47	0.27	0.16	0.25	0.08	0.69	0.29	0.07	0.29	0.20	0.37
m/p-xylene	0.04	0.03	0.03	BDL	0.19	0.10	0.26	0.04	0.02	2.19	0.32	0.26	0.25	0.04	1.33	0.68	0.38	0.63	0.24	1.61	0.75	0.18	0.75	0.54	0.96
o-xylene	BDL	BDL	BDL	BDL	0.07	0.04	0.10	0.02	BDL	0.84	0.15	0.15	0.11	0.02	1.01	0.24	0.13	0.21	0.09	0.54	0.28	0.07	0.29	0.20	0.38
alkanes	1.64	0.92	1.39	0.60	7.11	2.32	1.04	2.05	1.07	8.21	7.02	3.46	6.17	2.42	23.03	7.58	3.26	7.18	3.86	12.59	9.71	2.26	10.39	5.81	11.99
alkenes ³	0.68	0.44	0.58	0.31	3.30	1.47	0.92	1.17	0.63	5.60	2.44	1.72	2.23	0.59	13.42	7.56	4.60	5.42	2.36	15.78	3.79	1.35	3.61	1.95	6.11
alkynes	0.39	0.35	0.31	0.04	2.97	0.94	0.64	0.78	0.05	4.01	2.18	0.93	1.90	0.79	4.54	4.35	2.19	3.55	1.42	7.45	1.84	0.67	1.89	0.85	2.83
aromatics	0.40	0.51	0.31	0.13	4.63	0.79	0.95	0.54	0.25	7.54	4.40	3.99	3.51	0.62	23.66	3.75	2.03	3.40	1.69	8.44	3.64	0.95	3.54	2.51	4.97
biogenics	0.59	0.54	0.35	0.01	2.28	0.13	0.15	0.10	0.02	1.36	0.55	0.46	0.46	0.01	2.14	0.25	0.15	0.20	0.13	0.58	0.57	0.41	0.58	0.09	1.12
NMHC ⁴	3.70	1.85	3.55	1.56	15.08	5.65	3.01	4.89	2.56	18.97	16.59	8.21	15.32	7.24	48.15	23.50	11.78	19.47	9.95	44.73	19.56	4.51	19.85	12.04	24.95

1: the total number of samples; 2: BDL= below detection limit; 3: isoprene and alpha-pinene are not included in alkenes, but in biogenics; 4:

ΣNMHC: the total mixing ratio of all hydrocarbons measured.

Table 5.3 Comparisons of statistical data in Tengchong County, Ledong County and Lin'an City.

Item	Unit	Ledong County*	Tengchong County	Lin'an City
Area	km ²	2747	5845	3124
Population	ten thousands	48	62	52
Population in rural	ten thousands	40	57	45
GDP from primary industry	million	1479	807	1501
GDP from secondary industry	million	107	556	7562
Gross output value of grain	ton	171,184	248,358	93,139
No. of industry above designated size**	unit	14	19	428
Gross industry output value for the industry above designated size	million	68	393	13,980

* Jianfeng Mountain is under the administration of Ledong County

** Industry above the designated size means all state-owned enterprises and non state-owned enterprises with an annual sales revenue over 5 million Yuan.

Table 5.4 Percentages of hydrocarbons in propylene-equivalent concentrations.

hydrocarbon	JM	TM	LA	TC	SY
ethane	0.2%	0.5%	0.5%	0.2%	0.1%
propane	0.2%	0.4%	1.0%	0.3%	0.9%
isobutane	0.1%	0.1%	0.8%	0.4%	0.8%
n-butane	0.2%	0.2%	1.2%	0.4%	1.6%
isopentane	0.8%	1.2%	1.2%	1.6%	1.7%
n-pentane	0.6%	0.8%	0.8%	0.7%	1.0%
ethene	3.5%	12.2%	10.3%	15.5%	6.1%
propene	3.2%	7.2%	6.1%	8.7%	5.0%
isoprene	58.8%	11.4%	28.0%	4.8%	21.4%
alpha-pinene	2.8%	4.0%	6.3%	2.6%	0.9%
ethyne	0.4%	1.1%	1.3%	1.5%	0.7%
benzene	0.2%	0.5%	0.6%	0.5%	0.3%
toluene	1.0%	1.8%	10.4%	2.3%	2.9%
ethylbenzene	0.2%	0.4%	1.6%	0.7%	0.8%
m/p-xylene	0.8%	2.5%	4.2%	4.9%	5.7%
o-xylene	0.0%	0.8%	1.4%	1.3%	1.6%
alkanes	5.2%	7.9%	10.7%	8.1%	11.4%
alkenes	28.7%	61.3%	30.1%	67.6%	47.2%
alkynes	0.4%	1.1%	1.3%	1.5%	0.7%
aromatics	4.0%	14.2%	23.7%	15.4%	18.5%
biogenics	61.7%	15.5%	34.2%	7.4%	22.3%



Figure 5.1 Map showing geographic locations of the sampling sites-Jianfeng Mountain, Tengchong Mountain and Lin'an.

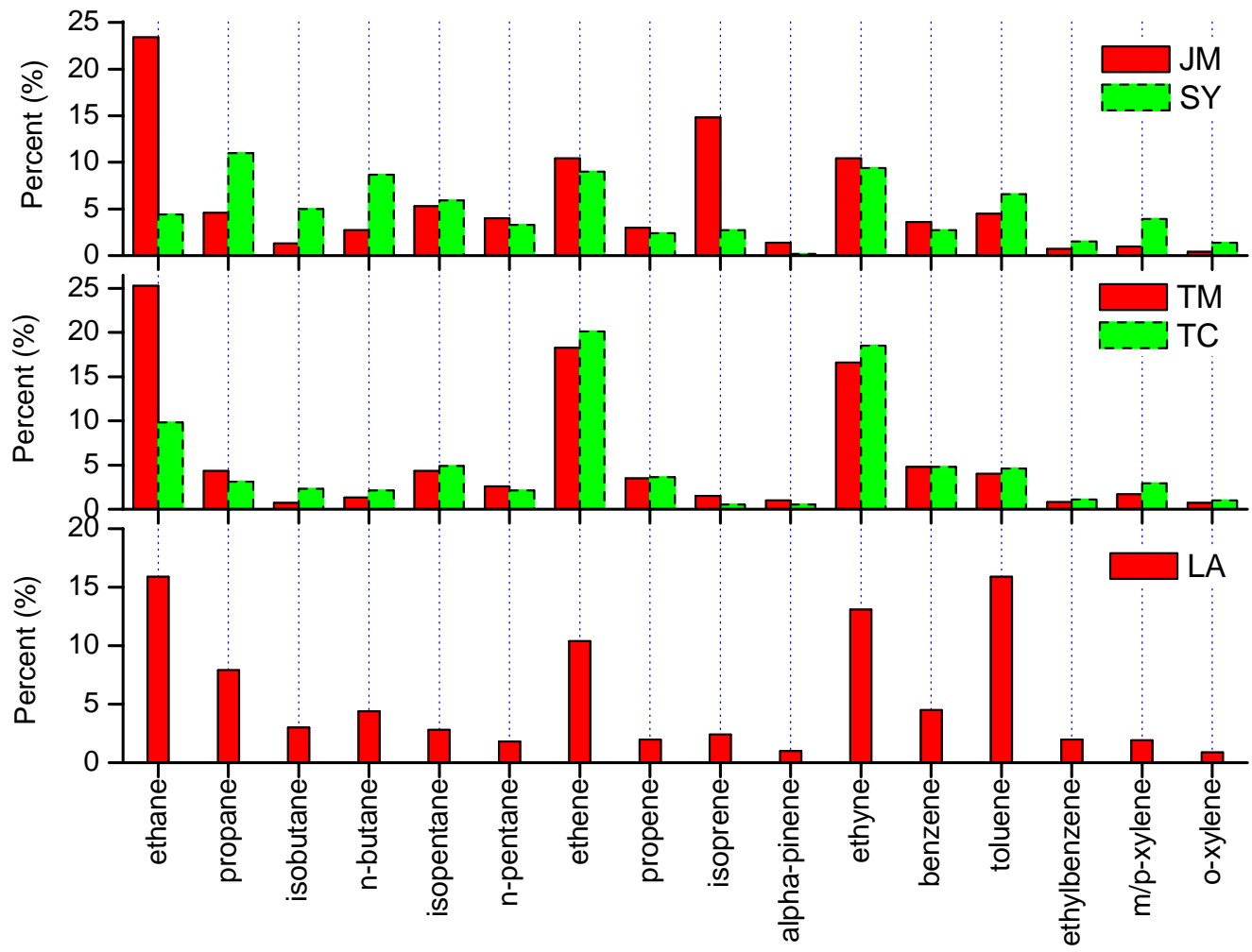


Figure 5.2 Percentage contributions of hydrocarbons at the five sites.

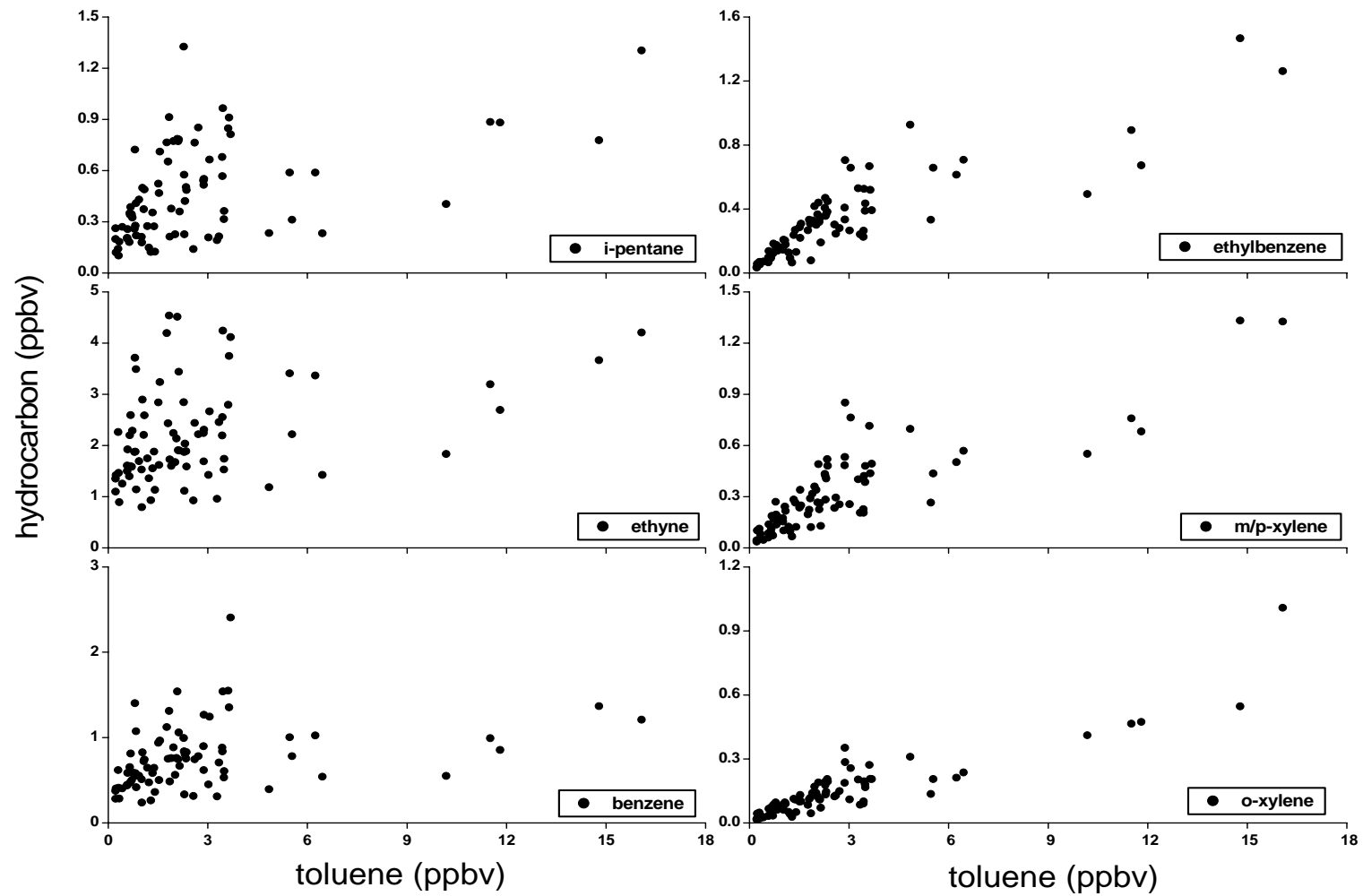


Figure 5.3 Scatter plots of several hydrocarbons versus toluene at LA.

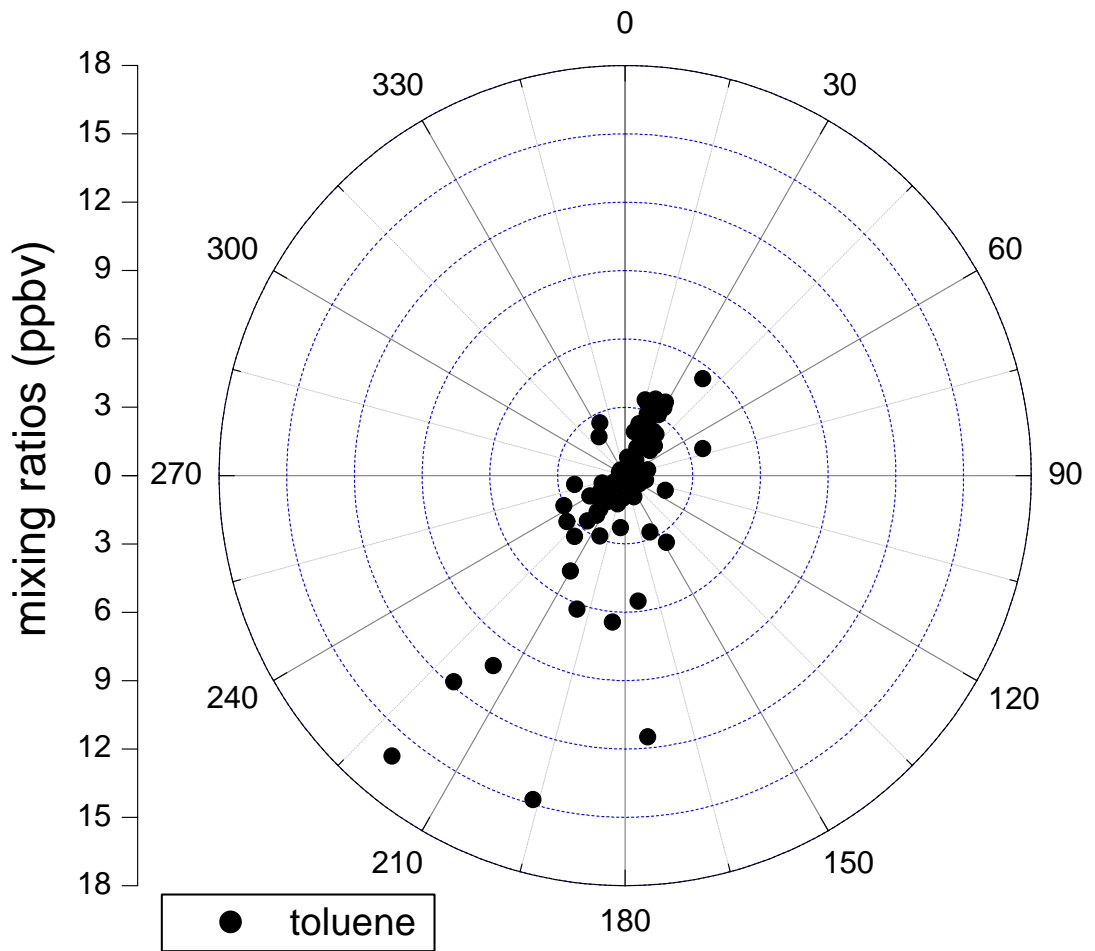


Figure 5.4 Wind rose of toluene at LA.

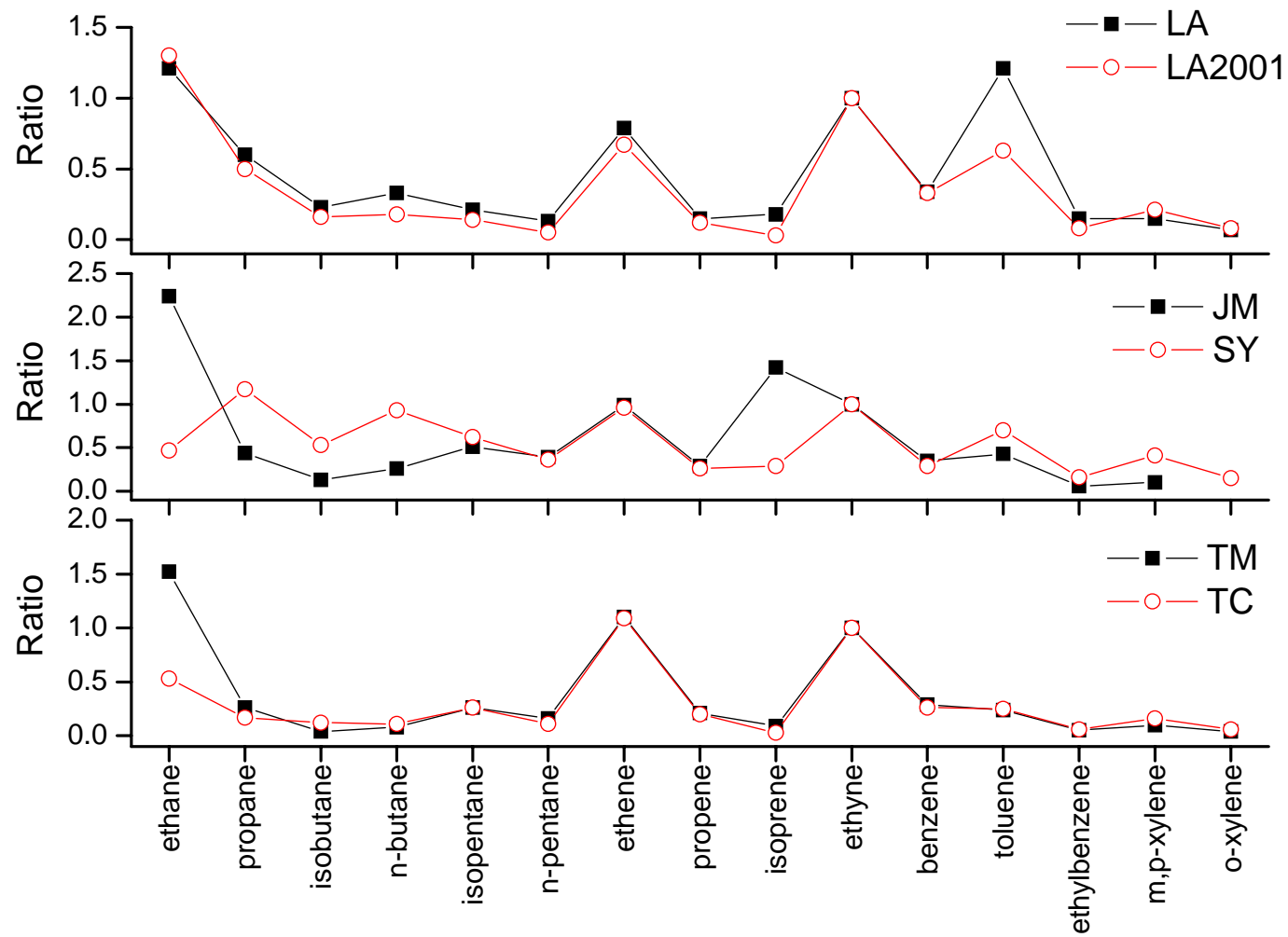


Figure 5.5 Hydrocarbon/ethyne ratios at five sites and plus data at Lin'an in spring 2001

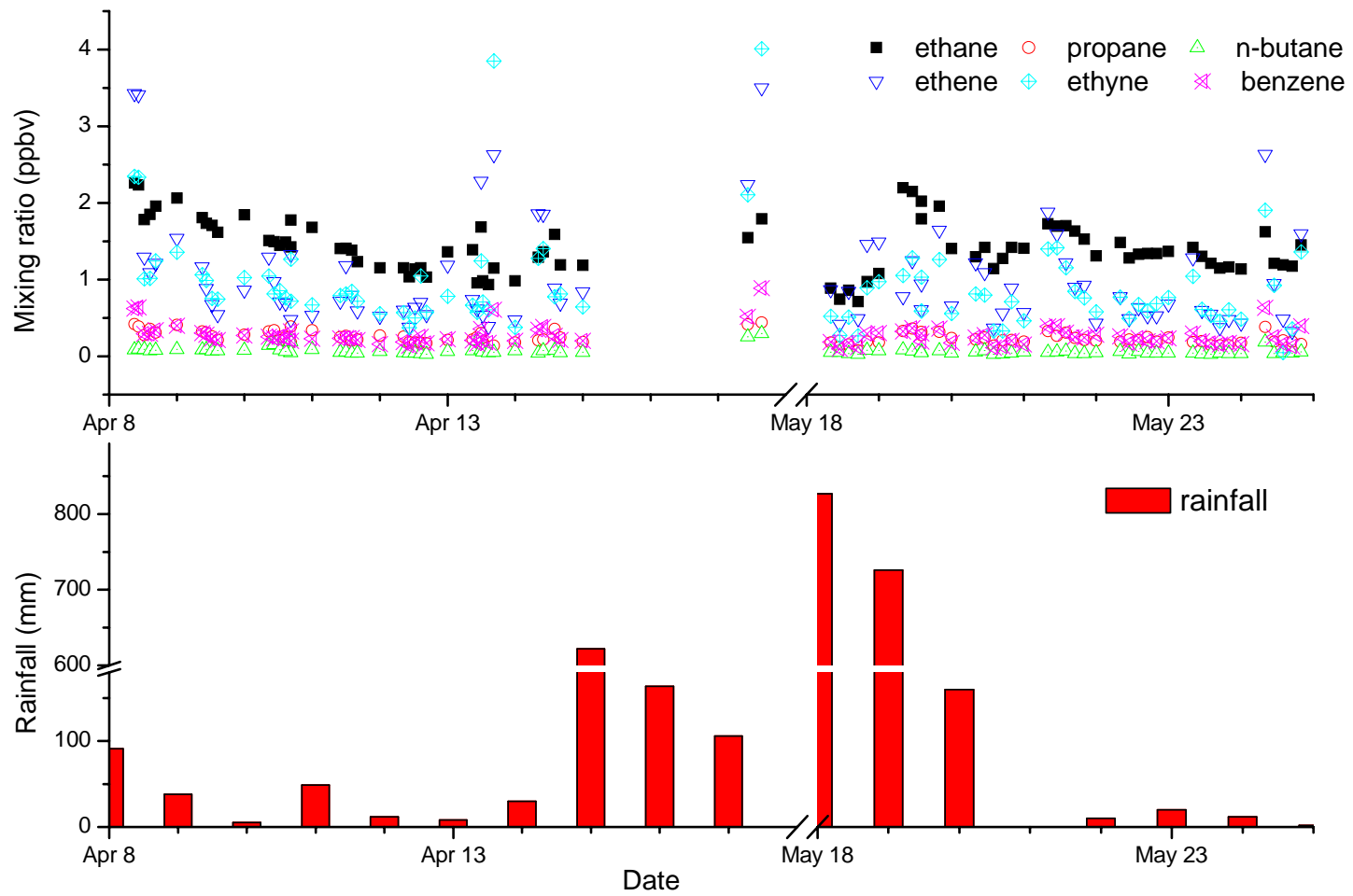


Figure 5.6 Variations of selected hydrocarbons and rainfall at Tengchong Mountain during the study period.

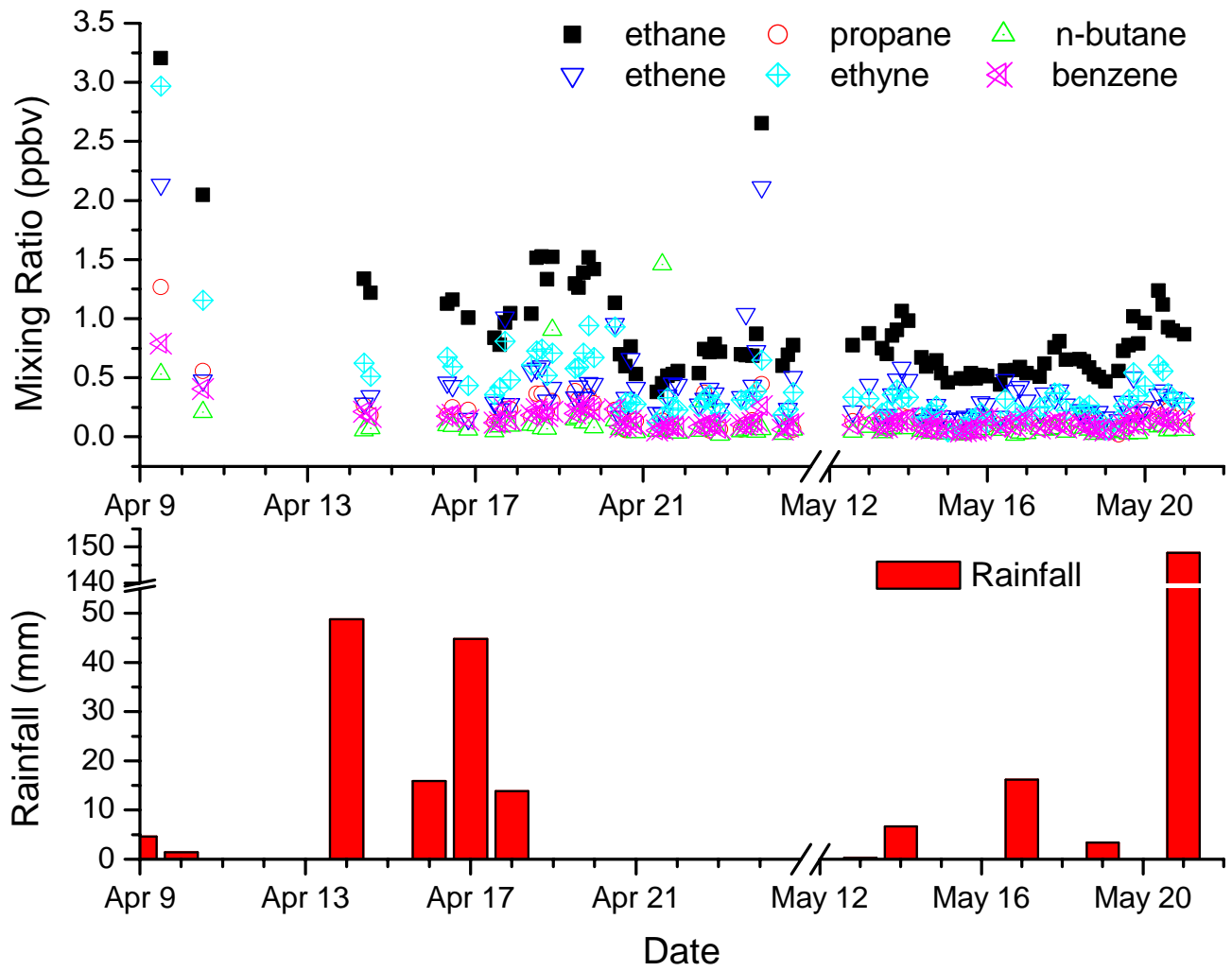


Figure 5.7 Variations of selected hydrocarbons and rainfall at Jianfeng Mountain during the study period.

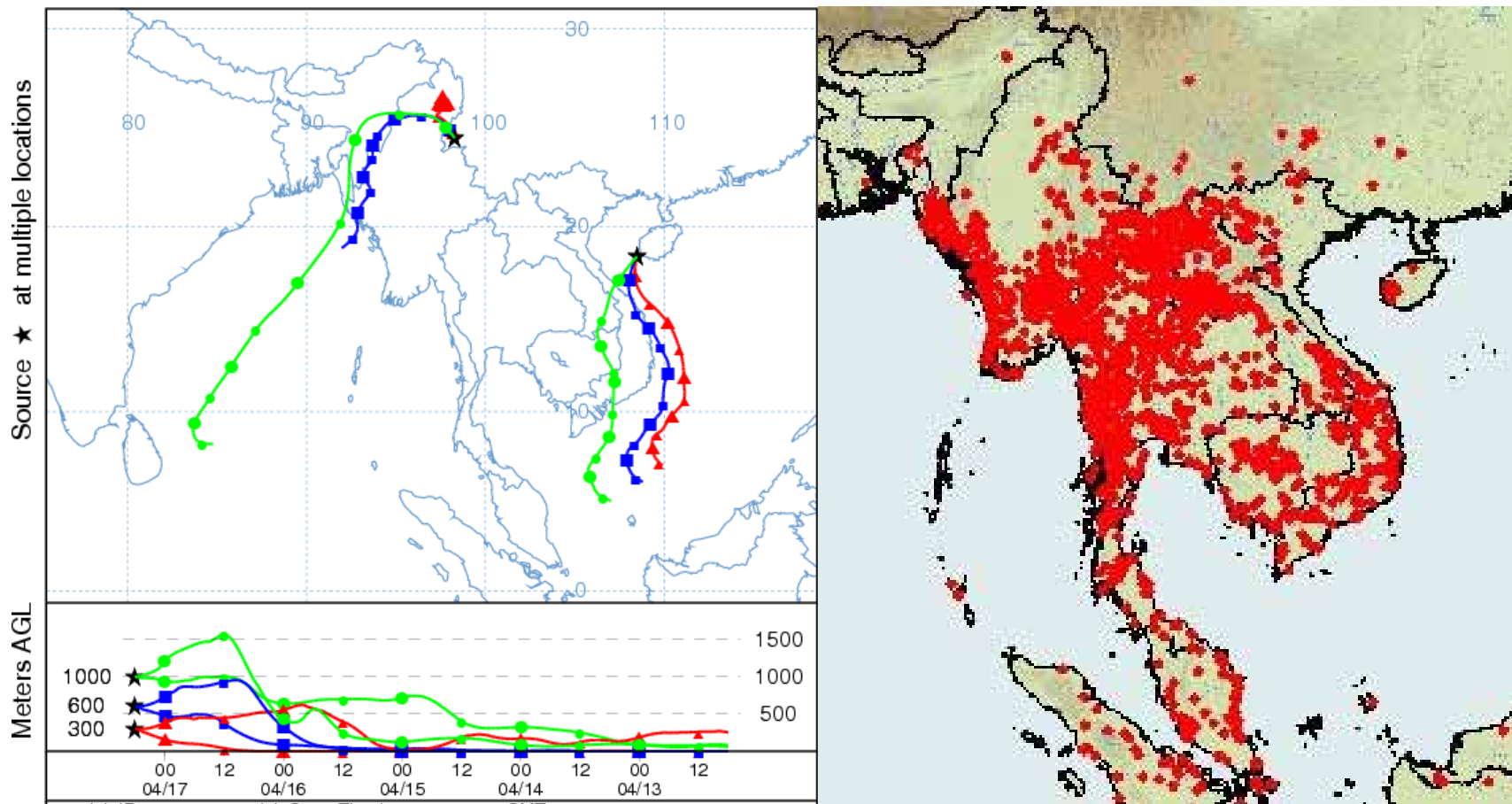


Figure 5.8 Backward air trajectory on April 17 (left) and fire account map (right) during April 12-15, 2004.

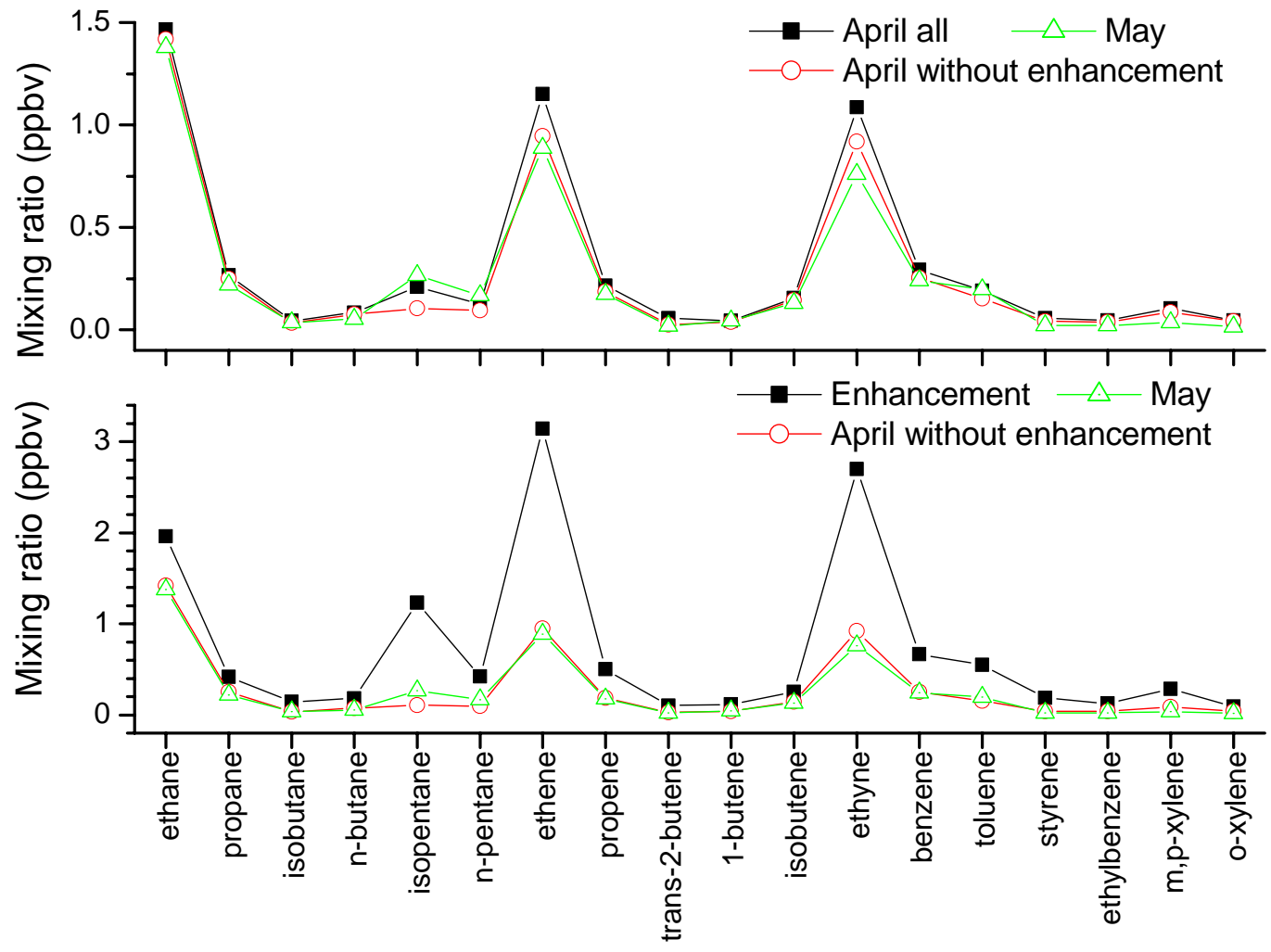


Figure 5.9 Comparison the average mixing ratios of selected hydrocarbons in enhanced days of April, April and May, 2004.

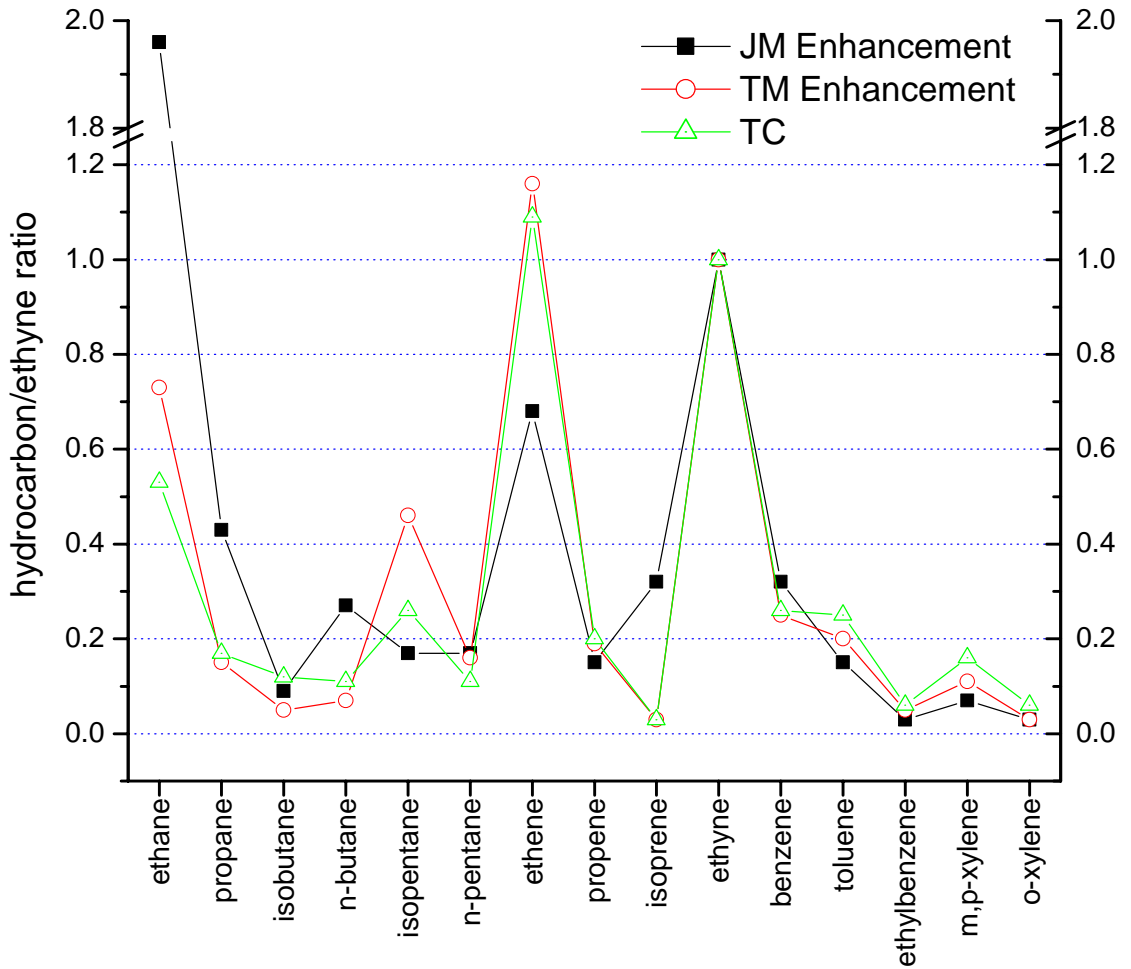


Figure 5.10 Comparison of hydrocarbon/ethyne ratios at the enhanced concentration samples in Jianfeng Mountain and Tengchong Mountain with those at Tengchong County.

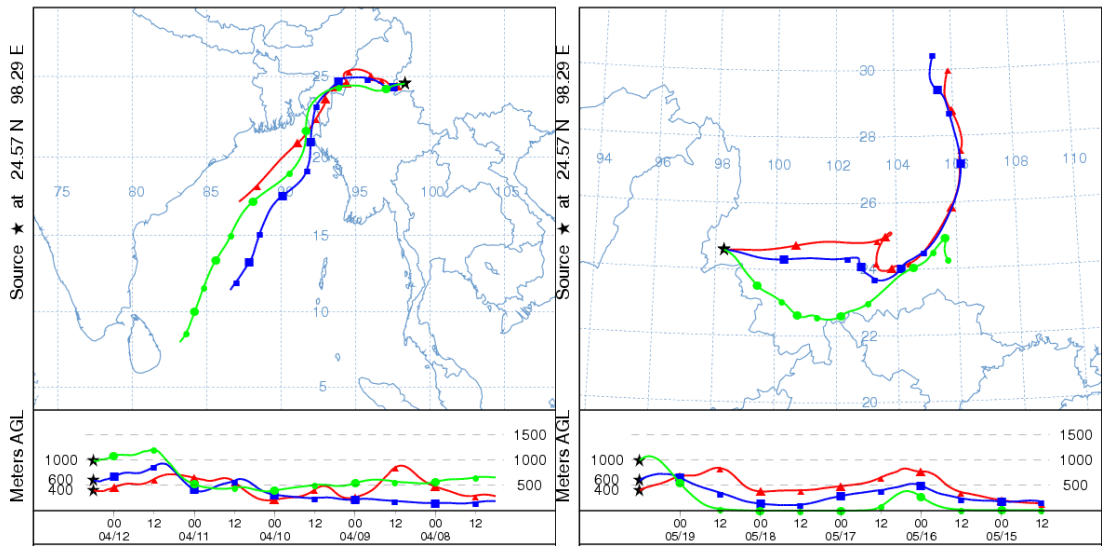


Figure 5.11 Typical back air trajectories reaching at TM in April (left) and May (right), 2004.

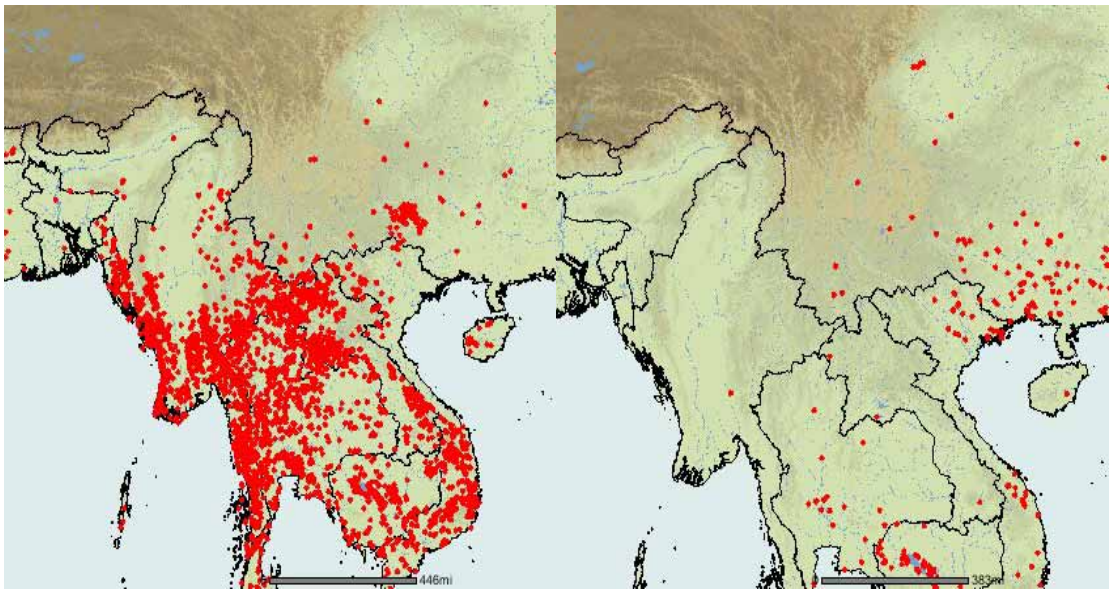


Figure 5.12 Maps showing active fire spot during April 8-18 (left) and May 18-25 (right), 2004.

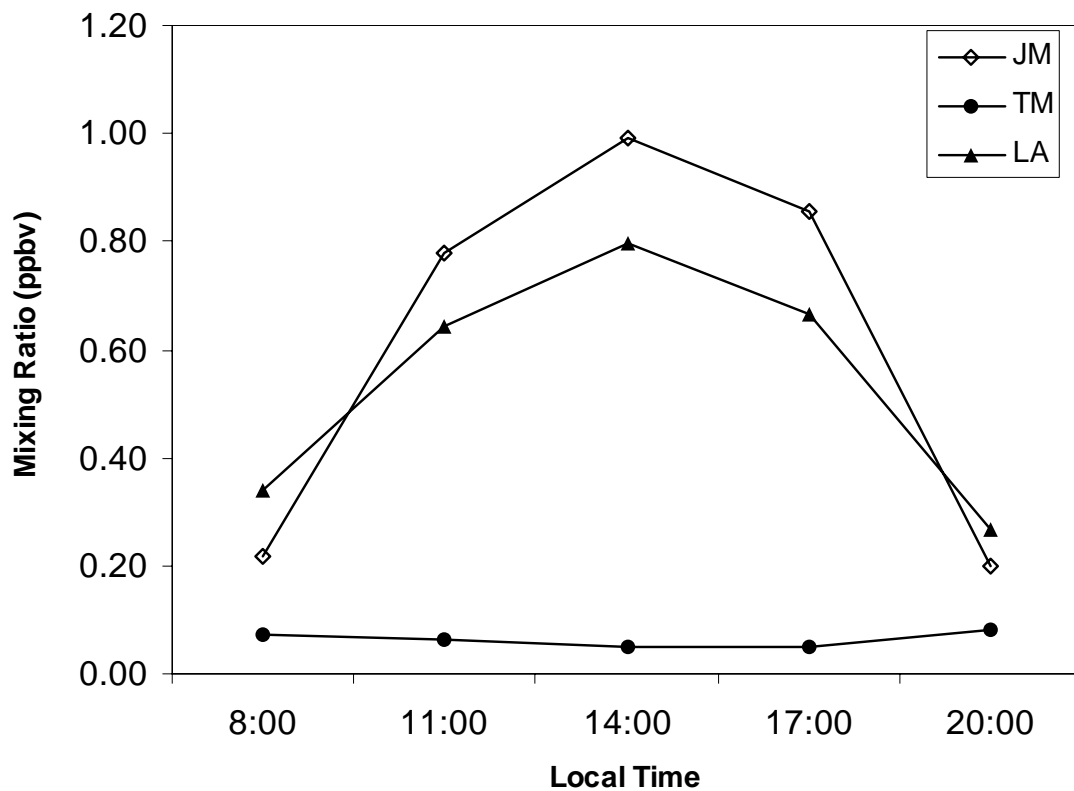


Figure 5.13 Diurnal variations of isoprene at three sites.

Chapter 6

NMHCs at representative urban, suburban, rural and remote sites of South China

6.1 Introduction

This chapter presents the NMHCs collected at four sampling sites including one each of urban, suburban and rural site of the PRD and a remote site of South China in April 2005. Ambient canister samples were collected at urban, suburban, and rural sites of the PRD during April 16-22, and a remote site in South China during April 7-13 and 16-18. To study the impacts of NMHCs from vehicular emissions, six roadside samples were collected at Xingang Road in Guangzhou, on 8th September 2006. Three roadside samples were also collected at a roundabout of Qingxi town (QX), Dongguan, at 11:40-11:55 for the days January 7-9, 2006. Qingxi is a small town with dense industrial factories.

6.2 Sampling sites

Four sites were selected for the study of urban, suburban, rural and remote atmosphere: Guangzhou (GZ), Panyu (PY), Dinghu Mountain (DM) and Jianfeng Mountain (JM). Figure 6.1 shows their geographical locations and Table 6.1 describes the characteristics of the sampling sites.

Guangzhou is the capital city of Guangdong Province with a total population of 7.5 millions. It is the economic and cultural center of the PRD. The sampling site is located in the urban center - the Dongshan district and is surrounded by residential houses and business offices. There are two main roads with very high traffic volume,

one about 100 meters to the north and the other the same distance to the south. This site represents a typical Guangzhou urban site which is influenced by residential and traffic emission sources.

Panyu (PY) is a satellite city of Guangzhou with a total population of one million in an area of 1300 km². The sampling site is located in a PY suburban site. This site is about 20 km from the urban center of Guangzhou to the north, 25 km to Dongguan to the west, 30 km to Zhongshan to the south. There is no obvious anthropogenic source nearby except for a road about 50m to the south. Air samples were collected at the rooftop of an environmental monitoring chamber (about 4 m above ground).

Dinghu Mountain (DM) is located in the middle region of Guangdong Province in South China. It is about 85 km to the west of Guangzhou, 18 km to the northeast of Zhaoqing, and is surrounded by less developed counties compared to other areas of the PRD. There is a small town (the Guicheng district, with a population of 20,000) and a highway near the sampling site about 3 km to the south. This site area is covered by tropical forest. The sampling site is located at the top of a hill in the Dinghushan Biosphere Reserve which is one station of the Man and Biosphere Programme, United Nations Educational, Scientific and Cultural Organization.

The characteristics of Jianfeng Mountain (JM) are described in Chapter 4 and Chapter 5.

6.3 Result and discussion

6.3.1 General characteristic of NMHCs

The average mixing ratios and standard deviations of selected hydrocarbons in the ambient and roadside samples are listed in Table 6.2. These species accounted for about 82-97% of the sum of measured hydrocarbons (Σ NMHC) for ambient samples. At the three PRD sites- GZ, PY and DM, toluene, ethyne, ethene, and propane were the most abundant hydrocarbons, although their orders differed. For the roadside samples of GZ, propane, ethene, n-butane and ethyne were the dominant hydrocarbons; while at the roadside samples of QX, toluene, ethyne and ethene were the dominant hydrocarbons. The major sources of toluene in the PRD were industrial solvent emission and gasoline evaporation (Chan L. Y. et al., 2006; Tsai et al., 2006). The major source of ethyne and ethene is incomplete combustion of fossil fuel (Wadden et al., 1988), and those were also the most abundant hydrocarbons found at the roadside in PRD cities (Chan et al., 2006; Tsai et al., 2006). Propane is the major component of liquefied petroleum gas (LPG), and its major source in the urban area is LPG leakage (Tsai et al., 2006). At JM, ethane, ethyne, ethene and isoprene are the four dominant species. As expected, most hydrocarbons show decreasing mixing ratios progressing from an urban site to a suburban, to a rural and finally to a remote sites. This is a match with more anthropogenic emissions in urban and suburban areas compared with rural and remote areas.

6.3.2 Comparison with other studies in Asian cities

Comparison of the mixing ratios of hydrocarbons in different Asian cities is shown in Table 6.3. Many factors affect the mixing ratio of hydrocarbons found in different studies, such as the nature of the sampling sites and periods, meteorological

conditions, human activities and fuel composition in the target cities (Hsieh et al., 2003). So, direct comparison of hydrocarbon mixing ratio in different studies needs careful interpretation. In this study, the mixing ratios of most hydrocarbons did fall within the range of variation measured in the other 43 Chinese cities (Table 6.3). However, toluene and isobutane were the two species placed at the upper range. Propane, toluene, ethyne, ethene, isobutene and butane showed higher levels in Guangzhou than in other Asian cities (Ulsan, Korea, Na et al., 2001; Kathmandu, Nepal, Sharma et al., 2000; Hong Kong, So and Wang, 2004; Ahmedabad, India, Sahu and Lai, 2006; and Kaohsiung, Taiwan, Chang et al., 2005), except for Taipei, Taiwan (Wu et al., 2006) and Karachi, Pakistan (Barletta et al., 2005).

The high levels of NMHCs indicate that the higher emission strength and lower efficiency of emission control strategy in Guangzhou. In Taipei, air samples were collected at afternoon rush hour (6 pm), vehicular emissions contributed largely to the high levels of most NMHCs, such as ethene, ethyne, i-pentane, and toluene, while leakage from Natural Gas (NG) contributed to the high levels of ethane. These species showed higher levels in Taipei than in Guangzhou. Although LPG leakage contributed greatly to propane and n-butane levels, the two species showed lower levels in Taipei than in Guangzhou (Wu et al., 2006). However, in Karachi, propane and i/n-butane levels (mainly from LPG leakage) were approximately 3 times higher and ethane levels (mainly from NG leakage) were approximately 23 times higher than those in Guangzhou. Hydrocarbons from vehicular emissions also showed higher levels in Karachi than in Guangzhou. It indicates the lower efficiency in emission control in this city (Table 6.3).

6.3.3 Source signatures of NMHCs at the four sites

Figure 6.2 shows the contribution of individual hydrocarbon to Σ NMHC at the four sites. At the three PRD sites, fluctuations were found in the percentages of ethane, ethyne, propane, n-butane, toluene and m/p-xylene making up the Σ NMHC. At GZ, propane accounted for 12.7% of Σ NMHC, which is much higher than that of PY (7.0%) and DM (8.1%). LPG-fueled vehicles have been promoted in Guangzhou since 2003, and in November 2005, there were about 5060 and 9200 LPG-fueled buses and taxis in Guangzhou, which accounted for 67% and 58% of the total numbers of buses and taxis, respectively (New Express, 18/11/2005). Very fewer LPG-fueled vehicles were in use at the other two areas, although domestic use of LPG was also prevalent. Hence, the excess contribution of propane in the urban area of Guangzhou can be attributed to leakage from LPG-fueled vehicles. This finding is supported by the high abundance of propane and n-butane in the GZ roadside atmosphere. The percentages of propane and n-butane in GZ were also the largest among the four sites. Ethane contributed significantly at DM (10.9%), a percentage about two times higher than in GZ and PY (both were about 4.5%), while the contribution of ethane to Σ NMHC at the remote JM site (31.5%) was the highest. Ethane is a relatively long-lived species (about 40 days, Tang et al., 2007) in the atmosphere compared with other hydrocarbons, and its removal rate in the atmosphere is lower than those of other hydrocarbons. In the rural and remote sites where there are less anthropogenic sources, the major sources of ethane are transport from upwind source regions with ethane accumulation during the transport. Further examine of this upwind transport will be performed with illustration by backward air trajectories in the following section. Thus, the percentages of ethane follow the order: remote>rural>suburb>urban. This is also the situation for ethyne, which has an atmospheric lifetime of about 11 days. The

contributions of ethyne to Σ NMHC were also highest in the remote JM site (19.6%), and higher than the rural DM site (17.2%), the suburb PY site (12.7%), and the urban GZ site (11.0%). The contributions of toluene to Σ NMHC were the highest at the suburb PY site (15.5%), and second highest at the rural DM site (12.4%). Among the four sites, aromatic hydrocarbons also showed the highest percentages at PY among the four sites, such as ethylbenzene, m/p-xylene and o-xylene. The major sources of toluene in the PRD have been shown to be industrial emissions and gasoline evaporation (Chan L. Y. et al., 2006). The high content of aromatic hydrocarbons at PY indicates that industrial emissions from neighborhood industrial zones play a very important role at this suburban site. It is also consistent for the recent trend of industry to move out from the Guangzhou urban area to the outskirts as well as the dispersion of industry into other less developed regions (Chan L. Y. et al., 2006). Among the four sites, besides ethane and ethyne, isoprene was also shown to be among the highest contributors to NMHCs at the remote JM site.

Ethyne had been used as a tracer for vehicular exhausts (Barletta et al., 2002; 2005). To assess the impact of vehicular emission on the ambient NMHC level, NMHC/ethyne ratios were calculated. Figure 6.3 shows the NMHC/ethyne ratios in the samples at the two roadside sites and the four ambient sites. Among the four sites, all hydrocarbons showed the lowest NMHC/ethyne ratios at JM, except for ethane and isoprene. This is due to the longer lifetime of ethane than ethyne in the atmosphere, and the local biogenic emission of isoprene. It confirmed that long range transport and biogenic emission were the major sources of NMHCs at this remote site.

For the roadside samples, propane/ethyne, n-butane/ethyne, i-butane/ethyne and ethene/ethyne showed higher values at GZ than at QX, while toluene/ethyne and m/p-xylene/ethyne showed higher values at QX than at GZ. At the roadside in GZ, LPG-fueled buses and taxis were common while this type of vehicles was not used at QX. This explains the high propane/ethyne, i/n-butane/ethyne ratios at GZ. QX was an industrial site, and industrial emissions of toluene may contribute greatly to the ambient toluene levels. The higher toluene/ethyne ratios at QX reflect the influence of industrial emissions on the roadside atmosphere. The profile of NMHC/ethyne ratios in the ambient air of GZ was very similar to that of the roadside air of GZ, except for the toluene/ethyne and m/p-xylene/ethyne ratios, which were close to those at the roadside samples of QX. This indicates that the major source of NMHCs at GZ was vehicular emission, although it is still influenced by industrial emissions from its outskirts. The profiles of NMHC/ethyne at PY and DM were more similar to those at the QX roadside. It illustrates the influence of the PRD regional industrial emission on the ambient atmosphere where there is no heavy traffic.

6.3.4 Diurnal variations of NMHCs

The diurnal pattern of hydrocarbons was driven by the interaction of the sources and sinks. The sources of hydrocarbons included direct anthropogenic emissions and transport from upwind source regions. The sinks of hydrocarbons include photochemical reactions with OH radical and dilution by the background air. The mixing ratio of the OH radical increased with the available solar ultraviolet radiation (Rohrer and Berresheim, 2006), and reached their highest levels at noon (Ren et al., 2003). The dilution of hydrocarbons is caused by meteorological factors. The nocturnal inversion caused by radiation cooling is thought to be the dominant force

driving the diurnal patterns of long-lived species like ethane as their reaction rates with OH were relatively slow (Yang et al, 2005). The mixing height of the planetary boundary layer (PBL) decreases in the evening and early morning, and increases with solar radiation, and reach the highest at noon. The mixing ratios of hydrocarbons are reduced at noon due to the pronounced dilution effects, but are concentrated in the evening and early morning due to the decrease of mixing height in the urban area.

Actually, the diurnal variation of NMHCs is also highly affected by changes in the environment, such as traffic, industry, landuse, etc. Average diurnal variations of several hydrocarbons together with Σ NMHC measured at the four sites are shown in Figure 6.4. Hydrocarbons and Σ NMHC show remarkable diurnal variations. Their variation patterns were also quite different at the four sites.

In GZ, high levels were observed in the morning and evening for most hydrocarbons and Σ NMHC. They showed high mixing ratios in the morning (8:00 – 9:00), decreased to the lowest at noon (14:00 – 15:00), and later, increased gradually to the highest value in the evening (20:00 – 21:00). This two peak pattern has also been observed at many other urban sites, such as Changchun, northeast China (Liu et al., 2000); Taichung, central Taiwan (Yang et al., 2005); Bilbao, Spain (Durana et al., 2006). It indicates that the major sources of these hydrocarbons are traffic emissions, as traffic volumes in the urban area reached their highest levels at rush hour in the morning (8:00-10:00) and afternoon (17:00-19:00). The lowest hydrocarbon levels at 14:00-15:00 were due to the interplay of reactions with OH and increased mixing height of the PBL. However, toluene showed a different pattern from that of other hydrocarbons. Its peak levels occurred at 11:00-12:00 and 17:00-18:00. Toluene

showed a decreasing trend in the evening (20:00 – 21:00) rather than in the afternoon (17:00 – 18:00). This demonstrates that the sources of toluene were different from those of most of the other hydrocarbons. As mentioned above, industrial emission was the major contributor to the high levels of toluene in the PRD region. Most industrial activities reached their full operation in the afternoon and stopped running at night. In the urban GZ area, the industrial sites are at the outskirts of the city. This again shows that the impacts of the industrial emissions are area-wide in the PRD.

The major difference in the hydrocarbon diurnal patterns between PY and GZ was that a peak was observed at 11:00-12:00 at PY rather than in the morning rush hour (8:00-9:00). As PY is located in a suburban area, no high traffic volume was observed during the morning rush hour (8:00-9:00). Observations show that the diurnal variation of hydrocarbons at PY was highly influenced by aged air masses from the urban areas.

The explanation is given below. The major sink of hydrocarbons in the atmosphere was the reaction with the OH radical, and the reactivity of individual hydrocarbons varied greatly. The concentration ratio of the two hydrocarbons with common sources but different reaction rates in the atmosphere can be used to assess the photochemical ages of air masses (Nelson and Quigley, 1983). Ethene and propene were both derived from vehicular exhaust in the urban area (Wadden et al., 1988), but showed different reaction rates with OH ($K_{OH} = 8.5$ and $26.3 \times 10^{12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K for ethene and propene, respectively, Atkinson and Arey, 2003). After being emitted, propene would decay more quickly than ethene in the atmosphere. And as stated above, their concentration ratios would be good indicators of the photochemical ages

of the air masses. Figure 6.5 shows the scattered plot of propene to ethene at the four sites. The high correlation coefficients ($R > 0.87$) indicate that they were from the same sources. The slopes of propene to ethene decreased from GZ (0.30), to PY (0.21), to DM (0.20), and to JM (0.13), indicating the increase in photochemical age of air masses. The effect of aged air masses on the ambient atmosphere is illustrated by the lagged appearance of the two NMHC peaks in PY.

The diurnal variations of hydrocarbons at the rural DM site showed different features from those at the urban GZ site and suburban PY site. Most hydrocarbons and Σ NMHC showed a peak at 11:00-12:00 such as at PY but a high plateau from 17:00-21:00. The variation of propane was mainly due to the domestic usage of LPG.

At the remote JM site, most hydrocarbons showed a one-peak pattern. Their mixing ratios reduced slightly at 11:00-12:00 compared with those at 8:00-9:00, and then increased to the maximum at 17:00-18:00, and decreased between 20:00-21:00. The major sources of hydrocarbons at this remote site were long-range transport from the upwind source regions as there were very little local anthropogenic emissions (Tang et al., 2007). In this study, backward air mass trajectory analysis is used to determine the possible transport pathways of air masses. Using the NOAA HYSPLIT model (Rolph, 2003), ten-day backward air trajectories were calculated for the air masses reaching at Jianfeng Mountain. Figure 6.6 shows a typical trajectory during the sampling periods. Air masses originated from the North China, traveled through the western Pacific Ocean, and passed over Philippines and in some extent over the Southeast Asian subcontinent before approached at JM (Figure 6.6). This site was far away from the source region, and several hours were needed to transport the air masses from upwind

source regions, such as South China, and Southeast Asia. Hence, the lowest propene to ethene ratio was found here. In the evening (20:00-21:00), the sea-land breeze brought the fresh air from the South China Sea, and diluted the air pollutants at this site. The NMHC levels are greatly affected by the meteorological conditions.

In this study, we also noted that the average mixing ratio of isoprene at JM (0.48 ppbv) was much higher than at the other three sites (0.12-0.27 ppbv) (Table 6.2). Figure 6.7 shows the diurnal variations of isoprene at the four sites. At the mountainous sites of JM and DM, isoprene showed similar diurnal patterns, which increased between 8:00-9:00 and 14:00-15:00 and then decreased at 20:00-21:00. These patterns were opposite to those of other NMHC patterns shown in Figure 6.4, and were mainly driven by the local biogenic emission of isoprene, which was strengthened with the increase of solar radiation and temperature in the early afternoon (Kesselmeier and Staudt, 1999). The levels of isoprene at JM were much higher than those at DM. The diurnal variations of isoprene at the urban GZ site and the suburban PY site were negligible.

6.3.5 Comparison of the reactivities and ozone formation potentials of NMHCs for the selected sites

Photochemical reactions of NMHCs are mainly initiated by the OH radical, and the mechanism of ozone formation for each hydrocarbon varies greatly. To compare the reactivity and the contribution to photochemical ozone formation of individual hydrocarbons, propylene-equivalent concentration method proposed by Chameides (1992) and the Maximum Incremental Reactivity (MIR) method proposed by Carter (1994) were used. The details of these methods are discussed in chapter 2.

The top 10 hydrocarbons ranked by their propylene-equivalent concentrations and ozone formation potentials were listed in Table 6.4 and Table 6.5, respectively. These NMHCs accounted for about 60% of the total propylene-equivalent concentration and about 70% of the total OFP at the three PRD sites, and 90% of total propylene-equivalent concentration and 80% of total OFP at the remote site JM. Ethene, toluene and m/p-xylene were among the highest reactive hydrocarbons (based on reaction with OH) in urban, suburb and rural sites, and they accounted for 24-29% of the total propylene-equivalent concentration. They were also the largest contributors to the OFP at the three PRD sites, which accounted for 45-52% of the total OFP. The high contributions of ethene, toluene and m/p-xylene to ozone formation has also been reported in other Asian cities, such as Karachi, Pakistan (Barletta et al., 2002); Hong Kong (So and Wang, 2004), and Kaohsiung, Taiwan (Chang et al., 2005). Almost all the remaining top 10 hydrocarbons were alkenes and aromatics at the three PRD sites. The major source of alkenes was motor vehicular exhaust, and the major sources of aromatics were industrial emissions and vehicular emissions in the PRD region (Chan et al., 2006; Tsai et al., 2006; Tang et al, 2007). So, vehicular emissions and industrial emissions play a dominant role in ozone pollution in this region. At the remote site, isoprene was the dominant species and accounted for 60% of the total propylene-equivalent concentration and about 40% of the total OFP. So, biogenic emission was the major contributor to the ozone formation at this remote site.

6.4 Conclusion

Vehicular emissions were the common sources of NMHCs at the GZ urban, PY suburban, and DM rural sites, although the magnitudes of the effects differed. In

addition, LPG leakage from LPG-fueled vehicles contributed significantly to the high levels of propane and n-butane in the urban GZ area. The impact of industrial emissions was widespread and they contributed greatly to the levels of aromatic hydrocarbons and in particular toluene at the three PRD sites investigated. The remote JM site was affected more by long range transported air masses and isoprene was the only highly contributing local NMHC source.

Σ NMHC and most hydrocarbons showed noticeable diurnal variations. These patterns were different from each other. Propene/ethene ratios demonstrated the degree of contributions from vehicular emissions. At the urban GZ site, the levels of NMHCs were affected by fresh vehicular exhausts, whereas at the suburban PY site and rural DM site, transport from nearby urban areas was the major source of NMHCs. Long-range transport from the upwind source regions was the major source of NMHCs at the remote JM site. Toluene showed a different diurnal pattern to those of other hydrocarbons from vehicular exhausts in urban GZ, because its major source consisted of industrial emission from the GZ outskirt areas.

Ethene, toluene, and m/p-xylene showed the highest propylene-equivalent concentrations and were the largest contributors to the OFP at the three PRD sites, indicating vehicular exhaust and industrial emission were the two major contributors to regional ozone pollution. This is consistent with other studies of Asian cities. At the remote JM site, however, isoprene showed the highest propylene-equivalent concentration and was the dominant contributor to the OFP at that site.

1 Table 6.1 Characteristics of the four sampling sites.

Site	Abbr.	Location	Altitude, m asl	Sampling periods	Site Characteristics
Guangzhou	GZ	23.08 °N, 113.18 °E	88	April 16-22, 2005	Urban site, at the rooftop of a 21-story building
Panyu	PY	22.56 °N, 113.19 °E	16	April 16-22, 2005	Suburban site, 4 m above the ground
Dinghu Mountain	DM	23.10 °N, 112.32 °E	320	April 16-22, 2005	Rural site, at the top of a hill
Jianfeng Mountain	JM	18.40 °N, 108.49 °E	820	April 7-13 & 16-18, 2005	Remote site, at the rooftop of a 2-story building

Table 6.2 Mixing ratios of selected hydrocarbons at different sites (unit: ppbv).

Hydrocarbon	Ambient				Roadside	
	GZ (n=28*)	PY (n=33)	DM (n=30)	JM (n=52)	GZ (n=6)	QX (n=3)
ethane	3.98 ± 1.17	2.71 ± 0.95	2.72 ± 0.48	1.51 ± 0.40	3.63 ± 0.83	5.42 ± 0.69
propane	11.29 ± 5.69	4.27 ± 2.20	2.03 ± 0.94	0.32 ± 0.19	29.85 ± 12.31	5.39 ± 0.68
i-butane	4.48 ± 2.31	1.87 ± 1.01	0.78 ± 0.41	0.07 ± 0.05	5.72 ± 1.27	3.22 ± 1.63
n-butane	6.31 ± 3.21	2.98 ± 1.64	1.17 ± 0.64	0.10 ± 0.09	10.71 ± 2.59	7.15 ± 3.69
i-pentane	3.81 ± 1.93	2.27 ± 1.20	0.90 ± 0.46	0.08 ± 0.04	3.73 ± 1.06	4.26 ± 1.33
n-pentane	1.76 ± 0.87	1.32 ± 0.73	0.52 ± 0.29	0.04 ± 0.04	1.63 ± 0.45	1.75 ± 0.72
n-hexane	1.24 ± 0.59	0.93 ± 0.56	0.32 ± 0.18	0.05 ± 0.03	0.66 ± 0.27	1.71 ± 0.51
n-heptane	1.12 ± 0.65	1.04 ± 0.67	0.30 ± 0.23	0.02 ± 0.01	0.49 ± 0.22	0.76 ± 0.28
ethene	8.60 ± 4.28	5.42 ± 3.42	2.45 ± 1.17	0.52 ± 0.43	12.67 ± 5.29	11.90 ± 1.96
propene	2.36 ± 1.34	1.10 ± 0.76	0.43 ± 0.25	0.13 ± 0.07	2.91 ± 1.28	2.19 ± 0.41
isoprene	0.27 ± 0.14	0.18 ± 0.10	0.12 ± 0.08	0.48 ± 0.47	1.13 ± 0.88	0.18 ± 0.02
ethyne	9.80 ± 3.95	7.71 ± 4.13	4.30 ± 1.38	0.94 ± 0.46	10.20 ± 5.14	16.98 ± 2.89
benzene	2.75 ± 1.19	2.67 ± 1.58	1.17 ± 0.54	0.21 ± 0.11	2.07 ± 0.52	3.62 ± 0.46
toluene	10.02 ± 4.69	9.39 ± 5.59	3.09 ± 1.79	0.09 ± 0.06	4.01 ± 2.34	18.94 ± 4.19
ethylbenzene	1.91 ± 1.04	1.87 ± 1.07	0.48 ± 0.28	0.02 ± 0.01	0.91 ± 0.36	3.16 ± 0.33
m/p-xylene	3.03 ± 1.69	3.10 ± 2.11	0.66 ± 0.48	0.04 ± 0.02	1.92 ± 0.64	8.17 ± 0.93
o-xylene	1.16 ± 0.62	1.16 ± 0.75	0.27 ± 0.18	0.02 ± 0.01	0.63 ± 0.19	2.22 ± 0.46
ΣNMHC	88.79 ± 38.56	60.79 ± 31.47	23.40 ± 9.84	4.78 ± 1.85		

* Number in the parentheses indicates the total number of samples at each site.

Table 6.3 Comparison of selected NMHCs in Guangzhou and other Asian cities (units: ppbv).

hydrocarbon	Ulsan ^a Korea Jun. 97	Taipei ^b Taiwan Aug. 98	Kathmandu ^c Nepal Nov. 98	Karachi ^d Pakistan Dec. 98 - Jan. 99	Hong Kong ^e China Nov. 00 - Oct. 01	43 Cities ^f China Jan.-Feb. 01	Ahmedabad ^g India April 02	Kaohsiung ^h Taiwan Oct. 02	Guangzhou ⁱ China April 05
ethane	1.6	6.03	1.86	93		3.7-17.0	2.59	4.5	3.98
propane	5.0	5.65	1.14	41	4.01	1.5-20.8	2.93	3.1	11.29
isobutane	1.4		1.10	11.0	2.87	0.4-4.6	0.97	0.7	4.48
n-butane	3.5	4.26	3.32	19.8	6.53	0.6-14.5	2.15	2.3	6.31
isopentane	2.0	10.30	1.15	12.1	4.48	0.3-18.8	1.43	3.8	3.81
n-pentane	1.5	5.38	1.13	13.4	1.71	0.2-7.7	0.54	1.3	1.76
ethene	6.9	13.80	3.27	19.0		2.1-34.8	2.34	7.5	8.6
propene	2.1	3.92	0.63	5.5	2.8	0.2-8.2	0.77	2.2	2.36
isoprene			0.02	0.8	0.65	0.04-1.7		0.6	0.27
ethyne	1.9	12.80	1.25	18.0		2.9-58.3	1.90	4.9	9.8
benzene	1.1	3.22		5.2	1.58	0.7-10.4		1.1	2.75
toluene	3.9	23.50		7.1	8.24	0.4-11.2		8.2	10.02
ethylbenzene		2.84				0.1-2.7		0.7	1.91
m/p-xylene	2.1	8.87		3.1		0.4-15.3		1.2	3.03
o-xylene	0.9	4.45		1.1		0.1-6.9		0.6	1.16

a. Na et al., 2001; b. Wu et al., 2006; c. Sharma et al., 2000; d. Barletta et al., 2002; e. So and Wang, 2004; f. Barletta et al., 2005; g. Sahu and Lai, 2006; h. Chang et al., 2005; i. this study.

Table 6.4 Top 10 NMHCs ranked according to propylene-equivalent concentrations (unit: ppbv).

Rank	Guangzhou			Pianyu			Dinghu Mountain			Jianfeng Mountain		
	Species	Conc.	%	Species	Conc.	%	Species	Conc.	%	Species	Conc.	%
1	ethene	2.78	9.5	m/p-xylene	2.21	10.9	ethene	0.80	11.7	isoprene	1.82	59.4
2	propene	2.36	8.0	toluene	2.01	9.9	toluene	0.66	9.7	isobutene	0.26	8.6
3	m/p-xylene	2.15	7.3	ethene	1.75	8.6	alpha-pinene	0.64	9.4	ethene	0.17	5.5
4	toluene	2.00	7.3	styrene	1.25	6.1	m/p-xylene	0.47	6.9	propene	0.13	4.2
5	isobutene	2.03	6.9	isobutene	1.10	5.4	isoprene	0.44	6.4	styrene	0.09	3.0
6	cis-2-butene	1.53	5.2	propene	1.57	7.7	propene	0.43	6.3	alpha-pinene	0.08	2.6
7	trans-2-butene	1.52	5.2	isoprene	0.70	3.4	isobutene	0.35	5.2	2-methyl-2-pentane	0.07	2.1
8	2-methyl-2-butene	1.20	4.1	o-xylene	0.60	3.0	styrene	0.23	3.4	1-butene	0.06	1.9
9	isoprene	1.03	3.5	2-methyl-2-butene	0.58	2.9	cis-2-butene	0.16	2.4	trans-2-pentene	0.05	1.6
10	1-butene	0.93	3.2	ethylbenzene	0.50	2.4	1-butene	0.15	2.2	1,2,4-trimethylbenzene	0.04	1.2

Table 6.5 Top 10 NMHCs ranked according to ozone formation potentials (unit: ppbv).

Rank	Guangzhou			Pianyu			Dinghu Mountain			Jianfeng Mountain		
	Species	OFP	%	Species	OFP	%	Species	OFP	%	Species	OFP	%
1	toluene	51.8	16.7	m/p-xylene	50.8	21.4	toluene	16.0	20.8	isoprene	6.2	37.9
2	m/p-xylene	49.5	15.9	toluene	48.7	20.4	m/p-xylene	10.8	14.0	ethene	2.3	13.9
3	ethene	37.2	12.0	ethene	23.5	9.9	ethene	10.6	13.8	propene	1.0	6.4
4	propene	19.4	6.2	o-xylene	16.7	7.0	o-xylene	3.8	5.0	isobutene	0.8	5.1
5	o-xylene	16.7	5.4	ethylbenzene	11.2	4.7	propene	3.5	4.6	1,2,4-trimethylbenzene	0.6	3.9
6	ethylbenzene	11.4	3.7	propene	9.0	3.8	alpha-pinene	3.0	3.9	m,p-xylene	0.6	3.7
7	1,2,4-trimethylbenzene	9.9	3.2	1,2,4-trimethylbenzene	7.6	3.2	ethylbenzene	2.9	3.7	1-butene	0.5	3.0
8	cis-2-butene	8.3	2.7	isopentane	4.7	2.0	isopentane	1.9	2.4	toluene	0.5	2.9
9	1-butene	8.1	2.6	isobutene	4.0	1.7	1,2,4-TMB	1.7	2.3	alpha-pinene	0.4	2.3
10	isopentane	7.9	2.5	n-butane	3.7	1.5	isoprene	1.5	1.9	1,3,5-trimethylbenzene	0.3	1.7



Figure 6.1 Map showing the sampling sites- Guangzhou, Panyu, Dinghu Mountain and Jianfeng Mountain.

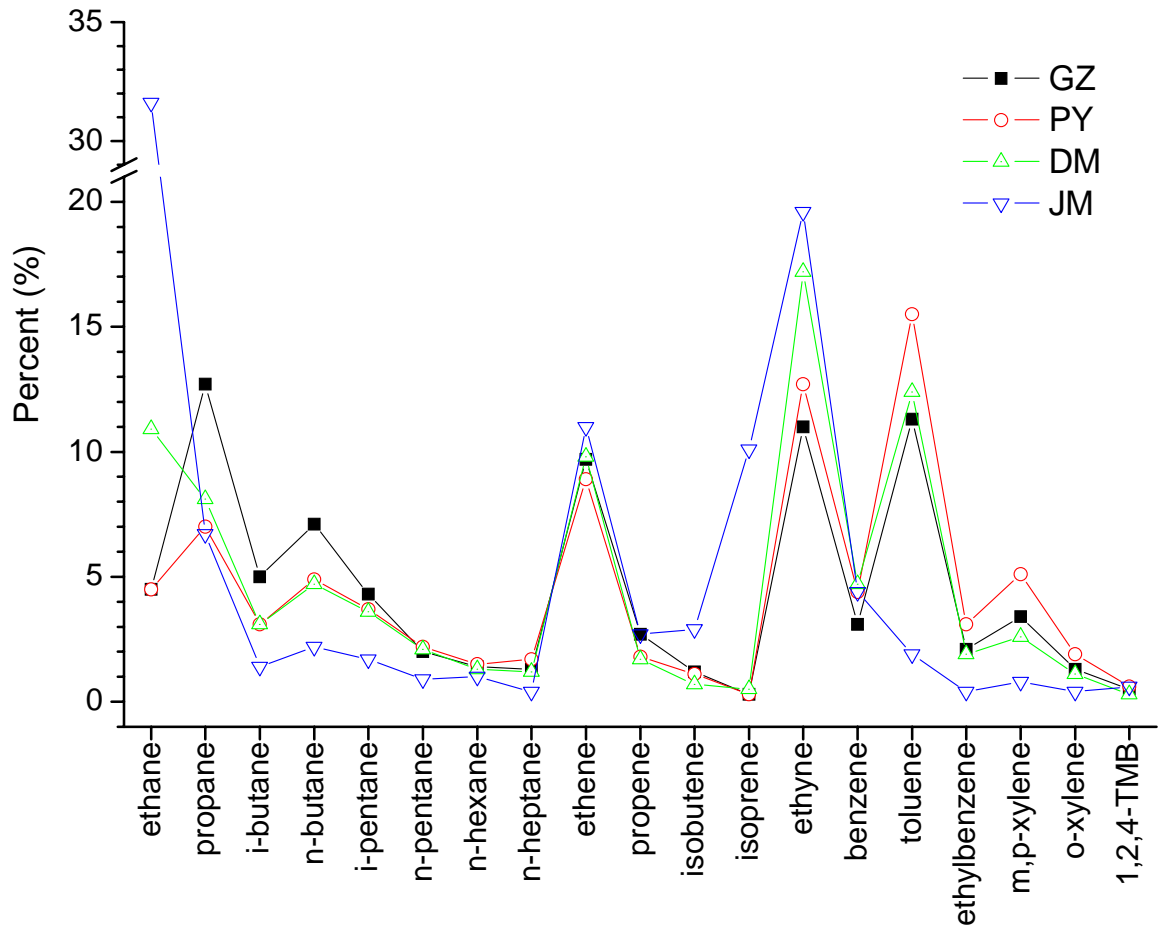


Figure 6.2 Percentage contributions of different hydrocarbons to Σ NMHC.

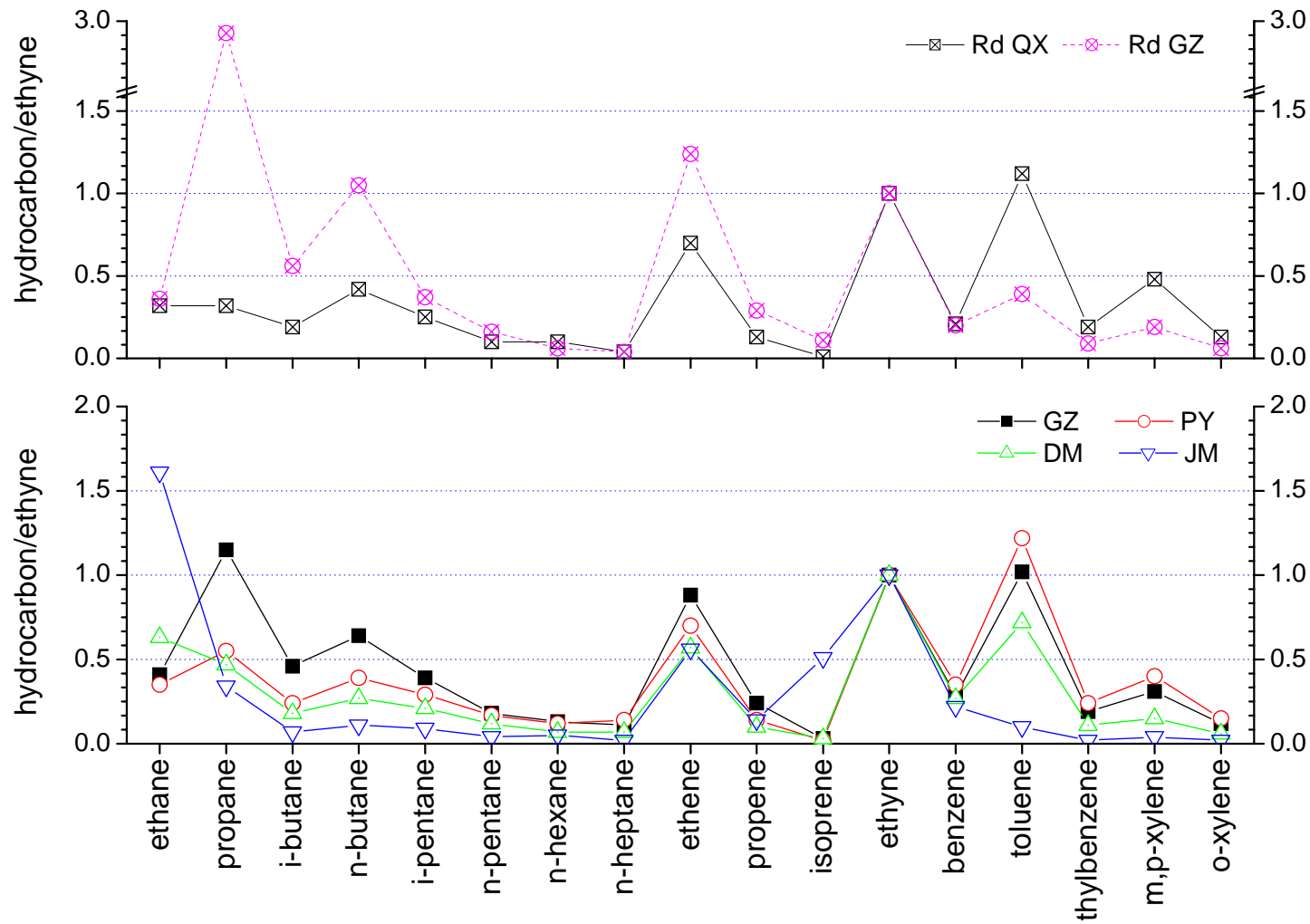


Figure 6.3 Comparison of hydrocarbon/ethyne ratios at different sites.

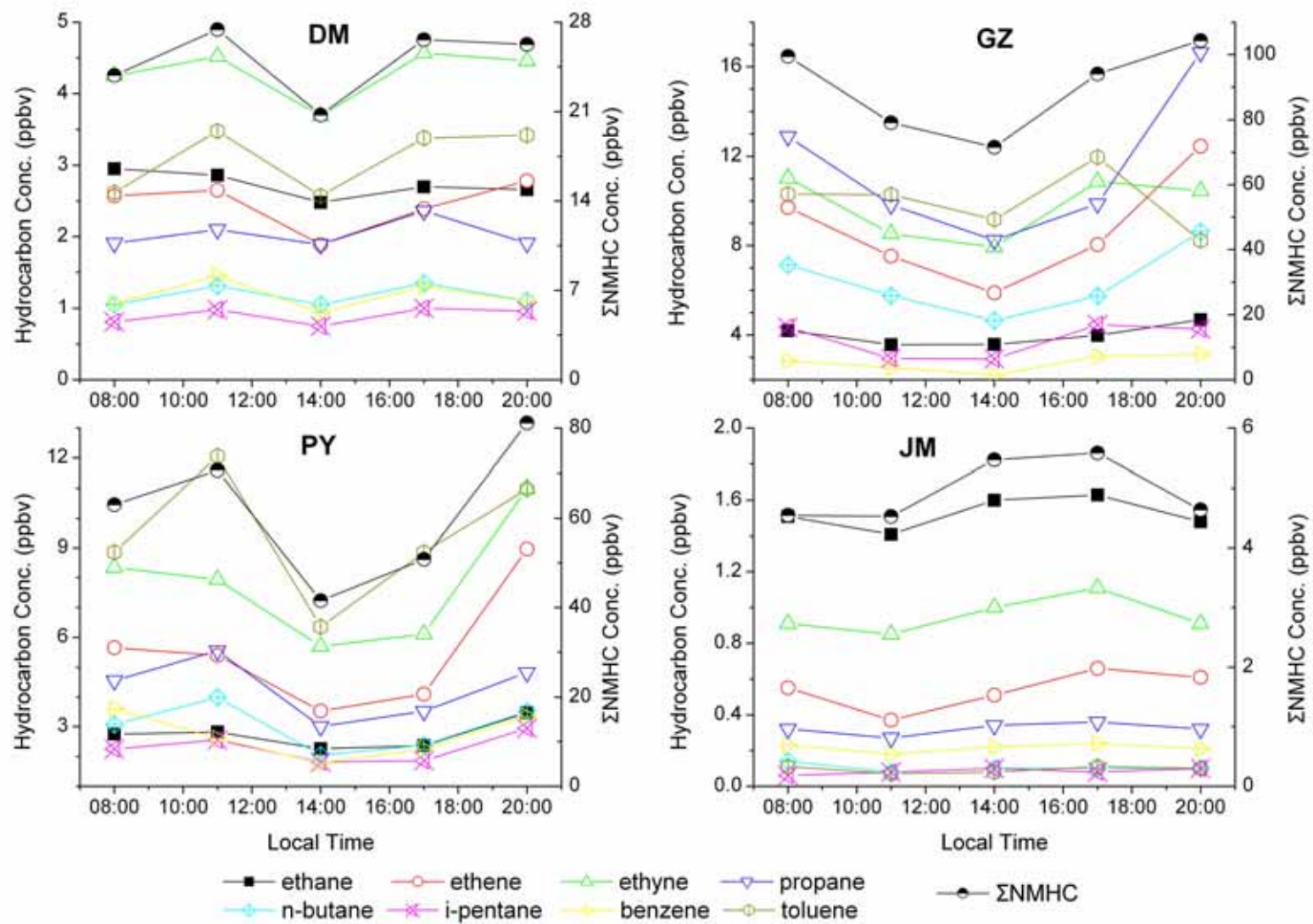


Figure 6.4 Diurnal variations of selected hydrocarbons at the four sites.

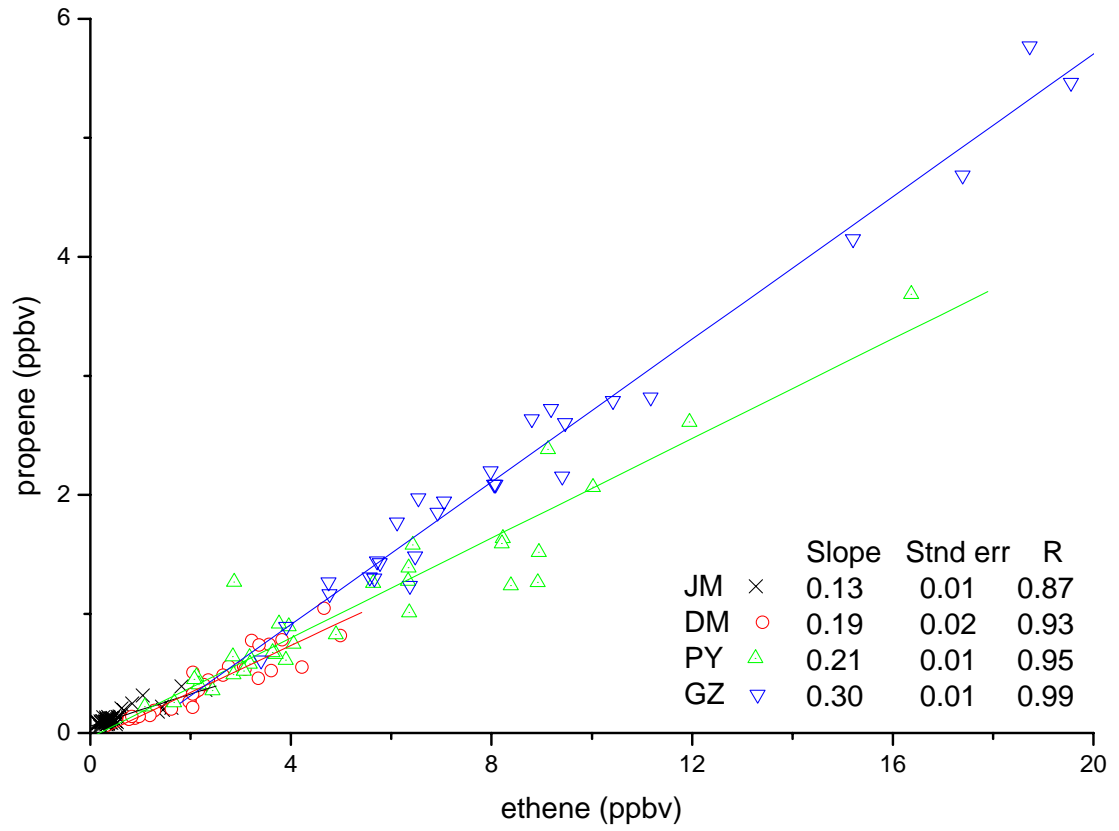


Figure 6.5 Scatter plot of propene against ethene at the four sites.

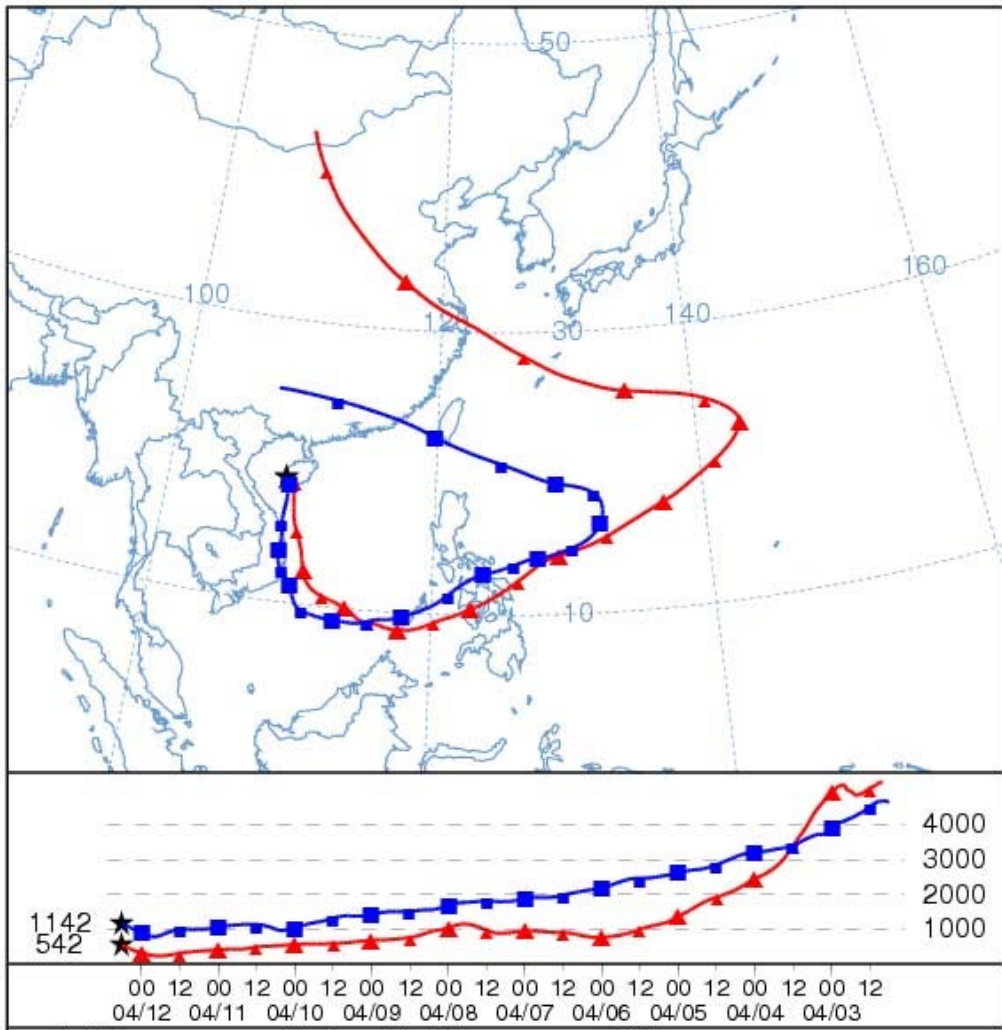


Figure 6.6 Typical of backward air trajectory at Jianfeng Mountain during sampling periods.

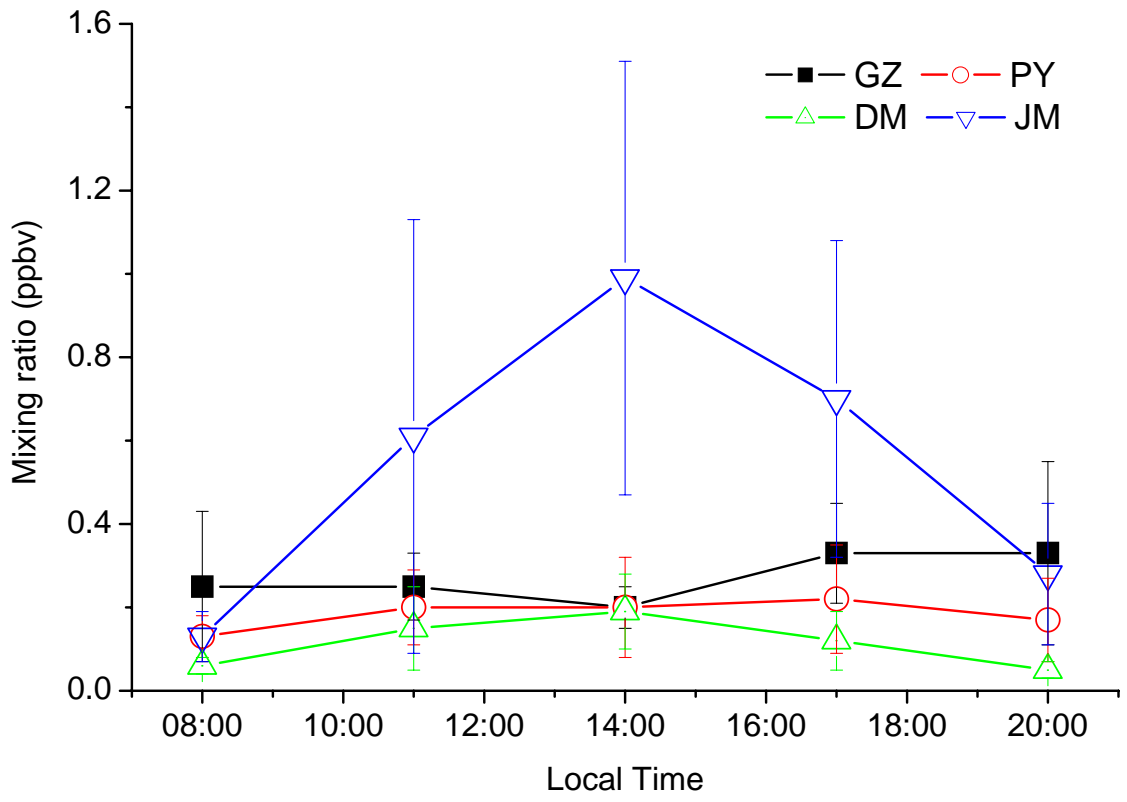


Figure 6.7 Diurnal variations of isoprene at the four sites.

Chapter 7

Implication of Changing Urban and Rural Emissions on atmospheric NMHCs in the PRD

7.1 Introduction

This Chapter compares the NMHC data in one rural site (Dinghu Mountain) and two urban sites of Guangzhou in the PRD in spring of 2001 and 2005, aimed at determining the effects of economic, industrial and urban changes on the modification of NMHC profiles in rural and urban environments.

7.2 Sampling sites

Figure 7.1 shows the maps of sampling sites. Ambient whole air samples were collected at one rural site and two urban sites in the PRD region. Between March 3 and 19, 2001, 39 air samples were collected at a forest site on the Dinghu Mountain (PRD). The sampling site is located on a hilltop in Dinghushan National Natural Reserve. Detailed information about Dinghu Mountain has been introduced in Chapter 6. During April 16 and 21, 2005, 30 samples were collected from the Dinghu Mountain sampling site. Paralleling the March 3 and 26, 2001 Dinghu Mountain forest sampling, 43 canister samples were from the rooftop of a nine-story building located in the Liwan district in Guangzhou. Liwan is an old city centre and the sampling site is surrounded by traffic congested roads, residential buildings, restaurants and schools. Paralleling the Dinghu Mountain sampling, April 16-21, 2005, 30 urban ambient samples were collected in the Dongshan District of Guangzhou. The sampling site this time was located on the rooftop of a 21-story building, and this site was surrounded by crowded roads and residential building.

The samples in 2001 were mainly collected at noon. 15 samples were also collected within two days at both sites to study the diurnal variations of NMHCs. On average, the 2001 sampling canisters were filled in about two minutes. All ambient samples in 2005 were collected between 08:00-21:00 at intervals of 3 hours. A flow controlling device was used to collect one hour integrated samples. The sampling sites locate at the top of mountain in rural site and the rooftop of high buildings in urban sites, and it helps to collect well mixed and representative air samples.

In addition, roadside and tunnel samples were also collected in Guangzhou. On February 6, 2000, two samples were collected at a roundabout on the Xingang Road at 09:00 and 10:00, and two samples were collected from the Zhujiang Tunnel at 10:30 and 15:30 in the same day. Xingang Road is a very busy traffic road and Zhujiang tunnel links the two urban areas of Liwan and Fangcun. Later, on August 13, 2000, one sample was collected at a roundabout of Xingang Road at 09:30, and another sample was collected at a roundabout of a traffic congested road (Tianhe Road) at noon. Six samples were collected on September 8, 2005, between 07:00 and 20:00 at the Xingang roadside. The entire roadside and tunnel samples were two-minute integrated samples.

In this comparison study, the samples collected between April 16 and 22 at Guangzhou and Dinghu Mountain were analyzed by RCEC, and the other samples were analyzed by UCI. So, conversion factors were also used to adjust the data from RCEC like that in Chapter 4.

7.3 Results and discussion

7.3.1 Variations of the NMHC profiles in between 2001 and 2005

Thirty-five hydrocarbons were quantified and compared in this study. The statistics of selected hydrocarbons are listed in Table 7.1. Two of the ambient samples collected in Guangzhou (2005) were removed from the data set as they showed extraordinarily high levels of certain hydrocarbons. Average mixing ratios for most hydrocarbons showed large standard deviations; therefore, median mixing ratios are used in the following discussion. Toluene, ethyne, ethane, ethene and propane were the most abundant hydrocarbons in the ambient air of Guangzhou and Dinghu Mountain. The total mixing ratio of measured hydrocarbons (Σ NMHC) was about 3 ~ 4 times higher in Guangzhou than at Dinghu Mountain (Table 7.1). This is consistent with more anthropogenic emissions in urban areas than in rural areas.

The sampling periods between 2001 and 2005 took place during different months. The question whether the difference in wind directions could have had an effect on the levels of hydrocarbons has been explored. Figure 7.2 shows the wind roses of Guangzhou and Zhaoqing in March 2001 and April 2005, respectively. The wind directions were dominant from the Southeast in Guangzhou and from the Northeast in Zhaoqing in both sampling periods.

Figure 7.3 compares the percentage distribution of hydrocarbons at the two sites for 2001 and 2005. The percentage was calculated by dividing the median mixing ratio of each hydrocarbon by the median mixing ratios of Σ NMHC. From Table 7.1 and Figure 7.3, several common features are found between the urban and rural sites. The median mixing ratios of light alkanes (C_3 ~ C_5) in 2005 were enhanced with respect to

those in 2001 at both sites, particularly urban propane. The percentage of propane went up to 170 % in Guangzhou between 2001 and 2005. Additionally, the mixing ratio of toluene had decreased by about 15 % in 2005 compared with those found in 2001 in Guangzhou. At Dinghu Mountain, the median mixing ratio of toluene had increased by approximately 150% in 2005 compared with that found in 2001. The median mixing ratios of ethene had increased about 20% at Dinghu Mountain and 25% in Guangzhou, while ethyne had increased about 37% at Dinghu Mountain, but had less increased at Guangzhou (only 4%). However, considering the uncertainty in data analysis, this minor increase of ethyne in Guangzhou is negligible.

7.3.2 Effects of changes in vehicular emissions and road conditions on atmospheric NMHCs

Figure 7.4 shows the average daily usage of LPG and gasoline in Guangdong Province and the number of motor vehicles in Guangzhou and Guangdong Province between 1998 and 2004 (Guangdong Statistical Bureau, 1999-2005; Guangzhou Municipal Statistics Bureau, 1999-2005). With the rapid urbanization and economic development in recent years, the number of motor vehicles has soared both in Guangzhou and throughout Guangdong Province, by about 125% between 1998 and 2004 (Guangdong Statistical Bureau, 1990-2005). Similarly, the motor vehicle fleet has increased by about 80% in Zhaoqing, from 29,000 in 2000 to 52,000 in 2004 (Zhaoqing Municipal Statistical Bureau, 2005). However, the increases in concentration of certain NMHCs from vehicular emissions such as ethyne were more noticeable on Dinghu Mountain than in Guangzhou (Table 7.1). The reasons for these observations are discussed as follow.

Firstly, the implementation of the EURO-I emission standard in Guangzhou for motor vehicles began in October 2000, with EURO-II following in 2005. The new registered vehicles after 2000 were designated to be equipped with electric injection technology and 3-way catalytic converters, significantly reduced hydrocarbon emissions when old vehicles were replaced by new. Secondly, the road conditions in urban sites improved in 2005. Vehicle speeds were generally higher in 2005, resulting in a more even and smooth traffic flow than in 2000. This, in turn would result in lower hydrocarbon emissions from vehicles and improve roadside air quality. To solve the crowded traffic situations in urban areas and to promote the development of the suburban and rural areas, huge highway lengths were built in the PRD. During the government's tenth five-year plan (2000-2005), about 2000 km of highways were built, reaching 3100 km in Guangdong Province. During the eleventh five-year plan, 25,000 km of roads, including 2000 km of highways, are to be built in Guangdong Province. This will further increase road traffic and will encourage the spread of industrial activity to less developed regions.

Although only six roadside and tunnel samples were collected in 2000, and six roadside samples in 2005, these limited roadside data supported our hypothesis that tighter emission standards and improved roadways helped to limit the increase in NMHC emissions from vehicles relative to the increase in vehicular fleet. For example, Xingang Road was widened from 3 lanes in both directions in 2000 to 4 lanes in 2005, and several overpasses and connections were built after 2000 to decrease the traffic jams and deadlock situations, which were common in 2000. These changes are expected to have contributed to the significant decrease of most roadside and tunnel hydrocarbon levels in 2005 as compared to 2000. Although, we also noted

that the 2000 samples were collected at a roundabout, where vehicle speeds were slower than for the 2005 roadside samples, and therefore emissions were expected to be higher.

7.3.3 Effect of increasing vehicle numbers on the levels of ethene and ethyne

The median mixing ratios of ethene and ethyne had both increased in Dinghu Mountain between 2001 and 2005. This is attributed to the increased number of vehicles in the region and the resulting increase in the usage of gasoline. Ethene and ethyne are well correlated in the roadside and tunnel samples (Figure 7.5), consistent with their common vehicular source in urban areas. The slopes between ethene and ethyne on Dinghu Mountain and in Guangzhou are very close to that of roadside samples, indicating that traffic emissions are the major sources of these two species. Although the median ethene and ethyne levels increased by 20-35% in the Dinghu Mountain samples between 2001 and 2005, in Guangzhou, the median mixing ratio of ethyne showed little change (<5%) compared to the 25% increase in ethene (Table 7.1). Bearing in mind the uncertainty in these data, it is possible that ethyne may have other sources than vehicular emissions in Guangzhou. In a previous study in urban centre of Bilbao, Basque, Durana et al. (2006) found that vehicular emissions were not the only urban source of ethyne, and industrial emissions also played very important roles. In this study, ethyne may have other contributing sources (for example, industrial emissions) in Guangzhou. Due to the decrease of industrial enterprises in the Guangzhou urban area (which will be discussed in detail in the following section), the emission of ethyne from industrial sources would have decreased, thereby, mitigating the increased trend of ethyne from vehicular sources. The relocation of

industries to more rural areas would also explain the relatively larger increase in ethyne compared to ethene at Dinghu Mountain.

7.3.4 Effects from LPG emissions and leakage

The consumption of LPG increased drastically from 2000 to 2004 in Guangdong Province (Figure 7.4; Guangdong Statistical Bureau, 1999-2005). In Guangzhou, approximately 700,000 tons of LPG was consumed in 2004, of which 450,000 tons was for residential use (Guangzhou Municipal Statistical Bureau, 2005). Figure 7.6 shows the residential use and total supplied LPG in Guangzhou from 1998 to 2004 (Guangzhou Municipal Statistical Bureau, 1999-2005). The rapid increase in the use of LPG is the likely cause of the significant increase of propane observed in Guangzhou.

LPG-fueled buses and taxis were first introduced in Guangzhou in 2003, and more buses and taxis are now running on LPG (Guangzhou Yearbook Committee, 2004). To mitigate the air pollution problem from vehicle exhausts, the Guangzhou municipal government began promoting the use of LPG-fueled buses and taxis in 2003. By the end of that year, there were 207 and 874 LPG-fueled buses and taxis in service respectively (Guangzhou Yearbook Committee, 2004). In November 2005, there were approximately 5060 and 9200 LPG-fueled buses and taxis in Guangzhou, which accounted for 67% and 58% of the total buses and taxis numbers (New Express, 2005). By the end of 2006, all taxis and buses will be LPG fueled.

Figure 7.7 shows the correlation of propane and n-butane. Both of them are the major components of LPG (Tsai et al., 2006). Propane and n-butane are strongly correlated in the ambient samples of Guangzhou, Dinghu Mountain, and in the roadside and

tunnel samples, indicating that they originated from common sources. The two hydrocarbons were strongly correlated ($R^2 > 0.97$) at the roadside and tunnel samples in 2000 and 2005. However, the slope in roadside samples of 2005 (3.66) was much higher than in roadside and tunnel samples of 2000 (0.59). It is likely attributed to the introduction of LPG-fueled buses and taxis since 2003. The drastically increased propane compared with n-butane in the roadside samples indicates that LPG-fueled vehicles emitted more propane than n-butane, although it was unknown about the composition of LPG used in Guangzhou. In Hong Kong, the composition of LPG is 46.4% of n-butane, 26.0% of propane and 22.4% of i-butane (Tsai et al., 2006). However, LPG contained high percentage of propane was also reported in other cities, for example, Mexico City (propane:n-butane:i-butane = 67.7:16.3:12.1, Vega et al., 2000) and Ciudad Juárez, Mexico (propane:n-butane:i-butane = 85.6:9.6:2.5, Fujita, 2001). At both sites in 2001, the slopes are nearly the same (0.96 in Guangzhou and 1.07 at Dinghu Mountain). It appears that before the introduction of LPG-fueled buses and taxis, the characteristic ratio of propane/n-butane in ambient air was about 1.0 in these regions. The slopes are higher in 2005 than 2001, especially in Guangzhou. This suggests that the introduction of LPG-fueled vehicles greatly affected the ambient levels of propane. The slopes of propane vs. n-butane at both sites are lower than that of roadside samples in 2005 (3.66), which indicate that n-butane has a significant source other than LPG, likely gasoline evaporation (Tsai et al., 2006).

7.3.5 Effects of changing industrial emissions on level of toluene

In the PRD region, several studies have shown that transportation is the largest contributor to VOC emission (CH2M HILL, 2002; Streets et al., 2006). However, Chan et al. (2006) found that industrial activities greatly contribute to ambient VOC

levels. Their study on NMHCs in industrial, industrial-urban and industrial-suburban environments showed that toluene was the most abundant hydrocarbon in the PRD atmosphere, and industrial solvents and vehicular emission were its major sources.

Toluene was also the most abundant atmospheric hydrocarbon found in Guangzhou in 2001 and 2005. At Dinghu Mountain, toluene was the fourth most abundant species in 2001 and the second most abundant one in 2005, after ethyne (Table 7.1). Both the mixing ratio and the percentage of toluene decreased from 2001 to 2005 in the ambient air of Guangzhou. However, both of them increased at Dinghu Mountain from 2001 to 2005.

Figure 7.8 shows the correlation of toluene with benzene. In previous studies, the toluene to benzene (T/B) concentration ratio was used to infer their sources in many studies (Barletta et al., 2005; Chan et al., 2002; Wang et al., 2005b; Lee et al., 2002). A high T/B ratio was found in the ambient air of Hong Kong urban area (T/B= 5.0, Lee et al., 2002) and rural area (T/B=5.4, Wang et al., 2005) compared with other cities (0.7~2.0), and in the gasoline evaporation samples of Hong Kong (22.1 ± 12.7), Guangzhou (3.7 ± 1.5), Zhuhai (3.9 ± 0.7) and Macau (23.0 ± 1.8) (Tsai et al., 2006). The high level of toluene was attributed to the use of aromatic-rich unleaded fuels and industrial solvents. A previous study in five cities of the PRD found that the T/B ratio in the ambient samples of industrial, industrial-urban, and industrial-suburban sites was 6.3 ± 8.0 , 6.0 ± 4.7 and 6.9 ± 5.6 , respectively (Chan et al., 2006). In this study, ambient air T/B ratios decreased in 2005 compared with 2001, in both sites. The median ratios decreased from 4.3 to 3.4 in Guangzhou and from 3.0 to 2.6 at Dinghu Mountain, while it was nearly the same in the roadside and tunnel samples for 2000

(1.4) and the roadside samples for 2005 (1.4, when excludes one sample, which is 4.9). This indicates that an additional source(s) (i.e. industrial solvents) other than motor vehicle emissions contribute to ambient levels of toluene in Guangzhou and Dinghu Mountain. The higher T/B ratio in Guangzhou than on Dinghu Mountain indicates that the emission strength of toluene is greater in Guangzhou than on Dinghu Mountain and is consistent with the existence of many industrial enterprises in Guangzhou.

It was reported that 157 highly polluting factories were forced to close, or relocate, or if they did not comply with the emission standards set by the government in the year 2004 (Guangzhou Yearbook Committee, 2005). Additionally, many factories in this region, in recent years had voluntarily relocated out of Guangzhou in pursuit of cheaper labor, less stringent pollutant emission standards and lower running costs. Some large factories in Guangzhou had closed down due to high energy consumption, high pollutant emissions, low efficiency, and changes in government policy on large pollutant emitters. Figure 7.9 shows the number of industrial enterprises above a designated size in the Guangzhou urban area. The number of large industrial enterprises decreased dramatically from 2002 to 2003 (Figure 7.9). Industrial enterprises here refer to all state-owned enterprises and non state-owned enterprises with an annual sales revenue over 5 million Yuan (unit of RMB) in the Guangzhou urban area. The medium sized industrial enterprises refer to those with a work force below two thousands but above three hundreds, or with sales below three hundreds millions but above thirty millions Yuan, or with a capital investment below four hundreds millions but above forty millions Yuan. Although the number of medium and small sized industrial enterprises increased between 1999 and 2004, these new enterprises were less polluting than the older ones. Due to the closing or moving of

large industrial enterprises and other control efforts, ambient levels of toluene in the Guangzhou urban area decreased between 2001 and 2005. However, the levels of toluene on Dinghu Mountain increased from 2001 to 2005. This may be attributed to the increase in industrial enterprises in this less developed region compared to that in Guangzhou.

7.3.5 Ozone formation potentials in ambient air of GZ and DM

To assess the relative contribution of individual hydrocarbon to ozone formation, the maximum incremental reactivity (MIR) estimates developed by Cater (1994) were used. Table 7.2 lists the calculated ozone formation potential (OFP) of selected hydrocarbons and their sum values. Toluene, m/p-xylene and ethene are the three largest contributors to the formation of ozone in both sites. The total OFPs of these three species account for about 60 % and 55 % of the total on Dinghu Mountain and about half in Guangzhou city in 2001 and 2005, respectively. The total OFPs had slightly increased in 2005 compared with 2001 in Guangzhou (about 6 %), but significantly increased on Dinghu Mountain (40 %). In Guangzhou, the increase of OFP by light hydrocarbons from vehicular emissions and LPG leakage was mitigated by the decrease of OFP by aromatic hydrocarbon from industrial emissions. On Dinghu Mountain, almost all the OFPs for the hydrocarbons from these emission sources increased in 2005 compared with 2001. This made a significant increase of total OFP in the rural regions.

7.4 Conclusion

From 2001 to 2005, NMHC profiles varied greatly in both ambient atmosphere of the urban city of Guangzhou and a rural site Dinghu Mountain. The increase of vehicle

numbers contributed to the increased levels of ethene and ethyne at Dinghu Mountain in 2005 compared with that found in 2001. In the urban area of Guangzhou, only ethene levels had increased. This is due to the streamlining of traffic flow and the improve of road conditions in Guangzhou urban sites, and hence resulted in less emission from vehicular emissions, and is also due to other sources of ethyne in Guangzhou. Leakage of LPG is a major source of propane in Guangzhou and on Dinghu Mountain. The increasing use of LPG-fueled buses and taxis, especially in Guangzhou, has significantly affected ambient levels of propane. The relocation of some industries to less developed outskirts towns, the closing of some heavily polluting industries, and the introduction of LPG fueled vehicles, which emit less toluene, are the main reasons for the decrease of ambient toluene observed in Guangzhou, while the increase of industrial factories may have contributed to the enhanced toluene levels on Dinghu Mountain.

With a fast growing economy and continuing industrialization and urbanization, the number of motor vehicles and usage of LPG will continue to increase in Guangzhou and the PRD region. Emissions from vehicular exhausts and leakage of LPG into atmosphere will further degrade the local and regional air quality. The closing and/or relocation of polluting factories from developed urban areas to less developed outskirts towns, or rural areas, however, will spread pollution to a larger part of the PRD, while perhaps decreasing industrial pollution in central cities. The observed toluene/benzene reductions indicate the effectiveness of local/regional emission regulations. However, it is imperative that the PRD government institutes additional emissions regulations and modifies existing ones in order to address continuing emission changes in the PRD, otherwise air quality will further deteriorate.

Table 7.1 Statistics of selected hydrocarbons in ambient and roadside samples (unit: ppbv).

hydrocarbon	Dinghu Mountain				Guangzhou				Guangzhou roadside & tunnel samples			
	Mar 2001 (n=39)		Apr 2005 (n=30)*		Mar 2001 (n=43)		Apr 2005 (n=28)*		Rd & Tun 2000 (n=6)		Roadside 2005(n=6)	
	Median	Average ± S.D.	Median	Average ± S.D.	Median	Average ± S.D.	Median	Average ± S.D.	Median	Average ± S.D.	Median	Average ± S.D.
ethane	3.17	3.18 ± 0.89	2.67	2.60 ± 0.46	3.89	4.06 ± 1.21	3.63	3.80 ± 1.12	10.98	10.56 ± 4.13	3.94	3.63 ± 0.83
propane	1.28	1.59 ± 0.83	1.84	1.85 ± 0.85	4.31	5.39 ± 3.01	8.82	10.26 ± 5.17	10.33	11.42 ± 6.16	36.21	29.85 ± 12.31
isobutane	0.37	0.58 ± 0.46	0.77	0.76 ± 0.40	2.40	3.11 ± 1.97	3.97	4.33 ± 2.23	9.95	11.41 ± 6.30	6.36	5.72 ± 1.27
n-butane	0.49	0.88 ± 0.73	0.96	0.94 ± 0.51	3.37	4.60 ± 3.04	4.36	5.04 ± 2.56	12.43	15.43 ± 10.24	11.97	10.71 ± 2.59
isopentane	0.28	0.50 ± 0.42	1.10	1.06 ± 0.54	2.60	3.00 ± 2.00	3.68	4.49 ± 2.28	37.20	47.04 ± 30.17	3.43	3.73 ± 1.06
n-pentane	0.13	0.27 ± 0.25	0.54	0.56 ± 0.31	0.80	0.99 ± 0.69	1.72	1.90 ± 0.94	8.54	10.55 ± 6.35	1.53	1.63 ± 0.45
2-methylpentane	0.10	0.26 ± 0.35	0.32	0.40 ± 0.22	1.09	1.28 ± 0.83	1.43	1.73 ± 0.78	8.06**	8.06 ± 0.10	1.33	1.22 ± 0.39
3-methylpentane	0.18	0.25 ± 0.18	0.23	0.25 ± 0.16	0.88	1.02 ± 0.58	0.99	1.14 ± 0.52	4.56**	4.56 ± 0.15	0.88	0.79 ± 0.24
n-hexane	0.09	0.19 ± 0.19	0.32	0.40 ± 0.23	0.90	1.13 ± 0.85	1.43	1.57 ± 0.75	5.01	6.30 ± 3.72	0.67	0.66 ± 0.27
ethene	1.82	2.18 ± 1.32	2.16	2.40 ± 1.14	5.83	7.37 ± 3.92	7.34	8.40 ± 4.18	76.76	82.20 ± 34.00	13.01	12.67 ± 5.29
propene	0.27	0.40 ± 0.36	0.50	0.50 ± 0.29	1.40	1.79 ± 1.17	2.38	2.76 ± 1.57	21.76	22.07 ± 8.44	2.93	2.91 ± 1.28
isoprene	0.26	0.41 ± 0.39	0.07	0.10 ± 0.08	0.24	0.26 ± 0.18	0.20	0.24 ± 0.13	7.95	8.06 ± 4.19	1.22	1.13 ± 0.88
ethyne	2.58	2.86 ± 1.39	3.54	3.86 ± 1.23	7.31	8.83 ± 4.64	7.58	8.79 ± 3.54	89.74	94.28 ± 43.49	9.09	10.20 ± 5.14
benzene	0.59	0.85 ± 0.55	1.18	1.32 ± 0.61	2.42	2.80 ± 1.43	2.71	3.10 ± 1.35	16.79	18.10 ± 7.43	2.21	2.07 ± 0.52
toluene	1.32	3.36 ± 3.67	3.35	3.52 ± 2.04	11.98	14.09 ± 10.15	10.12	11.40 ± 5.34	26.09	25.90 ± 10.50	3.38	4.01 ± 2.34
ethylbenzene	0.16	0.56 ± 0.71	0.42	0.45 ± 0.26	1.78	2.21 ± 1.76	1.59	1.78 ± 0.98	3.32**	3.32 ± 0.24	0.87	0.91 ± 0.36
m/p-xylene	0.84	1.24 ± 1.28	0.65	0.75 ± 0.55	3.31	5.16 ± 5.11	3.48	3.46 ± 1.93	15.73**	15.73 ± 1.23	2.10	1.92 ± 0.64
o-xylene	0.16	0.64 ± 1.30	0.26	0.30 ± 0.20	2.00	2.63 ± 2.24	1.24	1.29 ± 0.69	8.02**	8.02 ± 0.97	0.75	0.63 ± 0.19
ΣNMHC	15.10	21.40 ± 13.28	22.16	23.50 ± 10.09	61.38	76.71 ± 43.52	75.79	84.11 ± 36.24				

*Samples were analyzed by the RCEC, Taiwan and adjusted by a conversion factor.

**Only two data from the samples collected on Aug. 13 2000 at roadside.

Table 7.2 Ozone formation potential of selected hydrocarbons at Guangzhou
and Dinghu Mountain (unit: ppbv).

hydrocarbon	DM2001	DM2005	GZ2001	GZ2005
ethane	0.50	0.42	0.61	0.57
propane	0.57	0.81	1.90	3.89
isobutane	0.54	1.12	3.51	5.81
n-butane	0.60	1.18	4.16	5.38
isopentane	0.58	2.28	5.40	7.63
n-pentane	0.20	0.84	1.25	2.69
2-methylpentane	0.27	1.07	2.93	3.84
3-methylpentane	0.49	0.68	2.37	2.68
n-hexane	0.16	0.72	1.59	2.51
ethene	7.89	9.36	25.27	31.82
propene	2.19	4.10	11.57	19.62
isoprene	3.35	0.92	3.08	2.61
ethyne	0.55	0.76	1.57	1.63
benzene	0.41	0.81	1.65	1.86
toluene	6.84	17.35	62.08	52.43
ethylbenzene	0.95	2.50	10.62	9.50
m/p-xylene	13.79	10.67	54.15	56.91
o-xylene	2.27	3.70	28.77	17.81
Σ NMHC	48.36	68.22	264.10	280.81



Figure 7.1 Map showing the Pearl River Delta and the sampling sites.

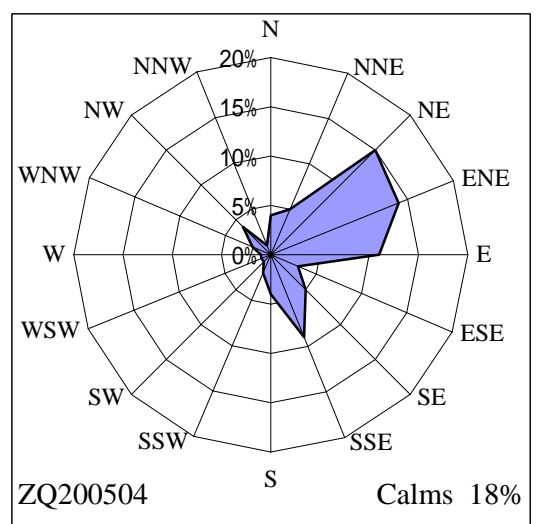
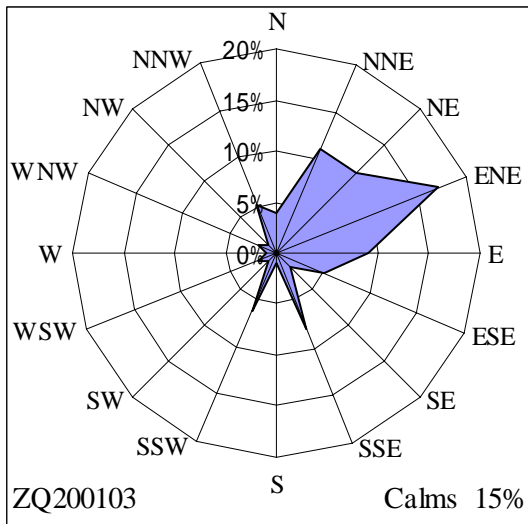
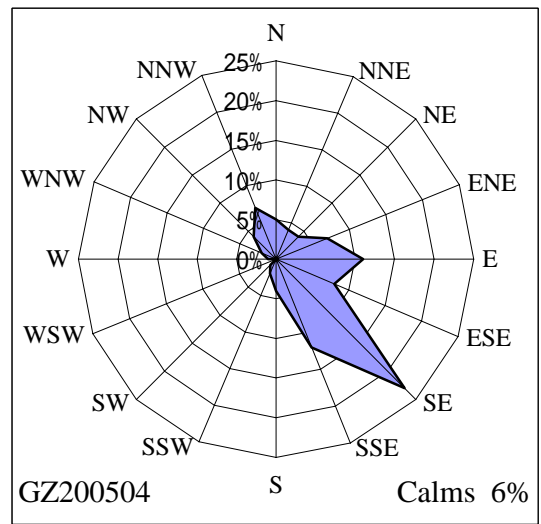
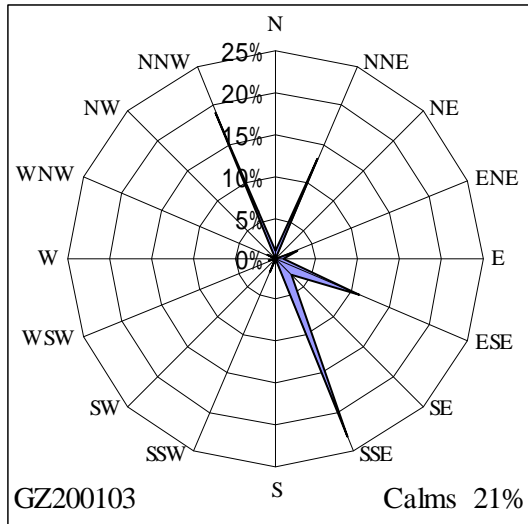


Figure 7.2 Wind roses of Guangzhou (GZ) and Zhaoqing (ZQ) in March 2001 and April 2005.

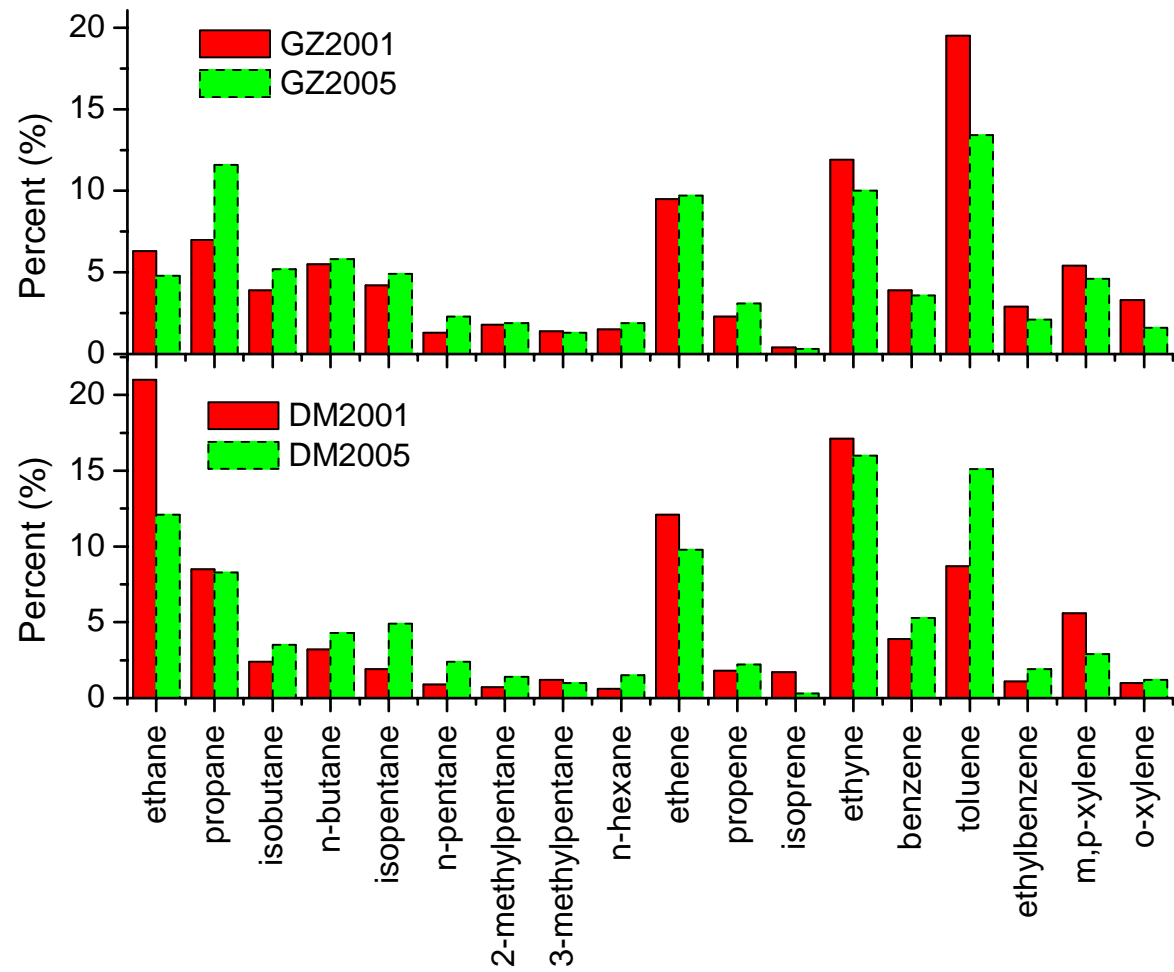


Figure 7.3 Percentages of hydrocarbons in Guangzhou and Dinghu Mountain.

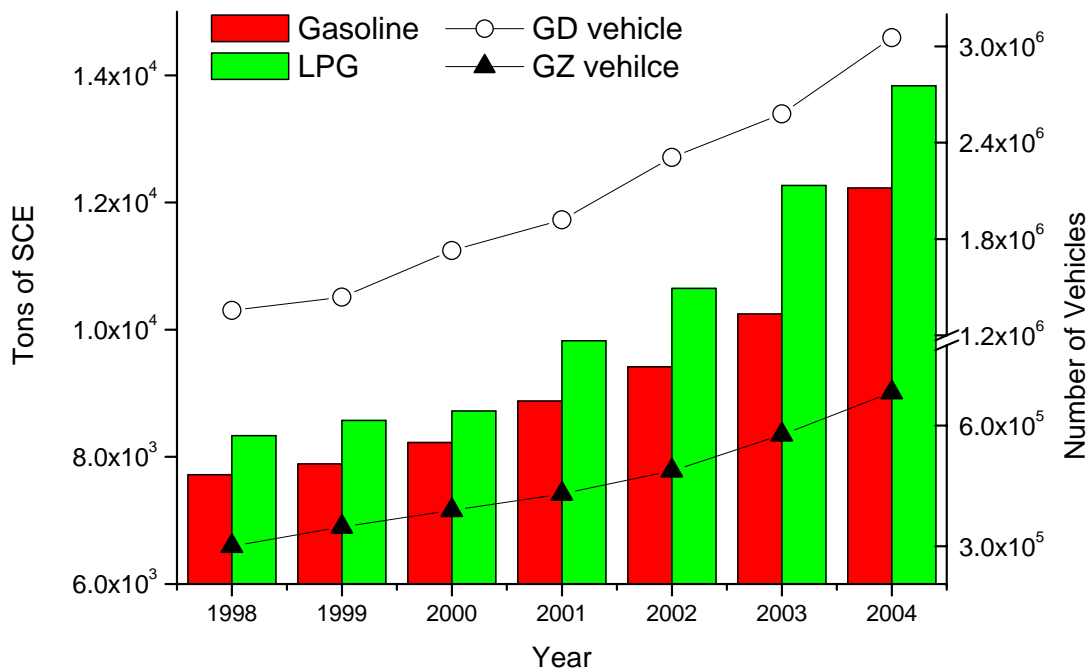


Figure 7.4 Average daily usages of LPG and gasoline in Guangdong Province (unit: tons of Standard Coal Equivalent) and total number of motor vehicle in Guangdong Province (GD) and Guangzhou (GZ) (Source: Guangdong Statistical Yearbook 1999-2005 and Guangzhou Municipal Statistics Bureau, 1999-2005).

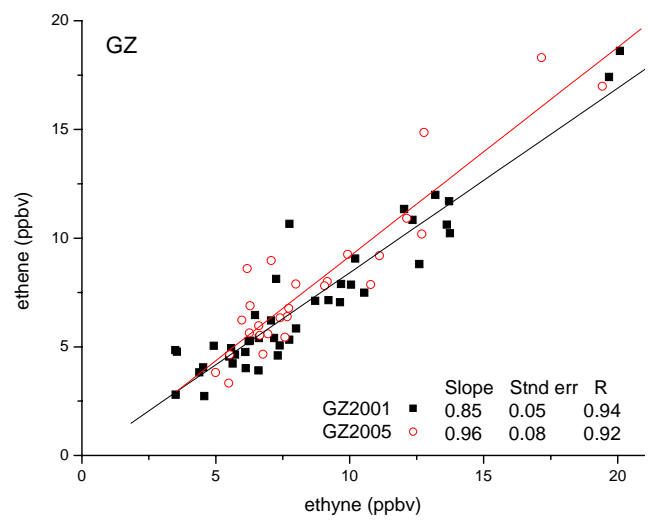
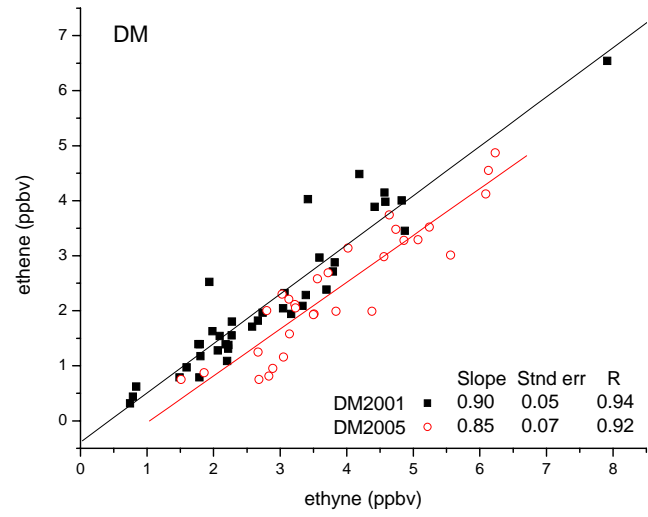
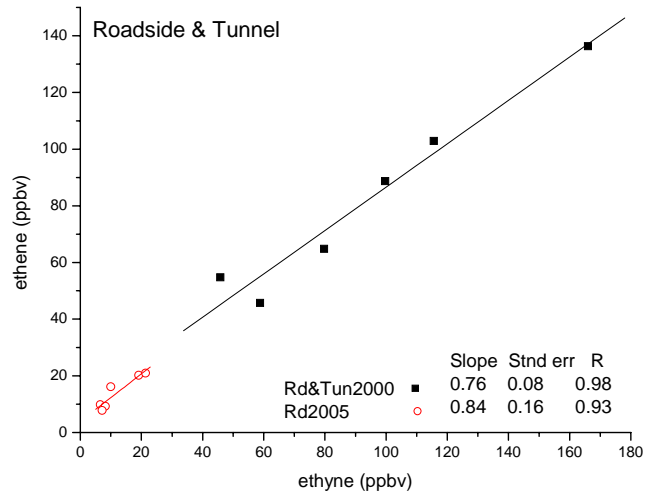


Figure 7.5 Correlation between ethene with ethyne.

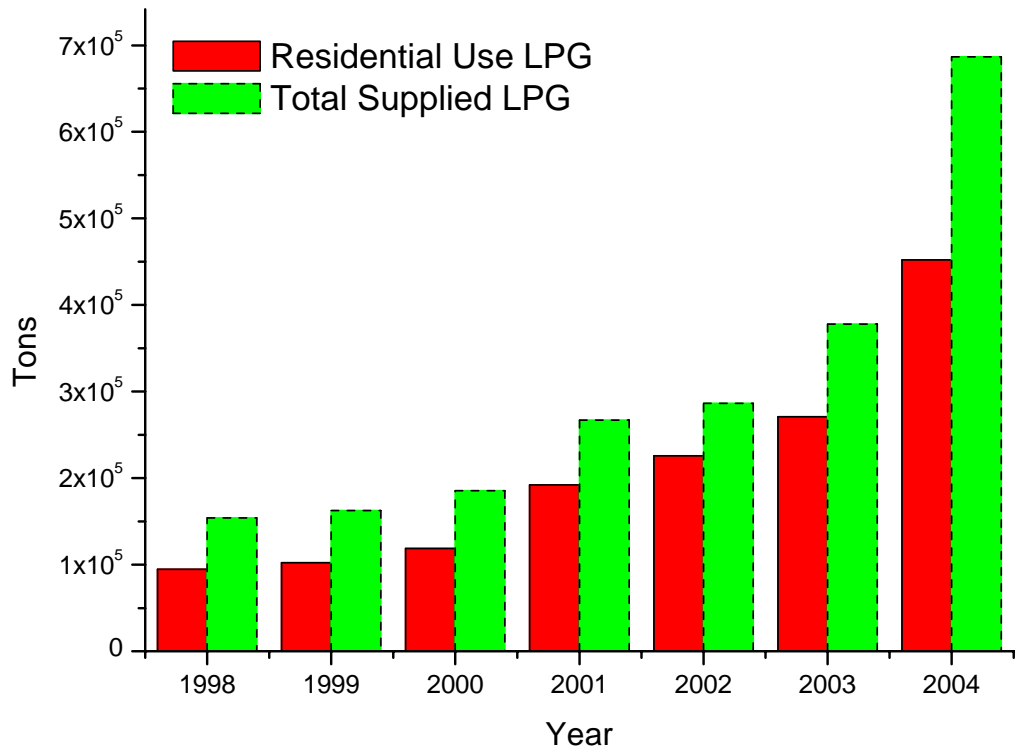


Figure 7.6 Residential usage and total supplied LPG in Guangzhou (Source: Guangzhou Statistical Yearbook 1999-2005).

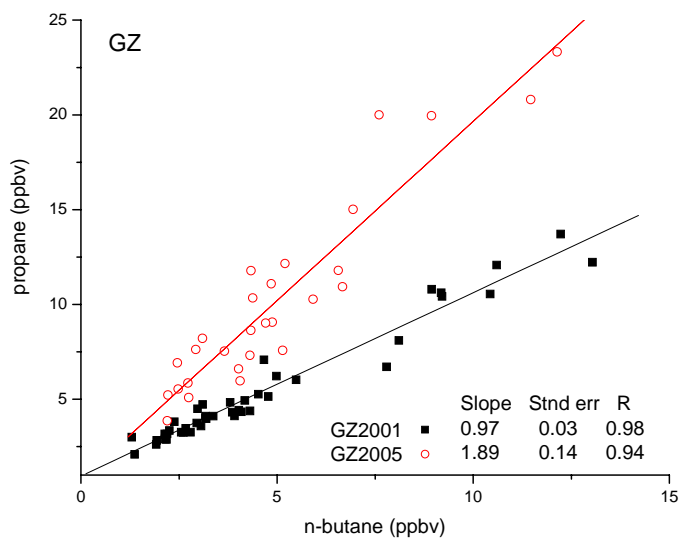
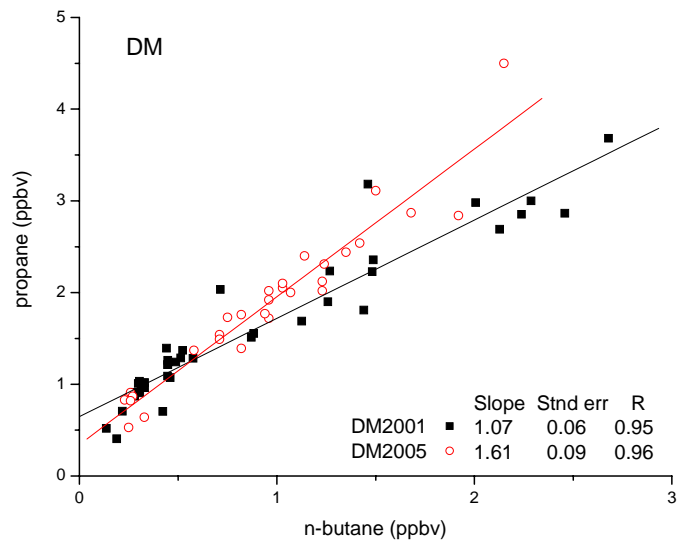
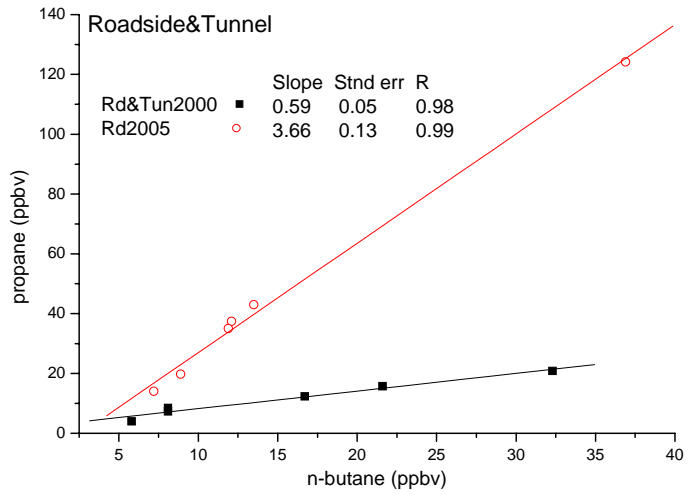


Figure 7.7 Correlation between propane with n-butane.

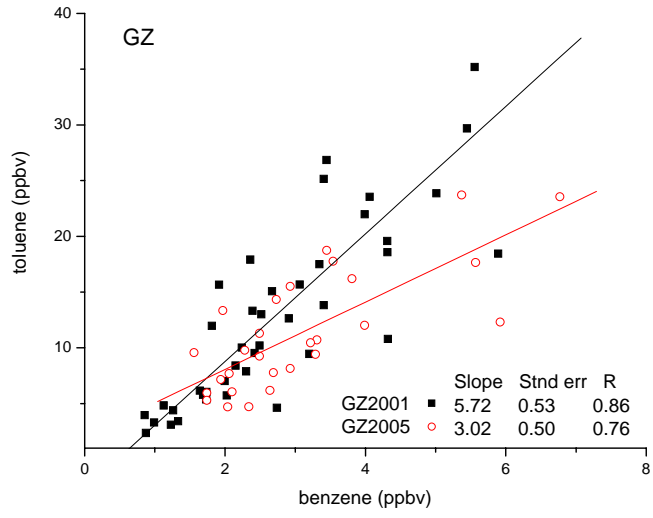
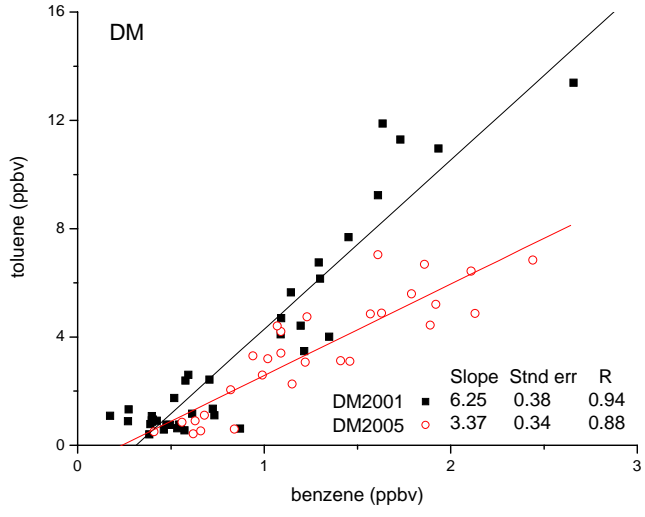
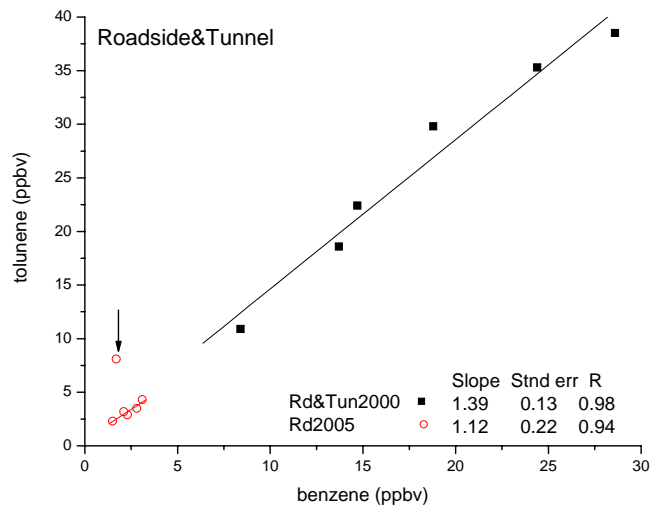


Figure 7.8 Correlation between toluene to benzene

(One sample was excluded in the regression of roadside sample in 2005).

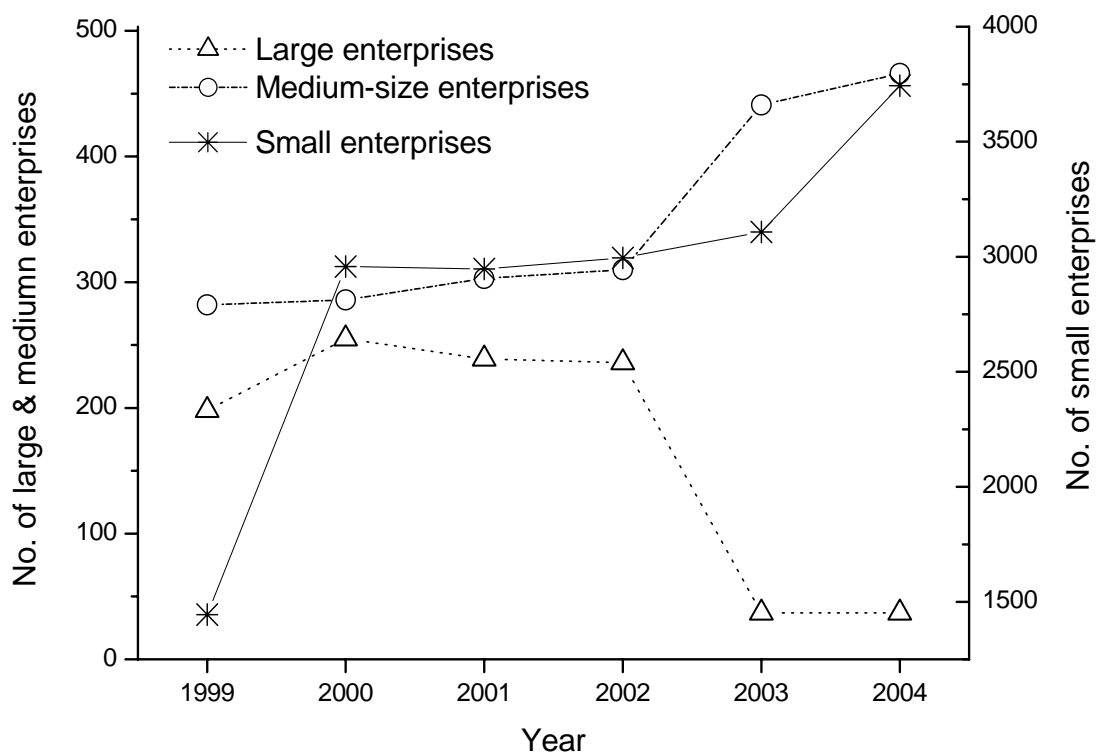


Figure 7.9 Change of numbers of industrial enterprises designated by size in the urban area of Guangzhou from 1999 to 2004

(Source: Guangzhou Statistical Yearbook, 2000-2005).

Chapter 8

Conclusion

In this study, I have performed a series of ambient and source air sampling and subsequent analysis of C₂-C₁₀ NMHCs in various selected roadside, urban, rural and remote sites of South China with an aim to investigate the characteristic and the speciation of NMHCs and their implications on atmospheric NMHC pollution in this region. The studied areas extended from the relatively less developed Hainan Province and Yunan Province to the more developed Zhejiang Province and Guangdong Province. More in depth studies have been performed for Guangzhou and Dinghu Mountain within the PRD. The sources and source regions of prevalent NMHC species and associated pollution were assessed. NMHC spectrum between ambient and source samples were compared. Characteristics ratios of NMHC species, backward air trajectory and satellite images were utilized in the data analysis.

NMHCs have complex characteristics in the atmosphere of South China respective to the predominant species among these sites. High mixing ratios of NMHCs including those health impairing species were found in Guangzhou and Lin'an, highlighting the poor air quality in the PRD and YRD regions. In these well developed regions, NMHCs are dominated by aromatics and unsaturated alkenes and alkynes which were closely related to industrial and vehicular emissions in urban areas. The pollution from these regions affects their leeward sites in the southeast coast of China. However, in rural and remote areas such as at Jiangfeng Mountain on Hainan Island and Tengchong Mountain in southwest of China, long-range transports of biomass burning

pollution from the SE Asia subcontinent in addition to contributions from in situ biogenic and other local emissions, are important sources of NMHCs in Spring.

We have explored the implications of urban and rural changes on atmospheric NMHC in the PRD region. The number of vehicles had doubled from 2001 to 2005 in Guangdong Province while the industrial activity had also increased significantly during this period. Our study shows that the mixing ratios of traffic and industrial related NMHC species such as ethyne and toluene had increased much higher in the rural Dinghu Mountain than in the urban Guangzhou city. This was due to the streamlining of urban traffic, upgrading of road networks not only in the urban area but throughout the whole of Guangdong Province, the implementation of stringent emission standards for vehicles as well as polluting industries especially in the urban cities, the relocation of polluting industries from urban to the less developed parts of the PRD and the significant increase in vehicular traffic in the rural areas. We have found for the first time that the mixing ratio of propane, a major component in LPG, has increased substantially from 2001 to 2005 in Guangzhou. Such propane increases were due to the introduction of LPG-fueled buses and taxis in Guangzhou. Such signatures of LPG influence are also found in Sanya of Hainan Province, where LPG is used as a fuel in taxis. In addition, the modification of the NMHC emission patterns in the rapidly developing PRD was also due to the shifting of prevalent fuels and implementation of better air pollution control strategy in this region.

Due to the limited data utilized and the large regional area covered, this study can only provide a preliminary assessment, and much more research efforts are needed to

understand thoroughly the impacts of the changing atmospheric NMHC on the regional air quality and local atmospheric environment in South China.

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