Characterization of Volatile Organic Compounds (VOCs) in Emissions from Industrial Sources

by

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Declaration

I hereby declare that this thesis is my own work and that, to the best of my knowledge and belief, it reproduces no material previously published or written, nor material that has been accepted for award of any other degree or diploma, except where due acknowledgement has been made in the text.

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Abstract

In this research, observation based methods were used to characterize a wide range of VOCs in emissions from PRD industries. Corresponding VOC source signatures from emissions of particular industrial work processes or activities were obtained, and then used to further analyze the PRD ambient air composition. This research comprises three VOC field studies. Impact of industrial emissions on the PRD region was firstly examined. The year-2000 field VOC data preliminarily gave VOC compositions of industrial, industrial-urban and industrial-suburban atmosphere of the PRD, and showed the impact on the local air quality due to the spread of industrial activities from urban area to suburban and rural areas. Toluene was the most abundant VOC. Instead of vehicular emission, industrial solvent usage contributed to the high atmospheric toluene levels. Also, some samples showed that the adjacent industrial activities greatly affected the neighbourhood atmospheric VOCs.

In the 2003 study, the impact of the transported industrial pollutants on Zhuhai, a south coastal city, was then investigated. By the classification of three different characteristic prevailing wind directions in three sampling days, the result showed that strong polluted sources from inland PRD cities and upwind industrial areas greatly affected the whole Zhuhai city, because strong north wind frequently transported polluted air masses from

the upwind PRD industrial regions, carrying enriched toluene, dichloromethane and other industrial organic pollutants to Zhuhai. In addition, mild east wind could transport polluted plume from a suburban-industrial area to the downwind suburban sampling site. Under the influence of clean sea air, local vehicular emission became the major anthropogenic source in the downtown and roadside microenvironment.

The 2005 VOC study was conducted in Qingxi, an inland PRD town in Dongguan. VOC source signatures of different work processes of electronic industry and printing industry were collected, and then used in explaining the general impact of industrial activities. The rooftop TVOC of the printing factory was about 20 times higher than that of the electronic factory. Most of the abundant VOCs collected on the rooftop of the electronic factory were produced by the corresponding work processes inside the factory. In the case of the printing factory, toluene contributed more than half of the total VOCs in three examined work processes. The role of respective industries on local ambient atmosphere was also discussed in the study.

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Chapter 1 Introduction

1.1 Background

A wide range of volatile organic compounds (VOCs) participates in photochemical reactions in the troposphere resulting in ozone (O_3) enhancement and photochemical smog formation. Both VOCs and ozone may have adverse effects on human health and plant growth (Burnett et al., 1994; USEPA, 1998a). The environmental and health impacts of these pollutants have become the major concerns in the Pearl River Delta (PRD) region, South China. The PRD is the first special economic zone characterized with special economic systems and policies different from typical China economic practice. Emphasis is generally placed on foreign direct investment and export. This special condition leads to its fast industrial development. It eventually becomes a massive manufacturing center in South China in the past two decades. Vast industrialization and urbanization worsen the PRD air quality in recent years, as industrial activities and automobiles emitted large quantities of VOCs and other air pollutants. In general, the dominant anthropogenic VOC sources are vehicular and industrial emissions that are emitted from fossil fuel combustion, liquefied petroleum gas (LPG) leakage, fuel evaporation, petroleum distillation and industrial solvent utilization (Cheng et al., 1997; Chen et al., 2001; Na et al., 2001; Seila et al. 2001;

Watson et al., 2001; He et al., 2002).

These air pollution problems affect not only the PRD cities, but also other downwind perimeters. The medium and long-range transport of the ozone precursors (VOCs, CO and NO_x) from inland PRD cities can enhance tropospheric ozone formation and haze formation in downwind regions such as Hong Kong. According to the HKEPD (2002) report, the number of hours with visibility impairment (lower than 8 km) in Shenzhen, Guangzhou and Hong Kong had substantially increased from 1991 to 2000. Therefore, tackling the deteriorating air quality of the PRD and Hong Kong is in urgent needed.

However, there are problems in developing the formulation of emission control strategies. One such problem is the lack of emission data. The contribution of VOC emission from anthropogenic sources (automobile and industry) has been drastically changed due to the fast urbanization and industrialization in recent years. Outdated and questionable emission inventories make it difficult to study the PRD air pollution. Running air quality models with inappropriate input parameters and VOC tracers could lead to inaccurate and unreliable results, such as the underestimation of industrial emission or the overestimation of vehicular emission. According to Hidy (2000), one main reason for unsatisfactory modeling results is the deficiency in VOC source profiles

that are needed to build a comprehensive picture. Otherwise, it could pose failures to source apportioning. In the past, limited VOC measurements were conducted to characterize the VOC source profiles of industrial and vehicular emissions and the atmospheric VOC composition in the PRD. It is clear that the characterization of VOC sources should be performed in order to have a better understanding of the current air quality of the region.

1.2 Objective of study and scope of work

This research used field VOC data collected in three case studies conducted in 2000, 2003 and 2005, to investigate the characteristics of the VOC emission from PRD industries, so that the contribution of respective industrial VOC emissions to the air quality of the PRD and its perimeters can be assessed. There are three objectives in this research:

1. To provide general background information of atmospheric VOC distribution profiles in the PRD and to illustrate the change of atmospheric VOC levels due to the fast industrialization.
2. To briefly characterize vehicular emission source that is useful for the interpretation of the atmospheric VOC mixing ratio and speciation, and for the

assessment of the significance of PRD industrial emission.

3. To characterize VOC profiles from different work processes for selected PRD industries, and to examine their VOC contribution to the local ambient air quality.

The scope of work mainly focuses on the three VOC field studies. Firstly, the VOC data, which were collected by members of our research group in 2000, is analyzed. As an outcome of this preliminary analysis, the composition of atmospheric VOCs in the whole PRD region associated with industrial activities in this region is examined. Secondly, the effects of the transport of air pollutants from inland PRD cities and neighboring sources on Zhuhai sites were studied. Thirdly, information collection is included in the scope of research. Understanding the landuse and the industrial development through interviews and site visits gives substantial information on the change of the PRD situation. This helps the selection of target industry in the third VOC study conducted to characterize industrial VOC emissions from printing and electronic manufacturing industry.

According to the results of the three main VOC measurements, some methods for the evaluation of changes in atmospheric VOC mixing ratios and for the extraction of representative VOC markers for specific industrial emissions are examined. This study

serves to pinpoint a direction for future extended research.

1.3 Structure of the thesis

In Chapter 2, the basic photochemistry of VOCs and O_3, and some relevant studies on VOC measurement, and sampling technique are reviewed. In Chapter 3, the research approach and the method of measurement are described. Chapter 4 reports VOC speciation and mixing ratio in the three industrial-related environments of the PRD. In addition, a case study on the air quality of Zhuhai relative to the transport of air masses under different wind directions is shown in Chapter 5. Chapter 6 presents characterization of VOCs for printing and electronic industries. Chapter 7 summarized changes in atmospheric VOC levels. In Chapter 8, potential VOC markers for PRD industries are studied. Finally, conclusion and recommendations are given.

Chapter 2 Literature Review and Implication on Research Direction

2.1 General and specific definitions of volatile organic compounds (VOCs)

Among various air pollutants such as ozone (O_3), carbon monoxide (CO), oxides of nitrogen (NO_x), sulphur dioxide (SO_2), particulate matter (PM) and volatile organic compounds (VOCs), the definition of VOCs is the most unclear one. Many definitions are adopted by different organizations and in different fields of interests. This section provides some general and specific definitions of VOCs.

In general, organic compounds include a wide range of hydrocarbons, halocarbons, oxygenated hydrocarbons, organic nitrates and organic sulphides. These organic chemicals are carbon-based chemical substances, containing element carbon. Natural organic chemicals are basic constituents found in living organisms and in products derived from living organisms such as fossil fuel and petrochemical products. Synthetic organic chemicals that are derived from reaction of hydrocarbons with other chemicals, such as halogens, are manufactured in laboratories and chemical processing industries. Volatile chemicals are characterized by their tendency to evaporate at room temperature and atmospheric pressure. More precisely, the vapor pressure of volatile chemicals is

greater than that of mercury by one tenth millimeter at room temperature. Broadly speaking, highly evaporative organic compounds can be defined as volatile organic compounds.

More specific definitions of VOCs are selectively adopted for different purposes. According to the National Pollutant Inventory VOC definition (NPI, 2003), “any chemical compound based on carbon chains or rings (and also containing hydrogen) with a vapor pressure greater than 2mm of mercury (0.27 kPa) at 25°C, excluding methane. These compounds may contain oxygen, nitrogen and other elements. Substances that are specifically excluded are: carbon dioxide, carbon monoxide, carbonic acid, carbonate salts, metallic carbides and methane.”

The U.S Environmental Protection Agency (USEPA) applies an additional requirement to limit the large number of VOCs for their interests, emphasizing their ozone formation property and toxicity. Volatile organic compounds are defined as a group of carbon compounds, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which are reactive to participate in atmospheric photochemical reaction to form ozone and ozone precursors. They also pose health effects to human beings, animals and plants (40 CFR 51.100 (s)). Health

impacts include eye irritation, dizziness and headaches. Some VOCs are classified to be carcinogenic such as benzene and 1,3-butadiene.

Although the focus of environmental impact of VOCs is usually placed on the production of ground level ozone and health effects, some VOCs are not involved in photochemical reactions in the troposphere and they are neglected from the USEPA definition. Yet they can have important impacts on the destruction of the stratospheric ozone layer. Most halocarbons, including CFCs, HCFCs, Halons, and most of the substances which have been determined to have negligible photochemical reactivity described in 40 CFR 51.100 (s), can be transported to the stratosphere due to their inert nature to photochemical reactions in the troposphere. They can react with stratospheric ozone, and then cause the depletion of the ozone layer. Excess ultraviolet radiation can pass through ozone hole to harm human health and reduce crops. Thus, these halocarbons have started to be routinely monitored and phased out under international treaty obligations, such as the Montreal Protocol (1987). Decreases in Northern Hemisphere baseline halocarbon mixing ratio were reported in recent years (Derwent et al., 1998; WMO. 2002).

This research project tries to characterize VOC emission from industrial sources in the

PRD. So, the measurement of nonmethane hydrocarbons (NMHCs) is an important task. Saturated, unsaturated and aromatic hydrocarbons are three main groups of NMHCs to be measured in the study. In addition to NMHCs, most halocarbons that are contained in various industrial solvent emissions are also considered (Wadden et al., 1991; He et al., 2002). There are some basic knowledge related to VOCs, such as health effects, general atmospheric reaction mechanisms and modeling parameters, which is needed to be considered, reviewed below though they are not included in the aim of this thesis.

2.2 Health effects of VOCs and ozone (O_3)

With regard to its highly evaporative nature, VOCs can easily escape into the atmosphere and then be breathed into the human respiratory system. Acute and chronic health effects may be induced by everyday exposure in high-level VOC environment. Eye, nose and throat irritation, headaches, vomiting, dizziness and asthma exacerbation are classified as actual effects, while liver, kidney and central nervous system damage and cancer are chronic effects (WHO, 2000). Benzene is a known human carcinogen and its detrimental effect on health is supported by evidence from human epidemiologic studies (USEPA, 1998a). Benzene undoubtedly becomes one of the target VOCs to be measured in the research on health and environment. Recent studies investigating passenger and pedestrian exposure to toxic VOCs in Guangzhou in the Pearl River

Delta region found relatively high benzene mixing ratios in public transportation vehicles and along urban roadsides (Chan et al., 2003; Zhao et al., 2004). In addition to benzene, total VOCs was also examined to evaluate health impacts on workers in a sheetfed offset printing shop (Wadden et al., 1995b). High total VOCs (30-51 g) were emitted from each press cleaning which endangered the safety of workers.

Apart from the direct health effects, VOCs could subsequently participate in photochemical reactions to form ozone and photochemical smog. These secondary air pollutants deteriorate the air quality and have harmful effects on human health. Ozone causes eye irritation and some respiratory disease symptoms, including coughing, wheezing, chest pain and labored breathing. Positive and statistically significant relationships were found between hospital admission related to the acute respiratory health effects and ambient ozone mixing ratio (Burnett et al., 1994). In addition, ground level ozone could impair the ability of plants to produce and store food. As a result, plant growth was inhibited and vegetable health was weakened. In order to tackle it, many atmospheric researches had been conducted to investigate the relationship between VOCs and ozone in urban, industrial and suburban atmospheres in recent decades (Jobson et al., 1994; Chen et al., 2001; Kang et al., 2001; Seila et al., 2001; Jimenez and Baldasano, 2004).

2.3 Photochemistry between VOCs and O_3

In general, ozone and NO_x are in the null cycle described in reactions (R1) and (R2) resulting in no net change in ozone (Sillman, 1999). Photolysis of NO_2 produces ozone when the oxygen atom formed in reaction (R1) rapidly recombines with molecular oxygen (O_2). Then NO and ozone are consumed in reaction (R2) to balance the reaction cycle.

$$NO_2 + h\nu \rightarrow NO + O \qquad (R1)$$

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (R2)$$

However, there are two situations that the ozone null cycle would be disturbed. Net ozone reduction occurs through reaction (R2) at nighttime because the rate of ozone formation reaction (R1) becomes zero without sunlight. The second situation is that the rate of ozone reduction reaction (R2) largely elevates in condition that large NO_x sources exists. In contrast, net ozone production is resulted. Consequently, the null cycle between ozone and NO_x will be destroyed, if daytime NO_x-VOC-CO chemistry is considered. Firstly, RO_2 and HO_2 radicals are produced by means of the reaction of hydrocarbon (RH) or CO with OH radical shown in reactions (R3) and (R4).

$$RH + OH + [O_2] \rightarrow RO_2 + H_2O \qquad (R3)$$

$$CO + OH + [O_2] \rightarrow HO_2 + CO_2 \qquad (R4)$$

These radicals generated from reactions (R3) and (R4) subsequently convert NO to NO_2 with molecular oxygen. These processes are described in reactions (R5) and (R6).

$$RO_2 + NO + [O_2] \rightarrow R'CHO + HO_2 + NO_2 \quad (R5)$$

$$HO_2 + NO + [O_2] \rightarrow OH + NO_2 \quad (R6)$$

RO_2 and HO_2 in reactions (R5) and (R6) replace O_3 in reaction (R2) to convert NO back to NO_2 in ambient air. The rate of ozone reduction (R2) decreases while photolysis of NO_2 (R1) keeps steady to form ozone. Thus, VOCs increase tropospheric ozone in daytime with NO_x and a plenty of sunlight in general.

The complex photochemistry related to the sensitivity of VOCs and NO_x to ozone production will be reviewed below, because VOC-sensitivity and NO_x-sensitivity are two very crucial factors to influence the mechanism of photochemical reactions that are more complex than the general view of tropospheric ozone formation presented in this section. In addition, it is crucial to understand the VOC composition of polluted air masses transported from upwind regions, as ozone formation during transport is also very sensitive to the mixing ratio of these two ozone precursors.

2.3.1 Sensitivity of VOCs and NO_x on ozone production photochemistry

Ozone formation is a highly nonlinear process varied with NO_x and VOCs (Sillman,

1999). The rate of ozone formation depends on different conditions that can be briefly divided into NO_x-sensitive, VOC-sensitive and NO_x-saturated regimes.

1. The NO_x-sensitive regime refers to situations in which a percent reduction in NO_x results in a significant greater decrease in O_3 relative to the same percent reduction in anthropogenic VOCs.
2. The VOC-sensitive regime refers to situations in which a percent reduction in anthropogenic VOCs would result in a significantly greater decrease in O_3 relative to same percent reduction in NO_x.
3. The NO_x-saturated regime refers specifically to conditions in which increased NO_x would result in lower O_3.

These three regimes should be carefully selected to apply in different types of situation, including urban, industrial, and rural, because different, even opposite, results could be obtained if a wrong sensitive regime was applied to models. Jimenez and Baldasano (2004) studied precursor controls in response to ozone production in some very complex situations. Effective ozone reductions were observed with decreasing either sensitive precursor in different situations according to the NO_x-VOC sensitive regime. They found that the NO_x-sensitive regime would be likely applied to low NO_x domains

and at low absolute precursor mixing ratios, such as in rural areas, while the VOC-sensitive regime was likely applied to high NO_x domains and at high absolute precursor mixing ratios, such as in urban and industrial areas, or in rural areas that were largely influenced by upwind polluted air masses. However, there are some specific situations that these two sensitive regimes are not applicable to explain the ozone production phenomenon. The NO_x-saturated regime is more appropriate than the VOC-sensitive regime when applying to regions in the remote troposphere and to large power plants. For example, limited VOCs were found surrounding a large power plant in which large NO_x source existed, so the VOC-sensitive regime cannot be applied.

Understanding atmospheric VOC compositions and mixing ratios in various environments of the PRD and Hong Kong could probably help in the classification of which sensitive regimes are likely to be applied in corresponding areas. Then, more effective and efficient emission control strategies could be formulated.

2.3.2 Temporal and spatial variations on the sensitive regimes

The dependence of sensitive regimes on temporal and spatial factors is illustrated in study on the history of an air mass. During the evolution of an air mass, the sensitive regime would change due to the different reduction rates of the two ozone precursors

and dilution on their mixing ratios with cleaner background air (Kleinman, 2005). The reactivity of NO_x was relatively higher than that of the average VOCs in tropospheric photochemistry (Duncan and Chameides, 1998), so that the ratio of VOCs to NO_x would increase during the evolution of an air mass. Fresh emissions from urban and industrial areas were typically characterized by the VOC-sensitive regime because low VOCs to NO_x ratios are usually measured in these polluted ambient atmospheres (Navazo et al., 2003). When polluted air masses were transported to downwind areas, VOCs/NO_x increased with faster reduction rate of NO_x relative to average VOCs. The chemical regime would convert from the VOC-sensitive in downtowns to the NO_x-sensitive in downwind areas (Kleinman et al., 2001). If the initial mixing ratio of polluted plume from downtown areas was high, the VOC-sensitive regime may also remain in downwind areas due to insufficient time for NO_x reduction by photochemical reactions and background air dilution.

2.4 The usefulness of observation based methods in air quality models

The application of air quality models (AQMs), including meteorological, emission and chemical transport models, to stimulate air quality assessment and air pollution events has become more prevailing and important in the field of atmospheric research and environmental policy over the past decades (Talbot et al., 1996; McCulloch et al., 1999b;

Fujita, 2001; Jimenez and Baldasano, 2004). However, use of unreliable inventories would lead to unsatisfactory results in various modeling studies. Other reasons for unsatisfactory modeling results include parameter uncertainties, model uncertainties, temporal and spatial dependence, and human error in the process of data input. Human errors will not be discussed here, while the other three causes and suggesting solutions will be briefly reviewed below.

2.4.1 Parameter and model uncertainties

A large difference between two different inventory records may cause completely different predicted results. Placet et al (2000) performed comparisons between two inventory records collected through different methods. Although the two inventories (the Interim Inventories and the Ozone Transport Assessment Group Inventories) were compiled in a similar period, significant differences in terms of total VOCs and NO_x emissions were discovered. The reason for this variation has not been explained yet. They also found that the difference of NO_x between USEPA and State of California estimates was associated with different definitions on “point sources” and “area sources”. In addition to different inventory collection methods, lack of consensus on specific terms in inventories could also cause serious errors for a wide range of inventory data that input to the models.

Quality Assurance/Quality Control (QA/QC) and specific conditions for determining inventory estimates and emission factors are very crucial for uplifting of the data quality and reducing the uncertainty of estimates. VOC source profile is among the input parameters for models. Traditional VOC database that have been used by atmospheric modelers called “SPECIATE” were compiled in the late 1980s. These VOC speciation data is already outdated due to the dramatic change in VOC compositions emitted in production processes and from product themselves within the last 20 years. As most manufacturing activities tend to emit VOCs, small uncertainties of VOC emission factor and speciation are likely to pose large uncertainties to model predications. In fact, very limited VOC speciation of industrial emission and industrial solvents had been obtained in the PRD in the past. This becomes a crucial factor that affects the reliability of modeling results of air quality in the PRD and Hong Kong.

Regarding the three major components of AQMs, meteorological sub-models appear to be better developed than emission and chemical transport sub-models. For example, the back air trajectory (HYSPLIT) model that is provided by NOAA Air Resource Laboratory on network is a prevailing and important tool to predict where air masses came from. This technique leads to our better understanding of the evolution of an air

mass. So, the effectiveness of ozone precursor control could be evaluated. In contrast to horizontal meteorological transport, vertical mixing and transport between different boundary layers pose larger uncertainties to meteorological modeling results because these processes greatly depend on temporal and spatial variations (Solomon et al., 2000).

The uncertainty of emission models could be revealed in the comparison of the chemical mass balance (CMB) results and emission inventories. For example, the contribution of vehicular emission determined by the CMB was larger than the proportion in current emission inventories whereas the CMB result for solvent-related emissions was smaller than the proportion in emission inventories (Watson et al., 2001). These failures are mainly caused by the quality of emission inventories and the uncertainty of the CMB method. The former cause that is subjected to parameter uncertainties has been discussed in the previous section. The limitations of CMB method were described in Hidy (2000). First, insufficient VOC source profiles to build a comprehensive picture pose failures to source apportionment which leads to incorrect comparison with inventories. Second, different sources probably share some common VOCs, but the CMB model could not successfully separate them. For example, dominant VOCs (ethene and benzene) are commonly contributed by both mobile and

industrial combustion. Third, the CMB model could not deal with sources of precursors capable of forming secondary reaction products in the atmosphere.

Chemical transport models involve many very complex reaction mechanisms, so model predictions greatly depend on the selected mechanisms and simplification of reaction. The previous discussion on VOC and NO_x chemical sensitive regimes demonstrates the significance of this area for chemical models. Tropospheric ozone production is a non-linear way varied with VOC and NO_x mixing ratios. Therefore, inconsistent results will likely be obtained from models if wrong chemical regimes are adopted in interested domains. The VOC-sensitive regime (the NO_x-saturated regime), for example, was likely to be applied in metropolis and urban areas. If the NO_x-sensitive regime was incorrectly used in models, NO_x reductions that could reduce ozone in low NO_x may elevate ozone mixing ratio in a high NO_x domain. In addition to sensitive regimes, assumptions and simplifications for chemical reaction calculation in models could speed up the calculation processes in the expense of model uncertainties increment (Jimenez and Baldasano, 2004). Carter and Atkinson (1989) developed the incremental hydrocarbon reactivity to describe the influence of ozone production based on their reactivities with hydroxide radical. In fact, VOCs are involved in different types of photochemical reactions other than reacting with OH. For example, highly reactive

ethene could fast react with ozone within several hours. As a result, the incremental hydrocarbon reactivity could not completely represent their practical photochemical reactivities in a complex environment, though more comprehensive maximum incremental reactivity has been continuously updated to provide a better simulation (Carter, 2000).

2.4.2 Temporal and spatial dependence

Air pollution is an international problem due to long-range transport of air pollutants, but it is also regional specific due to the difference in meteorological and emission parameters. In fact, both parameters are temporally dependent. For instance, the emission of biogenic VOCs varies with change in temperature and light intensity to cause daily and seasonal variations (Jobson et al., 1994; Riemer et al., 1998; Kang et al., 2001). This variation, subsequently, affects the formation of ozone. Anthropogenic VOC emission rate, related to fuel combustion and solvent utilization, also depends on temperature and hence may cause error of emission inventory. The mixing ratio of ozone precursors, VOC speciation and meteorological data are essential parameters for model input and they are very sensitive to spatial and temporal change. The previously discussed O_3-NO_x-VOC photochemistry also pointed to the importance of temporal and spatial variations for ozone production. Using an inappropriate chemical regime would

result in unreasonable or opposite modeling results.

While using models to study atmospheric ozone mixing ratio, one common uncertainty broadly recognized by researchers in recent years (Sillman, 1999; Kleinman et al., 2001; Jimenez and Baldasano, 2004; Kleinman, 2005) is that the reactivity of each VOC plays more significant roles than that of the total VOCs in model calculations. Kleinman (2005) pointed out that more diverse VOC emission mixture would worsen the modeling results in the narrow transition range. Nevertheless, the result of the two limiting cases would still be successfully predicted. Areas involving various industrial emissions generally showed higher uncertainties than other areas where emissions were dominated by narrow sources, such as mobile exhaust. In the PRD study, wide areas of the region, covering urban, suburban and rural areas, have been greatly affected by industrial emissions due to the fast industrialization in the past two decades. In addition, the atmospheric VOC composition and mixing ratio greatly depend on the distribution of industrial activities. It is essential to use more updated VOC source profiles of industrial activities to run air quality models in this complex domain. Also, understanding the VOC composition and mixing ratio of the PRD outflow are important to the study of the air quality of its downwind regions (e.g. Hong Kong).

2.4.3 Improvements of modeling uncertainty by incorporating observational based methods

Regarding the large number of uncertainties found in modeling based methods, there is a high motivation to apply observational based methods in environmental field study to improve modeling results. Field measurements are very important in the building up of emission database or emission profiles for a specific domain at the beginning of relevant studies, thus it is important to collect VOC source fingerprints from industrial and vehicular emissions in the PRD before using models to study the air quality.

The basic function of observation-based methods is to evaluate the accuracy of emission inventories. In the past two decades, many studies were conducted to do comparison between modeled and measured VOCs and NO_x as part of general model evaluation. In addition, uses of continuous emission monitors technique could greatly improve site-specific emission estimates from a major stationary source of NO_x such as power plants (Placet et al., 2000). Measuring mixing ratios of the two ozone precursors, especially NO_x, has significant contribution to modeling results. In contrast to NO_x, VOCs are more complex as it is a large group of chemical species with different evaporative rates and photochemical reactivities. A large number of VOCs could not be easily qualified and quantified in real time scale measurements. As a result, the emission

uncertainty of VOCs for modeling error remains large in complex areas where different types of VOC emission are involved. The PRD region is a complex domain in which industrialization leads to very complicated landuses everywhere.

Measuring these two ozone precursors provides a better understanding of the chemical regime for the highly non-linear ozone production process and their photochemical mechanisms can be more accurately modeled to reduce model uncertainties. With regard to the largest source of uncertainty in VOC-NO_x predictions from emission-based models, ambient VOCs and NO_x obtained in a field measurement were intentionally used as input parameters to model ambient ozone. Better modeling results were always obtained when removing unreasonable parameters from modeling input. Thus, the combination of observational based and model based methods is useful in the selection of input parameter and chemical mechanism in models. This provides more accurate predictions compared to the model based method only. Overall, more field measurement data and VOC emission profiles should be collected from industries and automobiles of the PRD, in order to improve the accuracy of the model predication of tropospheric ozone and air pollution events.

2.5 Technique of VOC sampling

Volatile organic compounds have different vapor pressures and photochemical reactivities, therefore an appropriate sampling method should be selected to cope with the properties of interested VOCs in this study. There are three common sampling methods which are broadly applied to collect VOCs from various ambient environments and emission exhaust: 1) air bag sampling, 2) absorbent tube sampling, and 3) canister sampling. These sampling techniques have their advantages and disadvantages and are adopted for different sampling purposes. The canister sampling method tends to be more popular in VOC measurement in recent years. These sampling methods are briefly reviewed below.

2.5.1 Air bag and adsorbent tube samplings

In general, Tedlar gas sample bag is used to collect VOC samples. A battery operated pump that was calibrated by a flow meter was used to draw air into the bag. This sampling technique was adopted for VOC measurements of indoor air quality and motorcycle exhausts (Srivastava et al., 2000; Tsai et al., 2003). The capacity of the gas sample bag is flexible and sampling volume can be conveniently adjusted on the basis of sampling environment and sampling purpose. However, a sample-loaded air bag is too bulky and can be easily damaged to cause leakage during transport. These

disadvantages make it difficult to transport the sample from a sampling site to a laboratory for chemical analysis. In addition, the storage of reactive VOCs cannot last for a long time, so chemical analysis should be carried out within several hours after the sampling. Thus, this sampling method is appropriate to collect air samples from a place close to a laboratory for chemical analysis.

In addition to the air bag sampling, an adsorbent tube was commonly used for sampling VOCs in air in the situations related to vehicular emission and industrial emission (Lin, 2001; Jo and Song, 2001; Cetin et al., 2003). A portable sampling pump, coupled with a flow meter, was used to draw air into an adsorbent tube. Its portable size makes it convenient to transport between a sampling site and a laboratory for chemical analysis. In addition, VOCs could be stably stored in the adsorbent tube for several days. Depending on different sampling environments, sampling volume could be adjusted to prevent the adsorbent tube from overloading. However, breakthrough of certain VOCs could possibly occur under adverse conditions such as high pollutant mixing ratio. Another disadvantage was that limited VOCs could be collected in each sampling. How many and which VOCs could be trapped in the adsorbent tube depend on the types of adsorbent packed. Jones et al. (1998) compared the canister and adsorption method for VOC sampling and showed that hexane, benzene and toluene were less suitable to be

collected by graphitized carbon black (carbontrap C) adsorbent tube. Thus, using multi-bed adsorbent tubes to collect more interested VOCs in air have become more popular in recent years (Wang et al., 2002; Wu et al., 2003).

2.5.2 Canister sampling

Since the early 1990s, the canister sampling become the most widely used sampling method for a wide range of atmospheric research in different countries (Sweet and Vermette, 1992; Blake et al., 1994; Cheng et al., 1997; Kang et al., 2001; Na et al., 2001; Lee et al., 2002; Gautrois et al., 2003; Guo et al., 2004b). This sampling method was also adopted to measure VOCs in large-scaled VOC characterization studies such as the global tropospheric experiment Pacific Exploratory Mission Tropics A and B (Colman et al., 2001), as it can collect and stably store a wide range of VOCs, including hydrocarbons, halocarbons and organic nitrates. According to the USEPA compendium method TO-14A (USEPA, 1999), which clearly describe the procedures of VOC sampling using specially prepared canisters, the canister sampling provides a number of advantages: convenient integration of ambient sample over a specific time period; ease of storing and shipping samples; analysis of samples from multiple sites with one analytical system; sufficient sample volume for QA/QC; and storage stability for many VOCs over periods of up to 30 days. Thus, the canister-based method is appropriate to

characterize VOC emission from industrial sources in the PRD due to a large variety of VOCs emitted from various industrial activities.

2.6 Past studies of VOC measurement

In the past decades, the impacts of VOCs on the air quality of various environments, including metropolitan cities, roadside, industrial areas and remote sites, had been assessed. Published studies in other developed countries show that many factors affects the results of VOC study, especially those regional specific ones such as, landuse planning, fuel and solvent composition, meteorological condition, types of industry and situation of development. It should be carefully considered whether their results can be appropriately integrated into the case of the PRD. Nevertheless, reviewing the past VOC studies could help to the understanding of the influence of these factors in the atmospheric VOC mixing ratio and their roles on the region. These relevant results could be useful in the interpretation of the results in this PRD study. In general, vehicular exhaust and industrial emission were the focuses of past studies, as they are the two major anthropogenic VOC sources. The following review mainly concentrates on VOC emissions from different industrial sources. Vehicular VOC emission is also reviewed to provide the knowledge of its impact on air quality.

2.6.1 VOC source profiles of vehicular emissions

In general, vehicular emission was found to be the most dominant VOC contributor in urban and roadside atmospheres (Derwent et al., 1995; McLaren et al., 1996; Sharma et al., 2000; Barletta et al., 2002). As the results of these measurement studies showed, ethene, ethyne, propene, i-butane, n-butane, i-pentane, n-pentane, benzene, toluene, ethylbenzene and xylenes emitted form automobile, were dominant in roadside and urban atmospheres. These abundant VOCs were consistent with VOC sources profiles of vehicular exhausts, gasoline and gasoline vapor which were developed to run CMB models (Doskey et al., 1992; Kenski et al., 1995; Fujita, 2001; Watson et al., 2001). Propane was also reported as one of the abundant VOCs in urban and roadside atmospheres in Latin American cities (Blake and Rowland, 1995; Cheng et al., 1997; Chen et al., 2001; Seila et al., 2001). Leakages from LPG fuelled vehicles and other uses are the leading source of propane in these cities. These results indicate that the type and composition of fuel made significant contribution to the composition of vehicular emission and atmospheric level.

A number of studies measured the mass concentration of VOCs in urban atmosphere and reported benzene-to-toluene ratios (B/T, wt/wt) as an indicator of VOC sources. Gee and Sollars (1998) compared B/T ratios of four Latin and two Asian cities. Similar

B/T ratios were found in the Latin cities (0.3-0.5) and that in US (0.5) (Sweet and Vermette, 1992), whereas lower ratios were found in the Asian cities (0.1). The major source of toluene and benzene in the urban atmosphere was vehicular emission. The difference of B/T ratio between the Latin and Asian cities was probably attributed to the aromatic contents of fuels. Similar to Latin cities, the ratios of 0.41 and 0.45 were measured in the microenvironments of trafficked roads and automobiles in UK, respectively (Kim et al., 2001b). Lower mean B/T ratios (0.11-0.23) were obtained in the urban atmospheres of Hong Kong (Lee et al., 2002; Guo et al., 2004a). Some studies indicated that the B/T ratio was largely affected by neighboring industrial point sources. Higher B/T ratio (1.25) was obtained when the monitoring site (E. St. Louis) was affected by a chemical plant (Sweet and Vermette, 1992). However, very low B/T ratio (0.06) was also contributed by industrial emissions from the Nylon-dyeing plant (Lin, 2001), like many industries, such as printing and painting, which heavy solvent consumption is involved. This would lead to abundant toluene in their emissions. In addition to vehicular emissions, industrial emissions play a significant role on atmospheric VOC compositions.

2.6.2 VOC source profiles of emissions from various industries

It is evident that VOC source fingerprints are very crucial data for performing source

apportioning and for the interpretation of atmospheric VOC compositions. In the validation study of VOC emission inventory using receptor modeling (Kenski et al., 1995), summarized VOC profiles of industrial sources from past studies were used as input parameters. These source profiles included refinery, architectural coatings, graphite arts, polyethylene production and coke oven. Relatively simple source fingerprints were utilized for solvent-related industrial activities and their profiles involved a small number of major VOCs. For example, toluene and m-/p-xylene were enriched in the emission of graphite arts (Scheff and Wadden, 1993). Similar VOC species were found in the source profiles of automobile paint shop in Mexico (Seila et al., 2001) and ink for printing in Korea (Kim et al., 2001a). In contrast, the VOC profiles of fuel combustion activities (vehicle exhaust and coke ovens) and refinery were more complex, with more VOCs species included. More importantly, the source fingerprint of polyethylene production indicated that ethene could largely be emitted from petrochemical industry other than fuel combustion of automobiles and industries. It is the reason why similar VOC markers for different categories of emission source would lead to overestimation or underestimation of either source category in CMB modeling results (Watson et al., 2001).

Printing is one of the target industries in this study, so similar studies were reviewed.

Wadden et al. (1995a, 1995b) determined the VOC emission rates and compositions for offset printing, because the impact of uncontrolled fugitive VOC emissions from printing on public health and urban air quality was significant. Corresponding VOC compositions measured in three printing shops included benzene, toluene, xylenes, ethylbenzene, hexane and a group of C_9 substituted aromatic hydrocarbons (Wadden et al., 1995a). The high toluene and xylenes levels were consistent with source fingerprints of graphite arts used in verifying VOC emission inventory by receptor modeling (Kenski et al., 1995). Similar VOC compositions were also obtained in the solvents of the three shops. It was evident that the process of press cleaning significantly contributed fugitive VOCs in the room due to the use of cleaning solvents

2.6.3 Ambient VOC measurements outside the PRD region

In Illinois, US, Sweet and Vermette (1992) studied 13 toxic VOCs in urban air. They found similar average airborne VOC mixing ratios in the study areas compared to other previous studies in the same city. The average urban mixing ratios were 2-10 times higher than the regional background level. Vehicular emission, gasoline evaporation and solvent emission were found to be the general sources of urban emissions of the target VOCs. Benzene level increased in some cases when polluted air masses were transported from the local industrial area. This is consistent with a chemical plant's

source emission profile obtained in the study (Sweet and Vermette, 1992). Benzene was the major component of emission together with small amounts of m/p-xylene and 1,1,1-trichloroethane. This result suggested that specific industrial sources had significant contribution to specific VOCs in the air within 1 or 2 km of the source.

In Canada, Cheng et al. (1997) placed the focus on seasonal variations (winter and summer) of VOCs at the downtown and industrial sites. The total VOCs of downtown sampling site was highest in winter and lowest in summer due to higher vertical mixing in summer and other meteorological conditions. However, no seasonal variation was found at the industrial site and the highest mixing ratio was found in summer because of strong emission strengths of neighborhood industrial sources. Propane, butane and i-pentane were the most abundant VOCs in both sites, but there were different emission sources largely contributed to them. Propane-fuelled taxis and automobiles contributed high propane level at the downtown site. Petroleum refineries and hydrocarbon storage tanks made significant contribution to these VOCs in the industrial atmosphere. Na et al. (2003) studied diurnal characteristics of VOCs in Korea. High VOC levels were observed in the morning and the evening. Lower mixing ratio was measured in the afternoon. This was due to higher emissions from the traffic during rush hour, dilution effects by an increase of the mixing depth during daytime and photochemical

destruction. In the afternoon, higher mixing ratios of toluene, ethylbenzene, m-/p-xylene and o-xylene may be due to the increase in evaporative emissions derived from the increase in ambient temperature and the solvent uses of painting, printing and dry cleaning activities (Kim et al., 2001a).

Understanding the global mixing ratios of long lifetime halocarbons could help in the analysis of VOC composition in industrial emissions, as trichlorofluoromethane (CFC-11), dichlorodifluoromethane (CFC-12), 1,1,2-trichloro-1,2,2-trifluoromethane (CFC-113), tetrachloromethane (CCl_4) and 1,1,1-trichloroethane (CH_3CCl_3) were commonly used as industrial solvents in many developing countries. Derwent et al. (1998) measured their North Hemisphere baseline mixing ratios from 1987-1996 and found that their baseline mixing ratios, except for CFC-12, dramatically decreased annually, because the uses of these halocarbons were gradually banned in various developed countries. However, CFC-11, CFC-12 and CCl_4 were still emitted from many developing countries such as China. It was believed that they were enriched in the ambient atmosphere of the PRD.

Talbot et al. (1996) studied chemical characteristics of continental outflow from Asia to the troposphere over the western Pacific Ocean using results from the Pacific

Exploratory Mission-West A. Direct and fresh outflow of industrial emissions from Japan and China was observed at altitudes below 2 km. Halocarbon compounds, such as CH_3CCl_3 and tetrachloroethylene (C_2Cl_4), which were used in various industrial activities were enhanced about threefold compared to aged Pacific air, and they were much reduced in outflows observed at higher attitudes. This study provided VOC tracers for interpretation of the VOC composition of industrial emissions in China at the beginning of early 1990s, when industrialization began in the Pear River Delta region and the Yangtze River Delta (YRD) region.

One long-time VOC measurement (Guo et al., 2004b) was carried out at the rural site of Lin'an in eastern China. They showed that vehicular emission and industrial emission from neighboring urban cities significantly affected the rural monitoring site. In addition, local biomass and biofuel burning also contributed much to the VOC composition of the rural site, as chloromethane that was mainly contributed by biomass burning (Lobert et al., 1999) was abundant there. A principal component analysis showed that 71% of the total VOC emissions were contributed from a combination of vehicle emissions and biofuel burning, while 11% of the total VOC emissions were from industrial emissions. The VOC contribution from industrial activities may be underestimated when using a single VOC, C_2Cl_4, as a tracer for industrial emission in the study, because many

industrial activities did not involve C_2Cl_4 in their emissions. Thus, it is essential to obtain more VOC source fingerprints of different industries and vehicular emissions in China, so that more accurate source apportionment could be performed.

2.6.4 Past VOC measurements in the PRD region

Limited VOC studies had been conducted in China and in the PRD region, especially those related to industrial VOC emission. Lack of such data poses difficulties to study the air quality. Wang et al. (2002), Chan et al (2003) and Zhao et al. (2004) put the focus on urban roadside and in-vehicle levels of benzene, toluene, ethylbenzene and xylenes (BTEX) in some PRD cities. Increases in BTEX levels were frequently observed in public transportation modes and roadside ambient atmosphere. These aromatic VOCs were mainly contributed by vehicular emissions, especially in Macau. With regard to other industrial active PRD cities (Guangzhou and Nanhai), Wang et al. (2002) found that benzene and toluene were emitted from different sources other than vehicle emissions. Industrial emissions were the potential emission sources of benzene and toluene in these PRD cities. However, a small number of measured VOCs in this study could not provide a comprehensive picture of industrial VOC emissions in the PRD.

Transportation of various VOC sources to a Hong Kong rural site, Tai O was examined

in 2001-2002 (Wang et al., 2005; Guo et al., 2006). High toluene levels were identified in PRD regional outflow and in Hong Kong local emissions. The possible reasons included evaporation loss of gasoline in Hong Kong and solvent uses in PRD industries. A mean T/B ratio (5.4 ppbv/ppbv) in the PRD regional outflows was similar to those measured in the urban atmospheres of Hong Kong (5.2 and 6.4) (Guo et al., 2004a). These similar ratios suggest that the PRD regional outflows frequently contributed high toluene levels to the general atmosphere of Hong Kong. In addition, about 300 canister samples were collected in 17 sampling locations throughout the PRD (e.g. Guangzhou, Dongguan Shenzhen and Jiangmen) and Hong Kong in 2000 by HKEPD. The result showed that atmospheric toluene levels have a large spatial variation. In general, the highest median toluene mixing ratios were observed in the atmospheres of industrial and rural areas, followed by urban and roadside ambient atmospheres (HKEPD, 2002). It implies that industry has become a significant toluene contributor in recent years due to the fast industrialization.

Chapter 3 Research Approach and Methodology

3.1 Research approach

In the United States and other countries, various statistical parameters, emission inventories, air quality models and mathematical models are commonly used to evaluate and predict the air quality and ozone event. Uncertainties discussed in the last chapter raise the importance of observation based results and updated inventories which can enhance the accuracy of modeling result. However, this weakness is more pronounce in the PRD, as its emission inventories and statistics have become outdated and inaccurate in view of the fast industrialization and loose environmental management policy in the past two decades. The full permeation of industrial activities throughout urban, suburban and rural areas of the whole PRD region increases the spatial complexity for air quality modeling. In addition, VOC profiles of industrial emission are specific in the PRD and are different from other countries. These limitations pose significant uncertainties to the air quality modeling result of the PRD and Hong Kong. The reliability of the air quality of the PRD (HKEPD, 2002) compiled by the model based methods will not be much improved until more accurate and updated model parameters are obtained.

After all, the first step to understand the air quality of the PRD is to use the observation based method to characterize VOC emissions from different anthropogenic sources. Hence, I have designed a more organized research approach to study the influence of industrial VOC emission in the PRD. A simple flow chart of the research approach is shown in Figure 3.1. The flow chart clearly describes the relationship between respective parts of research. In general, this research involves three field measurement studies and fact finding survey-type site visits.

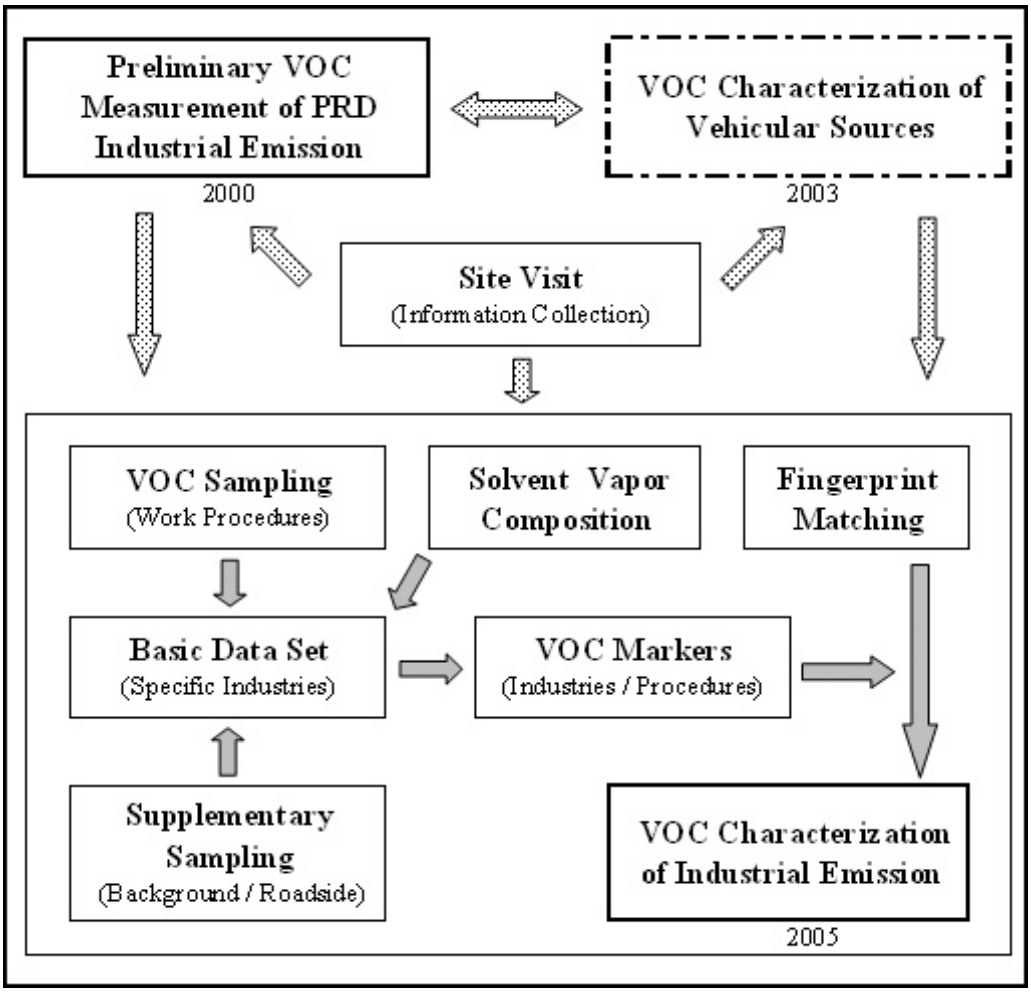


Fig. 3.1 Flow chart of the research approach

Characterization of VOCs in emission from industrial sources is the main aim of the research. The whole research plan and follow-up works are based on the result of a preliminary VOC measurement, which had been conducted for various industrial environments throughout the PRD region in 2000. This preliminary measurement is to achieve the objective 1 presented in Chapter 1.2. In this study, an initial scanning of VOC contribution from various high impact industrial emission sources had been performed. The measurement provides a yardstick for the selection of industries in further intensive studies.

The second step is to briefly characterize vehicular emission source. Automobile and industry are the two most important anthropogenic VOC sources. Understanding vehicular VOC emission in the region can provide more comprehensive VOC profiles to achieve objective 2 (Chapter 1.2). Research on vehicular emission is done by another research group's member. Thus, only one VOC sampling related to vehicular emission had been carried out in 2003 winter, in the second field measurement study. In addition, the VOC composition of industrial polluted air masses transported from inland PRD cities was examined.

A third field measurement study on VOC fingerprints for two selected PRD industries

was performed in January of 2005. The third step is to achieve the objective 3, so that the actual PRD industrial emissions could be examined.

Within the period between the second and third sampling studies, four site visits were conducted in various PRD cities and districts in 2004. The detail of these site visits is listed in Table 3.1. The first two visits were conducted in October to explore the development plan in Zhuhai and to understand the situation of industrial development in the whole PRD region. The phenomenon of industrialization and the category of industry in the PRD were observed in the five-day site visit trip. The experience and background information about industrial development in the PRD were utilized to analyze the VOC data collected in 2000 and 2003 studies, and to select industries for further studies.

Table 3.1 Description of the four site visits in the PRD

Date, Location and Purposes	
14-Oct-2004	
Understanding the plan of development in Zhuhai and the shift of industrial activities	
Zhuhai	1. Interview of the official of Zhuhai Environmental Protection Bureau (Zhuhai EPB) 2. Site visits to Zhuhai downtown and Nanping industrial area
26-Oct-2004 - 30-Oct-2004	
Seventy-two industrial sites were visited throughout seven active PRD cities. 1. Inspecting the shift of industrial activities from urban to suburban areas 2. Understanding the distribution of industrial activities in respective cities	
Zhuhai	One industrial area in downtown and three industrial areas in neighboring suburban towns were visited.
Zhongshan	Four industrial areas/towns were visited.
Jiangmen	Three towns were visited.
Foshan	Seven industrial areas/towns were visited.

Guangzhou	Four industrial areas/towns in its perimeters (Huadu, Conghua and Zengcheng) were visited.
Dongguan	Eleven industrial areas/ towns were visited.
Shenzhen	Two industrial areas in the downtown were visited.
30-Nov-2004	
Selecting appropriate industrial activities and sampling sites for next intensive study	
Qingxi, Dongguan	1. Six factories (Electronic, printing, plastic film and metal processing) were visited. 2. Various work processes of each industry were inspected for their VOC emissions.
09-Dec-2004	
Selecting appropriate industrial activities and sampling sites for next intensive study	
Shipai, Dongguan	1. Three factories (Electronic, plastic and toy) were visited. 2. Various work processes of each industry were inspected for their VOC emissions.

The objective of the other two site visits in November and December is to select appropriate industries for the VOC characterization study in 2005. In the light of the result of previous site visits, the quantity and diversity of industry in Dongguan were more involved than those in other PRD cities. Thus, Qingxi and Shipai, which are two towns in the suburban-industrial areas of Dongguan with more sample industrial mix, were targeted for industrial activity field study. Nine factories were visited and a variety of work processes were inspected. Finally, two industries in Qingxi were selected for intensive industrial VOC characterization sampling: electronic manufacture and printing. Electronic manufacture is one of the prevailing industries in Dongguan as well as other PRD cities according to the result of the five-day site visit trip. Printing is prone to emit VOCs in large quantities due to its heavy solvent and ink consumption and fugitive emission. In addition, both include one or two common work processes that are involved in other industries. For example, plastic molding and spray painting are

involved in toy and plastic film manufacturing. It is believed that the VOC emission from these common work processes is likely to pose significant impact to neighboring air quality.

3.2 Canister sampling

Air bag sampling, adsorbent tube sampling and canister sampling are the three common sampling methods to measure VOC levels. Their methodologies were reviewed in the last chapter. Among the three sampling methods, canister sampling is the most appropriate method for VOC measurement in the PRD, because a sample-loaded air bag is too bulky to transport between sampling sites and the laboratory for chemical analysis. In addition, there is a risk that leakage occurs during transport and storage. Limited VOCs that can be collected for quantification by an adsorbent tube is the major reason for rejection of this sampling method. It is more convenient to transport 2 l electro-polished stainless canisters compared to 6 l Summa canisters, and hence they were selected.

Prior to sampling, the canisters were cleaned and evacuated in the Rowland and Blake's Laboratory at University of California, Irvine (UCI). The procedures of canister preparation and pre-conditioning are described in Blake et al. (1994). The sampling

canisters were manufactured by the group and are currently a seventh generation design. Canisters are conditioned and tested regularly to ensure reliability. All reported gases have been tested for stability inside the canister.

In general, short duration time-integrated air samples are collected by a canister equipped with a vacuum gauge and a critical orifice flow controller. The flow rate is adjusted and calibrated in the air laboratory before taking to sampling sites, so that the flow controller can serve different sampling durations in accordance with particular sampling purposes. The flow controller connecting to a 2 l evacuated electro-polished stainless steel canister is calibrated against a digital flow meter (DC-Lite, BIOS, USA). At the beginning of sampling, the initial flow rate must be checked and within 5% error of the required flow rate, otherwise the critical orifice flow controller is needed to be calibrated again. The sampling height above ground level and the distance from the source depend on respective sampling environments and types of sample. After sampling, all canisters are shipped to the Rowland and Blake's Laboratory at UCI for chemical analysis.

3.3 Chemical analysis using multiple gas chromatograph (GC) system

A variety of compounds, including carbon monoxide (CO), methane (CH_4), halocarbons,

nonmethane hydrocarbons (NMHCs), are qualified and quantified in the chemical analysis of each sampled canister. Based on the category of sample (ambient air samples and source samples) and the purpose of study, the number and species of quantified compounds are different. In general, all these compounds are quantified in whole air samples. The chemical analyses of samples were carried out using the multiple GC system at the Rowland and Blake's Laboratory, UCI.

3.3.1 Carbon monoxide and methane

Anthropogenic sources of carbon monoxide and methane are mainly emitted from incomplete combustion. It is important to measure them when studying the impact of industrial and vehicular emissions on air quality. The details of the GC analytical system for CO and CH_4 analyses are described in Barletta et al., (2002). Carbon monoxide analyses were carried out using a gas chromatograph (HP 5890) equipped with a flame ionization detector (FID) and a 3 m molecular sieve column. The samples were injected and then converted to CH_4 in a catalyst (2% coating of nickel on Chromosorb G) after the chromatographic separation. Methane was also analyzed using an HP 5890 GC equipped with an FID detector. The samples were injected into an 1/8" stainless steel 0.9 m column packed with 80/100 mesh Spherocarb.

3.3.2 Halocarbons and nonmethane hydrocarbons

Halocarbons are tracer gases in the atmosphere. Due to their very low mixing ratios and different functional groups, another multiple GC analytical system is adopted to analyze them. A variety of nonmethane hydrocarbons (NMHCs) are simultaneously quantified. This multiple GC system comprises a cryogenic pre-concentrator and three GCs with five different detector/column combinations. Barletta et al. (2002) describe the configuration of the GC system. The cryogenic pre-concentrator was used to trap air sample in a stainless steel loop (1/4" O.D.) filled with 3 mm glass beads and immersed in liquid nitrogen (-196 ^{o}C). The pre-concentrated sample was subsequently vaporized with hot water and split into five different streams directed to three GCs (all HP 6890). These three GCs output to five detectors, including two electron capture detectors, two flame ion detectors and one quadrupole mass spectrometer (MS) detector (HP 5973). Additional analytical details are given by Blake et al. (1994) and Colman et al. (2001).

Smaller quantity of air sample was diluted and loaded to the same multiple GC system when performing the chemical analysis of direct source sample, as the mixing ratio of source sample was several order higher than that of the ambient air sample. While the sample of vehicular fuel and tailpipe exhaust were analyzed, the GCs with specific detector/column combinations used to analyze alkyl nitrates and halocarbons were

bypassed, as vehicular fuel and exhaust were mainly composed of hydrocarbons and CO.

3.3.3 Quality assurance and quality control (QA/QC)

The Blake and Rowland research group has performed trace gas analysis of whole air samples at UCI since 1977. In order to improve encountered difficulties due to a wide range of environments and air mass histories, and a correspondingly large range of compound abundances and ratios, new idea and new technology have been introduced to modify the procedure of analysis. The analytical system and procedures consistently yield accurate identifications of a wide range of unknown hydrocarbons and produce excellent quantitative results. The system described above is used to analyze samples collected in the atmosphere of industrial, urban and remote, and from tailpipe exhaust and fuel source. The routine calibration procedure and detailed quality control are described in Colman et al. (2001). The measurement precision, accuracy and detection limits for all reported species are briefly summarized in Table 3.2. All parameters of trace gases (alkyl nitrates and halocarbons) show larger variation and those of CO, CH_4 and NMHCs are less variable.

Table 3.2 The measurement precision, accuracy and detection limits of the system

	Detection limits	Precision	Accuracy
CO	5 ppbv	2 ppbv	5 - 7%
CH_4	2 ppbv	4 ppbv	1%
NMHCs	3 pptv	0.5 - 16%	5%
Alkyl nitrates	0.02 pptv	1 - 2%	10 - 20 %
Halocarbons	0.01 - 10 pptv	0.7 - 9%	2 - 20%

3.4 Analysis of industrial solvent vapor composition

Nine industrial solvents and one wastewater odor sample were collected from the electronic and printing factories during the third VOC study conducted in Qingxi in 2005. Chemical analysis for industrial solvent vapor compositions was carried out using GC (HP 6890A) with a MS detector (HP 5973) in the Air Laboratory of the Hong Kong Polytechnic University (HKPU). For the solvent analysis in the third study, 21 interested VOCs were quantized: dichloromethane, 1,1,1-trichloroethane, tetrachloromethane, trichloroethylene, tetrachloroethylene, 1-butene, n-butane, i-pentane, n-pentane, 3-methylpentane, n-hexane, methylcyclopentane, benzene, 2-methylhexane, n-heptane, methylcyclohexane, 2-methylheptane, toluene, ethylbenzene, p-/m-xylene and o-xylene.

3.4.1 Preparation of solvent vapor samples

Prior to preparing solvent vapor samples, all air bags and canisters were cleaned by repeated evacuating and filling of humidified zero air for five cycles. The solvent vapor sample was prepared by injecting 2 μl of liquid solvent into a 12 l air bag. The air bag

was filled with 10 l humidified zero air in two minutes. A hair dryer was used to evaporate the solvent droplet inside the air bag. 2 l of the solvent vapor sample was transferred from the air bag to an evacuated 6 l Summa canister with a flow controller and a vacuum gauge. It was then diluted in the 6 l canister to which humidified zero air was filled. The solvent vapor in the pressurized canister was released to another air bag, and the total NMHC mixing ratio of the vapor sample was measured by the NMHC analyzer (Thermo Environmental Instruments Inc. Model 55). The same dilution procedure was repeated until the range of the total NMHC mixing ratio was appropriate for GC analysis system. Finally, the sample-loaded canister was slightly pressurized before performing GC/MS analysis.

3.4.2 Chemical analysis using GC/MS

Prepared industrial solvent vapor samples were analyzed using a combined cryogenic concentrator (NUTECH 3350A, USA) with GC with MS detector. Four types of sample volume (50 ml, 100 ml, 150 ml and 250 ml) were loaded in accordance with the total NMHC mixing ratio of the diluted solvent vapor samples. Interested VOCs were trapped in the cryogenic concentrator with liquid nitrogen and were rapidly desorbed from -190 to 150 ^{o}C, followed by transferring vaporized analytes to GC/MS. A capillary column (J&W Scientific, DB-1 column, 60 m x 0.32 mm ID x 0.5 μm) was used with an

initial oven temperature of 30 to 80 ^{o}C at a rate of 5 ^{o}C/min, and then was raised to 125 ^{o}C at a rate of 15 ^{o}C/min. The oven temperature continuously increased to 160 ^{o}C at a rate of 7 ^{o}C/min (held for 3 mins), and was finally raised to 220 ^{o}C a rate of 5 ^{o}C/min (held for 6 mins). Three-point calibration curves of 21 interested species were obtained from the two canisters of standard gases (Spectra gases Inc., TO-14A and PAM gases), and their corresponding mixing ratios ranged from 6 ppbv to 30 ppbv. Regarding QA/QC, solvent vapor samples were analyzed in different mixing ratio levels in two separate GC runs. The relative average deviation of the percent composition of two runs in all cases was within ±10%. The method detection limit (MDL) of the VOCs which is defined as the product of the standard deviation of seven replicate measurements and a student t-test value of 3.143 (99% confidence for seven replicates) is listed in Table 3.3.

Table 3.3 The method detection limit (MDL) of target VOCs (ppbv)

dichloromethane	1.15	i-pentane	0.40	n-heptane	0.42
1,1,1-trichloroethane	1.14	n-pentane	0.75	methylcyclohexane	0.50
tetrachloromethane	1.10	3-methylpentane	0.58	2-methylheptane	0.32
trichloroethylene	1.22	n-hexane	0.52	toluene	0.64
tetrachloroethylene	1.01	methylcyclopentane	0.45	ethylbenzene	0.35
1-butene	0.68	benzene	0.44	p-+m-xylene	0.67
n-butane	0.84	2-methylhexane	0.38	o-xylene	0.41

Chapter 4 Characteristics of VOCs in Industrial (T1), Industrial-urban (T2) and Industrial-suburban (T3) Atmosphere of the PRD Region

4.1 Introduction

Since the past two decades, industrialization has led the Pearl River Delta (PRD) region to develop into the leading manufacturing center in South China. The industrial output value of the PRD had increased from 105 billion yuan (1990) to 1,287 billion yuan (2000) (HKMPRD Development Information Net). This dramatic industrial growth implies the enormous increase in the air pollutants, such as VOCs and NO_x, emitted from industrial activities. It is believed that VOCs from industry is one of the most important contributors to the deteriorating air quality of inland PRD and its perimeters. Automobile is the other important VOC contributor in the PRD.

Because of the lack of landuse planning and emission control, industrial activities including heavy polluting ones are everywhere. Fast industrialization leads to the spread of industrial activities from urban to suburban areas and even to rural areas. For example, there are 18,084 industrial organizations and approximately 20,000 small sized village- and privately- owned factories and mills within the Dongguan city. This is

about 15 times the number in 1980. This phenomenon will result in much bigger VOC contribution from industry compared to that from automobile in the coming years. The high spread of industrial emission increases the impact on air quality of the whole PRD region instead of only concentrating on industrial and urban areas.

In order to have a better understanding of the changes in atmospheric VOC mixing ratio and speciation resulted from increasing number and type of industry in the past two decades, a preliminary field VOC study was conducted throughout five industrial active cities of the PRD in 2000. The aim of this observation based study is to obtain a general VOC spectrum in industrial, industrial-urban and industrial-suburban atmosphere, and to compare the differences of VOCs in the three sampling environments. In addition, VOC profiles of some polluting industries were obtained. They could be utilized to select appropriate VOC tracers for model input and then employed to improve the accuracy of modeling result, as well as the effectiveness of emission control strategy. More importantly, the preliminary results can lead the way in the selection of representative industries for further intensive VOC studies.

4.2 Sampling design basics

Between 11 August and 19 September 2000, a total of 78 ambient air samples were

collected using evacuated 2 l electro-polished stainless steel canisters throughout five industrial active cities in the PRD region. Thirty-two air samples were collected in Dongguan on 11 and 12 of August 2000, and the remaining samples were collected in Foshan, Guangzhou, Jiangmen and Zhongshan between 7 September and 19 September. To fully evaluate the influence of industrial emissions on air quality, all samples were collected between 09:00 and 17:00 local time, when factories were under normal operation. In addition to the 78 ambient air samples, two samples were collected in two dense urban traffic roadsides in Guangzhou to examine the profile of vehicular VOC emission in the PRD.

4.2.1 Background on the PRD region in 2000

The Pearl River Delta (PRD) region is situated within Guangdong province in the southeast corner of China, and is comprised of nine smaller cities (Figure 4.1). Each smaller city consists of a densely populated and developed central city surrounded by its county-level cities, districts and towns. For example, Guangzhou is the center city of the Guangzhou city, whose area covers other relatively less developed county-level cities and districts such as Huadu, Conghua, Zengcheng and Panyu, to form the greater Guangzhou city. The total area of the PRD is about 42,000 km^2.

Fig. 4.1 Map of five target cities in the PRD, Guangdong, China

In order to understand the VOC speciation and examine the impact of industrialization on the air quality in the PRD, the five most industrially developed cities were targeted for sampling. Seventy-eight ambient air samples were collected throughout Dongguan, Foshan, Guangzhou, Jiangmen and Zhongshan focusing on three categories of sampling environment: industrial, industrial-urban and industrial-suburban, henceforth referred as T1, T2 and T3, respectively (Table 4.1). The number of samples collected in each city was determined according to their industrial activities and their significance to the PRD industrial production output. Dongguan, Foshan and Guangzhou are more industrially developed than Jiangmen and Zhongshan, and therefore a greater number of samples were collected there. Over 40% of the air samples were collected in Dongguan while about 20% of the samples were collected in both Foshan and Guangzhou. The sampling

locations were selected to study the characteristic industrial VOC emissions and the effect of these emissions on dense populated neighborhoods. As such, the urban city/town centers with heavy traffic, the commercial areas and residential areas with little industrial activities were excluded from this study. However, the increasing VOC contribution from automobiles is still a concern in the PRD, though it is not the focus in this study. For example, by June 2000, the number of private cars in Guangzhou totaled 116,587, which is 28.6% more than that at the end of 1999 (Guangzhou Yearbook, 2000). Hence, two additional roadside samples were collected in high density traffic urban areas to examine the effect of traffic emission on the urban atmosphere.

Table 4.1 Sample collection throughout the five cities based on the three categories of sampling environment

	Sample Collection			
Cities	Type 1 (T1)	Type 2 (T2)	Type 3 (T3)	Total
Dongguan	5	7	20	32
Foshan	3	7	5	15
Guangzhou	7	5	5	17
Jiangmen	0	3	4	7
Zhongshan	0	3	4	7
Total	15	25	38	78

T1: Sampling outside the boundary of a significant industrial point source or an industrial complex (industrial)

T2: Sampling in an open area mixed with industrial and urban areas (industrial-urban)

T3: Sampling in an open area mixed with industrial and suburban areas (industrial-suburban)

4.2.2 Classification of sampling environments

Ultimately, the sampling design enabled the collection of air characteristic of industrial

emissions and the study of the impact of these emissions on the region. The three categories of air samples collected are as follows:

Type 1 (T1) samples were collected next to either an industrial point source or a cluster of industries. Facilities associated with paper production, shoemaking, cement and ceramic manufacture and food processing were next to sampling sites, as well as a steel plant and a petrochemical plant. Steel plants and cement factories consume huge amount of fuel while the shoemaking industry involves heavy solvent utilization and they are selected for later discussion in this chapter. T1 samplings were focused on Dongguan, Foshan and Guangzhou, where a wide variety of industries are distributed throughout these cities. Speciations of VOCs for different industries were also obtained.

Type 2 (T2) samples were collected so as to measure the ambient air in town/city sectors with active industrial activities, in the five cities. The sampling sites were located in open areas to prevent direct influence from any point sources giving a sample with an integrated VOC composition typical of ambient urban air. For instance, the rooftops of government buildings and primary schools were selected. Industrial emission and vehicular emission were expected to contribute to the air pollution.

Similarly, Type 3 (T3) samples were collected in open areas and away from any point sources. However, these sampling sites were located in suburban and rural areas with industrial activities. These sites experienced less contribution by vehicular emissions than T1 or T2 sites, while the recent spread of industry into suburban and rural areas increased the role of industrial emissions on the speciation of atmospheric VOCs.

4.3 Result and discussion

Forty-two interested compounds were analyzed for each of the 78 PRD samples. Average mixing ratios and standard derivations for the three sampling environments were quantified for methane (CH_4), carbon monoxide (CO), 12 halocarbons, and 28 non-methane hydrocarbons (NMHCs) which include 13 saturated hydrocarbons, 9 unsaturated hydrocarbons and 6 aromatic hydrocarbons (Table 4.2). The total VOC value given at the bottom of the table is the sum of all 40 quantified VOCs, excluding the two most abundant species CH_4 and CO. In general, these two species are not included in the term of VOCs when used in this thesis. In addition, there were three VOC mixing ratio values removed in the overall statistical analysis. The omitted values were one toluene value (77.28 ppbv) in T2, one CCl_4 value (16.01 ppbv) in T2 and one CH_3CCl_3 value (9.33 ppbv) in T3. These three cases involved exceptionally high values measured in the corresponding category. They may be the result of sampling near

unknown sources.

Table 4.2. Mean mixing ratios of measured species [a]

	*T1 (n = 15)	*T2 (n = 25)	*T3 (n = 38)
CH4 (ppmv)	2.07 ± 0.14 [b]	2.02 ± 0.13	1.99 ± 0.11
CO (ppmv)	1.40 ± 2.38	0.73 ± 0.60	0.46 ± 0.19
H-1211 (pptv)	50.3 ± 65.1	33.9 ± 56.1	18.1 ± 13.5
CFC-11 (pptv)	285 ± 34.6	303 ± 89.7	314 ± 174
CFC-12 (pptv)	638 ± 115	619 ± 88.5	572 ± 22.4
CFC-113 (pptv)	156 ± 24.6	169 ± 18.2	169 ± 30.1
HCFC-22 (pptv)	334 ± 351	254 ± 94.8	275 ± 293
CH_3Cl (pptv)	764 ± 136	698 ± 111	699 ± 92.9
CH_2Cl_2 (pptv)	1020 ± 1560	674 ± 474	748 ± 656
$CHCl_3$ (pptv)	44.5 ± 42.7	46.4 ± 46.8	27.3 ± 8.45
CCl_4 (pptv)	125 ± 32.5	109 ± 7.18 [d]	110 ± 9.55
C_2Cl_4 (pptv)	115 ± 237	70.6 ± 70.4	162 ± 577
C_2HCl_3 (pptv)	68.2 ± 104	63.7 ± 84.3	69.3 ± 90.5
CH_3CCl_3 (pptv)	105 ± 111	84.3 ± 33.2	90.2 ± 41.1 [d]
ethane	2.33 ± 1.33	1.85 ± 0.60	1.40 ± 0.61
propane	3.74 ± 2.52	2.49 ± 1.36	2.08 ± 1.69
n-butane	2.56 ± 1.70	1.53 ± 0.88	1.27 ± 0.96
i-butane	1.57 ± 0.83	1.04 ± 0.55	0.82 ± 0.59
n-pentane	1.29 ± 2.26	0.52 ± 0.36	0.37 ± 0.24
i-pentane	2.24 ± 1.48	1.32 ± 0.67	0.86 ± 0.44
2-methylpentane	0.99 ± 1.15	0.48 ± 0.27	0.53 ± 0.68
3-methylpentane	0.56 ± 0.62	0.27 ± 0.17	0.35 ± 0.62
n-hexane	1.06 ± 2.09	0.36 ± 0.25	0.53 ± 0.90
2-methylhexane	1.12 ± 1.48	0.59 ± 0.66	0.51 ± 0.38
3-methylhexane	0.89 ± 1.14	0.46 ± 0.50	0.40 ± 0.32
2,3-dimethylpentane	0.28 ± 0.36	0.16 ± 0.19	0.13 ± 0.11
n-heptane	1.37 ± 2.33	0.44 ± 0.56	0.38 ± 0.32
ethene	5.08 ± 3.84	2.56 ± 1.29	1.98 ± 1.15
ethyne	6.04 ± 3.01	3.96 ± 1.48	3.12 ± 1.74
propene	1.10 ± 0.76	0.57 ± 0.32	0.39 ± 0.24
trans-2-butene	0.33 ± 0.31	0.16 ± 0.12	0.10 ± 0.11
cis-2-butene	0.26 ± 0.23	0.14 ± 0.09	0.08 ± 0.09
1-butene	0.38 ± 0.33	0.20 ± 0.13	0.12 ± 0.09
i-butene	0.42 ± 0.31	0.27 ± 0.15	0.21 ± 0.21
1,3-butadiene	0.17 ± 0.10	0.14 ± 0.21	0.09 ± 0.12
isoprene	0.63 ± 0.33	0.37 ± 0.17	0.52 ± 0.71
benzene	2.75 ± 1.70	1.97 ± 1.06	1.30 ± 0.82
toluene	13.54 ± 11.78	11.51 ± 11.56 [d]	7.30 ± 5.38
ethylbenzene	1.98 ± 3.48	0.91 ± 0.98	0.82 ± 0.74
o-xylene	1.19 ± 1.44	0.71 ± 1.05	0.53 ± 0.52
m-xylene	3.58 ± 7.08	1.61 ± 2.22	1.08 ± 1.21
p-xylene	1.33 ± 1.80	0.92 ± 1.65	0.57 ± 0.64
Total VOCs [c]	62.52 ± 40.16	40.23 ± 21.17	31.16 ± 13.76

[a] Mean mixing ratio in ppbv, unless otherwise specified
[b] Mean ± Standard deviation
[c] CH_4 and CO are excluded

[d] One value each is excluded in the calculation of the mean of CCl_4, CH_3CCl_3 and toluene, due to their exceptionally high values.
* T1, T1 and T3 refer to industrial, industrial-urban and industrial-suburban samples, respectively (Table 4.1).

4.3.1 General VOC characteristics in T1, T2 and T3

The average mixing ratios of the four VOC groups are given for each category in Figure 4.2. Aromatic, saturated and unsaturated hydrocarbons were the three major groups of VOCs, followed by halocarbons. The lowest mean ratio of saturated hydrocarbons to unsaturated hydrocarbons (1.39) and with the smallest standard deviation (0.33) was observed in T2. This is consistent with greater vehicular emissions in the more developed urban areas as opposite to a larger contribution from fresh industrial emissions in T1, and a smaller vehicle density in T3. The unsaturated hydrocarbons (ethene, ethyne and propene) were frequently the dominant component in vehicular exhausts and on roadsides in the PRD like elsewhere (Derwent et al., 1995; McLaren et al., 1996; Watson et al, 2001). The PRD roadside spectrum will be discussed later. Additionally, alkane mixing ratios were elevated in T1 areas, most likely as a result of solvent use or by-product emissions and vaporization from poorly controlled industrial facilities. Relatively smaller traffic densities at suburban sites decreased olefins in T3. Thus, similar ratios, were obtained in T1 (1.54 ± 0.88) and T3 (1.56 ± 0.79) and these were higher than in T2 (1.39 ± 0.33).

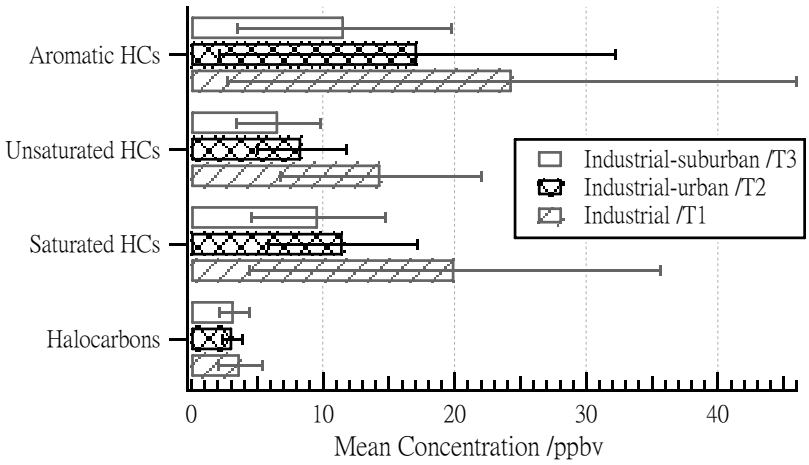


Fig 4.2 Mean mixing ratios of the different VOC groups in the three sampling environments

The maximum average mixing ratio of each VOC group occurred in T1 (Figure 4.2), where ambient air was directly influenced by local industrial sources. Halocarbons, including trichlorofluoromethane (CFC-11) and dichlorodifluoromethane (CFC-12), which have been banned in many developed countries, were still used for industrial purposes in the PRD. The highest total halocarbon mixing ratio was measured in T1. Lower mixing ratio was found in T3 and the lowest mixing ratio was found in T2. The major reason for why the NMHC pattern (T1 > T2 > T3) was different from that of halocarbons (T1 > T3 > T2) is that halocarbons are more specific to particular industrial and non-industrial applications while a wide range of NMHCs are commonly involved in industrial related emissions.

Table 4.3 Mean mixing ratios (ppbv) of the ten most abundant VOCs among the three categories

	*T1	Mean	*T2	Mean	*T3	Mean
1	toluene	13.54	toluene	11.51	toluene	7.30
2	ethyne	6.04	ethyne	3.96	ethyne	3.12
3	ethene	5.08	ethene	2.56	propane	2.08
4	propane	3.74	propane	2.49	ethene	1.98
5	m-xylene	3.58	benzene	1.97	ethane	1.40
6	benzene	2.75	ethane	1.85	benzene	1.30
7	n-butane	2.56	m-xylene	1.61	n-butane	1.27
8	ethane	2.33	n-butane	1.53	m-xylene	1.08
9	i-pentane	2.24	i-pentane	1.32	i-pentane	0.86
10	ethylbenzene	1.98	i-butane	1.04	ethylbenzene	0.82

* T1, T1 and T3 refer to industrial, industrial-urban and industrial-suburban samples, respectively (Table 4.1).

The ten most abundant VOCs are tabulated in Table 4.3. Toluene was the most abundant species and was significantly higher than the second most abundant species. This observation was similar to the result of HKEPD (2002). Most of the median toluene values were the highest for 15 PRD sampling sites in 2000. In addition to the increase in toluene from vehicular emission, it is also the major component of many industrial solvents and paints in the PRD (He et al., 2002) and other countries (Scheff and Wadden, 1993; Kim et al., 2001a; Seila et. al., 2001). Printing, shoemaking, toy manufacturing and electronic industries that use large amount of solvent and paint prevailed in the PRD and these industrial activities accounted for the high abundance of toluene and m-xylene (He et al., 2002), particularly in T1. Ethane, ethene, ethyne, propane, i-pentane, n-butane, toluene, benzene and m-xylene observed among all three categories were

associated with fuel combustion emissions, gasoline evaporation, LPG leakage and solvent usage (Doskey et al., 1992; Scheff and Wadden, 1993; Chen et al., 2001; Watson et al., 2001). The indication of this study is that these potential sources are likely to affect a wide area of the PRD with the spread of industrial activities over the whole PRD. In addition, as discussed later, gasoline evaporation from vehicles, in particular motorcycles and LPG leakage from refueling centers and domestic usages were found to contribute to atmospheric propane, butanes and i-pentane mixing ratios.

4.3.2 The impact of industrial emissions

The average mixing ratios of NMHC (ppbv) and CO (ppmv) measured in the three categories are plotted in Figure 4.3. Their average mixing ratios generally followed the trend: T1 > T2 > T3. Industrial emissions made significant contribution to the elevated average mixing ratios of NMHCs and CO. Fresh emissions from industries resulted in the maximum average mixing ratios measured in T1. Three serious polluting industries with certain VOC emission were selected for discussion. They were found to contribute greatly to several species in the nearby ambient atmosphere (Figure 4.4).

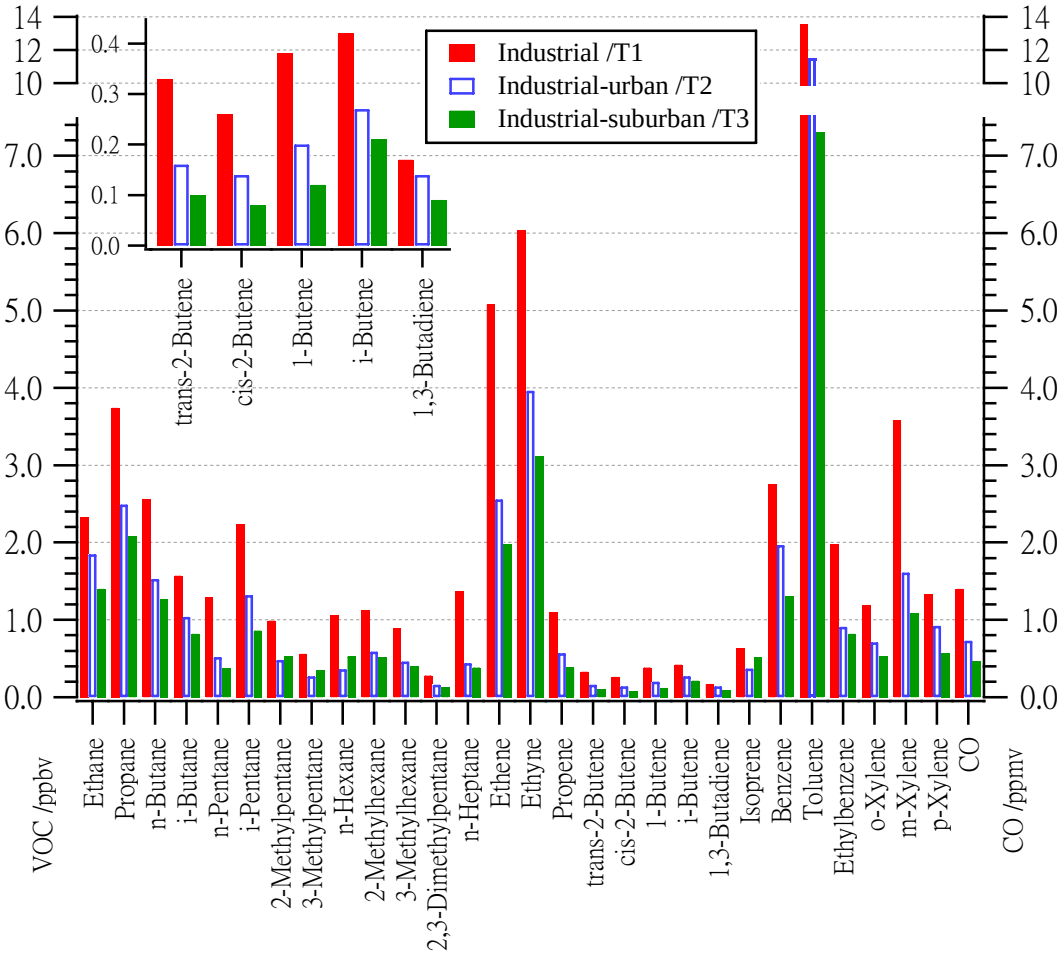


Fig. 4.3 Mean mixing ratios of NMHC (ppbv) and CO (ppmv) among the three categories of sampling environment

Shoemaking is a major industry in Dongguan and its factories widely spread over the city. Toluene, 2+3-methylhexane, n-hexane, n-heptane, ethylbenzene and xylenes were found to be enhanced in the sample collected outside shoemaking factories where their products are immersed in these solvents overnight to enhance the oil-resisting property. These VOCs can easily escape into ambient air when the solvent evaporates. Toluene and n-hexane are major components in various solvents which are commonly used in shoemaking industries and other prevailing industries involving furniture, toy and

leather manufacturing, printing and electronic production (He et al., 2002).

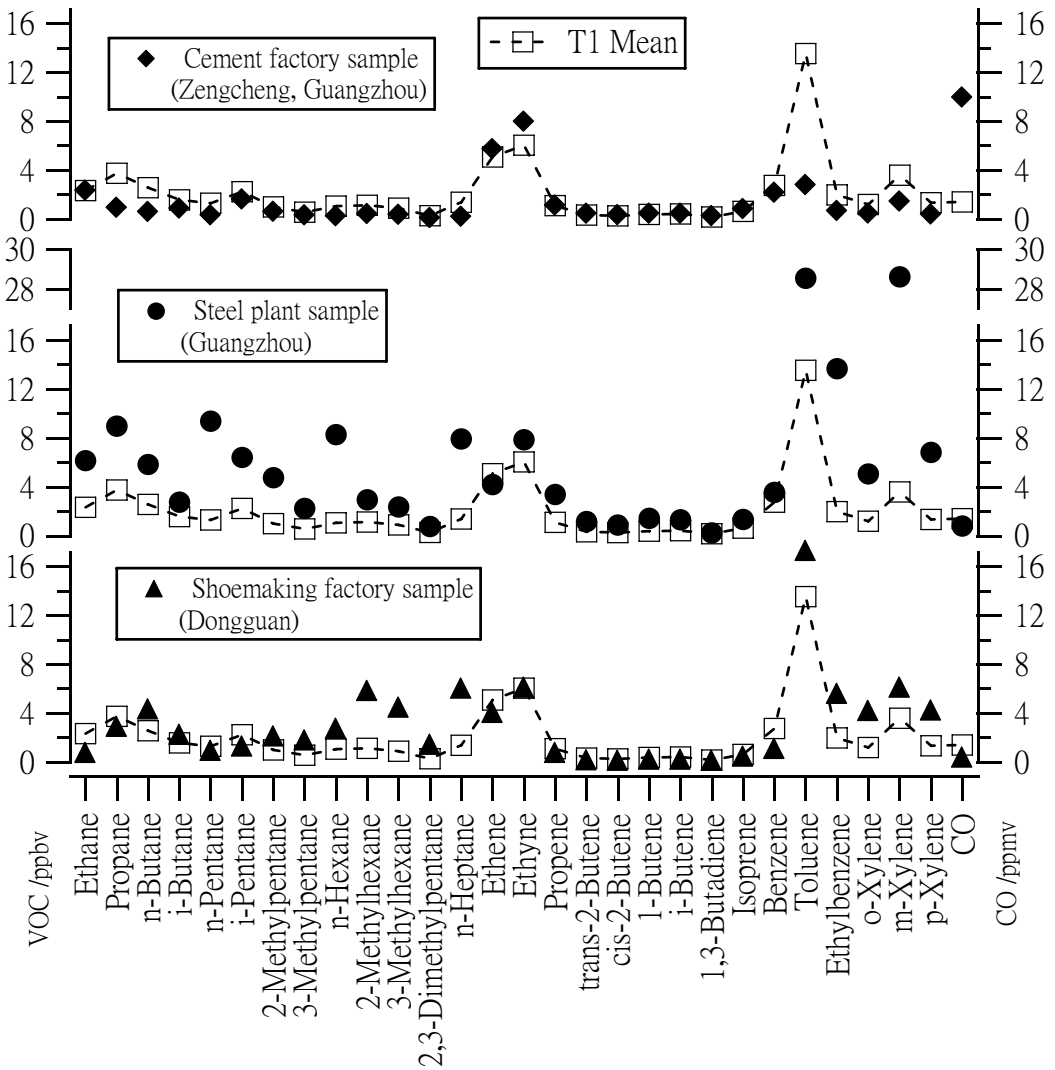


Fig. 4.4 Three ambient VOC profiles neighboring polluting industries were compared to VOC mean mixing ratios in T1

Cement industries are concentrated in Zengcheng of Guangzhou. Relatively high mixing ratios of ethene and ethyne were measured outside cement factories that consume huge amounts of fuel used in industrial boilers. Extremely high CO outside

many cement factories was associated with low-temperature fuel combustion and poor ventilation systems. In one T1 sample collected outside a large steel plant in the urban region of Guangzhou, almost all NMHC mixing ratios, especially aromatic hydrocarbons, were much higher than the mean mixing ratios of the corresponding species in T1, but CO was lower than the mean in T1. Chattopadhyay et al. (1996) also found higher benzene mixing ratios inside three steel plants, relative to the surrounding residential areas. Significant NMHCs were produced by the heating and cooling cycles in the plants' coke ovens. CO levels comparable to the residential areas were found because there is sufficient oxygen input to the coke ovens, which led to complete combustion in high temperature. Hence, incomplete combustion product of CO was greatly reduced in the steel industry compared to the cement industry, which requires lower oven temperature for cement production.

The T1 sampling sites are in the proximity of industrial activity, so direct emissions from major industries highly contribute to the neighborhood atmosphere. This leads to spatial variation of the VOC spectrum in the five PRD cities and the high standard deviations in several VOCs.

4.3.3 The impact of vehicular emission

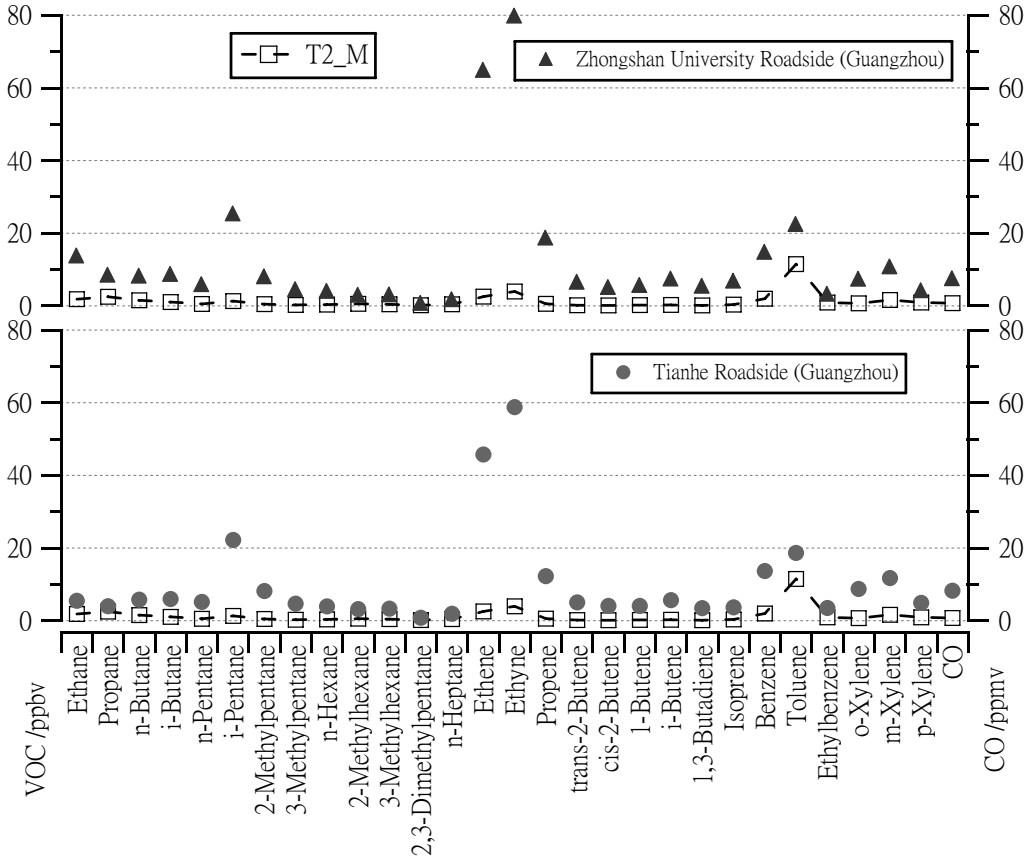


Fig. 4.5 Two extra vehicular source samples compared to the mean in T2

It is hard to separate the industrial and vehicular contribution in the industrial-urban atmosphere. Hence, two urban roadside samples were collected to examine the impact of vehicular emission. Figure 4.5 shows the patterns of the two samples and the mean values in T2. It was observed that the mean mixing ratios for the unsaturated and aromatic hydrocarbons at the roadside sites were much higher than the mean levels in T2. Several important vehicular emission markers such as toluene, and especially ethene and ethyne, exhibited substantially higher mixing ratios in the roadside samples. This

illustrates the high contribution from vehicular emission near urban centers with heavy-traffic and few industrial activities.

In the five PRD cities, motorcycles were very popular either in urban or suburban areas due to its low cost and mobility. The number of motorcycles was dominant in automobiles with about 75% of all automobiles being motorcycle. In addition, poor maintenance and poor control on motorcycles lead to high VOC emission and significant adverse impact on the ambient air quality. Tsai et al. (2003) investigated the emissions of VOC from motorcycle engine exhaust at different driving modes. The result showed that i-pentane, toluene, 2-methylpentane, 3-methylpentane, n-pentane and benzene were frequently emitted from exhaust gas of motorcycles under the whole driving cycle. It was observed that these motorcycle exhaust-related VOCs also prevailed in the two roadside samples.

The ranking of the six most abundant VOCs in roadside samples (ethyne > ethene > i-pentane > toluene > propene ≈ benzene) and their corresponding counterparts in T2 (toluene > ethyne > ethene > propane > benzene > ethane) were further examined (Figure 4.5). Several VOC contributors, such as background dilution and photochemical reaction play an important role in their rankings. The mean ratios of benzene to toluene

(B/T, wt/wt) in the three sampling environments and roadside samples are tabulated in Table 4.4. The mean B/T ratio in the T2 category (0.24) was 2.3 times lower than that in the roadside sample (0.59). A similar mean B/T ratio (~0.6) was observed in 25 Chinese cities' roadside in 2001 (Barletta et al., 2005). Furthermore, in T3 where the contribution from vehicles further decreased, the B/T ratio decreased further to 0.22, indicating high toluene emission from industrial activities rather than emission from automobiles in T2 and T3. Similar B/T ratios in the three selected environments with large standard deviations and ranges suggest that toluene were very commonly used in industrial activities and varied with the density and type of industry in that area. Unlike T1 that was affected by dominant clustered point sources, some samples in open areas (T2 and T3) were influenced by scattered industries using heavy toluene-containing solvents (He et al., 2002).

Table 4.4 Mean ratios of benzene to toluene (B/T, wt/wt)

Types	Mean ± S.D.	Range
*T1	0.27 ± 0.18	0.03 - 0.66
*T2	0.24 ± 0.18	0.04 - 0.76
*T3	0.22 ± 0.17	0.03 - 0.77
Roadside	0.59 ± N.A.	0.56 - 0.62

* T1, T1 and T3 refer to industrial, industrial-urban and industrial-suburban samples, respectively (Table 4.1).

We further noted that propane was not high in the roadside air but ranked fourth in T2. LPG vehicles were small in the PRD in 2000. Thus, propane was not emitted from LPG

leakage from automobiles. It was believed to be released from leakage of natural gas and LPG from refuelling centers and domestic usages. In the PRD region, the total LPG consumption was nearly $3.5x10^6$ tones in 2000 (Tian, 2002) and LPG was mainly consumed by heating and cooking.

4.3.4 Anthropogenic isoprene in industrial emissions

In general, isoprene is dominant in rural areas as it is emitted from a variety of vegetation (Jobson et al., 1994; Riemer et al., 1998). However, isoprene was also identified as an anthropogenic hydrocarbon, a good correlation with the well known combustion product of 1,3-butadiene, especially when air samples were collected next to a roadside (McLaren et al., 1996). In this study, linear coefficients (r^2) between isoprene and other quantified unsaturated hydrocarbons and benzene are listed in Table 4.5. The correlation between isoprene and 1,3-butadiene was poor in our study and it indicated that their major sources were not vehicular exhaust. However, isoprene in T1 (Figure 4.6) had much better correlations with the six combustion products (propene, trans-2-butene, cis-2-butene, 1-butene, i-butene and 1,3-butadiene) than in T2 and T3. Relatively photochemically stable hydrocarbons, such as ethene, ethyne and benzene, had no correlations to isoprene as they have longer atmospheric lifetimes and their mixing ratios are affected by the transport of air pollutants. The fair correlations

between isoprene and the six short lifetime unsaturated hydrocarbons in T1 indicate (that) they were emitted from local sources. The correlation between isoprene and the six shorter lifetime combustion VOCs was low in T2 and no correlation was observed in T3. This indicates a shift in the source of isoprene from combustion (T1) to biogenic emissions (T3). Weaker correlation observed in T2 is attributed to dilution with distance from industrial emissions and biogenic sources, and the removal of these shorter lifetime hydrocarbons by photochemical reaction. No correlation to these combustion VOCs were found in T3 where isoprene was contributed by biogenic sources. Lower isoprene in T3 and T2 than in T1 was also a result of its increased photochemical reactivity and faster reduction rates in NO_x-rich conditions (Carter and Atkinson; 1989; Kleinman, 2005). It is anticipated that the contribution of isoprene from combustion sources will increase and the contribution from biogenic sources will decrease in T3 in the coming years, because the farmland near T3 is giving way to housing and factory in recent years.

Table 4.5 Linear correlations between isoprene and other quantified combustion VOC products (r^2)

	ethene	ethyne	propene	trans-2-butene	cis-2-butene	1-butene	i-butene	1,3-butadiene	benzene
*T1	0.01	0.07	0.41	0.55	0.53	0.51	0.49	0.20	0.05
*T2	0.00	0.00	0.01	0.14	0.18	0.03	0.06	0.03	0.00
*T3	0.01	0.00	0.01	0.01	0.01	0.01	0.00	0.00	0.00

* T1, T1 and T3 refer to industrial, industrial-urban and industrial-suburban samples, respectively (Table 4.1).

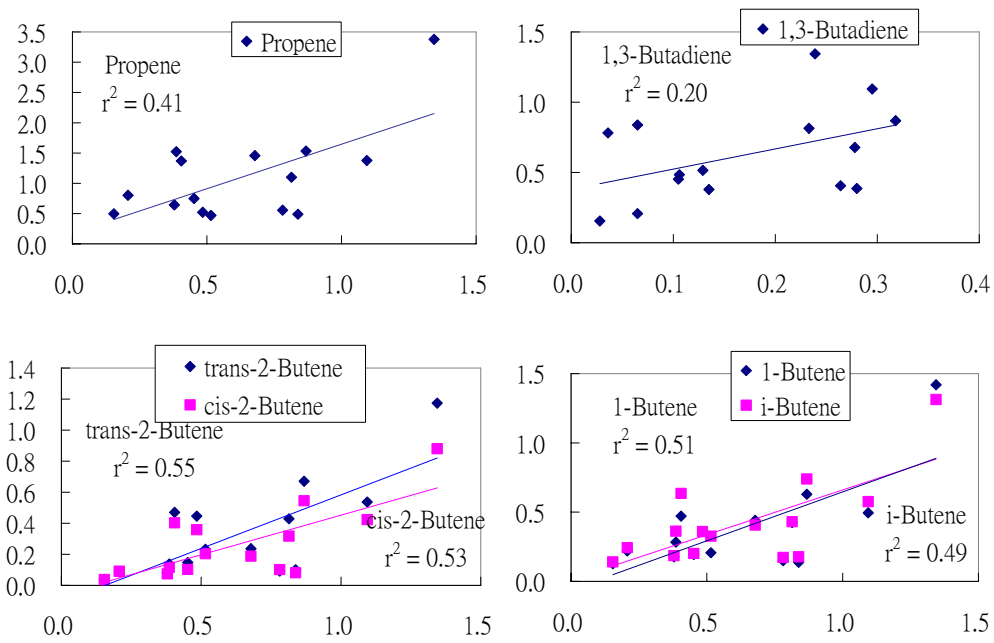


Fig. 4.6 Correlation between isoprene to the six combustion products in T1

4.3.5 <u>High hexane level in industrial-suburban atmosphere</u>

The n-hexane levels were the highest in T1 and slightly higher in T3 than in T2 (Table 4.2). In addition, their standard deviations were found higher in T3 than in T2. Hexane is a common component in architectural coatings-composite solvents (Fujita et al., 1995) and paint thinners. Solvent emission from industrial usage contributed to the high n-hexane level in T1. Enhancement of hexane in T3 relative to T2 could be related to the rapid industrialization and residential development in the PRD in recent years, which had extended to the suburban areas where land is cheaper and readily available. So it may lead to higher contribution and spatial variation in suburban and rural areas where large housing estates and factories kept poping-up.

4.3.6 Characteristics of halocarbons

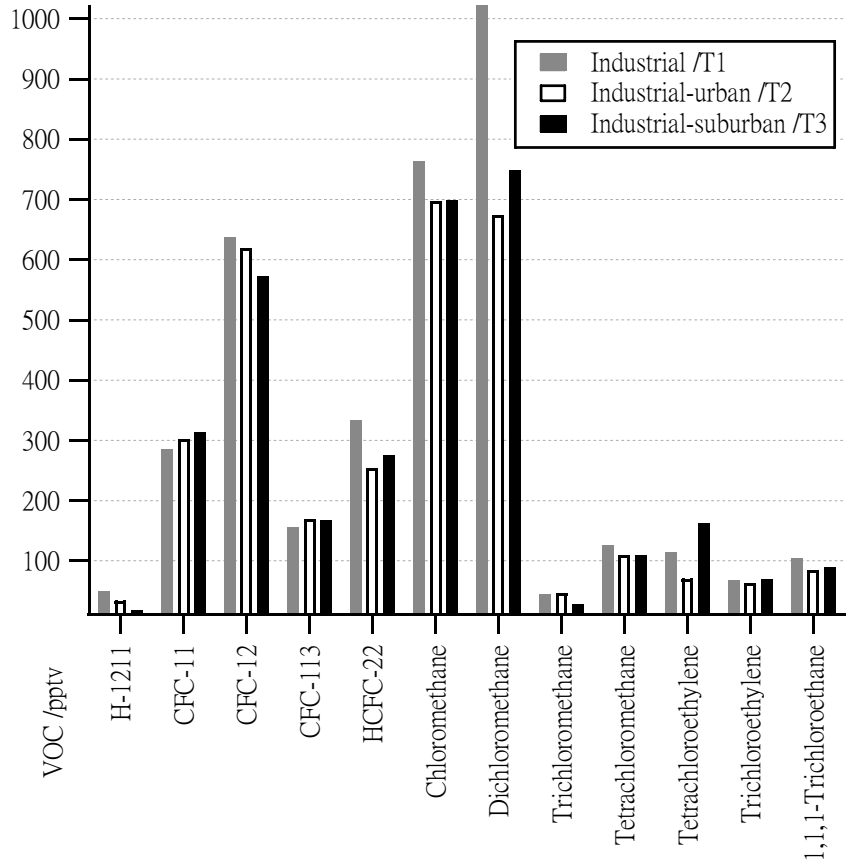


Fig. 4.7 Mean mixing ratio of halocarbons

The average mixing ratios of the halocarbons are shown in Figure 4.7. Major industrial emission characteristics were frequently observed in T1. The mean mixing ratios of CFC-12, chlorodifluoromethane (HCFC-22), chloromethane (CH_3Cl), dichloromethane (CH_2Cl_2), tetrachloromethane (CCl_4), and 1,1,1-trichloroethane (CH_3CCl_3) were the highest in T1 as these compounds are typically used as industrial solvents, cleaning agents and refrigerants for air conditioner. In contrast, CFC-11 had the highest mean mixing ratio with the highest standard deviation in T3.

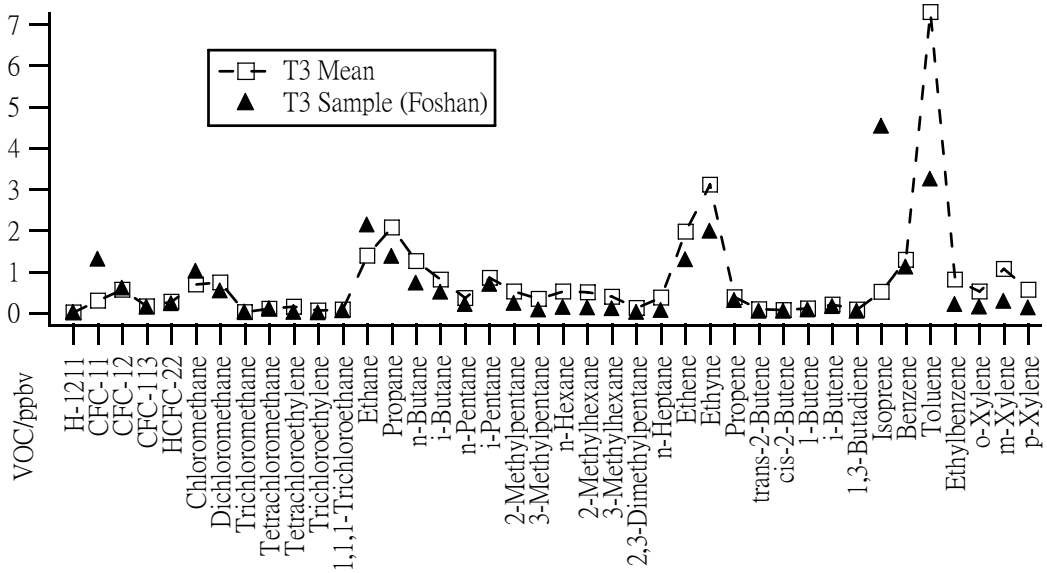


Fig. 4.8 Comparison between T3 mean to one T3 sample suspected to be influenced by the application of insecticide in suburban areas

Among the T3 sample set, one sample collected in Foshan had high mixing ratio of CFC-11 (1.31 ppbv), about four times higher than the mean in T3. This special case was suspected to be influenced by a neighboring polluted plume. The atmospheric mixing ratio of selected VOCs (NMHC and halocarbons) of the plume is plotted in Figure 4.8. It can be seen that short-lifetime species isoprene that is mainly emitted from neighboring plants and vegetations at this suburban site was found to be about eight times higher than its T3 mean. One of the reasons for the higher CFC-11 level in the Foshan sample may be due to the application of insecticide, as CFC-11 is often used as propellant of insecticide in the PRD. Pesticide application contributed 3.09% of the total VOCs (tonnes/yr) in the PRD in the 2000 annual emission inventory (HKEPD, 2002).

Slight elevation of CFC-11 with increased isoprene was also observed in a few other samples of T3. The other VOCs in the plume were lower than the T3 mean.

The two most abundant halocarbons were CH_3Cl and CH_2Cl_2 (Figure 4.7). Their highest mean mixing ratios in T1 could be the result of evaporative emissions from solvent utilization in factories. For example, CH_2Cl_2 are common components of metal degreasers and paint strippers (McCulloch and Midgley, 1996), and CH_3Cl are used as extractants and low-temperature solvents for organic synthesis. The other source of CH_3Cl is biomass/biofuel burning (McCulloch et al., 1999a). One recent VOC study were conducted at a rural site in Lin'an, which is a county close to another China's leading economic and industrial region, the Yangtze River Delta. This study reported that the high mixing ratio of CH_3Cl (1.29 ppbv) was due to biofuel/biomass combustion emission (Guo et al., 2004b). Much lower CH_3Cl mixing ratio (0.76 ppbv) in T1 indicated that CH_3Cl emission in the PRD was relatively less important in terms of the contribution from biofuel/biomass burning to the global atmospheric CH_3Cl mixing ratio. The mean CH_2Cl_2 mixing ratios had the largest variation ranging from 674 pptv (T2) to 1020 pptv (T1). Apart from general industrial uses for degreasing and cleaning purposes, CH_2Cl_2 was also used in chemical processing to manufacture pharmaceutics, especially in suburban Dongguan, where pharmaceutics is one of the two major

developing industries. In general, CH_2Cl_2 can also be used as a tracer for industrial emissions associated with solvent use and pharmaceuticals in the PRD, because these industries have been drastically increasing since the 1990s (Talbot et al., 1996). There is less variation in CH_3CCl_3 mixing ratio, which ranged from 84.3 pptv (T2) to 105 pptv (T1). CH_3CCl_3 had been suggested in the 1991 Asian Continental-North Outflow study as a tracer for industrial emission.

Tetrachloroethylene (C_2Cl_4), trichloroethylene (C_2HCl_3), CH_2Cl_2 and HCFC-22 were found higher in T3 than in T2. Bromochlorodifluoromethane (H-1211) and trichloromethane ($CHCl_3$), were in very low mixing ratio in the three sampling environments. Most of them were only used by specific industries and were not broadly used. Their abundance only affects residences nearby. C_2Cl_4 is a common dry cleaning solvent (McCulloch and Midgley, 1996). Recently, there was a tendency to perform dry cleaning of clothing in massive dry-cleaning centers with centralized emission control facilities in suburban/rural areas rather than in individual retail shops in the cities. This was due to the tightening of dry-cleaning emission control standards by the relevant authorities such as the Environmental Protection Bureau. Thus, large variations in respective halocarbon species were found among the three categories compared to the NMHC discussed before. More importantly, high halocarbon mixing ratios in T3

implied that industrialization had already spread to and substantially influenced the atmosphere of suburban areas in the PRD.

More importantly, the industrial and non-industrial uses of chlorofluorocarbons (CFCs) and other halocarbons have increased in the PRD at the end of the 20th century, and their increases was found to be related to the rapid industrialization. The details related to the increasing trend of halocarbons will be discussed in Chapter 7.

4.4 Concluding remarks

A total of 78 ambient air samples, covering a wide variety of VOCs, were collected throughout the five target cities in the PRD, which had high industrial activities. The result showed the highest mixing ratios in industrial areas, followed by industrial-urban areas and industrial-suburban areas. The nine most abundant species were the same for these three categories, though their rankings were different. Toluene (7.30-13.54 ppbv) was the most abundant species in the three sampling environments. Industrial solvent usage was the major toluene contributor in the PRD. Direct emissions from neighborhood industrial activities were found to contribute highly to the ambient air quality.

The levels of ethyne, ethene, i-pentane, toluene, propene and benzene were obviously high on dense traffic roadsides, but their contribution to the industrial-urban atmosphere was not clearly shown in this study. Comparing the mean benzene/toluene (wt/wt) of two extra roadside samples and the three sampling environments, the mean B/T ratio in the T2 category was 2.3 times lower than that in the roadside sample. This indicates that industrial activities had a larger contribution to atmospheric toluene level in T2. Dichloromethane (CH_2Cl_2) were significantly involved in the three sampling environments. The mean CH_2Cl_2 mixing ratios had the largest variation ranging from 674 pptv (T2) to 1020 pptv (T1).

This study demonstrated that industrial emission made a significant contribution to the atmospheric VOC mixing ratio in the PRD, in addition to vehicular emission. The distribution and density of industry, and direct emissions from different major industries resulted in the large spatial variation and high standard deviations of VOC mixing ratio in the five PRD cities. More importantly, the trend of the industrial development which spread from urban to suburban and rural areas implies that the whole PRD region will be more and more under the influence of industrial pollution in the coming decades.

Chapter 5 Contribution of Local and Transported Atmospheric VOCs on Roadside, Urban and Suburban Areas of Zhuhai, in the PRD of China – A Case Study in Winter of 2003

5.1 Introduction

Vehicular and industrial emissions are commonly identified as the two major anthropogenic VOC sources. Industrialization leads to an increase in the VOC contribution from various industrial activities in the whole PRD region as discussed in the last chapter. Vehicular emissions frequently affect the ambient atmospheres of roadside and urban area. This importance was clearly shown in the previous PRD study as well as other studies conducted at roadside and urban sites (Derwent et al., 1995; McLaren et al., 1996, Barletta et al., 2002; Zhao et al., 2004). Yet the small number of roadside sample in the previous PRD study did not provide sufficient information for examining the impact of vehicular VOC emissions on the PRD air quality. Obtaining the VOC profiles of vehicular sources, such as fuel vapor composition and vehicular exhaust, are necessary, so that the effect of industrial emissions can be further investigated.

Thus, a more comprehensive VOC field measurement was preformed to investigate the VOC contribution from automobile in Zhuhai, where tourism industry is intensively developed. Various manufacturing industries were forced to shift from urban areas to suburban areas due to stricter emission controls in recent years. More importantly, the inauguration of a proposed bridge providing a link across the estuary of the delta among Zhuhai, Macau and Hong Kong will greatly increase the traffic volume within these areas in the coming future. It is anticipated that the local air quality will subsequently deteriorate in the coming years. Taking a snapshot before the fast development is among of the aims of this study, because future development in the triangle economic zone will cause substantial change in the Zhuhai air quality, which was less reported in the past. In addition to the characterization of tailpipe exhausts, ambient samples of three different environments, covering roadside, urban and suburban, were also collected to study the contribution of tailpipe exhaust to the urban atmosphere. This study also focuses on the impact of transported air masses from upwind regions on the local air quality.

5.2 Sampling design basics

A total of 28 canister samples were collected using evacuated 2 l electro-polished stainless steel canisters in winter of 2003, including 18 ambient air samples and 10

tailpipe exhaust samples. The tailpipe exhaust samples were used to characterize the VOC emissions from common vehicles in Zhuhai, whereas the ambient samples were collected to study the local air quality.

5.2.1 Background of Zhuhai

Zhuhai is situated on the west bank of the PRD. Comparing with the eastern part of the PRD (Shenzhen and Dongguan), economic and industrial growth was slower due to its weaker logistic network to Hong Kong. In 2000, the industrial output value of Zhuhai (64,378 million yuan) was about one-fourth of that of Shenzhen (268,921 million yuan) (HKMPRD Development Information Net). Instead, tourism industry has developed in Zhuhai due to its good geographic position close to the two Special Administrative Regions (Hong Kong and Macau), which are situated in the southern China coastal area.

As a result, the urban planning and landuse in Zhuhai is different from other PRD cities where light and heavy industries distributed in urban, suburban and rural areas. In recent years, polluting industries are undergoing the process of transferring to the suburban districts/towns such as Doumen, Tangjia and Jinding (Figure 5.1). Stricter emission controls have been enforced to improve the air quality of urban area and to optimize the urban environment for the development of tourism in Zhuhai. Although the proposed

bridge could encourage the growth of tourism industry, it is considered that simultaneous traffic growth would also lead to the worsening of the local air quality.

5.2.2 Description of sampling locations and sample types

The 18 ambient samples were collected in three sampling environments, including: a roadside site next to a secondary school (SEZ roadside), an urban site on the rooftop of a four-storeys building in the same secondary school (SEZ rooftop), and a suburban site on the rooftop of an eight-storeys building in a university (ZSU rooftop). The secondary school is located in the downtown in the eastern coastal area as shown in Figure 5.1. The university is bounded by Zhongshan to the west, Jinding town to the north, Tangjia town to the east, and the Zhuhai downtown to the south. There are mountain regions isolating this suburban site from the downtown and there is a highway along the eastern coast to provide transport between these two sites. Prevailing winds from the east, northeast and north represent three typical surface pressure winds in November in Hong Kong (Chan et al., 1998), and similarly for Zhuhai. Thus, in the sampling periods, emissions from local industrial areas (Tangjia and Jinding) or from inland regions upstream of the Pearl River are expected to affect the Zhuhai ambient atmosphere, especially at the suburban sampling site. Sampling was carried out on 16th, 18th and 19th of November, henceforth referred as 16-Nov, 18-Nov and 19-Nov, respectively. Two

20–minute integrated ambient samples, with a calibrated flow controller, were collected in each sampling day. The morning sampling interval was between 08:00 and 10:00 local time and the early afternoon sampling interval was between 12:00 and 14:00 local time. Sampling height is about 1.5 m to the floor.

Fig. 5.1 Map of sampling locations in Zhuhai

Two idling tailpipe exhaust samples from each type of automobiles (bus, heavy-duty vehicle, motorcycle, taxi and private car) were collected. Each canister, coupled with a vacuum gauge and a calibrated flow controller, was used to collect ‘averaged’ tailpipe exhaust from five vehicles. For motorcycles, 2-stoke and 4-stoke samples were

separately collected. Only four 4–stoke motorcycles were averaged, as this type was not common in Zhuhai. Roughly equal proportion of exhaust from each vehicle was collected using a vacuum gauge. The distance between a tailpipe and a sampling inlet was 0.5-1.0 m.

5.3 Result and discussion

5.3.1 Major NMHCs of tailpipe exhaust at idling

Considering the NMHC composition of tailpipe exhaust, ethyne and ethene contributed over 84% of the total 58 identified NMHCs among the five types of vehicle, and ethane was the next abundant species (Table 5.1). Ethyne and ethene are the two major NMHCs found in the composition of tailpipe exhaust in Beijing, China (Lu et al., 2003) and elsewhere (Doskey et al., 1992; Fujita et al., 2001). In general, these combustion products are absent from the vapor composition of diesel and gasoline. However, n-butane and i-pentane which are abundant in the VOC profiles of evaporative gasoline (Lu et al., 2003) and hot soak (Doskey et al., 1992) were trivial in the tailpipe exhaust samples in this study, indicating that combustion VOC products, relative to fuel evaporation VOCs, had much higher tendency to be emitted from the tailpipe at idling. In addition, diesel-fuelled vehicles (bus and heavy-duty vehicle) emitted more ethene than ethyne from their tailpipes in contrast to gasoline-fuelled vehicles. Small

percentages of ethane were measured in both types of vehicles (Table 5.1). However, the Beijing study (Lu et al., 2003) showed a different result. Ethene and ethyne only accounted for about 30% and considerable amount of ethane was emitted from tailpipes of gasoline vehicle (15.3%) and diesel vehicle (26.3%) at idling. Much more unburned hydrocarbons, propane, *i*-pentane and toluene (Table 5.1), were emitted from tailpipes of gasoline vehicle (15.9%) and diesel vehicle (20.5%), but they were trivial in the tailpipe exhausts in this study. The variation may be due to a lower efficiency of fuel combustion at cold temperature in Beijing, as well as variations in the condition of vehicular fleet (e.g. age and maintenance), in the formulation of fuel (e.g. vapor pressure), and in the technology of emission abatement (e.g. catalytic converter).

Table 5.1 Comparison of NMHCs from tailpipe exhausts at idling (mol %)

Vehicle Types	Fuel Types	ethyne	ethene	ethane	propane	i-pentane	toluene
Bus [a]	Diesel	17.04	74.06	1.97	0.20	0.42	0.46
Heavy-duty vehicle [a]	Diesel	22.59	67.57	2.04	0.31	0.41	0.64
Private car [a]	Gasoline	21.30	63.58	9.60	0.50	0.51	0.77
Taxi [a]	Gasoline	51.42	35.79	4.33	0.29	0.80	0.73
Motorcycle [a]	Gasoline	70.93	25.57	2.75	0.30	0.06	0.03
Diesel vehicle [b]		9.91	19.22	26.27	17.72	0.61	2.19
Gasoline vehicle [b]		5.55	24.22	15.33	7.64	2.90	5.34
LPG vehicle [b]		2.68	5.82	6.10	63.79	0.18	0.04

[a] Averaged percentages of two samples (this study)

[b] Results of a Beijing study (Lu et al., 2003)

In Zhuhai in 2003 parts of the private car, other than other gasoline and diesel vehicle types, equipped a catalytic converter. The tailpipe exhausts of the two diesel vehicle

types and private car comprised higher percentages of ethene, relative to ethyne (Table 5.1). On the contrary, the other two gasoline vehicles emitted more ethyne than ethene. These results suggest that catalytic converter was important for the reduction of ethyne, relative to ethene, from gasoline vehicle types. Although ethene and ethyne were identified as the major components of tailpipe exhausts at idling, it was difficult to know their relative proportions in street conditions.

5.3.2 Analysis of VOC sources to Zhuhai using wind data

Fifty-three NMHCs and sixteenth halocarbons were quantified from each Zhuhai ambient sample. The NMHC mixing ratios of the three sampling sites for each sampling day (one weekend and two weekdays) are presented in Figure 5.2a–5.2c. In addition, their mixing ratios of halocarbons are presented in Figure 5.3. The results were briefly discussed and explained with simple physical observation, including the prevailing wind direction and the neighborhood environment. Based on the meteorological data (hourly wind speed and wind direction) measured in the Macau Taipa Grande Meteorological Station ($22^{o}10'$N $113^{o}34'$E), which is close to Zhuhai (Figure 5.1), three different characteristic wind directions were classified in the respective sampling days (Figure 5.4). North wind (N), which is most typically found in PRD winter, prevailed on 16-Nov. Regional outflows transported to Zhuhai were mainly from industrial regions of

Zhongshan and Guangzhou. East wind (E) on 18-Nov transported local industrial emissions from Tangjia to the suburban area (Figure 5.1). East-southeast wind (ESE) was prevalent on 19-Nov. Clean air masses from the sea affected the whole Zhuhai. According to these three prevailing wind directions, different VOC sources that affected Zhuhai were investigated below.

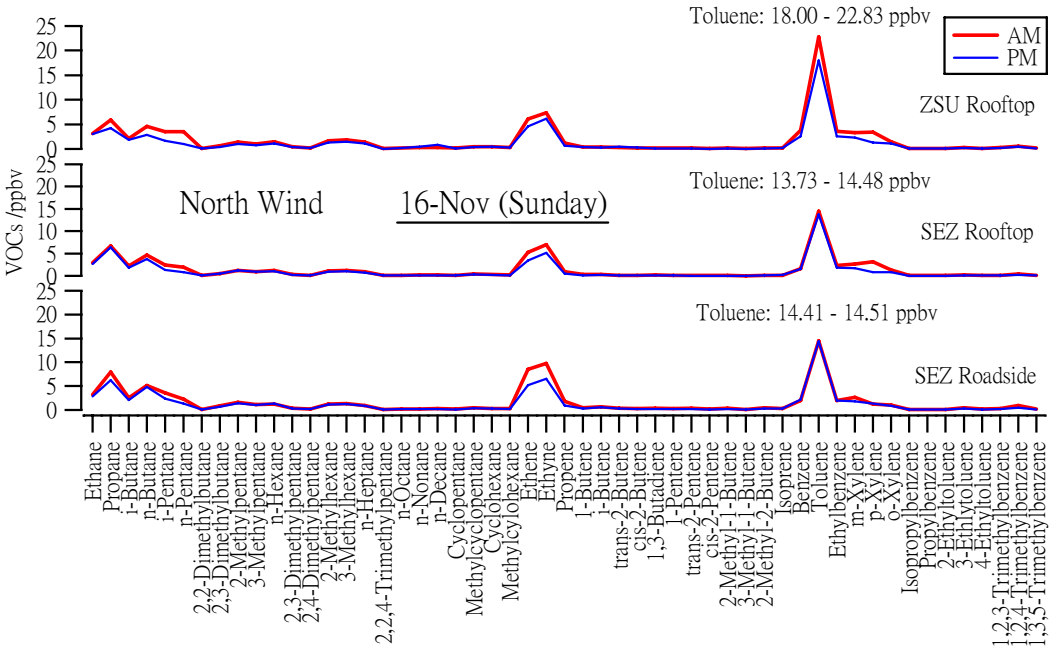


Fig. 5.2a The VOC profiles of all sampling locations on 16-Nov (N)

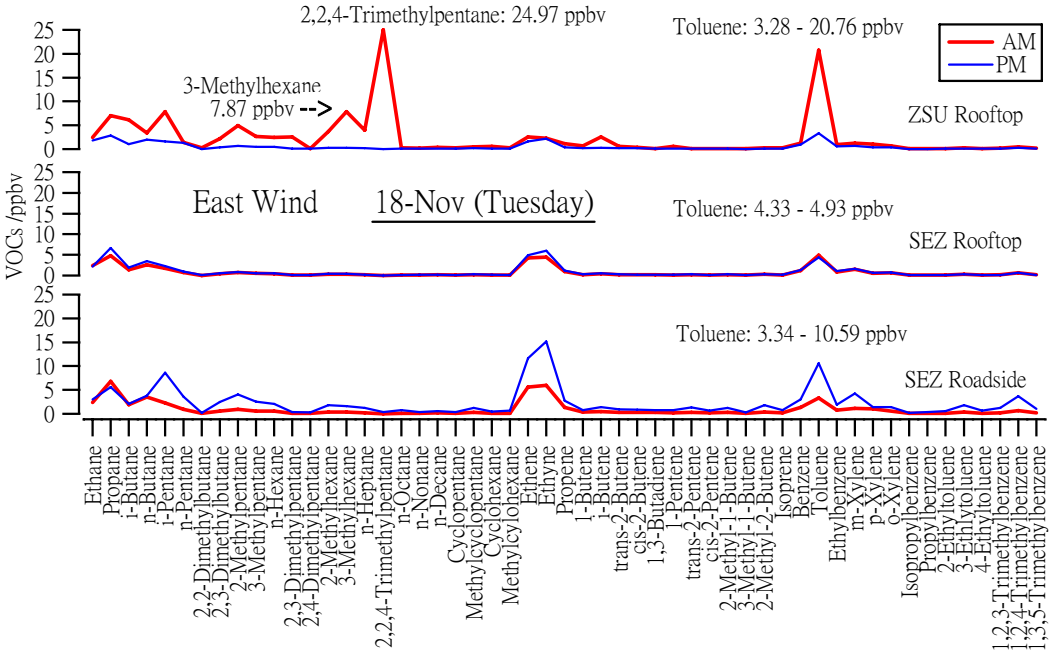


Fig. 5.2b The VOC profiles of all sampling locations on 18-Nov (E)

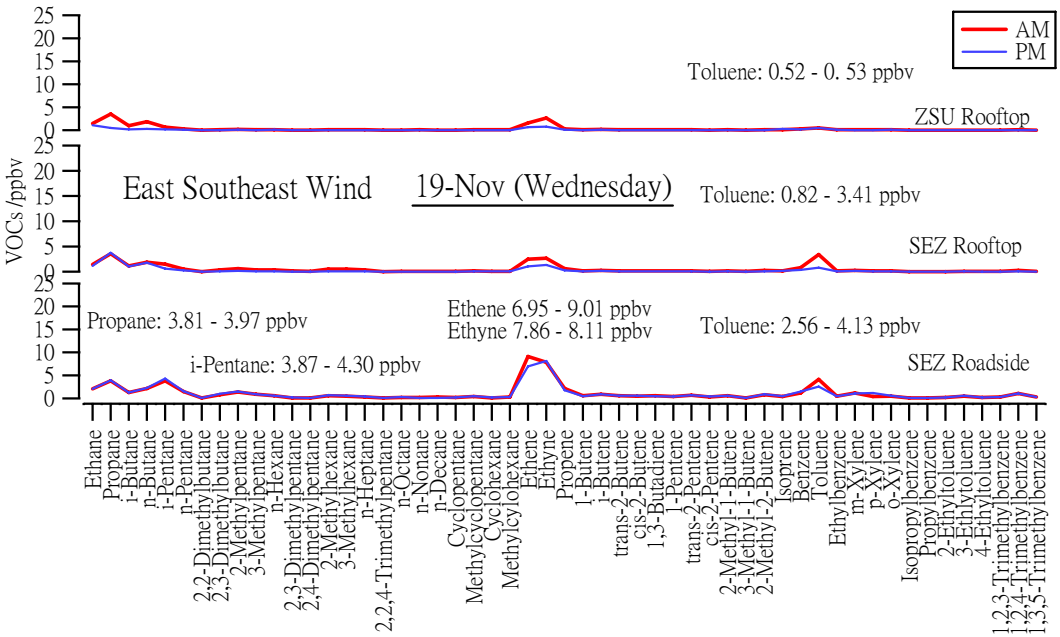


Fig. 5.2c The VOC profiles of all sampling locations on 19-Nov (ESE)

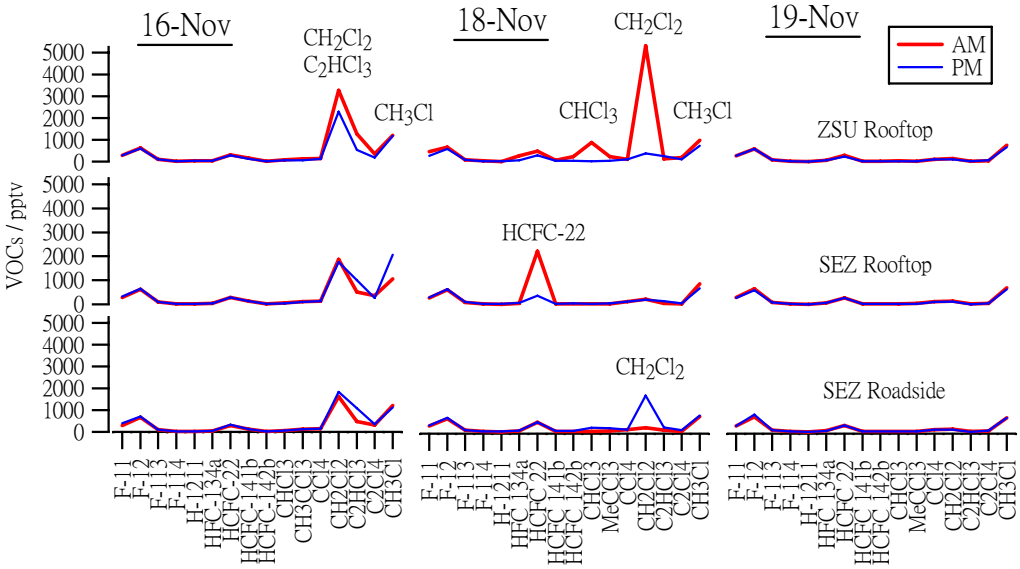


Fig. 5.3 Mixing ratios of halocarbons in the three sampling days

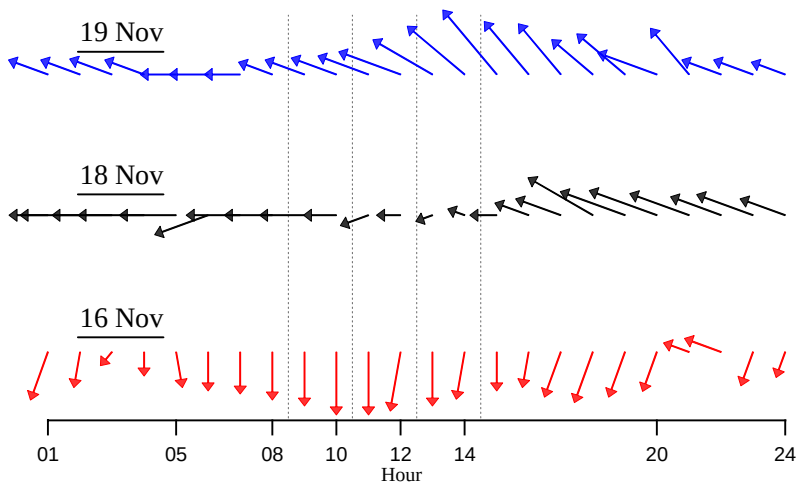


Fig. 5.4 Hourly wind vectors in the three sampling days (arrow head: wind direction and arrow length: wind speed)

A. VOC characteristics in Zhuhai on 16-Nov (Day 1)

Figure 5.2a presents the NMHC mixing ratio of the six ambient samples collected on 16-Nov. Significantly high toluene levels at the three sampling sites indicate Zhuhai being influenced by strong emission sources. An increase in toluene mixing ratio was

not a sudden case like the morning case of 18-Nov (Figure 5.2b), because similarly high toluene mixing ratios were measured in the morning and the early afternoon at all sampling sites. This high toluene plume provided a long and substantial effect for wide regions of Zhuhai. The highest toluene mixing ratios (18.00-22.83 ppbv) were measured at the suburban site. The toluene levels at roadside and urban sites were slightly lower. Similar to the result of the previous study (HKEPD, 2002), a significantly high toluene median value (12.1 ppbv) was also measured at a Panyu rural site, which is located in the northern direction of Zhuhai. Industrial emissions from Jinding industrial areas and other PRD cities should be the major sources on Day 1, as prevailing strong north wind (Figure 5.4) transported polluted air masses from inland PRD cities to Zhuhai. Several other aromatic hydrocarbons (benzene, ethylbenzene, m-/p-xylene and o-xylene) were also enhanced in the general ambient atmosphere. Some vehicular VOC markers dominated at all sampling sites, including ethene, ethyne, propene, n-butane and i-pentane (Figure 5.2a). It was believed that automobiles on the Beijing-Guangzhou-Zhuhai Expressway (East Line), which is located in the north of Zhuhai (Figure 5.1), were the major sources of these VOCs. Their mixing ratios were also enhanced in the roadside microenvironment due to local vehicular emissions. These results suggested that this PRD regional outflow air contained substantial industrial emissions and vehicular emissions.

In order to have a better understanding of the regional emission sources, the mixing ratios of halocarbons for the three sampling sites and the three sampling days are illustrated (Figure 5.3). Considering the lowest VOC mixing ratios on 19-Nov under the influence of clean sea air masses (Figure 5.3), dichloromethane (CH_2Cl_2) levels simultaneously increased in all sampling locations on Day 1. Both toluene and CH_2Cl_2 probably came from the same regional sources. The ratios of toluene-to-CH_2Cl_2 were similar in the three locations in the early afternoon (8) and slightly varied in the morning (7-9) (Table 5.2). These two VOCs were the most abundant NMHC and halocarbons in the industrial-related atmospheres reported in the year-2000 study (Chapter 4). Heavy toluene consumption of several working processes in electronic and printing industries in the PRD will be reported in Chapter 6.

Table 5.2 Ratios of toluene to CH_2Cl_2, C_2HCl_3 and CH_3Cl

	16-Nov AM			16-Nov PM		
	toluene/ CH_2Cl_2	toluene/ C_2HCl_3	toluene/ CH_3Cl	toluene/ CH_2Cl_2	toluene/ C_2HCl_3	toluene/ CH_3Cl
ZSU Rooftop	7.0	18.1	18.8	7.9	33.9	15.1
SEZ Rooftop	7.7	28.0	13.7	7.8	13.6	6.7
SEZ Roadside	9.0	30.9	12.1	7.9	13.3	12.9

Toluene from vehicular emissions and CH_2Cl_2 from domestic solvent uses led to a slight difference of toluene/CH_2Cl_2 found at the roadside (9.0) and urban (7.7) sites in the

morning of 16-Nov. The ratios of toluene to C_2HCl_3 and CH_3Cl showed larger spatial variations compared to toluene/CH_2Cl_2. Apart from the inclusion of regional unknown sources, local sources of C_2HCl_3 and CH_3Cl were temporally observed in the downtown (Figure 5.3). For example, double C_2HCl_3 mixing ratios and smaller toluene/C_2HCl_3 (Table 5.2) were measured in the downtown in the early afternoon, relative to in the morning. These increases were likely related to the general use of cleaning and degreasing solvents (Wadden et al., 1991; USEPA, 1998b) in domestic activities, such as outdoor car washing and maintenance in some urban auto maintenance shops.

B. VOC characteristics in Zhuhai on 18-Nov (Day 2)

There were two different VOC patterns at the suburban site in the morning and early afternoon periods of 18-Nov (Figure 5.2b). Toluene that was the most abundant VOC in the early afternoon (3.28 ppbv) was about six times lower than that in the morning (20.76 ppbv). Same wind direction (east wind) prevailed in both sampling periods (Figure 5.4), but the average wind speed of the morning period (13 km/h) was about twice that of the early afternoon period (6 km/h). Lower wind speed and less intensive industrial operations in lunch time period led to relatively low VOC mixing ratios. In the morning of Day 2, the transport of polluted plume from upwind regions affected the suburban sites. This polluted plume enriched extremely high mixing ratio of

2,2,4-trimethylpentane (24.97 ppbv), toluene (20.76 ppbv) and 3-methylhexane (7.87 ppbv). In Tangjia industrial zone, a petrochemical factory has been set up in the late 1989s-early 1990s. It mainly manufactures polyester slices, polyester films and water bottle chips, and its annual production totaled 140,000 tons in 2001 and 300,000 tons in 2002.

In general, 2,2,4-trimethylpentane is contained in industrial solvents, thinners and vehicular fuels, but it comprises small percent composition in these items and rarely emits into atmosphere in large quantities. This plume dominating with high 2,2,4-trimethylpentane level was likely associated with the leakage from fractional distillation columns in petrochemical industries under poor maintenance and emission controls, as this VOC is used as an azeotropic distillation entrainer (HCCD, 14th Edition). In addition, substantially high mixing ratios of toluene and 3-methylhexane were measured, but it was difficult to estimate whether they came from the same source as 2,2,4-trimethylpentane or from other factories. They are common components of various industrial solvents such as paints and thinners in the PRD. Considering mixing ratios of halocarbons (Figure 5.3) in this polluted plume, high levels of CH_2Cl_2 (5.30 ppbv) was measured at the suburban site in the morning. The ratio of toluene-to-CH_2Cl_2 was 3.9, which was lower than their counterparts (7-9) observed on Day 1. This

difference suggests that the source of these VOCs was not the same as the regional sources transported from inland PRD cities on Day 1. Instead, the higher CH_2Cl_2 level was probably emitted from solvent extraction in petrochemical industries and emitted through the leakage from solvent recover columns, as distillation and extraction are common work processes of the plastic resin and manmade fiber industries (USEPA, 1997).

Slight increases in the mixing ratios of almost all halocarbons, except for 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113), bromochlorodifluoromethane (H-1211) and tetrachloromethane (CCl_4), in this plume indicate that this industrial plume was partly contributed by various industrial activities together with the leakage from petrochemical factories. So, a number of C_3-C_7 straight-chain and branch-chain saturated hydrocarbons also increased in this industrial plume. Similar to the result of the year-2000 study, various C_6-C_7 saturated hydrocarbons elevated in the atmosphere outside shoemaking factories due to solvent uses. Other industrial working processes (e.g. plastic molding) also emitted various C_3-C_5 saturated hydrocarbons (Chapter 6). Low mixing ratios of ethene and ethyne indicate less VOC contribution from fuel combustion and vehicular exhaust.

The two downtown sampling sites were less influenced by industrial emissions from Tangjia, because of lack of emission sources above the sea. Instead of the industrial emissions from Tangjia, clean sea air decreased the VOC levels of the urban and roadside sites. However, there were some temporal sources of CH_2Cl_2 and toluene in the downtown area. A moderate increase in CH_2Cl_2 (1.66 ppbv) at the roadside site was observed in the early afternoon (Figure 5.3) and an increase in toluene level was simultaneously found (Figure 5.2b). The ratio of toluene-to-CH_2Cl_2 was 6.4 was closer to their counterparts (7-9) observed on Day 1. However, substantial increases in several vehicular VOCs markers (ethene, ethyne and i-pentane) that had been identified in tailpipe exhaust (in this study) and gasoline evaporation (Lu et al., 2003) suggest the overestimation of toluene-to-CH_2Cl_2 ratio due to the significant toluene contribution from automobile. As such, CH_2Cl_2 was likely emitted from small scale domestic activities such as painting and degreasing. Elevations of some halocarbon levels were sometimes observed in the downtown (Figure 5.3). For example, a high level of chlorodifluoromethane (HCFC-22; 2.21 ppbv) may be due to the use of propellants or refrigerants in air conditioning of school and neighboring housing estates (Aucott et al., 1999; McCulloch et al., 2003).

C. VOC characteristics in Zhuhai on 19-Nov (Day 3)

In contrast to Day 1 and Day 2, very different VOC patterns were characterized on Day 3 (Figure 5.2c), because of the dominant east-southeast wind and relatively higher wind speed (Figure 5.4). Clean sea air resulted in relatively lower atmospheric VOC mixing ratios at the three sampling sites. Especially at the suburban sampling site, which was often affected by industrial plumes on Day 1 and Day 2, the VOC mixing ratios of Day 3 were lower. The six samples had similar and lower halocarbons levels (Figure 5.3). Several industrial-related halocarbons (CH_2Cl_2, $CHCl_3$ and CH_3Cl) kept similar patterns and low mixing ratio levels at all sampling sites, though some refrigerant gases particular in CFC-12, HCFC-22 and HFC-134a (McCulloch et al., 2003), still slightly increased in the downtown atmosphere. Relatively low toluene mixing ratios were measured. We found its minimum value (0.52 ppbv) at the suburban site and its maximum value (4.13 ppbv) at the roadside site. These observations indicate less VOC contribution from industrial and domestic emissions, relative to vehicular emissions on that day.

Table 5.3 Benzene to toluene ratios (B/T, wt/wt)

		Day 1	Day 2	Day 3
Roadside	AM	0.12	0.34	0.24
	PM	0.13	0.24	0.49
Urban	AM	0.10	0.21	0.19
	PM	0.09	0.25	0.34
Suburban	AM	0.14	0.05	0.51
	PM	0.12	0.24	0.24

Table 5.3 lists the ratios of benzene to toluene (B/T, wt/wt) in each sample. Obviously, very low B/T ratios (0.05-0.13) were found in polluted air masses transported from inland PRD cities and local neighborhood industrial areas, because toluene is frequently involved in PRD industrial emissions. Higher B/T ratios (0.24-0.49) were measured from the roadside samples collected on Day 2 and Day 3. As such, automobile was the major contributor of toluene and benzene, while some domestic activities partly contributed toluene to these samples. However, the roadside B/T ratios obtained in this study were lower than those (~0.6) measured in the year-2000 PRD study (Chapter 4) and in 25 Chinese cities (Barletta et al., 2005). This may be due to the improvement of fuel quality by addition of toluene and reduction of benzene. The highest B/T ratio (0.51) was found at the suburban site in Day 3 morning. The benzene (0.32 ppbv) level significantly increased compared to its counterpart in the early afternoon, while very similar toluene mixing ratios (0.52-0.53 ppbv) were measured in the both cases. In addition, the mixing ratios of CH_3Cl (753 pptv), CH_2Cl_2 (143 pptv) and $CHCl_3$ (49 pptv) slightly increased in the morning, indicating that the source of benzene was probably emitted from biofuel/biomass burning (Lobert et al., 1999) in neighborhood mountain areas.

Table 5.4 Mean VOC mixing ratios (ppbv) on Day 3

	SEZ Roadside		SEZ Rooftop		ZSU Rooftop	
1	ethene	8.02	propane	3.65	propane	1.99
2	ethyne	7.98	toluene	2.11	ethyne	1.72
3	i-pentane	4.08	ethyne	2.00	ethane	1.26
4	propane	3.89	n-butane	1.81	n-butane	1.11
5	toluene	3.34	ethene	1.80	ethene	1.10
6	n-butane	2.20	ethane	1.30	i-butane	0.59
7	ethane	2.04	i-butane	1.08	toluene	0.53
8	propene	1.97	i-pentane	1.04	i-pentane	0.44
9	n-pentane	1.53	benzene	0.54	benzene	0.24
10	2-methylpentane	1.45	propene	0.44	propene	0.22

Vehicular emissions contributed much to the roadside site and less to the suburban site. Unlike the VOC ranking position of Zhuhai roadside (Table 5.4), the average mixing ratio of propane (1.99 ppbv) was higher than that of i-pentane (0.44 ppbv) at the suburban site. In the morning period, the mixing ratio of propane (3.51 ppbv) was much higher than that of i-pentane (0.65 ppbv) at the same site. Low i-pentane level indicates low contribution from automobile to the suburban site, because i-pentane is commonly identified as a VOC marker for gasoline evaporation and vehicular emission (McLaren et al., 1996). The source of propane was more likely related to the use of Liquefied Petroleum Gas (LPG) for cooking, rather than vehicular fuel evaporation. This will be further explained by investigating the VOC characteristics of vehicular emission in Zhuhai.

In order to study the characteristics of vehicular emission in Zhuhai, the six Day 3

ambient samples were selected for further analysis. Vehicular emission was the predominant VOC contributor in Day 3. Clean air masses from the sea minimized the influence of any large VOC contributors in upwind regions to the three sampling sites. Their mean VOC mixing ratios were calculated, and the ten most abundant VOCs are tabulated in Table 5.4. It was believed that the two roadside samples were mainly contributed by vehicular emissions. Ethene (8.02 ppbv) and ethyne (7.98 ppbv) were the two most abundant VOCs found on the roadside. It was consistent with the VOC composition of tailpipe exhaust of gasoline and diesel vehicles. They comprised more than 84% of the tailpipe exhaust at idling. Toluene and i-pentane that are dominant in gasoline vapor (Doskey et al., 1992; Lu et al., 2003) were in third and fifth position. They easily escaped into the ambient atmosphere through leakage and evaporation loss from fuel service stations and gasoline vehicles under running state. Propane was the fourth abundant VOCs on the roadside (3.89 ppbv), while it became the most abundant species on the urban rooftop (3.65 ppbv). Higher ranking on the urban rooftop showed that there were additional sources of propane in the downtown. Leakage from LPG cooking was the potential sources, as propane is the major component of LPG (Chen et al., 2001).

Thus, ethane, ethene, ethyne, propane, propene, i-butane, n-butane and i-pentane were

selected to study their linear correlations in the six roadside samples collected from Day 1 to Day 3. It was inappropriate to add toluene to the correlation analysis, as industrial emission was its major source on the first two days. According to the result of linear correlation (Table 5.5), two main VOC sources could be briefly characterized. Ethene, ethyne, propene and i-pentane were mainly associated with vehicular emissions through tailpipe exhaust and gasoline evaporation. Good correlations of i-pentane to the other three combustion VOC products (ethene, ethyne and propene) may be due to higher gasoline evaporation loss from aged vehicles with poor maintenance.

Instead of gasoline evaporation from vehicles, propane, i-butane and n-butane were mainly related to LPG leakage, as no correlation of propane to i-pentane was found on the roadside (Table 5.5). Because LPG vehicles were not common in Zhuhai in 2003, leakage from LPG cooking likely contributed to the high propane level in the downtown. Although no tailpipe exhaust samples of LPG vehicle were collected in this study, the result of a similar vehicular VOC study conducted in Beijing (Lu et al., 2003) was used as reference. The LPG tailpipe exhaust (by volume %) in northern China contained 63.79% of propane, 10.68% of n-butane, 8.53% of i-butane and 6.20% of ethane. The consumption of LPG in China in 2003 totaled 17.6 million tons. Domestic (cooking) use occupied about 72%, and consumption in industrial activities and vehicular fuel

occupied 16% and 3% respectively (Liu, 2005). So, the roadside propane level (3.89 ppbv) was partly contributed by gasoline evaporation and leakage from LPG cooking.

Table 5.5 Linear correlations (r^2) of light VOCs in the six roadside samples

	ethane	ethene	ethyne	propane	propene	i-butane	n-butane	i-pentane
ethane	1.00	0.09	0.27	0.58	0.01	0.90	0.82	0.09
ethene		1.00	0.82	0.04	0.94	0.01	0.02	0.79
ethyne			1.00	0.00	0.71	0.09	0.01	0.93
propane				1.00	0.12	0.86	0.79	0.06
propene					1.00	0.01	0.12	0.77
i-butane						1.00	0.90	0.00
n-butane							1.00	0.02
i-pentane								1.00

5.4 Concluding remarks

Atmospheric VOCs of three different environments, including roadside, urban and suburban, in Zhuhai were characterized in the three-day intensive sampling. Based on the three characteristic wind directions, different VOC sources that affected Zhuhai were investigated. On the first sampling day, the dominant north wind in PRD winter frequently transports polluted air masses from upwind PRD industrial regions, carrying enriched toluene, CH_2Cl_2 and other industrial organic pollutants to Zhuhai. On the second day, industrial emissions from local neighborhood industrial zone strongly affected the suburban site. Meanwhile, no upwind industrial sources in downtown resulted in significantly lower VOC mixing ratios.

On the last sampling day, clean sea air led to the lowest atmospheric VOC mixing ratio at all sampling sites. As such, local vehicular emissions became the major anthropogenic source in the downtown. Two roadside samples collected on the final day were used to study the VOC contribution from automobiles. Ethyne, ethene, i-pentane, propane and toluene were the most abundant species in the atmosphere of roadside. This was consistent with the result of tailpipe exhaust sampling that ethyne and ethene accounted for more than 84% of the tailpipe exhaust at idling.

The result of this study raised the importance of transported industrial emissions from inland PRD cities and local industrial areas. The PRD industrial emissions frequently deteriorate the air quality of wide areas of downwind region. Impact of local neighborhood industrial emissions was also observed at the suburban sampling site. The characterization of vehicular VOC emissions in Zhuhai provided substantial information to explain the VOC contribution from automobile in Zhuhai. This information may be applicable to the whole PRD region, before similar types of vehicle used in the PRD region.

Chapter 6 VOC Characterization for Printing and Electronic Industries and Their Contribution to Local Air Quality of Qingxi, Dongguan

6.1 Introduction

The two previous VOC sampling studies and the subsequent site visits provide relevant information on industrial activities in the Pearl River Delta (PRD) region. This information is used in the selection of appropriate industries for VOC characterization in this study. The VOC contribution from vehicular emission to Zhuhai local air quality was briefly discussed in Chapter 5. This chapter focuses the investigation of two prevailing industrial activities (electronic manufacture and printing) in Dongguan. It is decided to characterize their VOC emissions through more intensive measurements of corresponding work processes and industrial solvents. As such, the research approach for the VOC characterization (Chapter 3) was also examined.

Apart from characterizing VOC emissions from these two industries, an assessment of their impacts on local air quality in the study is intentionally included. Ambient air samples were collected at urban, roadside and background sites.

6.2 Sampling design basics

Thirty-four VOC samples were collected using evacuated 2 l electro-polished stainless steel canisters in Qingxi of Dongguan in January of 2005, including 19 source samples and 15 ambient air samples. The 19 source samples were used to characterize seven work processes of electronic manufacture and printing. The 15 ambient samples that were collected on the rooftop of the two industries, and at urban, roadside and background sites were designed to study the impact of these industrial VOC emissions on the local air quality. Nine industrial solvent were also collected to investigate their VOC vapor compositions.

6.2.1 Background of Dongguan

Dongguan is bounded by Guangzhou to the north, Huizhou to the east, Shenzhen to the south, and the Pearl River to the west (Figure 6.1). Its good geographical position and favourable economic systems and policies, corroborated by good infrastructure and logistics support, have attracted foreign direct investment and tremendous industrial development. As a result, it has developed an export-orientated economy and has grown to be one of China's largest exporting domains. The value of export was worth US$ 23.3 billion in 2002, up 25% from 2001, accounting for 7.3% of national total. Gross domestic product (GDP) increased 18.4% over 2001, and its GDP has been growing at

about 18% for six consecutive years (HKTDC).

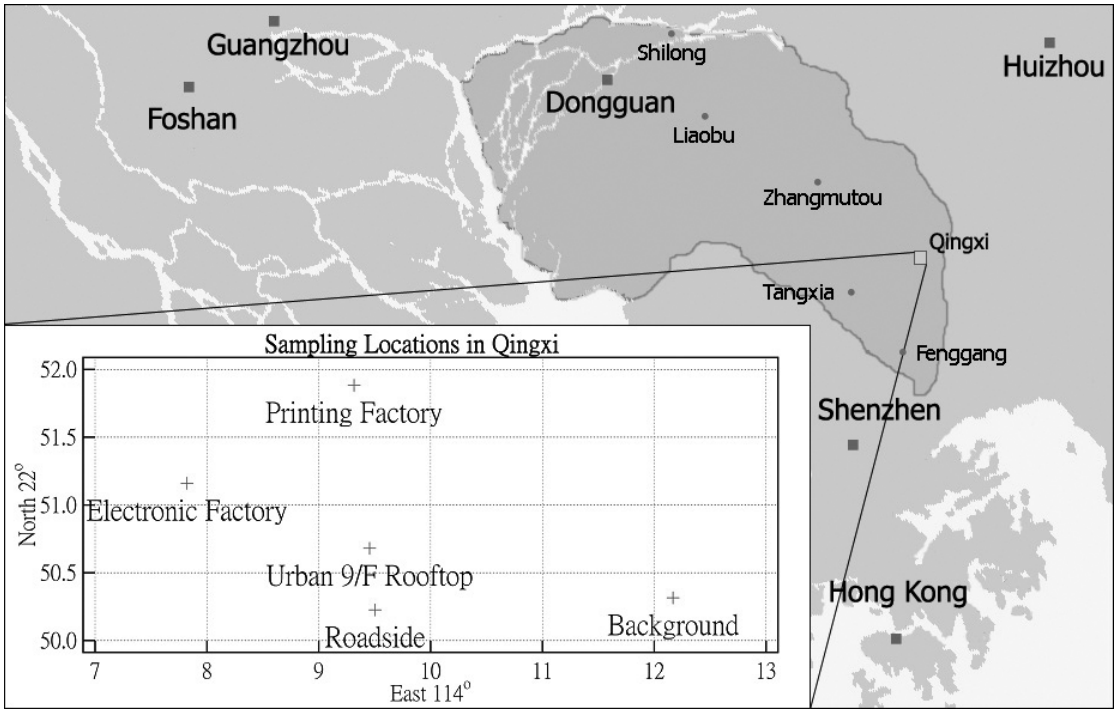


Fig. 6.1 Sampling locations in Qingxi of Dongguan

Apart from the main economic driving force provided by Hong Kong and foreign-invested enterprises, a strong supply chain backed by well-connected industrial system has also been developed in the past decade. A variety of industries have grown in Dongguan. There is a strong support to self-sufficient industrial development in recent years. For example, there is about 70-90% of electronic accessories and parts available locally. Various computer accessories like keyboard and printer are important high-valued component products. Decorated paper boxes are in high demand due to the enormous amount and diversity of manufacturing products which require packaging. As

such, the VOC characterization from electronic manufacture and printing industry is worth studying. Qingxi was selected because these two industries are prevalent there. Qingxi together with Zhangmutou, Tangxia and Fenggang (Figure 6.1) constitutes the south east economic zone, which is a comprehensive manufacturing base in Dongguan.

6.2.2 Description of sampling locations and sample types

Among the 34 canister samples, 33 source samples and ambient samples were collected in the three-day intensive sampling, started from 6th to 8th January in 2005. One extra source sample (soldering) was collected on 24th January to acquire a more complete data set. Table 6.1 lists the details of respective sampling periods. 15-minute “integrated” samples, totaled 1.4 - 1.5 l, were collected using evacuated 2 l electro-polished stainless steel canisters to which a critical orifice flow controller with a vacuum gauge was connected. The vacuum pressure changed from -30 psi to -8.5 psi in the 15-minute sampling period. Different critical orifice flow controllers were separately used to collect ambient and source samples. All critical orifice flow controllers were calibrated before sampling using a digital flow meter (DC-Lite, BIOS, USA), and their initial flow rates were within the range of requirement (100 ml/min ± 5%).

Table 6.1 Sample periods of 3-day intensive sampling

Sampling Period	Location	Sample Category
0600 - 0700	Background	Background (B)
0830 - 1030	Electronic Factory (F1)	Plastic Molding (PM) Logo Printing (LP) Spray Painting (SP) Soldering (S)
0930 - 1030		Rooftop (F1R)
1130 - 1230	Roadside	Roadside (R)
1330 - 1530	Printing Factory (F2)	Paper Printing (PP) Glossing (LSB) Gluing (G)
1430 - 1530		Rooftop (F2R)
1530 - 1630	Urban 9/F Rooftop	Urban (U)

* The sampling order of work processes was variable due to their different operation times or some of them out of operation for particular intensive sampling days.

The five sampling sites included electronic factory, printing factory, urban 9/F rooftop, roadside and background (Figure 6.1). The ambient air samples were collected for each sampling site in the three sampling days. The emission sources of various work processes were collected inside the electronic and printing factories. A total of 12 categories of VOC samples were divided into two main streams. Seven source categories corresponded to seven work processes of the two industries, while another five ambient categories were targeted for measuring the air quality of each sampling site. The source samples collected in the electronic industry (F1) included four samples from plastic molding and two samples from soldering, logo printing and spray painting (SP). In the case of printing industry (F2), three samples were collected from paper printing, glossing and gluing, respectively. Fifteen ambient samples were divided into five

categories, including background, roadside, urban and F1 rooftop (F1R) and F2 rooftop (F2R). Three samples were collected for each ambient category in each sampling day. In addition, nine samples of industrial solvent were obtained from the two factories. The chemical analysis of these industrial solvents was carried out in the Air Laboratory (HKPU) using GC/MS.

As the physical environment of each site is very important in understanding possible VOC source emissions to the neighborhood, it is essential to clearly understand the configuration of the two factories, so that the VOC contribution from respective work processes to the rooftop air quality of corresponding factories could be investigated. Their configurations are briefly presented in two non-scale figures (Appendix 1 and 2).

With regard to the configuration of the electronic factory (Appendix 1), the workshops for soldering and spray painting are separated, so that their VOC profiles are less likely influenced by other VOC sources. In contrast, the work processes of logo printing and plastic molding are located in the same workshop. It is believed that their VOC emissions partly integrated together, but the closer work process would make larger contribution to the samples. It is observed that the mixing ratio and composition of the rooftop ambient atmosphere greatly depends on the distance away from respective

workshops. For example, the soldering is likely to contribute much to the rooftop ambient atmosphere. Their different emission strengths are the other important factor to affect atmospheric VOCs, but this factor was too difficult to be considered in this study. In addition, three metal processing factories and on-road vehicles close to the factory probably also affected the rooftop VOC composition. The configuration of the printing factory (Appendix 2) is more complex than that of the electronic factory. It is located along dense traffic roads and in a dense area with houses and factories, which manufacture adhesive tape and electric appliance. The work processes are operated in the same large workshop, though some of them are partly separated by plastic curtains. It is considered that inter-contamination among different work processes is significant.

The remaining sampling locations have different environmental characteristics. A roadside site is situated in a dense traffic area, mainly with housings and restaurants. There are no industrial point sources nearby. A site used to measure the urban air quality is located on the rooftop of a 9/F residential building. It is far away from industrial areas and is situated within commercial and residential areas. A background site is located in the south east corner of Qingxi, where less anthropogenic emission sources are found nearby, except for a few small factories in the south west. However, the influence of these factories is minimized, due to the prevailing north and north east winds in PRD

winter and in the sampling periods. Also, factories did not start to operate in the early morning sampling period (0600 local time).

6.3 Result and Discussion

6.3.1 VOC composition of industrial solvent vapor

A total of 21 VOCs, including 5 halocarbons and 16 nonmethane hydrocarbons (NMHCs), were measured from the vapor samples of eight industrial solvents and one wastewater using GC/MS. The procedures of sample preparation and chemical analysis are described in Chapter 3.4. Their percent compositions (by volume) are presented in Table 6.2. Dichloromethane, trichloroethylene, n-hexane, benzene, toluene, ethylbenzene and xylenes that constitutes the majority of the VOC emission from most of the industrial solvent emissions (Fujita, 2001; Kim et al., 2001a; Watson et al., 2001; He et al., 2002) were quantified. Ethane, ethene, ethyne and propane, with very low boiling point, could not be trapped and analyzed by the GC/MS system. These VOCs are not commonly used as solvents. The GC peak areas of these 21 quantified VOCs ranged from 62.32% to 93.30% of the total GC peak area (Table 6.2), indicating that significant quantities of VOCs were not quantified. Graphite inks and a variety of industrial coatings used in the US mainly included paraffin, aromatic and oxygenated hydrocarbons, and the oxygenated hydrocarbons that were not the focus of this study

ranged from 32.77 to 91.17% of the total VOCs (Fujita and Campbell, 2003).

From the result of chemical analysis for the solvent of the electronic manufacture (Table 6.2), the mold releasing agent which is often sprayed on molds in plastic molding and logo printing mainly included n-butane (35.2%) and n-hexane (34.9%). Ethylbenzene, m-/p-xylene and o-xylene were the major VOC components in the silk-screen cleaning solvent and paint diluting solvent used in the logo printing. The cleaning solvent is used to remove residues of paint on silk screens when completing a batch of job. Toluene was the single VOCs quantified in the spray paint diluting solvent, whereas the thinner of the spray painting comprised n-heptane (31.1%), methylcyclohexane (30.5%) and toluene (15%). Methylcyclohexane and heptane were found to be abundant in thinning solvents in other countries (Censullo et al., 1996). The use of these two solvents contributed toluene (88.9%), n-heptane (6.0%) and methylcyclohexane (5.1%) in the sample of the spray painting's wastewater air sample. Regarding the three solvent samples of the printing industry, dichloromethane (CH_2Cl_2) was found in the fountain solution (63.9%) and the adhesive (53.8%). 1-butene constituted 36.1% of the fountain solution and n-hexane comprised 46.2% of the adhesive. Toluene was the only VOC component identified in the ultraviolet (UV) varnish.

Toluene was the most common VOC found in the industrial solvents of the two industries, especially in the spray paint diluting solvent and the UV varnish. Toluene was frequently found in industrial solvents of eight industries in the PRD, including electronic and printing industries (He et al., 2002). It can be seen from Table 6.2 that CH_2Cl_2 was only found in the fountain solution and adhesive used in the printing factory. In contrast, the industrial solvents used in the plastic molding, logo printing and spray painting in the electronic factory were free from CH_2Cl_2. In addition, no other halocarbons were quantified in these industrial solvents.

Table 6.2 The percent compositions of industrial solvent vapor (volume %)

VOCs	*Mold Releasing Agent (PM/LP)	Silk-screen Cleaning Solvent (LP)	Paint Diluting Solvent (LP)	Paint Diluting Solvent (SP)	Thinner (SP)	Wastewater (SP)	*Fountain Solution (PP)	*Adhesive (G)	UV Varnish (LSB)
dichloromethane	0.00	0.00	0.00	0.00	0.00	0.00	63.90	53.78	0.00
1,1,1-trichloroethane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
tetrachloromethane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
trichloroethylene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
tetrachloroethylene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1-butene	0.00	0.00	0.00	0.00	0.00	0.00	36.10	0.00	0.00
n-butane	35.23	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
i-pentane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
n-pentane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3-methylpentane	17.31	0.00	0.00	0.00	0.50	0.00	0.00	0.00	0.00
n-hexane	34.92	0.00	0.00	0.00	5.98	0.00	0.00	46.22	0.00
methylcyclopentane	5.16	0.00	0.00	0.00	5.30	0.00	0.00	0.00	0.00
benzene	0.00	0.00	0.00	0.00	2.61	0.00	0.00	0.00	0.00
2-methylhexane	7.38	0.00	0.00	0.00	6.21	0.00	0.00	0.00	0.00
n-heptane	0.00	0.00	0.00	0.00	31.13	5.13	0.00	0.00	0.00
methylcyclohexane	0.00	0.00	0.00	0.00	30.54	6.01	0.00	0.00	0.00
2-methylheptane	0.00	0.00	0.00	0.00	2.49	0.00	0.00	0.00	0.00
toluene	0.00	0.00	4.34	100.00	15.00	88.86	0.00	0.00	100.00
ethylbenzene	0.00	25.40	17.90	0.00	0.00	0.00	0.00	0.00	0.00
p-+m-xylene	0.00	54.85	62.81	0.00	0.24	0.00	0.00	0.00	0.00
o-xylene	0.00	19.74	14.94	0.00	0.00	0.00	0.00	0.00	0.00
**GC Peak Area (%)	62.74	91.43	79.38	93.30	63.64	88.43	72.62	62.32	91.61

* Average percent composition of two runs
** The percentage of the GC peak area of the 21 quantified VOCs

6.3.2 General VOC characteristics among the 12 categories

A total of 70 compounds, covering carbon monoxide (CO), methane (CH_4), 21 halocarbons and 47 NMHCs, were quantified in the 12 categories. For easy comparison of respective work processes, 52 interested and important VOCs were selected to calculate the total VOCs (TVOCs), and to convert mixing ratio to percent composition (by volume). The mean values for these 52 selected VOCs were calculated for each category, and are tabulated in Table 6.3. Most of the interested species were the top 20 abundant VOCs of each category. A few important VOCs were also included, such as isoprene, 1-butene, trichlorofluoromethane (CFC-11), tetrachloromethane (CCl_4), 1,1,1-trichloroethane (CH_3CCl_3) and tetrachloroethylene (C_2Cl_4). Among 18 excluded species, CH_4 and CO are generally excluded from the term of VOCs discussed in this thesis. Their mixing ratios are also reported in Table 6.3. The other species were in very low mixing ratio and were less significant in the calculation of percent composition. Thus, there were four VOC groups contained these 52 species, including 8 halocarbons, 17 saturated hydrocarbons, 13 unsaturated hydrocarbons and 14 aromatic hydrocarbons.

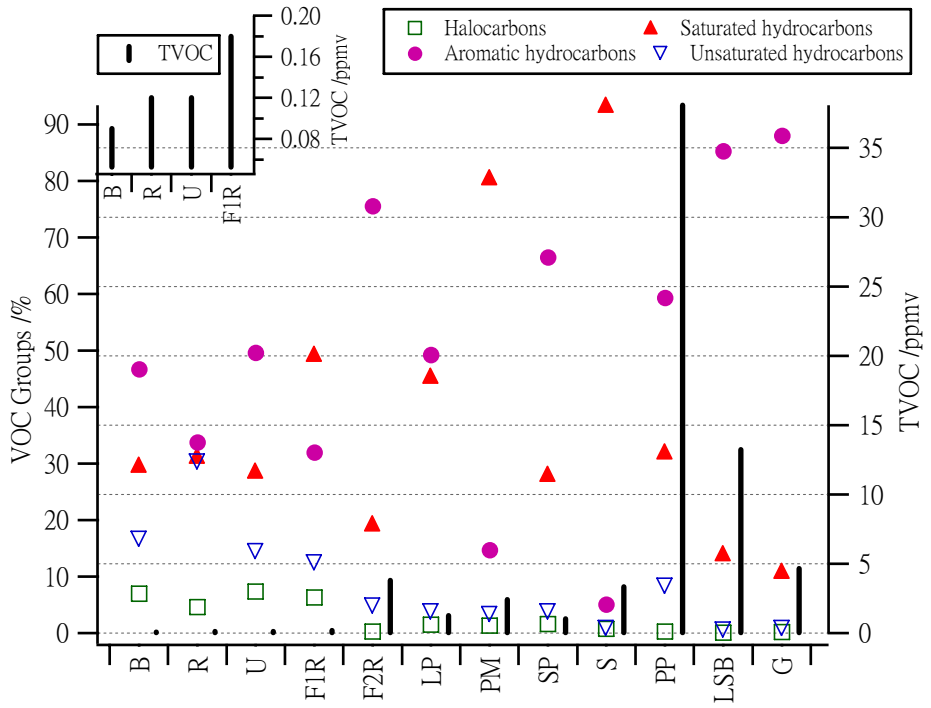
Table 6.3 VOC profiles (volume %) of the seven source and five ambient categories

	*Ambient VOC categories					**Source VOC categories						
Species	B	R	U	F1R	F2R	LP	PM	SP	S	PP	LSB	G
TVOCs (ppbv)	90.92	117.93	116.86	183.33	3809.22	1253.20	2411.54	1048.40	3329.49	38058.07	13208.34	4664.94
CO (ppmv)	1.23	2.30	1.37	2.05	3.73	2.28	1.79	1.60	1.94	1.18	1.30	1.22
CH4 (ppmv)	2.03	1.99	2.10	2.17	2.08	2.45	2.33	2.28	2.25	2.01	2.02	2.00
CFC-11	0.47	0.24	0.26	0.17	0.01	0.03	0.03	0.03	0.01	0.00	0.00	0.01
CFC-12	0.96	0.57	0.57	0.36	0.02	0.06	0.06	0.07	0.02	0.00	0.01	0.02
CH_3Cl	2.10	1.05	1.06	0.73	0.03	0.14	0.14	0.15	0.06	0.00	0.01	0.03
CH_2Cl_2	2.01	1.51	2.79	2.20	0.14	0.52	0.45	0.45	0.24	0.26	0.04	0.10
CCl4	0.19	0.11	0.11	0.08	0.00	0.02	0.02	0.01	0.01	0.00	0.00	0.00
C_2HCl_3	1.06	1.07	2.42	2.55	0.09	0.68	0.59	0.91	0.35	0.01	0.02	0.04
C_2Cl_4	0.12	0.05	0.05	0.14	0.00	0.05	0.04	0.02	0.01	0.00	0.00	0.01
CH_3CCl_3	0.07	0.04	0.06	0.06	0.00	0.01	0.01	0.01	0.02	0.00	0.00	0.00
Halocarbon	**6.97**	**4.63**	**7.33**	**6.28**	**0.30**	**1.52**	**1.33**	**1.65**	**0.72**	**0.27**	**0.09**	**0.22**
ethane	7.37	4.70	3.95	3.18	0.25	0.73	0.93	0.62	0.19	0.02	0.05	0.11
propane	5.22	4.58	5.15	9.41	1.43	15.60	33.78	3.06	3.53	0.06	0.07	0.16
i-butane	1.60	2.71	1.70	3.17	0.41	4.65	8.91	0.84	0.96	0.31	0.04	0.07
n-butane	3.37	6.01	3.41	7.17	0.76	10.91	20.00	2.00	2.02	0.73	0.08	0.16
i-pentane	1.59	3.58	2.10	1.80	1.71	0.71	0.69	1.25	1.11	8.42	0.43	0.55
n-pentane	1.09	1.46	0.98	1.45	0.60	0.66	0.53	1.34	0.72	2.68	0.17	0.20
n-hexane	1.67	1.43	1.91	7.86	0.65	4.11	4.80	3.10	0.75	1.23	0.41	0.33
2-methylpentane	1.26	1.68	1.62	4.20	0.90	2.52	3.60	1.50	25.58	2.66	0.30	0.32
3-methylpentane	1.06	1.20	1.32	4.29	0.61	2.45	3.13	1.16	30.03	1.85	0.23	0.24
2,2-dimethylbutane	0.10	0.15	0.13	0.23	0.07	0.15	0.33	0.09	0.77	0.20	0.02	0.03
2,3-dimethylbutane	0.42	0.67	0.57	0.98	0.41	0.63	0.93	0.36	5.85	1.59	0.13	0.15
n-heptane	1.46	0.63	1.60	0.97	3.61	0.33	0.39	4.85	0.27	3.01	3.70	2.76
2-methylhexane	1.32	0.84	1.57	2.12	3.05	0.93	1.23	2.14	12.67	2.97	3.36	2.29
3-methylhexane	1.70	0.95	2.03	2.02	4.12	0.84	1.17	2.28	8.73	3.76	4.73	3.27
n-octane	0.13	0.15	0.15	0.13	0.13	0.18	0.06	2.29	0.01	0.57	0.12	0.07
2,2,4-trimethylpentane	0.20	0.38	0.20	0.12	0.58	0.05	0.05	0.53	0.15	1.88	0.20	0.17
n-decane	0.16	0.21	0.22	0.16	0.06	0.06	0.05	0.66	0.02	0.15	0.03	0.05

Saturated Hydrocarbon	**29.73**	**31.33**	**28.63**	**49.28**	**19.34**	**45.50**	**80.59**	**28.07**	**93.37**	**32.10**	**14.07**	**10.95**
Species	B	R	U	F1R	F2R	LP	PM	SP	S	PP	LSB	G
ethene	6.41	10.22	4.60	5.07	1.42	1.47	1.34	1.18	0.32	0.02	0.09	0.14
ethyne	7.20	14.44	7.55	5.64	1.28	1.54	1.39	1.40	0.37	0.03	0.09	0.16
propene	1.11	1.88	0.71	0.75	0.29	0.23	0.21	0.28	0.05	0.01	0.01	0.01
i-butene	0.76	0.68	0.28	0.23	0.09	0.09	0.09	0.09	0.02	0.18	0.01	0.03
1-butene	0.27	0.42	0.18	0.18	0.06	0.07	0.06	0.37	0.02	0.24	0.01	0.02
cis-2-butene	0.07	0.29	0.13	0.07	0.16	0.04	0.03	0.12	0.01	0.74	0.03	0.05
trans-2-butene	0.09	0.29	0.13	0.07	0.14	0.05	0.03	0.10	0.01	0.74	0.03	0.04
1,3-butadiene	0.14	0.39	0.13	0.16	0.01	0.06	0.05	0.06	0.01	0.71	0.01	0.00
1-pentene	0.10	0.24	0.11	0.06	0.16	0.03	0.02	0.03	0.01	0.73	0.04	0.05
cis-2-pentene	0.08	0.24	0.10	0.04	0.21	0.02	0.01	0.02	0.00	0.94	0.05	0.06
trans-2-pentene	0.13	0.43	0.18	0.07	0.38	0.05	0.03	0.04	0.01	1.59	0.09	0.11
2-methyl-2-butene	0.18	0.60	0.22	0.08	0.58	0.06	0.03	0.05	0.01	2.33	0.13	0.16
isoprene	0.10	0.15	0.08	0.05	0.03	0.04	0.02	0.02	0.01	0.05	0.01	0.01
Unsaturated Hydrocarbon	**16.63**	**30.26**	**14.40**	**12.47**	**4.81**	**3.75**	**3.32**	**3.75**	**0.85**	**8.31**	**0.59**	**0.84**
benzene	2.97	3.09	2.22	1.77	0.49	0.80	0.64	2.09	0.36	0.95	0.20	0.21
toluene	29.65	15.93	31.23	19.54	67.42	4.40	4.37	58.13	2.22	52.18	72.01	69.25
ethylbenzene	2.56	2.69	1.93	1.96	0.30	10.33	2.09	1.38	0.54	0.48	0.27	0.32
o-xylene	1.61	1.88	1.32	1.31	0.34	5.58	1.42	0.61	0.29	0.67	0.39	0.43
m-xylene	4.53	5.14	3.64	3.78	0.94	17.73	4.04	2.25	0.86	1.59	0.79	0.86
p-xylene	1.26	1.81	0.90	1.19	0.29	8.01	1.07	0.52	0.50	0.48	0.40	0.28
o-ethyltoluene	0.28	0.23	0.68	0.17	0.47	0.24	0.09	0.08	0.02	0.19	0.97	1.50
p-ethyltoluene	0.37	0.28	0.78	0.22	0.54	0.28	0.10	0.10	0.03	0.26	1.09	1.74
m-ethyltoluene	0.76	0.63	1.71	0.46	1.25	0.61	0.23	0.22	0.05	0.84	2.52	3.25
i-propylbenzene	0.15	0.09	0.13	0.07	0.07	0.14	0.06	0.05	0.01	0.06	0.21	0.21
n-propylbenzene	0.26	0.20	0.50	0.16	0.34	0.47	0.12	0.11	0.02	0.18	0.70	1.02
1,2,3-trimethylbenzene	0.42	0.31	0.68	0.23	0.43	0.09	0.09	0.22	0.02	0.22	0.74	1.41
1,2,4-trimethylbenzene	1.46	1.15	3.09	0.87	2.08	0.42	0.36	0.56	0.10	0.86	3.81	5.72
1,3,5-trimethylbenzene	0.38	0.37	0.83	0.23	0.59	0.13	0.10	0.22	0.02	0.36	1.16	1.78
Aromatic Hydrocarbon	**46.66**	**33.78**	**49.64**	**31.96**	**75.55**	**49.23**	**14.76**	**66.53**	**5.06**	**59.31**	**85.25**	**88.00**

* Ambient categories: background (B), roadside (R), urban (U), electronic rooftop (F1R) and printing rooftop (F2R).
** Source categories: logo printing (LP), plastic molding (PM), spray painting (SP), soldering (S), paper printing (PP), glossing (LSB) and gluing (G).

In order to have a simple picture of the 12 categories, the mean percent compositions of the four VOC groups and the mean TVOCs are illustrated in Figure 6.2. Similar percent compositions were found in the ambient of background and urban. The aromatic hydrocarbon contributed about half of the total VOCs, followed by the saturated hydrocarbon (~30%), the unsaturated hydrocarbon (~15%) and the halocarbon (~5%). This was consistent with lower unsaturated hydrocarbons in aged air masses (early morning and late afternoon), as unsaturated hydrocarbons have generally shorter lifetimes in the troposphere. In contrast, the saturated, unsaturated and aromatic hydrocarbons occupied a similar percent composition (~30%) in the roadside ambient. Fresh vehicular exhaust mainly contributed the unsaturated hydrocarbon (ethene, ethyne and propene) to the atmosphere of roadside in the PRD (Chapter 4 and 5) and in other countries (Doskey et al., 1992; McLaren et al., 1996; Barletta et al., 2002). The highest mean CO mixing ratio (2.30 ppmv) was also found at the roadside site. Industrial activities were still the major sources of halocarbons in the PRD, though only small percents were found in these three ambient categories. For example, CH_2Cl_2 was dominant in the fountain solution and adhesive. It will be shown in following sections using the VOC source signatures of respective industrial work processes.



Note: background (B), roadside (R), urban (U), electronic rooftop (F1R), printing rooftop (F2R), logo printing (LP), plastic molding (PM), spray painting (SP), soldering (S), paper printing (PP), glossing (LSB) and gluing (G).

Fig. 6.2 Mean TVOC and percent composition of the twelve categories

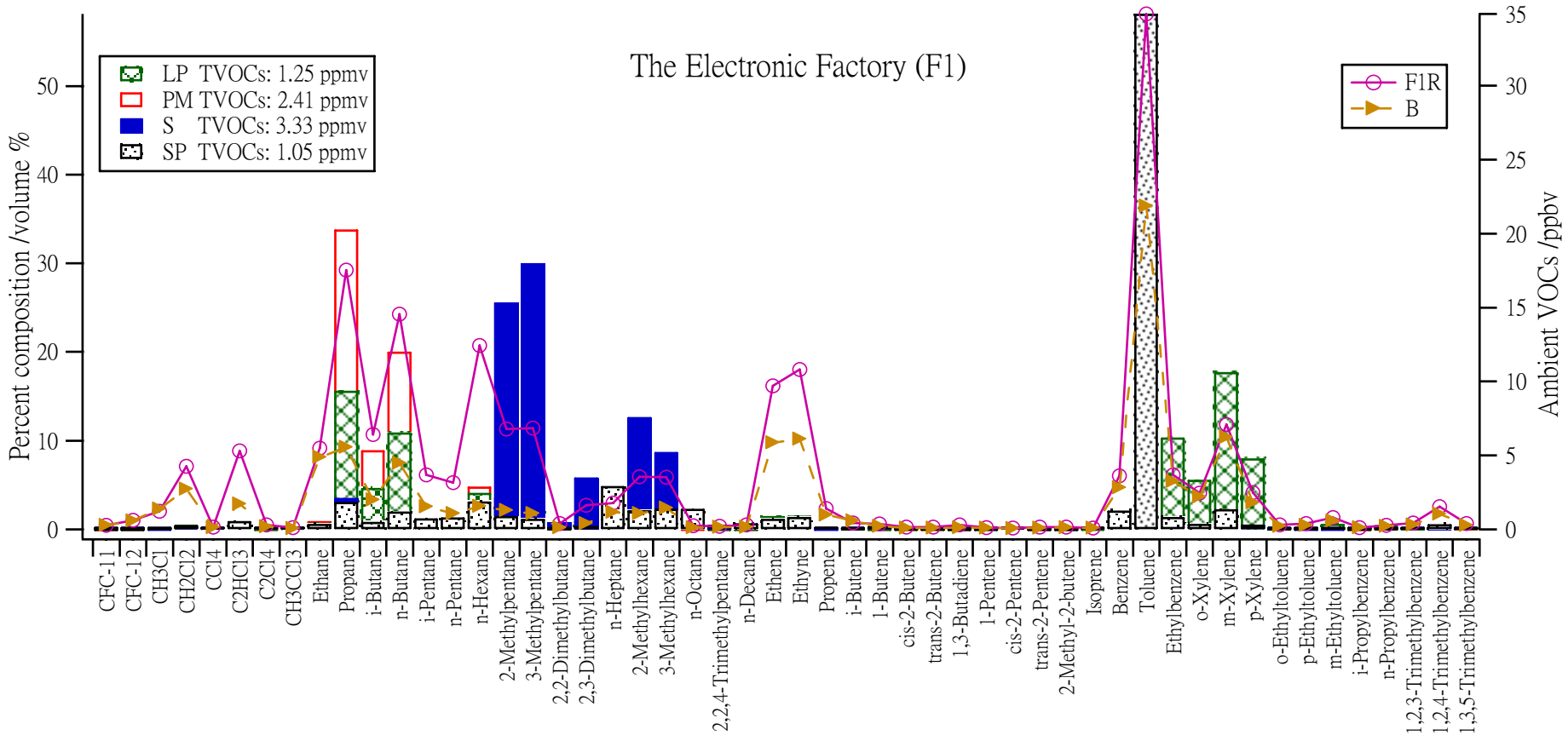
High mean TVOC level in the background (90.92 ppbv) was slightly lower than the level of urban (116.86 ppbv) and roadside (117.93 ppbv). In addition, the VOC composition of the urban and background were similar (Table 6.3). These observations suggested that VOCs from previous day frequently and significantly affected the atmospheric VOCs in the morning of following day.

Direct and fresh industrial emissions from the corresponding factories resulted in much higher total VOCs on the rooftop of the electronic factory and printing factory. In

addition, their VOC compositions greatly depended on the VOC source signatures of the related work processes. The saturated hydrocarbon contributed about half of the total VOCs to F1R, followed by one-third of the aromatic hydrocarbon. The rooftop ambient atmosphere of the printing factory contained over three-quarter of the aromatic hydrocarbon and about 20% of the saturated hydrocarbon. Similar to the VOC compositions for offset printing in the US (Wadden et al., 1995a), toluene, ethylbenzene, xylenes and a group of C_9 substituted aromatic hydrocarbons were greatly elevated in the neighboring atmosphere. The total VOCs of the printing factory (3.81 ppmv) was more than 20 times higher than that of the electronic factory (0.18 ppmv). This observation suggests that the emission strength of the printing factory was much higher. In terms of the total VOCs, the work processes of the electronic factory were one order smaller than those of the printing factory (except for gluing). Large contributions from neighboring industrial and vehicular emission sources also accounted for the great difference between these two ambient categories, because the neighboring environment of F2 was more complicated and the factory was relatively close to other factories and residential buildings. Thus, significant VOCs emitted from other industrial activities (e.g. electric appliances, adhesive tapes and metal products) highly contributed to the rooftop atmosphere of F2.

The four work processes in F1 were divided into two types. Plastic molding and soldering mainly emitted saturated hydrocarbons. Spray painting and logo printing mostly released aromatics. The increase in saturated hydrocarbons in logo printing was partly attributed to the influence of plastic molding, as both sites are placed 20 meters apart in the same workshop. The total VOCs of the four work processes in F1 (Table 6.3) ranged from 1.05 ppmv (SP) to 3.33 ppmv (S). Higher total VOCs in paraffin-involved work processes and closer distance between the soldering and the rooftop led to higher percent composition of saturated hydrocarbons in F1R.

Similarly, the three work processes in F2, including paper printing (PP), glossing (LSB) and gluing (G), mainly contributed to aromatics. Over three-quarter of the aromatic hydrocarbon was found on the F2 rooftop. More importantly, the inter-contamination of respective work processes prevailed in F2, because of close distance between each work process and their very strong emission strengths. The total VOCs of the three work processes in F2 were 4.66 ppmv (G), 13.21 ppmv (LSB) and 38.06 ppmv (PP).



Note: background (B), electronic rooftop (F1R),, logo printing (LP), plastic molding (PM), spray painting (SP) and soldering (S).

Fig 6.3 VOC source signatures (in percent composition) of F1 and background against the 52 interested VOCs

6.3.3 VOC fingerprints of the electronic factory (F1)

The VOC profiles of F1 and background are plotted against the 52 interested VOCs in Figure 6.3. VOC emission sources that contributed much to the rooftop ambient of F1 are illustrated. Most of the abundant VOCs on the rooftop were from corresponding work processes inside the factory. The saturated and aromatic hydrocarbons were the two major VOC groups.

The process of plastic molding transforms raw material into various types of plastic casting. Polystyrene, polypropylene and acrylonitrile butadiene styrene (ABS) are the three major plastic polymers used as raw material in the molding. Several light saturated hydrocarbons (Figure 6.3), including propane, n-butane i-butane and n-hexane, were mainly found in the workshop of the plastic molding. These four VOCs comprised 67.5% of the total VOCs. It was believed that they escaped from their corresponding polymers in the molding machine under high temperature. Among the four samples of the plastic molding (Table 6.4), PM4 was sampled during the maintenance and testing operations of a molding machine. The mixing ratios of the four abundant saturated hydrocarbons were one order higher than those under normal operation (PM1, PM2 and PM3). Both improper and normal cases showed similar ratios of i-butane, n-butane and n-hexane to propane, respectively (Table 6.4). There was no cover on the top of a

container that held molten polymers during the maintenance and testing operations. After testing, the residue of molten polymers remained and was free to escape into the atmosphere. Hence, it was anticipated that enormous quantities of propane, i-butane, n-butane, and n-hexane would evolve if poor emission controls were applied or machine operations failed. Also, using mold releasing agent contributed to n-butane and n-hexane (Table 6.2).

Table 6.4 Four abundant VOCs of the plastic molding (ppbv)

	*PM1	*PM2	*PM3	*PM4
propane (n-C_3)	225.72	284.68	420.74	2651.06
i-butane (i-C_4)	64.19	76.94	106.41	668.98
n-butane (n-C_4)	144.82	175.91	240.27	1464.72
n-hexane (n-C_6)	32.04	41.83	64.98	337.58
i- C_4/n- C_3	0.28	0.27	0.25	0.25
n- C_4/n- C_3	0.64	0.62	0.57	0.55
n- C_6/n- C_3	0.14	0.15	0.15	0.13

* Four source samples of plastic molding

In addition, the assembly of electronic parts was processed by soldering, and saturated hydrocarbon was significantly emitted. Five heavy branched-saturated hydrocarbons (2-methylpentane, 3-methylpentane, 2-methylhexane, 3-methylhexane and 2,3-dimethylbutane) that totaled 82.9% of the total VOCs were dominant in the separated workshop. After the soldering process, it was required to remove excess flux residue from a circuit board by acetone, alcohols or organic cleaning solvents. It was believed that their elevated mixing ratios were likely related to the utilization of

soldering flux thinner. Heat on the residue flux speeded up the evaporation of cleaning solvents. In recent years, other countries like US, deionized water instead of CFCs (CFC-113) and 1,1,1-trichloroethane, are used to remove flux (USEPA, 1995a). Similar mixing ratios of CFC-113 (not included in the calculation of percent composition) were found among the background (88.0 pptv), F1 rooftop (94.1 pptv) and soldering (109 pptv), while the mixing ratio of 1,1,1-trichloroethane in the soldering (511 pptv) was about seven and five times higher than those measured in the background (71 pptv) and F1 rooftop (119 pptv), respectively. It indicates that uses of 1,1,1-trichchloroethane as cleaning solvents was still common in the electronic manufacture in the PRD.

The other two work processes mainly emitted aromatic hydrocarbons. Toluene contributed about 60% of the total VOCs in the separated workshop of spray painting. Toluene is one of the most common components found in a variety of paint thinners in the PRD (He et al., 2002) and Korea (Kim et al., 2001a), and in emissions from paint activities in other countries (Srivastava et al., 2000; Seila et al., 2001). Slight increases in other solvent-related VOCs like n-heptane, n-hexane, 2-methylhexane, 3-methylhexane, benzene and m-xylene were also observed in the workshop. Most of these VOCs in the paint diluting solvent, thinner and spray painting wastewater were also quantified (Table 6.2).

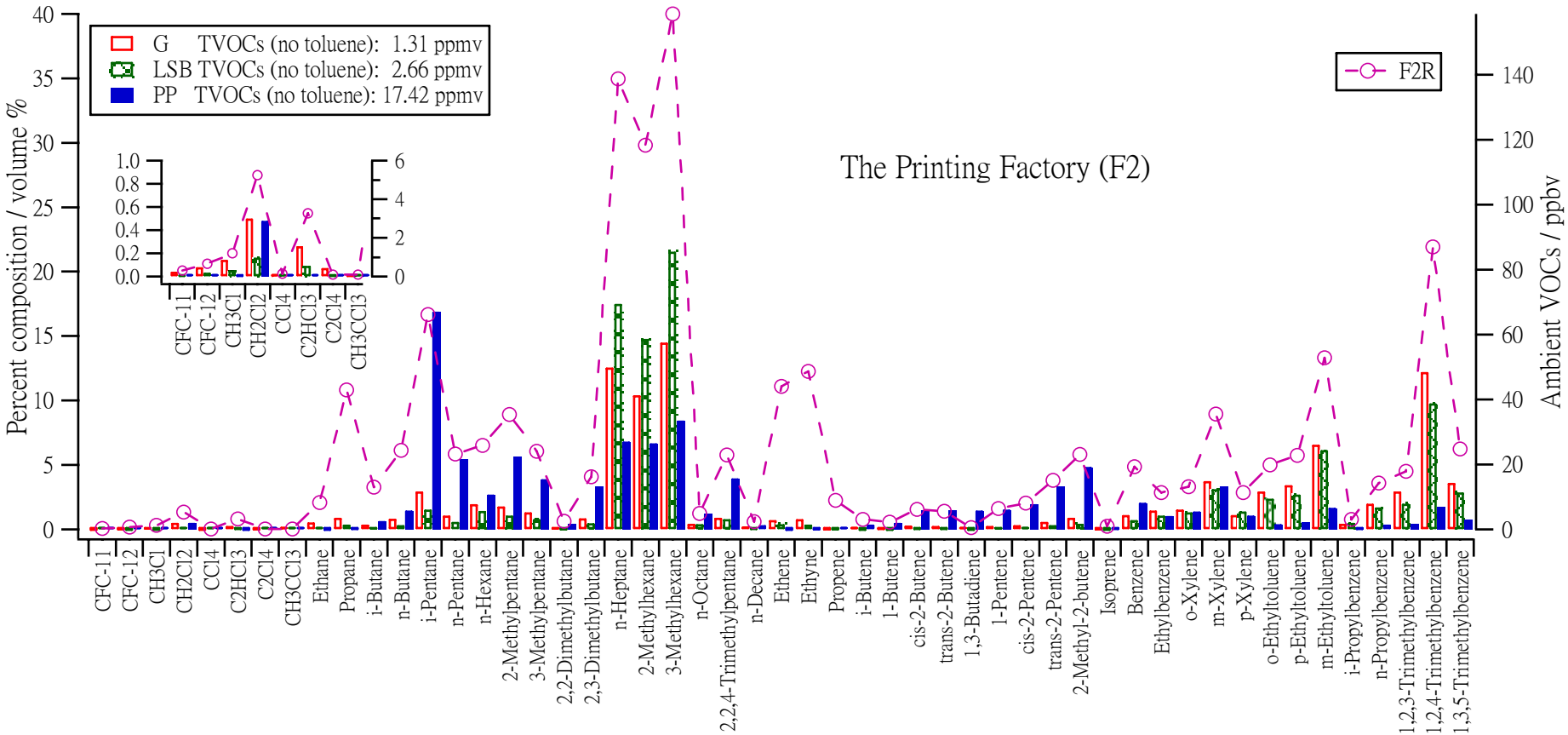
As logo printing and plastic molding shared the common workshop (Appendix-1), the four saturated hydrocarbons emitted from molding machines significantly contributed to the obtained VOC source signature of logo printing. Small emphasis was put on the saturated hydrocarbons (propane, i-butane, n-butane and n-hexane) when discussing the VOC source signature of logo printing. Printing small logo and symbol on the surface of product by paints and molds emitted four aromatic hydrocarbons (m-/p-xylene, o-xylene and ethylbenzene), totaled over 40% of the total VOCs. This percent had been largely underestimated due to the influence of the saturated hydrocarbon from the plastic molding, though n-butane and n-hexane were partly contributed by the mold releasing agent when cleaning the mold occasionally. Also, these four aromatic hydrocarbons were found to be dominant in the silk-screen cleaning solvent and paint diluting solvent (Table 6.2).

Table 6.5 Mixing ratios (ppbv) of some VOCs that were not directly emitted from various work processes in F1

VOCs	Logo printing	Plastic Molding	Soldering	Spray painting	Electronic rooftop	Background
CH_2Cl_2	4.86	6.29	7.77	4.31	4.26	2.73
C_2HCl_3	6.95	6.51	11.27	8.25	5.32	1.71
ethane	7.93	16.61	6.29	5.83	5.49	4.89
i-pentane	6.60	10.81	41.16	12.92	3.70	1.54
n-pentane	6.28	6.67	26.24	14.09	3.17	1.06
ethene	14.46	14.27	11.34	10.98	9.70	5.87
ethyne	15.41	14.58	12.74	12.57	10.82	6.11

Most of the abundant VOCs measured on the rooftop of F1 were attributed to the direct

emission of the four work processes. Propane, i-butane, n-butane and n-hexane were mainly from the plastic molding; 2-methylpentane, 3-methylpethane, 2-methylhexane, 3-methylhexane and 2,3-dimethylbutane were from soldering; toluene and n-heptane were from the spray painting; m-/p-xylene, o-xylene and ethylbenzene were from logo printing. However, a few VOCs were obviously not contributed from the four work processes and yet had higher mixing ratio than the background (Table 6.5). For example, ethene, ethyne, i-pentane and n-pentane were mainly emitted from vehicular exhaust and gasoline evaporation. Relatively high i-pentane and trichloroethylene (C_2HCl_3) mixing ratios measured in the soldering process indicate their significance contributions to the rooftop ambient atmosphere. Increases in C_2HCl_3 and CH_2Cl_2 on rooftop were likely related to industrial emissions from metal degreasing operations (Wadden et al., 1991; USEPA, 1998b) in several neighborhood metal processing factories. Similar mixing ratios of ethane to the background level indicate that there are no significant corresponding sources nearby.



Note: printing rooftop (F2R), paper printing (PP), glossing (LSB) and gluing (G).

Fig 6.4 VOC source signatures (in percent composition) of F2 against the 51 interested VOCs (without toluene)

6.3.4 VOC fingerprints of the printing factory (F2)

The mixing ratios of the F2 rooftop and the VOC sources signatures (%) of the three work processes are plotted against the 51 interested VOCs species in Figure 6.4. Toluene was excluded in the figure and the calculation of percent composition in this part, as it was enormously found in all sampling atmospheres, totaled 71.9% of the total VOCs in gluing (G), 79.9% in glossing (LSB), 54.2% in paper printing (PP), and 67.5% in the rooftop ambient. Toluene was the most abundant pollutants in 1992 Toxic Release Inventory (TRI) printing industry data and it comprised about 70% of the total chemicals released (USEPA, 1995b). VOC contribution to the F2 rooftop is simply illustrated in Figure 6.4. Most of the abundant VOCs in the rooftop ambient were from corresponding work processes, especially from paper printing. In contrast to the F1 rooftop, several VOCs (ethene, ethyne, propane and propene) were greatly contributed by neighboring unknown sources instead of the inside work processes. Strong inter-contamination of respective work processes and neighboring unknown sources was due to the complex and dense environment (Appendix-2).

Toluene was the major VOC in the printing industry. Examining the toluene levels of respective work processes showed that paper printing was the prevalent source of toluene in F2. The toluene mixing ratio of paper printing (20.63 ppmv) was twice that of

glossing (10.55 ppmv) and about six times higher than that of gluing (3.35 ppmv). A fivefold increase in the toluene level (22.63 ppmv) in a glossing sample was observed, while baking the surface of semi-products on which the UV varnish was smeared. Lower toluene level (4.51 ppmv) was measured without baking. As toluene is the single VOC component identified in the UV varnish (Table 6.2), baking could lead to an enormous evaporative emission under high temperature. No toluene was found in the fountain solution, therefore the fountain solution was not the sources of toluene. The high toluene level measured in paper printing was the result of the heavy use of solvent based inks, thinners and cleaning solvents. 93.1% and 69.1% of toluene (in wt %) were found in the quantified VOC compositions of graphic arts in US and solvent based inks in Korea, respectively (Scheff and Wadden, 1993; Kim et al., 2001a). In contrast, the adhesive was the only organic solvent in the process of gluing. The major VOC components quantified in the adhesive were CH_2Cl_2 and n-hexane. No toluene in the adhesive indicates that gluing did not contribute to the toluene level. Thus, the atmosphere of gluing was greatly affected by other work processes, especially paper printing. The toluene level of gluing (3.35 ppmv) was mainly related to solvent uses by the other two processes.

According to the total VOCs and toluene level of the three work processes in F2, their

emission strengths could be roughly ranked: paper printing > glossing > gluing. In addition, the source profiles of the industrial solvents (Table 6.2) could be used to simplify the interpretation of the VOC characteristics in F2 (Figure 6.4). Among the three work processes, glossing and gluing were simpler than paper printing. There were limited numbers and less diversity of industrial solvents for these two processes. Their VOC emission characteristics could be simplified as their vapor composition of the UV varnish and the adhesive, respectively. Toluene was a single VOC component identified in the UV varnish, contributing 79.9% of the total VOCs to the atmosphere of glossing (Table 6.3). CH_2Cl_2 (3.60 ppbv) and n-hexane (19.94 ppbv) slightly increased in the atmosphere of gluing, as they were the two VOCs quantified in the adhesive. However, there were large amount of other VOCs that were not contained in these two industrial solvents measured in the atmosphere of the corresponding atmospheres. It was believed that heavy fugitive and uncontrolled emission from paper printing contributed these VOCs.

CH_2Cl_2 and 1-butene were quantified in the fountain solution (Table 6.2). So, the observation of the increases in their mixing ratios in the atmosphere of paper printing was reasonable (Figure 6.4). There were other industrial solvents used for printing, such as solvent based inks and ink diluting solutions. Gasoline or other cleaning solvents

were used to clean plate cylinders and rollers that were frequently semi-immersed in fountain solutions.and inks, before starting a new batch of printing job. It can be seen from Figure 6.4 that the atmosphere of paper printing was enriched with the three groups of NMHCs. Abundant saturated hydrocabrons (i-pentane, n-pentane, n-hexane, n-heptane, 2-methylpentane, 3-methylpetanes, 2,3-dimethylbutane, 2-methylhexane, 3-methylhexane and 2,2,4-trimethylpentane) were properly emitted from gasoline and organic cleaning solvents. The use of gasoline as cleaning solvent in printing industry in other countries in recent years has been banned, but it was commonly used in China because of its low cost, good cleaning and easy to dry properties. Gasoline was also used to clean spirit dulplicators, cylinder roll and residues of ink fountain, and these cleaning porcesses largely increased VOC mixing ratio measured in workshops (Scheff et al., 1995b). In general, i-pentane is a VOC marker for gasoline evaporation (Doskey et al., 1992; McLaren et al., 1996; Watson et al., 2001; Lu et al. 2003). 2-methylpentane, 3-methylpentanes, 2,3-dimethylbutane, 2-methylhexane and 3-methylhexane were also dominant in the soldering atmosphere in the eletronic factory due to the use of cleaning solvents.

In addition, a number of unsaturated hydrocarbons were simultaneously enhanced, including 1-butene, cis-2-butene, trans-2-butene, 1-pentene, cis-pentene, trans-pentene

and 2-methyl-2-butene (Figure 6.4). These reactive unsaturated hydrocarbons were likely related to the fountain solution and ink, as 1-butene was dominant in the fountain solution. These unsaturated hydrocarbons were likely formed in the process of distillation and reflux, when the fountain solution and ink were heated up. In addition, increases in aromatic hydrocarbons were likely related to the use of ink and ink diluting solvents (Figure 6.4). Toluene, ethylbenzene, m-/p-xylene and o-xylene were common components of paint diluting solvents and thinners used in the electronic factory (F1) (Table 6.2). Various aromatic hydrocarbons were significantly found in the atmosphere of sheetfed offset printing shops and in their emissions (Wadden et al., 1995a).

6.3.5 The contribution of VOC sources to the local air quality of Qingxi

Comparing the 10 most abundant VOCs measured in the five ambient environments (Table 6.6), the influence of the two targeted industries on the local air quality (urban site) could be briefly interpreted. Obviously, toluene was the most abundant VOC in all sampling environments. An extremely high toluene level (21.88 ppbv) measured in the background indicates that large quantities of toluene that were emitted from the various local industries in a whole day could remain in the atmosphere to affect the air quality of following morning. Toluene together with m-xylene was emitted from various industries that included painting and printing activities (Seila et al., 2001; He et al.,

2002). Ethyne and ethene were the second and fourth in the ranking of the urban atmosphere. In general, these two combustion VOC products were contributed by vehicular exhaust. Significant increases of them were also observed in the roadside atmosphere, but the low roadside B/T ratio (0.16, wt/wt) was most likely related to the influence of high toluene emissions from neighborhood industries, similar to the roadside ratios (0.12-0.13) observed in Zhuhai under influence of PRD regional outflow (Chapter 5).

Table 6.6 The ten most abundant VOCs (ppbv) in the five sampling atmospheres

Background		Urban		Roadside	
toluene	21.88	toluene	36.58	toluene	18.94
m-xylene	6.25	ethyne	8.60	ethyne	16.98
ethyne	6.11	propane	5.83	ethene	11.90
ethene	5.87	ethene	5.26	n-butane	7.15
propane	5.55	ethane	4.32	m-xylene	6.04
ethane	4.89	1,2,4-trimethylbenzene	4.19	ethane	5.42
n-butane	4.48	m-xylene	4.07	propane	5.39
ethylbenzene	3.26	n-butane	3.80	i-pentane	4.26
benzene	2.82	CH_2Cl_2	3.19	benzene	3.62
CH_2Cl_2	2.73	C_2HCl_3	3.04	i-butane	3.22
Electronic Industry				Printing Industry	
toluene		34.86		toluene	2564
propane		17.53		3-methylhexane	158.7
n-butane		14.56		n-heptane	138.8
n-hexane		12.43		2-methylhexane	118.3
ethyne		10.82		1,2,4-trimethylbenzene	86.97
ethene		9.70		i-pentane	66.18
m-xylene		7.09		m-ethyltoluene	52.81
3-methylpentane		6.85		ethyne	48.61
2-methylpentane		6.79		ethene	44.01
i-butane		6.42		propane	42.88

High positions of propane and n-butane in the urban atmosphere (Table 6.6) were partly associated with electronic industry or other manufacturing industries related to plastic

molding, as these two VOCs were emitted during plastic molding. In addition, vehicular emission partly contributed to the n-butane level. Although no LPG profile was obtained in Dongguan, leakages from LPG use may be one of the propane sources (Chen et al., 2001). 1,2,4–trimethylbenzene was likely related to printing industry, and m-xylene were emitted from various industries that involved the uses of cleaning solvents and thinners (Kim et al., 2001a). High CH_2Cl_2 and C_2HCl_3 levels (Table 6.6) in the urban atmosphere may be due to the use of metal degreasing agents in local metal processing factories (Wadden et al., 1991) and the use of adhesive and fountain solution in printing factories or various other related industries.

6.4 Concluding remarks

The VOC emissions of electronic and printing industries were characterized using obtained VOC source signatures of corresponding work processes and industrial solvents. Extremely high toluene levels measured in the atmosphere of background (21.88 ppbv) and urban (36.58 ppbv) reveals the great VOC contribution from neighborhood industrial activates to the local air quality. Significant toluene levels were also found in the industrial emissions of the two targeted industries. Propane and n-butane that were abundant in the industrial emission of the electronic industry were enriched in the urban atmosphere. Ethyne and ethene were mainly emitted from

vehicular exhaust. CH_2Cl_2 and C_2HCl_3 were the two most abundant halocarbons. Except for a small increase in the workshop of soldering, C_2HCl_3 was not dominant in both targeted industries and it may be released from metal degreasing operations in local neighborhood metal processing factories.

The total VOCs of the printing factory (3.81 ppmv) was about 20 times higher than that of the electronic manufacturing factory (0.18 ppmv), indicating that the emission strength of the printing factory was much higher. Most of the abundant VOCs on the rooftop of the electronic factory were emitted from corresponding work processes inside the factory. Toluene was the predominant VOC in the atmospheres of the printing factory. It contributed more than half of the total VOCs in the processes of paper printing, glossing and gluing. The solvent profiles of the UV varnish and the adhesive showed that the work process of glossing released toluene, while gluing emitted small amount of CH_2Cl_2 and n-hexane. So, the work process of paper printing had the highest tendency to contribute toluene and other VOCs.

Chapter 7 Recent Changes in Atmospheric VOCs in the PRD

7.1 Change in the atmospheric toluene level

The three VOC studies reported in the three previous chapters showed that the atmosphere toluene levels were significantly high in the PRD region. Toluene was the most abundant VOC in the atmosphere of industrial, industrial-urban and industrial-suburban in 2000, in PRD regional outflow air transported to Zhuhai in 2003, and in the atmospheres of various sampling locations in Qingxi, an inland PRD town, in 2005.

The mixing ratios of toluene measured in the three studies are listed in Table 7.1. The air qualities of the three sampling environments that were characterized for different landuses, involving industrial activities, were investigated in the 2000 study throughout the five PRD cities. Toluene was the most abundant VOC found in all sampling environments. Direct influence by industrial emission led to the highest toluene mixing ratio measured in the atmosphere of industrial area, followed by the atmosphere of industrial-urban and industrial-suburban area. This was because the spread of industrial activity from urban area to suburban and rural areas just started at the end of the 20th

century, so that the number of industry in the suburban area was still low. Investigating the toluene levels in the atmosphere of different landuses provided important implication for relating the air quality of the PRD to industrialization in recent years.

Table 7.1 Toluene mixing ratios (ppbv) reported in the three PRD studies

2000 (Five PRD cities)		**2003 Zhuhai (16-Nov)**	
Industrial atmosphere	13.54	Roadside atmosphere	14.46
Industrial-urban atmosphere	11.51	Urban rooftop	14.11
Industrial-suburban atmosphere	7.30	Suburban rooftop	20.42
2005 (Qingxi, Dongguan)			
Roadside atmosphere		18.94	
Background		21.88	
Urban rooftop		36.58	
Electronic factory rooftop		34.86	
Printing factory rooftop		2564.37	

Toluene was suggested as an indicator of industrialization in the PRD. This suggestion was supported by the result of the VOC case study in Zhuhai (2003). The first sampling day (16-Nov) was selected to reveal the impact of the PRD regional outflow transport on the air quality of Zhuhai. High toluene mixing ratios (14.46 to 20.42 ppbv) measured in the three sampling environments (Table 7.1) were contributed by industrial emission from inland PRD cities, as prevailing north wind transported polluted air masses from Zhongshan and Guangzhou to Zhuhai. In addition, the atmosphere of the suburban site was strongly affected by local industrial sources on the second sampling day. This local industrial plume from the local neighborhood industrial area (Tangjia) enriched high

toluene level (20.76 ppbv). In contrast, low toluene mixing ratios on the third sampling day was due to the influence of clean sea air. As such, toluene (3.34 ppbv) was slightly enhanced in the atmosphere of roadside due to vehicular emission. Its contribution to the local air quality was much reduced, relative to those from industrial emissions on the two previous sampling days. In contrast to local vehicular emissions, industrial emissions became the major contributor of atmospheric toluene from 2000 to 2003 due to fast industrial growth in recent years.

The last study (2005) presented higher atmospheric toluene levels than those measured in the two previous studies (Table 7.1). The background atmosphere that was measured in early morning (local time 0600) was enriched with toluene (21.88 ppbv). No industrial activities operated in that period indicates that toluene from the previous day had substantial effect on the following day. Dilution of air pollutants by increasing tropospheric mixing height at noon resulted in slightly lower toluene level (18.94 ppbv) at the roadside site. There were huge amount of toluene emitted into the atmosphere from various industrial activates in a whole day, so that the highest toluene level (36.58 ppbv) occurred in the urban atmosphere in late afternoon. Also, toluene was dominant in the atmospheres of these two industries and their work processes. This observation was consistent with the VOC source profile of their solvents. Toluene was the major

component of spray paint diluting solution (electronic industry) and UV varnish (printing industry). As the toluene mixing ratio of the printing factory (2560 ppbv) was two orders higher than that of the electronic factory (34.9 ppbv), the printing factory contributed much more toluene to the local ambient atmosphere.

The findings in the three VOC studies reveal that toluene was the most common VOC involved in industrial emission in the PRD. It is important that toluene contribute to the increase in the number of high ozone day and hazy day, due to its high atmospheric mixing ratio, though its ozone formation potential was lower compared to the unsaturated hydrocarbon. Its growing events observed from 2000 to 2005 imply that the development of manufacturing industry had rapidly increased in recent years. Large contribution from printing industry was clearly revealed in the last study. If atmospheric toluene level continues to increase in the coming years, the air quality of the PRD and Hong Kong will be further deteriorated. In addition, high toluene mixing ratio has harmful effect on the health of industrial workers and public. It is necessary to develop and implement appropriate formulation of emission control strategy in order to reduce the industrial emission of toluene and other VOCs in the region.

7.2 Industrial use of halocarbons in the PRD

In general, the atmospheric mixing ratio of halocarbons is significantly lower than that of NMHCs, as halocarbons are not as common as NMHCs emitted from various anthropogenic sources. They were just emitted from certain specific industrial and domestic activities, such as the use of metal degreasing solvent and cleaning solvent, chemical processing in manufacturing pharmaceutics, refrigerant gases for air conditioning and freezer, and foaming agent (Aucott et al., 1999; McCulloch et al., 1999b; Sturrock et al., 2002; McCulloch et al., 2003). Although halocarbons are in trace level (in pptv) in the atmosphere, they also play an important role on the depletion of the ozone layer. Thus, some of the chlorofluorocarbons (CFCs) were banned or gradually phased out in other countries, but they were still used in China. In addition, halocarbons could be extracted as potential tracers for PRD industries.

7.2.1 Atmospheric mixing ratios of CFC-11, CFC-12, tetrachloromethane (CCl_4) and 1,1,1-trichloroethane (CH_3CCl_3)

CFC-11, CFC-12, CCl_4 and CH_3CCl_3 are usually well mixed in the global atmospheric environment due to their very long atmospheric residences, so that a small discrepancy in mixing ratios was often measured between urban and remote ambient air (Sweet and Vermette, 1992). The mixing ratios of CFC-11, CCl_4 and CH_3CCl_3 had decreased from

1987 to 1996 in the polluted European air masses measured at Mace Head, Ireland, after the Montreal Protocol was implemented. The baseline halocarbon mixing ratios in the Northern Hemisphere have begun to decrease, though CFC-12 was continuously increasing in Europe (Derwent et al., 1998). These four man-made halocarbons have not been completely phased out in many developing countries, such as China. The statistical results of these four halocarbons based on other studies and the 2000 VOC study in the PRD are tabulated in Table 7.2. Their mean mixing ratios in the atmosphere of industrial (T1), industrial-urban (T2) and industrial-suburban (T3) measured in the PRD are higher than those reported by Derwent et al. (1998). Small differences in the two CFC mixing ratios measured in 1991 in Asia when compared to North Hemisphere baseline in 1991, respectively, (Talbot et al., 1996; Derwent et al., 1998) suggest that they were used less frequently in Chinese industrial activities in the past. However, there had been obvious increases in their mixing ratios in the PRD from 1991 to 2000, most likely because of the rapid increase in various industrial activities, agricultural activities, and the growing installation of air conditioners using CFCs in the PRD at the end of the 20th century. Nevertheless, the level of CCl_4 did not change much in the past, and CH_3CCl_3 seemed to be gradually phasing out in the PRD in recent years.

Table 7.2 Comparison of the four halocarbons (pptv) with other studies

	CFC-11	CFC-12	CCl_4	CH_3CCl_3
1991 [a]	265	506	113	160
1991 [b]	266	504	105	150
1994 [b]	267	526	102	123
1995 [b]	267	532	102	109
1996 [b]	265	535	101	93.1
*T1 [c]	285	638	125	105
*T2 [c]	303	619	109	84.3
*T3 [c]	314	572	110	90.2

[a] Mixing ratio in Fresh (< 2 days) Asian Continental-North Outflow observed at < 2 km (Talbot et al., 1996)
[b] Northern Hemisphere baseline halocarbon mixing ratios by halocarbon sorting method (Derwent et al., 1998)
[c] Average mixing ratio of the three categories (T1, T2 and T3) in our study in the PRD
* T1, T1 and T3 refer to industrial, industrial-urban and industrial-suburban samples, respectively (Table 4.1).

The study on the air quality of Zhuhai (2003) provided more detailed VOC characteristics of industrial plume in the PRD. Examining the mixing ratio of these four halocarbons at the suburban site (Table 7.3) provide additional sight into the use of the halocarbons in the region. Based on the three characteristic winds, clean air masses from the sea (Day 3) could be used as the reference of the clean background level of the halocarbons in the region. The PRD regional outflow air (Day 1) and local industrial plume (Day 2) enriched these four halocarbons with respect to the background. Similar to the 2000 study, a small variation of CCl_4 level (95.5-137 pptv) was found. In addition, the remaining halocarbons were the highest in the local industrial emission, as the role of dilution was less significant in the short range transport. Much higher CH_3CCl_3 level from local industrial area, relative to that from inland PRD cities and the sea, most likely indicates that CH_3CCl_3 was more specific to a smaller number of industrial

activities and it was less commonly emitted from various PRD industries.

Table 7.3 Atmospheric mixing ratios of the four halocarbons (pptv) in the PRD

	CFC-11	CFC-12	CCl_4	CH_3CCl_3
Zhuhai suburban site (2003)				
Inland PRD cities*	288	615	137	96.5
Local industrial area*	462	660	101	235
The sea*	272	573	95.5	27.0
Qingxi, Dongguan (2005)				
Background	284	588	123	71.0
Roadside	276	676	126	42.3
Urban 9/F Rooftop	283	630	121	63.0
Electronic factory	291	607	154	119
Printing factory	304	672	128	96.7

*The source of air masses transported to the Zhuhai suburban sampling site

High background levels of these four halocarbons (Table 7.3) were measured in the inland town (Qingxi) compared to Zhuhai, which is located on the south coast of the PRD. Similar and high atmospheric mixing ratios were measured in background and urban rooftop. Higher halocarbon levels in the atmosphere of the electronic factory may be due to the metal degreasing operations from some neighborhood metal processing factories, because they were not found to be dominant in the composition of the industrial solvents and corresponding work processes. These four halocarbons in the atmosphere of the printing factory were also contributed by neighborhood sources. After all, the 2005 study showed that these four halocarbons were not used in the electronic manufacture and printing industries.

In general, the two CFCs (CFC-11 and CFC-12) were frequently dominant in the atmosphere of the PRD. They were still used by various industrial activities. The installation of air conditioning was another contributor in recent years due to fast housing development in the whole PRD region. Their uses in PRD industries as well led to the increase in their contribution to global mixing ratio. In contrast, CH_3CCl_3 was just found to be in high mixing ratio in certain environments. This phenomenon implies that it was gradually phased out in the region. The use of CCl_4 was not common in the PRD in recent years.

7.2.2 Atmospheric mixing ratios of dichloromethane (CH_2Cl_2), trichloroethylene (C_2HCl_3) and tetrachloroethylene (C_2Cl_4)

In contrast to the four long-lifetime halocarbons discussed previously, the three shorter-lifetime halocarbons (CH_2Cl_2, C_2HCl_3 and C_2Cl_4) were also used in various industrial activities. In general, they were used as cleaning solvents, paint strippers and metal degreasing solvents (McCulloch et al., 1999b). CH_2Cl_2 was also used as solvent in chemical processing to manufacture pharmaceuticals (McCulloch and Midgley, 1996). Their atmospheric mixing ratios reported in the three VOC studies are listed in Table 7.4.

Table 7.4 Comparison of the atmospheric mixing ratios (pptv) of the three halocarbons in the PRD

	CH_2Cl_2	C_2HCl_3	C_2Cl_4
Five PRD cities (2000)			
Industrial (T1)	1020	68.2	115
Industrial-urban (T2)	674	63.7	70.6
Industrial-suburban (T3)	748	69.3	162
Zhuhai suburban site (2003)			
Inland PRD cities	2780	897	262
Local industrial emission	5300	123	185
The sea	129	15.0	49.9
Qingxi, Dongguan (2005)			
Background	2730	1710	173
Roadside	1800	1300	62.3
Urban 9/F Rooftop	3190	3040	64.3
Electronic factory	4260	5320	315
Printing factory	5250	3260	94.3

Obviously, the atmospheric mixing ratio of CH_2Cl_2 and C_2HCl_3 had tendencies to increase in the period of the three studies (Table 7.4). CH_2Cl_2 was the most abundant halocarbon throughout the five PRD cities in 2000. Its highest mixing ratio (1020 pptv) was found in industrial area (T1), because of direct emission from neighborhood industrial activities. Slightly lower mixing ratios were found in T2 and T3. The second study (2003) showed that sharp increases in the CH_2Cl_2 level in polluted air masses transported from inland PRD cities (2780 pptv) and the local industrial area (5300 pptv). Their mixing ratios were one order higher than that quantified in clean air masses from the sea (129 pptv). This observation suggests that the use of CH_2Cl_2 in PRD industries became more and more common. The elevation of atmospheric CH_2Cl_2 levels in the five sampling environments in the third study (2005) was measured. CH_2Cl_2 was found in

the glossing solution and the adhesive used in the printing factory (Table 6.2), so that it was abundant in the rooftop atmosphere of the printing factory (5250 pptv). High CH_2Cl_2 mixing ratio found in the electronic factories (4260 pptv) may be due to the metal degreasing operations in some neighborhood metal processing factories.

Atmospheric C_2HCl_3 had been gradually increasing in the PRD (Table 7.4). Similar and low mixing ratios were measured in the three sampling environments throughout the five PRD cities. C_2HCl_3 probably corresponded to the use of cleaning and degreasing solvents in domestic activities (Wadden et al., 1991; USEPA, 1998b), but it was found that uses of C_2HCl_3 was not common at the end of the 20th century. Large and slight increases were observed in industrial emissions transported from inland PRD cities (897 pptv) and the local industrial area (123 pptv) to the suburban site of Zhuhai, respectively. It shows that VOCs in the transported air mass highly depends on the types of industry upwind of the site. Higher atmospheric mixing ratios of C_2HCl_3 were further observed in the five sampling environments of Qingxi (2005). The mixing ratio of the background sample (1710 pptv) was about twice the PRD regional outflow air to Zhuhai (2003). Its mixing ratio in the urban atmosphere was 3040 pptv and the highest mixing ratio was found on the rooftop of the electronic factory because of metal degreasing operations in neighborhood metal processing factories and slight contribution from the soldering

inside the electronic factory.

No significant increases in the atmospheric mixing ratio of C_2Cl_4 in the period of the three VOC studies suggest that C_2Cl_4 was not widely used by various PRD industries and was specific in a small number of industries such as dry cleaning. Its highest mixing ratio was found in the industrial-suburban area (T3). Slight increases in C_2Cl_4 were observed, when characterizing industrial plumes from inland PRD cities and the local industrial area to Zhuhai. Similarly, its atmospheric mixing ratios were kept low, but it varied largely in the five sampling environments in the study on the local air quality of Qingxi.

The results of the three VOC field measurement showed that CH_2Cl_2 and C_2HCl_3 became the two abundant halocarbons in the industrial emission of the PRD. Industrialization led to significant increases in their atmospheric mixing ratios in recent years in the same way as toluene.

Chapter 8 Potential VOC Markers for PRD Industries and Industrial Work Processes

8.1 Two main pathways of industrial VOC emission

Fuel combustion and solvent evaporation are the two major types of anthropogenic VOC emission. Apart from combustion VOC emission, a wide variety of VOCs escaped to the atmosphere are due to evaporative loss from fuels and solvents. Combustion VOC products (e.g. ethene, ethyne and propene) were mainly emitted from growing number of automobiles in the PRD. However, heavy fuel consumption from industrial activities could not be overlooked, as VOC contributions to neighborhood atmosphere of a steel plant and a cement production factory were significant (Chapter 4). The emission strength of this type of industry that frequently consume huge amount of fuel, was also much higher than automobiles, though they are smaller in number. As similar abundant VOCs were enriched in the emission of this type of industry and automobile, it was considered that potential VOC markers were more difficult to extract as compared to other type of industry, involving fugitive emissions from solvent uses, such as printing, painting and degreasing. Volatile organic compounds with high vapor pressure can easily escape to the neighborhood atmosphere. For example, 2-methylhexane, 3-methylhexane and n-heptane can easily escaped from a solvent tank that is used to

immerse their product overnight inside a shoemaking factory, and several other halocarbons that are not included in vehicular exhausts are frequently found in industrial solvents and cleaning solvents.

More importantly, the 2000 annual VOC emissions in the PRD (HKEPD, 2002) revealed that solvent emission was among the major VOC contributors in this region. Printing was the top VOC contributor in the industrial sector and totaled 19,072 tonnes (2.29%). Paint emitted 67,564 tonnes (8.13%) in the VOC containing product sector. These significant contributions led us to place our focus on them in the year-2005 VOC characterization study. Hence, the extraction of potential VOC markers to represent these corresponding industries is performed.

8.2 Electronic Manufacture

According to HKEPD (2002) report, electronic manufacture in the PRD just contributed 3 tonnes of VOCs in the ambient atmosphere in 2000. This small value shows that its VOC emission was significantly lower than other polluting industries, such as chemical/rubber/plastic (9,355 tonnes/yr), pulp and paper industries (8,864 tonnes/yr) and oil refinery (6,238 tonnes/yr). The result of the last study (2005) also confirms that the emission strength of the electronic factory was approximately two orders lower than

that of the printing factory, but a result was satisfactory in the trial of the designed approach of VOC source apportioning. This is because separated workshops led to clear source profile of respective work processes, thus the VOC composition on the rooftop ambient could be assigned to respective sources inside the factory. More importantly, spray painting and plastic molding are two very common work processes among the various industries in the region, such as toy making, metal castings, automobile body painting, rubber and plastic manufacture. Thus, their VOC source profiles could be applied to other industries and then help to study their VOC contributions to the air quality of the PRD region.

8.2.1 Spray painting

In fact, spray painting is the painting technique that use a device to sprays the paint on the surface of products. As such, VOC fugitive emissions into the atmosphere was tremendous when compared to traditional painting, as paint sprayers convert the paint into tiny droplets using air compressors to perform surface coating. In addition, this industrial work process is also commonly found in a variety of small-sized and large-sized factories in the PRD. It has important VOC contribution to the atmosphere of the PRD, as painting occupies 8.13% of the 2000 annual VOC emissions in the PRD.

Figure 8.1 presents the 10 most abundant VOCs collected in the workshop of spray painting and several abundant VOCs quantified in the corresponding solvents. Propane and 3-methylhexane were not reported in the solvent vapor analysis in the Air Laboratory (HKPU), as propane could not be analyzed by the GC/MS system and 3-methylhexane was not completely separated, while m-xylene was reported as the sum of m-xylene and p-xylene in the solvent vapor analysis. Obviously, the uses of solvents contributed the three most abundant VOCs. Toluene was the single component quantified in the diluting solvent for spray paint, and n-heptane, n-hexane, 2-methylhexane and benzene were enriched in the thinner. In addition, toluene and n-heptane were found to be the two major components of the wastewater air. These could explain why these two VOCs were the most abundant in the workshop atmosphere. However, n-octane was likely emitted from the paint, other than from these two solvents.

Toluene and n-heptane were the two dominant VOCs in the work process of spray painting in the electronic manufacture and other PRD industries related to spray painting. The high annual VOC emission from painting contributed greatly to the increase in atmospheric toluene level in wide areas of the region.

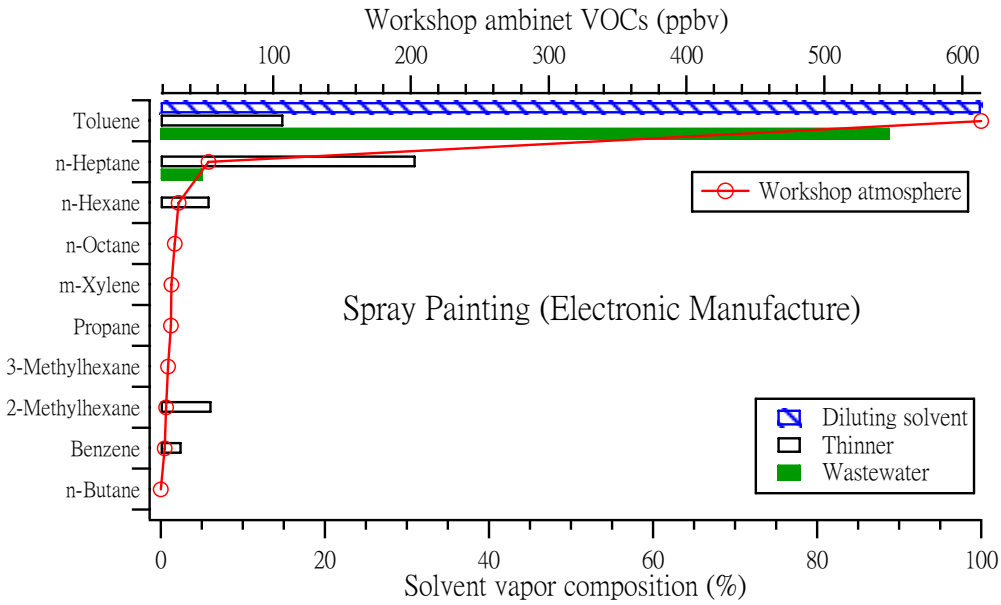


Fig. 8.1 Comparison of the VOC source signature of spray painting with corresponding solvent composition.

8.2.2 Plastic molding

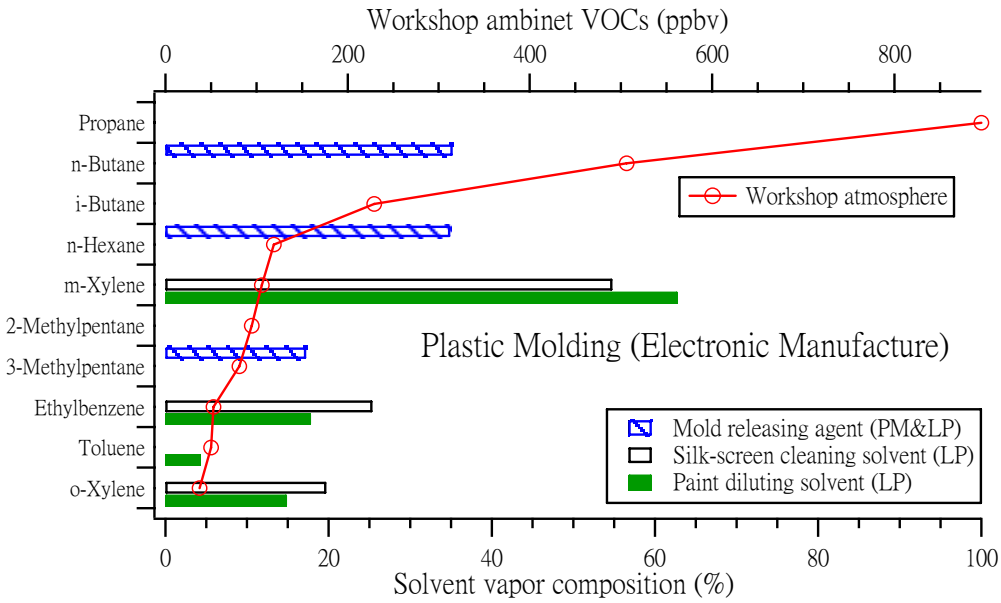


Fig. 8.2 Comparison of the VOC source signature of plastic molding with corresponding solvent composition

Plastic molding is the process of manufacturing by shaping molten plastic using a rigid

frame called a mold. A plastic cast is formed after the molten plastic is solidified inside the mold. The target electronic factory applied injection molding. Plastic pellets are molten under heating and molten plastic is forced into a mold. Fugitive emission from the molten plastic makes significant VOC contribution to neighboring atmosphere. This process is widely involved in various PRD industries (e.g. toy making and plastic film) that manufacture a variety of plastic parts.

The 10 most abundant VOCs measured in the workshop of the plastic molding and several abundant VOCs quantified in the corresponding solvents are presented in Figure 8.2. Propane and 2-methylpentane were not reported in the solvent vapor analysis in the Air Laboratory (HKPU), as propane could not be analyzed by the GC/MS system and 3-methylhexane was not completely separated, while m-xylene was reported as the sum of m-xylene and p-xylene in the solvent vapor analysis. The mold releasing agent was used in the work processes of plastic molding and logo printing, but the uses of cleaning solvent and diluting solvent were only found in the logo printing. The compositions of these two solvents were also reported in the figure because both work processes operated separately in the same workshop. In fact, solvent uses were not the major source of VOCs in plastic molding. The mold releasing agent was slightly contributed n-butane, n-hexane and 3-methylpentane as compared to strong fugitive emission from

the molding process.

The four most abundant VOCs, propane (i-butane, n-butane and n-hexane) were the major composition of the fugitive emission. Similar ratios of propane to the other three VOCs were observed between the normal operation and maintenance. The increase in the mixing ratios of these four VOCs is due to abnormal operation in maintenance (Table 6.4). These observations indicate that the emission of these four saturated hydrocarbons mainly from plastic molding. The silk-screen cleaning solvent and paint dilution solvent used in logo printing emitted the abundant aromatic hydrocarbons (m-xylene, ethylbenzene, toluene and o-xylene).

Light saturated hydrocarbons were mainly emitted from plastic molding. For example, propane, n-butane, i-butane and n-hexane were dominant in the electronic factory. It was believed that light saturated hydrocarbons were similarly emitted from other electronic factories and other industries that performed plastic molding. However, the abundant VOCs and their ratios were found to have variations due to different raw plastic pellets being used.

8.3 Printing

Printing emitted 19,072 tonnes of the VOCs in 2000 (HKEPD, 2002). It was the largest

VOC contributor in the industrial sector in the PRD. The result of assigning VOCs measured in the rooftop ambient atmosphere to the corresponding work processes was less satisfactory, because the closely packed and complex environment of the printing factory led to large extent of inter-contamination among the three sampling work processes and additional contribution from neighborhood VOC sources. Among the three sampling work processes, paper printing was the major VOC contributor. It largely affected the other two work processes and the rooftop ambient atmosphere. Thus, the source profile of paper printing was used to represent that of printing industry collected on the rooftop in this section.

The four-color offset printing technique is widely used in printing industry in the PRD. A variety of graphite inks, ink diluting solvents and glossing solutions were used. Gasoline or other cleaning solvents were commonly used to remove the residue of inks from printing rollers and plate cylinders. As a result, toluene level was frequently found to be extremely high and comprised 52.18% and 67.42% of the total VOCs in the atmosphere of paper printing and the rooftop atmosphere, respectively. A high mean rooftop toluene level was mainly contributed by paper printing. The toluene contribution from glossing increased to a comparable value as that from paper printing when the product of glossing was being baked. This toluene level was approximately

five times higher than that without baking. Toluene was the single VOC component quantified in the UV varnish, so that huge amount of toluene escaped into the ambient atmosphere with faster rate due to baking.

Table 8.1 Comparison of the ten most abundant VOCs (ppbv) in the printing factory

	Paper Printing (mean)		Printing Factory's Rooftop (mean)	
1	toluene	20600	toluene	2560
2	*i*-pentane	2820	3-methylhexane	159
3	3-methylhexane	1500	n-heptane	139
4	n-heptane	1210	2-methylhexane	118
5	2-methylhexane	1200	1,2,4-trimethylbenzene	87.0
6	2-methylpentane	991	i-pentane	66.2
7	n-pentane	905	m-ethyltoluene	52.8
8	2-methyl-2-butene	855	ethyne	48.6
9	2,2,4-trimethylpentane	705	ethene	44.0
10	3-methylpentane	673	propane	42.9

Table 8.1 lists the most abundant VOCs found in the atmosphere of paper printing and rooftop. The table could not completely reflect the VOC profile of paper printing, as the number of enhanced VOCs was at least 44. Isoprene that was commonly found in biogenic emission (Jobson et al., 1994; Riemer et al., 1998) and marginally measured in the fuel combustion exhaust (McLaren et al., 1996) was 17.39 ppbv (44th VOCs) in the atmosphere of paper printing. This observation indicates that a variety of NMHCs were enriched in the emission from paper printing, including saturated, unsaturated and aromatic hydrocarbons. Most of them were emitted from gasoline that was used for cleaning, and the portion of reactive species (unsaturated hydrocarbons) was likely

related to the distillation and reflux processes emissions from the ink fountain solution. However, ethene, ethyne and propene that are generally found in vehicular exhaust were excluded in these forty-fourth enhanced VOCs, since ethyne and ethene were dominant in the rooftop ambient atmosphere only. Instead of the printing factory, they were contributed by automobiles and neighborhood industries. CH_2Cl_2 was the only one halocarbon in these 44 enhanced VOCs, as it was one of the major components found in the fountain solution. It was also found in the glue used in the factory, but the emission strength of gluing was significantly weaker than that of paper printing.

Instead of several dominant VOCs in the emission of electronic manufacture, a variety of NMHCs (except for ethyne, ethene and propene) and CH_2Cl_2 were much enhanced in the emission of printing industry in the PRD. Furthermore, the result gives a conclusion that printing industry was one of the strongest VOC contributors in the PRD. More importantly, extremely high toluene levels in its emissions provide a substantial reason for interpreting the relationship between the growing atmospheric toluene level and industrialization in the region in recent decades, and for explaining why high atmospheric toluene levels were frequently measured in various environments in the region and in polluted air masses transported from inland PRD cities to downwind regions.

Chapter 9 Conclusion and Recommendation

9.1 Conclusion

Three case studies had been carried out from 2000 to 2005 in the PRD region. Although the duration of the respective sampling studies and the number of samples were limited, the impacts of industrial emission on the air quality of the PRD and its perimeters were assessed. Field VOC data was used to characterize industrial VOC emission in the region, to examine the changes of regional atmospheric VOC mixing ratio under the influence of industrialization, and to analyze the composition of polluted air masses transported from inland PRD cities to downwind regions.

The year-2000 study firstly revealed the influence of the spread of industry from urban area to suburban and rural areas. Industrial emissions greatly affected most suburban areas. Toluene (7.30-13.54 ppbv) was the most abundant species in the three sampling environments. B/T ratios (0.22-0.27, wt/wt) of the three industrial-related environments were lower than those of the roadside microenvironment (0.59). It indicates that toluene contribution from industrial solvent uses outweighed that from vehicular emissions. In addition, CH_2Cl_2 was the most abundant halocarbon in the atmosphere of the PRD, indicating its significant solvent utilization in various PRD industries.

The impact of transported industrial emission on Zhuhai, a south coastal city, was clearly revealed in the second study. High toluene (13.73-22.83 ppbv) and CH_2Cl_2 (1610 -3270 pptv) levels were involved in polluted air masses transported from inland PRD cities to Zhuhai in PRD winter. These dominant VOCs were similar to those observed in 2000. Although local vehicular emissions significantly contributed to Zhuhai downtown under the influence of clean sea air, the toluene level (~4 ppbv) was slightly enhanced and substantially lower than those under the influence of industrial plume transported from inland PRD cities and the local neighborhood industrial area. The result raises the importance of industrial toluene emissions and its regional effect due to the industrialization.

In the third VOC study, the measured VOC source signatures of printing and electronic industries provide substantial information for the analysis of the atmospheric VOC composition in the PRD. The total VOCs of the printing factory (3.81 ppmv) was about 20 times higher than that of the electronic factory (0.18 ppmv). Toluene contributed more than half of the total VOCs for each work process inside the printing factory. In effect, printing industry was the substantial toluene contributor among various PRD industries. This result helps to explain why the atmospheric toluene level had gradually

increased in the observations of the three VOC studies.

After all, the observation-based results of this research study help us to realize that toluene and CH_2Cl_2 were abundant in the atmosphere of the PRD. Atmospheric toluene level was frequently found higher than 20 ppbv in suburban areas or background environments though it is also dominant in various urban cities over the world. The implication of its substantial and widespread elevations agrees with the fast industrialization in the whole PRD region. More importantly, it seems that VOCs from industry poses larger regional effect to the local and downwind air qualities than that from automobile in recent years. In addition, some VOC source signatures of PRD industries (printing and electronic industries) were firstly obtained in the PRD. They are helpful to reduce the modeling uncertainty of input parameters. The updated VOC source signatures can further improve the result of observation-based and model-based study on the regional air quality.

9.2 Recommendation

This was a limited research study. The small number of samples and the limitation of time, resource and manpower restricted the scope of the research work. The results only provide preliminary information for investigating the impact of industrial VOC

emission on the air quality of the PRD and its perimeters. The change of atmospheric VOC mixing ratios due to the industrialization was shown. The following are a few suggestions that would contribute to the organization of a more comprehensive VOC characterization study in the region.

1. A growth trend of some interested VOCs (toluene and CFCs) was observed on the basis of the VOC data collected in the three field studies. The short-period of measurements and the variation in sampling locations could only give us a rough indication of the general atmospheric VOC levels in the PRD. Long-period measurements at some fixed sampling sites can provide more detailed and accurate atmospheric VOC mixing ratios. It can also give the trend of fluctuation for interested VOCs.

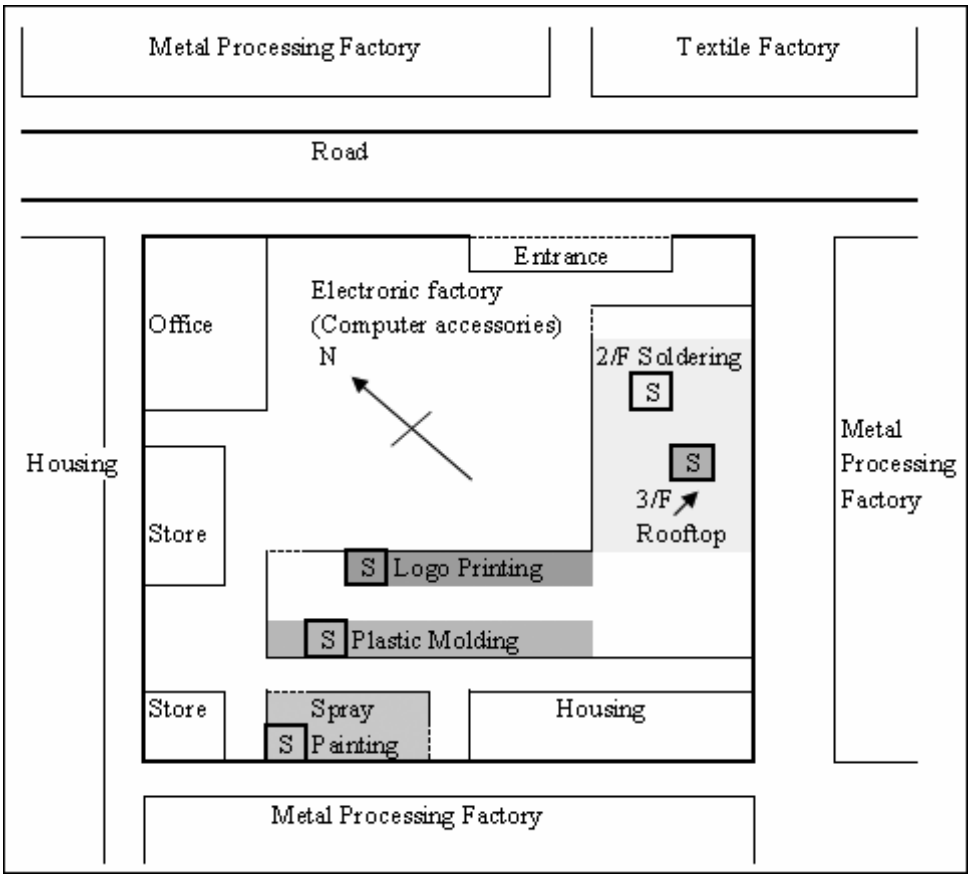
2. The three VOC sampling studies were carried out in autumn and winter. Prevailing north wind transports air pollutants from inland PRD cities and deteriorate the air quality of downwind regions. Similar measurements should be conducted in summer to observe different emission behaviors under the influence of different meteorological conditions, different evaporative emission strengths from industrial solvents, and varied vehicular emissions.

3. Source VOC source signatures were only characterized for two prevalent industries (printing and electronic manufacture). These two industries mainly contribute VOCs through evaporative loss from solvent uses. There are many other industries involved in heavy solvent utilization, such as toy, furniture and shoe manufacturing industries, which have not been characterized for the PRD region. The VOC profiles of other solvent related industries should be characterized for extensive comparison. In addition, the large contribution of fuel combustion by heavy fuel consumption industries was significant in the region. For example, VOC source profiles of cement and steel production should be obtained to build a more comprehensive VOC source database of PRD industries.

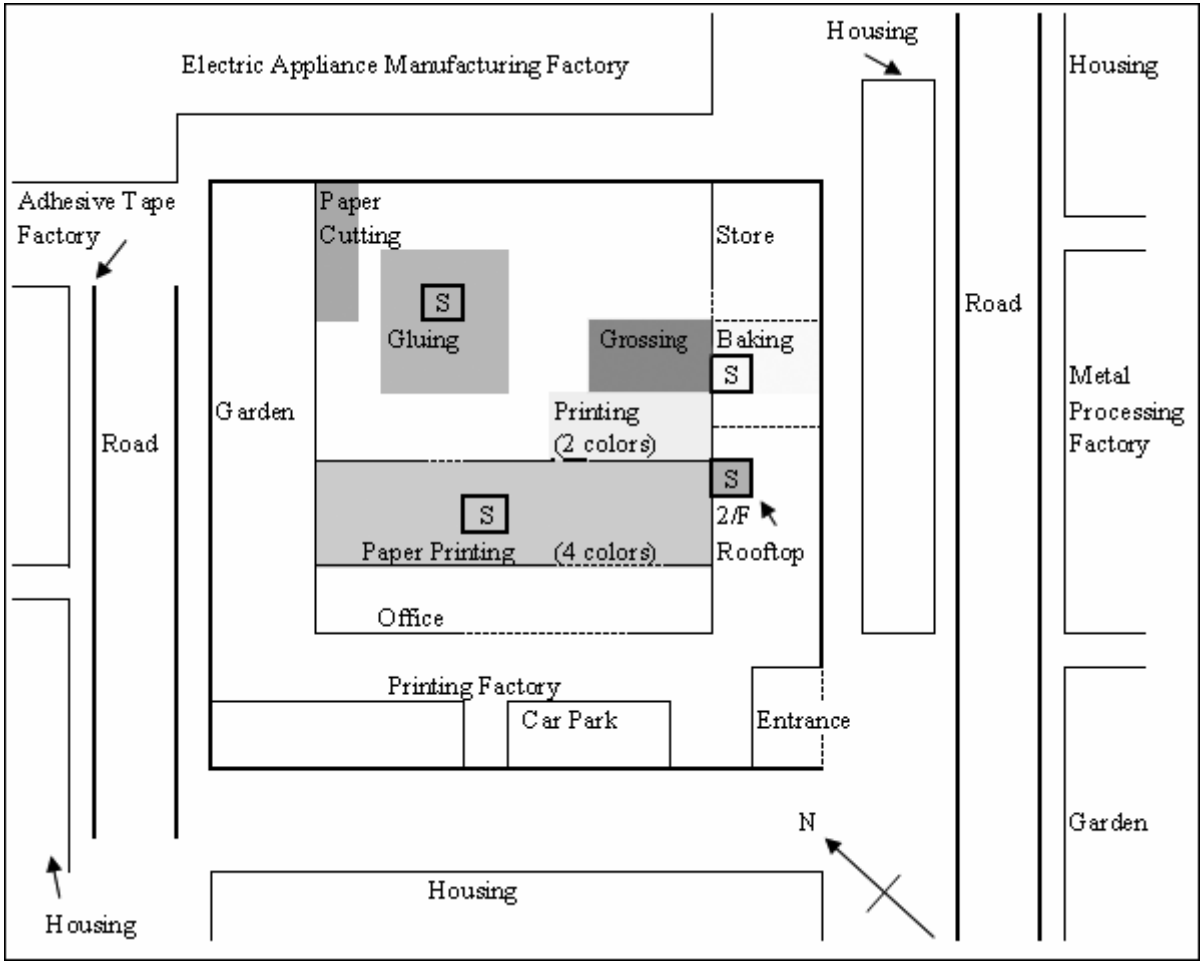
4. Although the solvent profiles obtained in VOC characterization study can successfully provide evidence to explain in situ industrial emissions, it was questionable whether they could apply to other similar factories in the PRD. As diversified industrial solvents could be used to perform the same job in different factories, analyzing more industrial solvents and grouping various solvents with similar purposes into respective classes can improve the representativeness of PRD solvent profiles.

5. Characterizing VOCs from industrial emissions is the main objective of this study. However, there was no field measurement of NO_x included. The important role of VOCs and NO_x on tropospheric ozone production is reviewed in Chapter 2. Their field measurement data are very important to develop an appropriate emission control strategy for the air quality of the PRD and Hong Kong. Thus, VOCs and NO_x should be simultaneously measured in future studies.

Appendices



Appendix-1 The configuration of the electronic factory (not in scale)



Appendix-2 The configuration of the printing factory (not in scale)

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