



**Study of VOC and Photochemical Ozone Pollution in the Pearl  
River Delta Region - Feasibility Study  
Agreement No. CE 2/2007 (EP)**

**Summary Report**

**January 2014**

Hong Kong Special Administrative Region  
Environmental Protection Department

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### **Remarks**

This report summarized the results found in Hong Kong SAR. Detailed results of the Pearl River Delta Economic Zone are not contained based on the agreement with Guangdong government.

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## 1 INTRODUCTION

### 1.1 Background

- 1.1.1 The rapid economic development in the Pearl River Delta (PRD) Region including Hong Kong Special Administrative Region over the past decade has resulted in changes in the nature of air pollutants emitted from various activities in the region. There has been a marked degradation in air quality and visibility over the region since the mid 90's.
- 1.1.2 The PRD Region has experienced more frequent regional photochemical smog (and also called regional haze) formation in recent years. Ozone is a major constituent of photochemical smog and elevated ground-level ozone concentrations have been recorded in the region. The ozone concentrations in Hong Kong have shown a moderate upward trend since the 1990s, with rural areas experiencing higher levels of ozone than urban areas<sup>1,2</sup>. Volatile organic compounds (VOCs) and Oxygenated Volatile Organic Compounds (OVOC) are important precursors to the formation of ground-level ozone. It is important to understand sources and strengths of photochemical ozone precursors as well as the spatial distribution of ozone, VOC and OVOC in order to understand the formation of photochemical smog in the region. Such information is essential to the formulation of appropriate regional smog controlling policy.
- 1.1.3 Environmental Protection Department (EPD) commissioned ENSR Environmental International, Inc (EEII) on September 27, 2007 to conduct Study of VOC and Photochemical Ozone Pollution In the Pearl River Delta Region - Feasibility Study (Agreement No: CE 2/2007 (EP)).
- 1.1.4 The main objectives of the study were collecting VOC and OVOC samples over the PRD Region covering a study area of 40,000km<sup>2</sup> (200km in length and width). The study area covered the whole territory of Hong Kong Special Administrative Region, (HKSAR) and the Pearl River Delta Economic Zone (PRDEZ) which includes Guangzhou, Shenzhen, Zhuhai, Dongguan, Zhongshan, Foshan, Jiangmen, Huizhou, and Zhaoqing. Please refer to Figure 1.
- 1.1.5 The aims of this Study are to identify the sources of VOC and OVOC, and to characterize the formation of photochemical smog. The collected data would enhance the understanding of the spatial distribution of VOC and OVOC in the PRD Region and aided the updating of the emission inventory for photochemical modeling. The Study included recommendations on the most suitable measures and strategies to reduce the regional smog problem. A total of eight measurements were conducted between Sept 2008 and Dec 2009 within four sampling days at 84 locations. Air quality modeling was used to help understand the characteristics of photochemical smog formation in the PRD

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<sup>1</sup> Wang et al., 2009, Increasing surface ozone concentrations in the background atmosphere of Southern China, 1994-2007. Atmospheric Chemistry and Physics 9, 6217-6227.

<sup>2</sup> EPD, 2010. Air Quality in Hong Kong 2009. Environmental Protection Department of the SARG, Hong Kong.

Region, and to support ozone control strategy development.

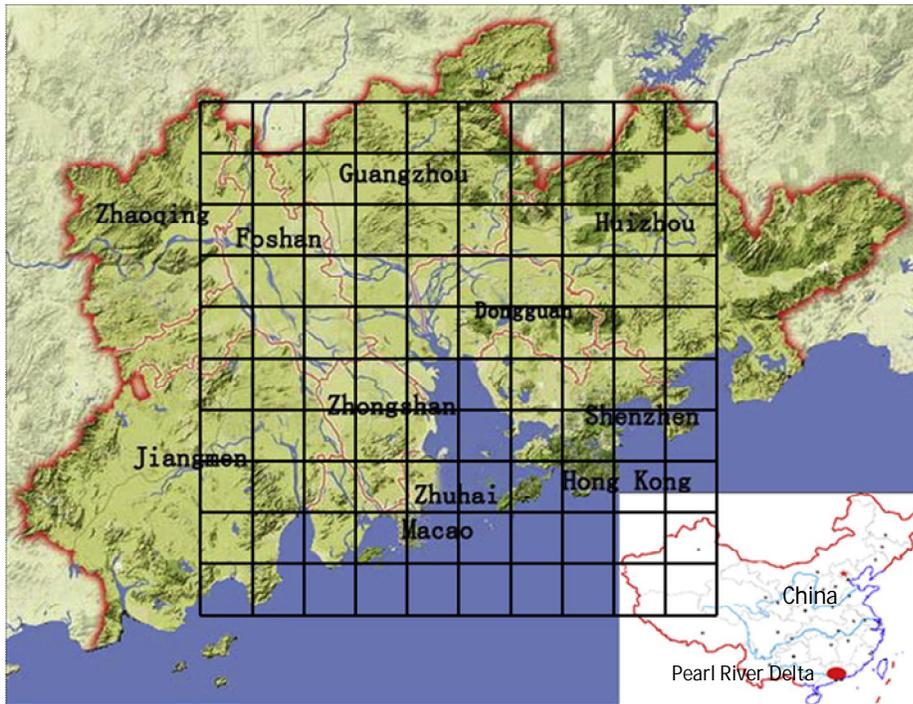
## 1.2 Significance of this Study

1.2.1 Some breakthrough results were obtained in this Study and summarized as follows,

- This is, perhaps, the first and foremost, and the largest regional grid sampling study including an area of 200kmx200km with VOCs and OVOCs field sampling and analysis. It helps better understand the VOCs and OVOCs' regional spatial and temporal variation.
- Based on data analysis, there are nine major VOCs sources in the PRD region which verifies that road transport is most influential emission sources among all and topped the ozone formation potential.
- By using PATH upgrade model, it simulates the ozone spatial and temporal variation and transportation characteristics. It identifies the ozone is affected by regional influence and the high ozone level is mainly related to local emissions.
- The finding further confirms the most effective emission reduction strategies would be targeted on road transport and industrial emissions.
- It also recommends strategies to augment the regional air quality monitoring network by setting up Photochemical Assessment Monitoring Stations (PAMS).

1.2.2 Various field data generated from the present study would complement national scientific programmes. The measurement data collected in this Study served an important source of reference on the smog formation mechanism in the PRD Region, and act as a major role during the formation of regional smog control strategy. The study findings shared and supported major scientific studies and topped up the smog formation mechanism in the PRD Region. The VOC data served as important scientific support and act as a major role during the formation of regional smog control strategy.

Figure 1 Study Area



## 2 STUDY FINDINGS AND DATA INTERPRETATION

### 2.1 Summary Findings

- 2.1.1 A total of 50 VOC species including methane (CH<sub>4</sub>), 39 non-methane hydrocarbons (NMHCs), 4 halocarbons, 5 alkyl nitrates and dimethyl sulphide (DMS), and carbon monoxide (CO) were quantified. In general, most VOC species had mixing ratios measured in the 4 sampling campaigns within ranges previously reported in the PRD Region or other cities in China.
- 2.1.2 VOC levels in the PRD Region were mainly dominated by C<sub>2</sub>-C<sub>5</sub> alkanes and alkenes, as well as benzene, toluene, ethylbenzene and xylenes (BTEX). VOC levels in Hong Kong, was relatively low within the study area.
- 2.1.3 Mixing ratios of most VOC species showed summer-low-winter-higher characteristics except alkyl nitrates and isoprene. This may result from dilution due to the increase in the mixing depth, more rainfall in the summer which caused a washout of pollutants, removal of VOCs by particulate matter by dry and wet deposition, and chemical removal, especially OH radicals, during the summer, etc. However, higher alkyl nitrates and isoprene formations due to atmospheric photochemical production and biogenic emission were found in summer respectively, resulting from more sunlight and higher temperature in summer.
- 2.1.4 Twenty-four hour passive OVOC samples were collected at all the 84 sampling sites, and active OVOC samples were collected in 2 time slots at 10 sampling sites in the first 2 sampling campaigns. The passive OVOC sampling was replaced by the more robust OVOC active sampling (extended to 20 sites) in the last 2 sampling campaigns to obtain more representative results. There were 19 targeted OVOC species considered in this study.
- 2.1.5 Although results of the passive OVOC sampling did not show a systematic spatial pattern for the quantified OVOC species, it was concluded that the order of magnitude of the OVOC concentrations measured with the passive sampling was in good agreement with those obtained with active sampling. This shows its capability for ambient OVOC measurement.
- 2.1.6 Based on the active OVOC sampling result, it was indicated that secondary formation was a significant source of OVOC. Moreover, it is observed that the total OVOC concentrations measured in Year 2 sampling were generally higher than the Year 1 sampling. This was consistent with the findings of VOC concentrations.

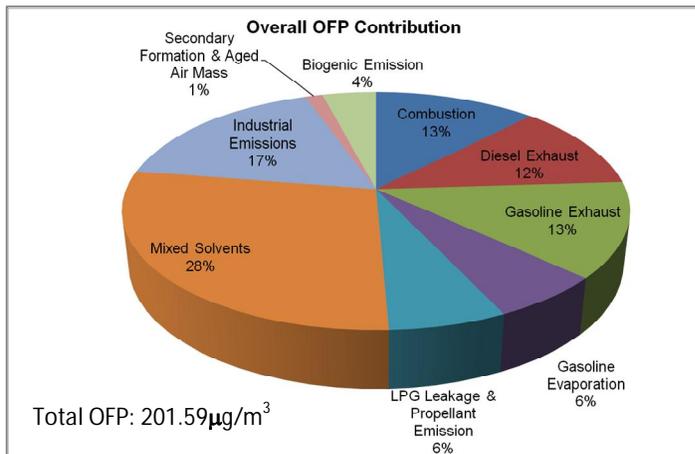
### 2.2 Source Apportionment and Ozone Formation Potential (OFP)

- 2.2.1 Principal Component Analysis (PCA) and Positive Matrix Factorization (PMF) models were applied to the collected VOC data to identify major air pollution sources and their contributions to ambient pollution levels.
- 2.2.2 A total of 9 VOC emission sources were found by PMF and similar sources were also

identified by PCA. Sources included combustion, diesel exhaust, gasoline exhaust, gasoline evaporation, liquefied petroleum gas (LPG) leakage & propellant emission, mixed solvents, industrial emission, secondary formation & aged air mass and biogenic emission, were identified by PMF and the source contributions at both 5:00am and 10:00am of the 4 sampling campaigns were estimated. Overall, the emission source contributions by gasoline exhaust was found to be the largest contributor (22.7%) to the ambient VOC concentration in the PRD Region, followed by industrial emission (15.9%) and LPG leakage & propellant emission (13.0%). The PMF results showed that traffic-related emissions (i.e. diesel exhaust, gasoline exhaust, gasoline evaporation and LPG leakage) and industrial-related emissions (i.e. industrial emission and mixed solvents) contributed to roughly an average of 50% and 25% of the ambient VOC levels respectively during the 4 sampling campaigns.

- 2.2.3 Ozone formation potential (OFP) indicates the potential of ozone formation caused by VOCs and understanding the OFP of individual emission sources would be helpful for policy makers to decide what direction of the control strategies should be focused on. The OFPs of different source categories identified by PMF analysis of the validated VOC data were further investigated to identify which particular emission source(s) had the highest potential for ozone formation in the PRD Region. In traffic-related emissions, OFP contributions from diesel exhaust and gasoline exhaust dominated (about 45%); while mixed solvents contribution was the most dominant one (28%) among the industrial-related emissions. Based on the above findings, the ozone control strategies for traffic-related sources should be developed focusing on the control of VOC emissions from diesel and gasoline exhausts; while those for industrial-related sources should be developed focusing on the control of VOC emissions from mixed solvents (Please refer to Figure 2).
- 2.2.4 OFP of OVOC was studied less frequent in previous researches. The average OFP was higher in the 2 summer sampling due to high level of photochemical reactions of most OVOC species in summer. Both VOC and OVOC have contributions to the ozone formation, the overall mean of total OFP contributed from OVOC ranged from 22.7% to 43.2% among the 4 sampling campaigns, revealed that OVOC is a main contributing group which warrants for further studies.

Figure 2 Overall OFP contribution percentages for the nine sources identified by PMF analysis



## 2.3 Air Quality Modeling Results

2.3.1 An upgraded PATH modeling technique was used to simulate the ozone concentrations in the PRD Region in the 4 sampling campaign periods. The emission inventory was updated for this study based on the information obtained from latest researches as well as the VOC measurement data and PMF results obtained from this study. The model outputs were compared against the observation values. Results showed that the PATH model can reasonably simulated ozone concentration, and the model performance was better for more remote sites.

2.3.2 Ozone Source Apportionment Technology (OSAT) was used to estimate the contributions of multiple sources areas, categories, and pollutant types to ozone formation in a single model run. It uses multiple tracer species to track the fate of ozone precursor emissions (VOC and NO<sub>x</sub>) and the ozone formation caused by these emissions within a simulation.

2.3.3 Based on the four campaigns results, ozone from the boundary condition (i.e. influence from outside of the study boundary) was a major source of ambient ozone at most sites. At Tap Mun site in Hong Kong, the averaged O<sub>3</sub> were formed under NO<sub>x</sub>-limited dominated situation generally because it was located at upwind position, whereas in Tung Chung and Yuen Long in Hong Kong, the ambient O<sub>3</sub> were dominated by boundary transport during the 2<sup>nd</sup> campaign and aggregate sources contributed at other times.

### **3 RECOMMENDATIONS**

#### **3.1 Implications on Emission Control Strategies in the PRD Region**

- 3.1.1 A typical ozone episode occurred in November 2006 was chosen for ozone control strategy development. CAMx OSAT analysis can give us the ozone source apportionment results, by which source region and source category could be controlled to attain the ozone air quality objectives. The OSAT results indicated that local emission sources were the dominant factor for the high ozone episode, while the transported ozone from outside of the PRD region was dominant factor for the background ozone level. The Observation-based model (OBM) was also used to identify the VOC-limited or NO<sub>x</sub>-limited conditions of all campaigns. Both OBM and OSAT showed comparable results although the OBM considered local emissions only.
- 3.1.2 Sensitivity analysis showed that reducing the VOC emission in the PRD Region would result in a general reduction of ozone concentration among the region especially the downwind area, and more significant reduction of ozone can be achieved by reduction the VOC emission from mobile sources in the region. Reduction of NO<sub>x</sub> emission in the PRD Region would result in a general reduction of ozone concentration in most area, but the ozone concentration would be increased in the directly downwind areas of the major emission sources. Reduction of NO<sub>x</sub> emission from mobile sources would have a general reduction of ozone concentration in the region except the downwind areas of Guangzhou and Hong Kong, while reducing NO<sub>x</sub> emission from point source would significantly increase ozone concentrations in areas immediately downwind of some major point emission sources.
- 3.1.3 Based on the results of source apportionment, OSAT analyses and sensitivity runs, traffic sources, area sources and point sources in the PRD Region were found to be the major contributors of ozone formation in the PRD Region including Hong Kong. Four ozone control scenarios were thus designed to investigate their impacts on the regional ozone concentrations. Modeling results revealed that reducing 50% of traffic in the PRD Region (control strategy 1) would be the most effective control scenario, and reducing 50% of VOC emissions from traffic and area sources on the PRD Region would have similar impacts. Reducing NO<sub>x</sub> emissions (50% and 85%) from point sources in the PRD Region would not be able to reduce ozone concentration in area directly downwind of major NO<sub>x</sub> emission sources.
- 3.1.4 Based on all the above findings, the ozone control strategies in the PRD Region should be focusing on controlling the emissions from traffic-related sources such as road traffic as well as industrial emissions including mixed solvents.

#### *Traffic-related sources*

- 3.1.5 Green measures for public transportation are especially suitable for Hong Kong since transportation network and facilities in Hong Kong are quite extensive and few extra infrastructures such as bus fleets rationalization are required for further optimization. On the other hand, marine emission is also one of the potential air pollution sources which

should be controlled by some possible measures such as reducing vessel speed when approaching port area, developing mandatory emission standards for engines, encouraging use of cleaner fuels and setting up emission control areas (ECAs) in PRD ports.

### *Industrial-related sources*

- 3.1.6 Based on the study findings, use of mixed solvents should be the major focus when developing the emission control strategies. In addition to the already implemented Air Pollution Control (VOC) Regulation (the VOC Regulation) and the Air Pollution Control (Petrol Filling Stations) (Vapour Recovery) Regulation in Hong Kong, the Pearl River Delta Clean Air Action Plan (廣東省珠江三角洲清潔空氣行動計劃<sup>3</sup>) also requires strengthened management of VOC content in products containing organic solvent for commercial and domestic consumption. The introduction on VOC emission standards covering both chimney discharges and fugitive emissions, and VOC content in industrial raw materials would be also looked for on VOC emissions control.
- 3.1.7 Others include strengthening of emission control of organic solvent consumption industries and control on VOC content in solvent products for commercial and domestic consumption. VOC emission standards for typical emission industries should also be developed.
- 3.1.8 Besides, strategies on energy utilization and other measures such as advocating energy efficiency, use of cleaner fuel, and promoting low carbon living can also help control ozone in the PRD Region.
- 3.2 Establishment of Photochemical Assessment Monitoring Stations (PAMS) Network
- 3.2.1 The precursors of photochemical smog such as NO<sub>2</sub> and ozone have been monitored in the regional air quality monitoring network. In Hong Kong, the measurements of VOC and OVOC have been measured in the toxic air pollutants (TAPs) programme in Tsuen Wan and Central/Western station, and project-based measurements such as real-time VOCs, NO<sub>y</sub>, TNMHCs, trace level CO, etc. are also measured to improve the understanding on the formation of photochemical ozone pollution in Tung Chung, Hong Kong. Results in this Study revealed that spatial distribution of emission sources in the PRD were not even, especially for different kinds of VOC sources. To accurately estimate the regional ozone contribution potential of a particular city cluster, emission source-oriented network design, such as the design philosophy of Photochemical Assessment Monitoring Stations (PAMS) and supersites air quality monitoring stations network, are applicable in the PRD Region. A more probable strategy would be the integration of these monitoring networks as one in the PRD Region, i.e. having both monitoring capability of photochemical oxidants as well as fine particles.
- 3.2.2 Based on the findings from PMF analysis, the source contribution hotspot stations of

<sup>3</sup> Reference: 2010. [http://www.gdep.gov.cn/dqwrzf/dqgl/dqfgwj/201008/t20100806\\_80179.html](http://www.gdep.gov.cn/dqwrzf/dqgl/dqfgwj/201008/t20100806_80179.html)

VOC are roughly located in three areas: 1) located right in the mouth of the Pearl River [Central PRD]; 2) Eastern PRD; and 3) Southwestern PRD. Three sub-PAMS Networks can be developed with these regions correspondingly.

3.2.3 To maximize current resources, several currently-in-operation PRD Network of Air Quality Monitoring Stations can be utilized and upgraded as PAMS station. For example, sites in the current two Network stations (Tsuen Wan and Tung Chung), the Hong Kong University of Science and Technology (HKUST) as well as Hok Tsui, which roughly lie northeast-southwest, can be transformed into PAMS stations network.

### 3.3 The Needs for Additional Air Pollutants Sampling in the PRD Region

3.3.1 As air pollution is getting complicated in the PRD Region, the monitoring capability should be enhanced and becomes more versatile in order to identify the root causes of the complex photochemical air pollution problems. On top of the criteria pollutants ( $\text{SO}_2$ ,  $\text{NO}_2$ ,  $\text{O}_3$  and  $\text{PM}_{10}$ ) that are monitored regularly in the PRD Regional Air Quality Network, more parameters are suggested to be included in the network stations. Similar to the suggestions on expansion of the network monitoring capability, the parameters should be added in view of the emission sources in the vicinity, location, meteorological conditions, resources constraints, etc.

3.3.2 In order to evaluate the complex air pollution issues such as photochemical ozone pollution, regional smog, visibility degradation, more comprehensive monitoring capacity is recommended. Recommended parameters on various types of monitoring network in the PRD Region were provided. For example, in urban monitoring stations, in addition to the currently monitored parameters, it is suggested including  $\text{PM}_{2.5}$ , CO,  $\text{NO}_y$  and meteorological observables in monitoring programme whereas more robust measurements are recommended in the PAMS stations network, e.g. HONO, PAN, fine particles ( $\text{PM}_1$  to  $\text{PM}_{2.5}$ ) etc.

## 4 OUTLOOK

### 4.1 Summary

- 4.1.1 Extensive VOC and OVOC data were collected in this Study. These data were useful for filling in the gaps to better understand photochemical pollution emissions sources and possible formation mechanism specifically in the PRD Region. The extensive VOC grab samples collected in this Study would be valuable for preliminary investigation on the spatial variations of air pollutants among the study area including transitional terrain. However, more intensive temporal sampling is suggested to help study the characteristics of secondary formation of ozone within the whole region.
- 4.1.2 OVOC was demonstrated to have significant contributions to ozone formation in this Study. This group of VOC was usually neglected in previous VOC studies conducted in the PRD Region. More intensive OVOC field measurements are thus recommended to fill the data gaps in this region.
- 4.1.3 VOC and OVOC samples collected showed different spatial and temporal variation patterns among the 4 sampling campaigns in this study; long term measurements of VOC, OVOC, and other ozone precursors such as NO<sub>x</sub>, as well we meteorological conditions are thus necessary for familiarizing their long-term trends and developing appropriate ozone control measures and strategies.
- 4.1.4 In demonstrating the ozone formation characteristics and the effectiveness of various ozone control strategies, it is suggested to include longer time period for modeling, for example, seasonal or yearly data should be included. More receptors should be considered in the analysis to seek appropriate measures among the whole region but not limited to specific sites. Continuous efforts should also be put on updating the emission inventory in the PRD Region due to the rapid development in the region.
- 4.1.5 Other than ground-based measurements, remotely-sensed data is also a possible source to monitor the air quality in the PRD Region at spatially wider scale. A comprehensive application system including satellite data with ground-based observation monitoring together is proposed to be set up because it could be useful to monitor temporal and spatial air quality properties at a larger regional scale at one time even though the availability of the remotely sensed gaseous pollutants in city scale may still be limited at present. The application of remote sensing technology is also one of the 863 programmes.
- 4.1.6 In summary, similar programmes with Guangdong and Hong Kong regional cooperation that demonstrated integrated and holistic approach will be useful for evaluating the effectiveness of wide-ranging control measures implement in the Guangdong province and Hong Kong. Some recently implemented measures such as the Guangdong Clean Air Action Plan of Pearl River Delta (廣東省珠江三角洲清潔空氣行動計劃), the Guangdong Air Pollution Control Measures of Pearl River Delta (廣東省珠江三角洲大

氣污染防治辦法<sup>4</sup>), a series of control measures implemented before and during the Asian Games in Guangzhou and Hong Kong's measures such as retrofitting coal-fired generating units with low-NOx burners and flue gas desulphurization systems; tightening emission standards for newly registered vehicles, reducing VOC emissions from printing process, paints and consumer products; encouraging the use of Euro V diesel; and launching the Incentive Scheme for Replacing Euro II Diesel Commercial Vehicles by New Commercial Vehicles, etc. would be much needed to gauge the effectiveness of these and many other control measures. Further regional cooperation should be encouraged to tackle the complex air pollution in the PRD Region in the years ahead to meet the goal of air quality at the level of developed world.

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<sup>4</sup> Reference: People's Government of Guangdong Province, 2009.  
[http://www.gd.gov.cn/govpub/zfwj/zfxxgk/gz/200903/t20090330\\_88639.htm](http://www.gd.gov.cn/govpub/zfwj/zfxxgk/gz/200903/t20090330_88639.htm)