Referee #1 comment

General comment

1. VOC/NOx ratio should only give a rough idea as to whether it is a NOx-sensitive or VOC-sensitive environment, which is crucial for ozone formation. However, VOCs are a complex mixture of compounds with large difference in reactivity with respect to ozone formation. The true impact of VOCs to ozone formation is more relevant to the reactivity of individual VOC species rather than to the total amount of VOCs.

We agree with the reviewer’s view. Instead of using the VOC/NOx ratio method to judge the VOC-limited or NOx-limited regimes, we mainly used the ozone isopleths diagram by observational data to judge the ozone formation regime, VOC/NOx ratio method was used only to further confirm the conclusion by ozone isopleths diagram in revised manuscript. It’s true that VOCs are a complex mixture of compounds with large difference in reactivity with respect to ozone formation, the truth is that we have already considered the reactivity of individual VOC species and rank the top ten VOC species by the traditional method (i.e. MIR and propylene-equivalent concentration) in original manuscript. We also used the VOC (reactivity)/NOx ratio to analysis the ozone formation regime in revised manuscript. Finally, considering the Ozone formation regime may be decided by the composition of VOCs, the VOC reactivity has been analyzed in O_3 isopleths diagrams in revised manuscript.

The analysis of VOC (reactivity)/NOx ratio has been added in revised manuscript (page9, line35-41), and the analysis of VOC reactivity in O_3 isopleths diagrams has been added in revised manuscript (page8, line29-41).

2. Only one site located in suburban Guangzhou is not appropriate for the formulation and implementation of ozone control strategies in Guangzhou.

The site we choose for this study is appropriate in some extent for the formulation and implementation of ozone control strategies in Guangzhou. The reasons are as follows:

Firstly, the previous studies show that high ozone episodes often occur in suburban Guangzhou, so choosing this suburban site to do some researches about ozone problems is targeted.

Secondly, the site selection has been demonstrated by many experts and is the main site of the observation network for atmospheric composition over Pearl River Delta in the CMA (China Meteorological Adminstration) network. You can see in figure 2 in revised manuscript, regardless of the large variation in concentration of the three types of VOCs, the relative contribution of the three groups remains fairly uniform throughout the observational time. Such uniformity implies that air was sufficiently homogenized from various point sources at the surface.

At last, you can monitor the typical air pollution processes in different seasons and under different weather conditions. You can see in figure 1 in revised manuscript that when the prevailing wind is northeasterly in December, the difference between weekends and weekdays for VOCs is very typical showing large amounts of pollutants are emitted from the downtown Guangzhou city. However, when the prevailing wind is southwesterly in July, the difference between weekends and weekdays for VOCs is not apparent for the reason that only small amounts of pollutants are emitted from the further suburban areas. So you can see two different typical air pollution processes in this site.

The description of the sampling site has been added in revised manuscript (page4, line 18-23 and line 30-36), the map has been changed and figure 2 has been added in revised manuscript.

3. There is no QA/QC of online VOC measurements. Any inter-comparison? Are all the instruments calibrated and how?

We agree with the reviewer's view. Actually, QA/QC of online VOC measurements has been done and the description needs to be added in manuscript. Inter-comparison is as follows：

(a) A zero gas check：It checks for memory effect or contamination.

(b) Drift check：It checks for a deviation between the original span value and the current span value.

(c) Deviation value ：It checks for a deviation between two current span values.

All the instruments need to be calibrated. Regarding the VOC calibration, we performed a zero gas check and a span gas check by using a five point calibration method. We qualified the VOC species by standard curve and quantified the VOC species by retention time.

The description of QA/QC has been added in revised manuscript (page5, line 21-30).

Specific comments

1) Very poor quality of Fig 1. Also, much more detailed map and surroundings should be plotted.

We agree with the reviewer’s view.

The map has been changed in figure 1 in revised manuscript. The surrounding cities are showed in the map. The VOCs concentrations in July when the summer prevailing wind is southwesterly and in December when the winter prevailing wind is northeasterly are also showed in the map. The description of sampling site has been added in revised manuscript (page4, line 18-23 and line 30-36).

2) Page 5 lines 10-12: why?

Two reasons are accounting for this. Firstly, the site selection has been demonstrated by many experts and became the main site of the observation network for atmospheric composition over Pearl River Delta in CMA network. Secondly, you can see the difference between weekends and weekdays for VOCs under different weather conditions.

The description has been added in revised manuscript (page4, line30-36).

3) How did you identify VOC species with GC-FID? What standards were used?

In a whole, the measurement is based on the principle that VOCs are absorbed by special materials in an enrichment tube, subsequently adsorbent VOCs are coming into a capillary column of a GC and separated, eventually detected by a FID detector (figure below).

The speeds of VOCs separation and the peak time in a capillary column of a GC are different, so we identify VOCs according to retention times of VOCs. The principle of FID is as follows：

(a) Sample gas effluent from analytical column passes by the flame and the hydrocarbons burn.

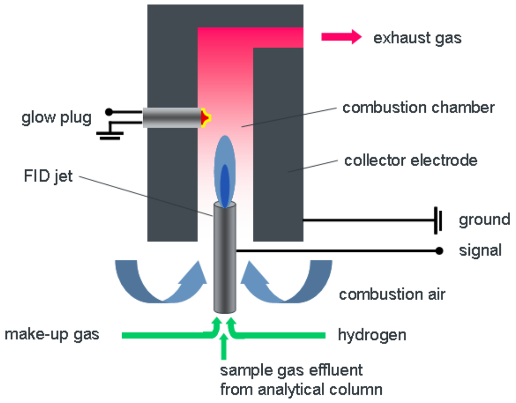
(b) Ions are formed in the flame.

(c) Charged gas ions flow to collector electrode and current (signal) is produced.

(d) current is measured and concentration is displayed on the built in computer.

(e) The original compound has been burned：carbon dioxide leaves the analyzer.

The standards we used were the same to the EPA/USA PAMs (Photochemical Assessment Monitoring Stations), which has been added in revised manuscript (page5, line 17-19).

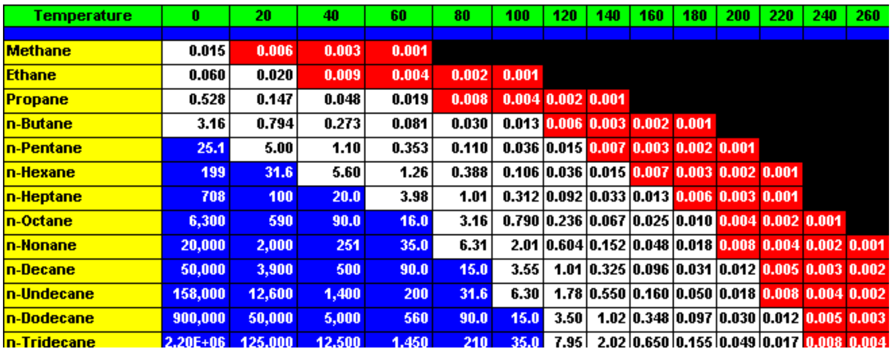


The design drawing of flame ionization detector

4) Lines 23-24, page 5: I don’t know how the analyzer contacted enriched concentration at 13℃, given that C_1-C_4 HCs have negative boiling points. In other words, it is impossible to concentrate these low boiling-points HCs at 13℃. More info about the operation principle of GC-FID is needed. Zou et al. (2013) is in Chinese.

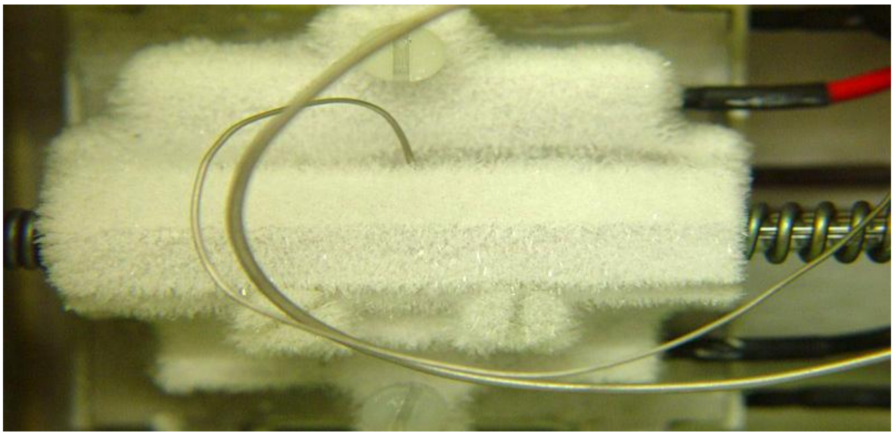
VOCs are pre-concentrated on a tube which is filled with special adsorption materials at 13℃. A case in point is that Tenax-TA (figure below), the analyzer enriched the VOCs by absorbents, lower temperature corresponds to more VOCs enriched by absorbents, but when the temperature is below 0℃, which would make the tube condensed(figure below).So we choose 13 ℃ to enrich VOCs by adsorption materials.

The sentence has been added in revised manuscript (page5, line3-4).



Temperature	0	20	40	60	80	100	120	140	160	180	200	220	240	260
Methane	0.015	0.006	0.003	0.001										
Ethane	0.060	0.020	0.009	0.004	0.002	0.001								
Propane	0.528	0.147	0.048	0.019	0.008	0.004	0.002	0.001						
n-Butane	3.16	0.794	0.273	0.081	0.030	0.013	0.006	0.003	0.002	0.001				
n-Pentane	25.1	5.00	1.10	0.353	0.110	0.036	0.015	0.007	0.003	0.002	0.001			
n-Hexane	199	31.6	5.60	1.26	0.388	0.106	0.036	0.015	0.007	0.003	0.002	0.001		
n-Heptane	708	100	20.0	3.98	1.01	0.312	0.092	0.033	0.013	0.006	0.003	0.001		
n-Octane	6,300	590	90.0	16.0	3.16	0.790	0.236	0.067	0.025	0.010	0.004	0.002	0.001	
n-Nonane	20,000	2,000	251	35.0	6.31	2.01	0.604	0.152	0.048	0.018	0.008	0.004	0.002	0.001
n-Decane	50,000	3,900	500	90.0	15.0	3.55	1.01	0.325	0.096	0.031	0.012	0.005	0.003	0.002
n-Undecane	158,000	12,600	1,400	200	31.6	6.30	1.78	0.550	0.160	0.050	0.018	0.008	0.004	0.002
n-Dodecane	900,000	50,000	5,000	560	90.0	15.0	3.50	1.02	0.348	0.097	0.030	0.012	0.005	0.003
n-Tridecane	2.20E+06	125,000	12,500	1,450	210	35.0	7.95	2.02	0.650	0.155	0.049	0.017	0.008	0.004

The relationships between penetration capacity and temperature by using the absorbent Tenax-TA



The scene of enriching tube freezing when the temperature is below 0℃

5) Lines 19-21, page 6: this is not fully correct. What about the emission strength of air pollutants?

We agree with the reviewer’s view.

The description “which is mainly due to the light, temperature and other meteorological factors being different in each season” in the original manuscript has been changed to “which is mainly due to the light, temperature , other meteorological factors and the emissions strength of air pollutants being different in each season” in revised manuscript (page5, line36-39).

6) Lines 16-24, page 6: no statistical analysis was conducted for all the comparisons. Are they really statistically different?

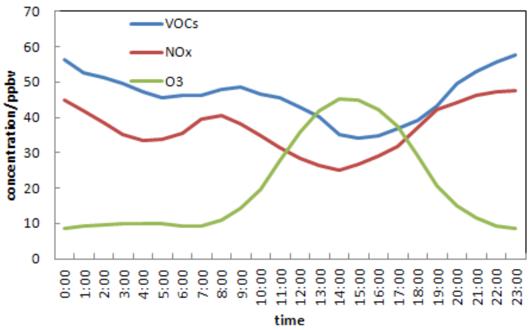
We agree with the reviewer’s view.

Statistical analysis for all the comparisons (page5, line 41-45 and page 6, line 1) and Table 3 have been added in revised manuscript.

7) Lines 25-26, page 6: I did not see this pattern from Fig 3.

You can see this pattern on one year average in the figure below though this pattern in some seasons may be not apparent.

The sentence “though variations may not be apparent among some seasons” has been added in revised manuscript (page6, line4).



The diurnal variations of VOCs ,NOx and ozone in four seasons (from June 2011to May 2012) at GPACS. Colored markers represent hourly mean values.

8) Line 26 page 6 – lines 1-2 page 7: how? What is the law of

atmospheric photochemical reactions?

In fact we didn’t mean the specific law of atmospheric photochemical reactions in original manuscript, Maybe, the description using “the law” could mislead the reader.

We replaced the sentence by “basic photochemical characteristic that is photochemical precursors gradually reduce and products increase accordingly” in revised manuscript (page6, line 4-6).

9) Lines 10-19, page 7: the discussion contains a conceptual mistake. The most important factor to affect the net production of ozone is not NO titration but the level of OH radicals which initiate the photochemical reactions. Simply, during nighttime, there was zero O_3 generation because there was no OH radical. NO titration could still consume O_3.

We agree with the reviewer’s view.

Lines 10-19, page 7 in original manuscript has been changed to “the results show that a negative growth of ozone concentration occurs between 15:00-18:00LT and 19:00-23:00LT…the concentration trend of ozone shows a positive growth during the period of time（8:00-14:00LT）due to the high OH radicals and strong photochemical reaction” in revised manuscript (page6, line 14-22).

10) The title of Fig 5 is not accurate. It should be diurnal variations of NO_2/NO and O_3.

We agree with the reviewer’s view.

However, according to the other reviewer suggestion, section 3.2 and Fig 5 (original manuscript) have been omitted in revised manuscript.

11) Lines 1-10, page 8: low morning O_3 is caused not only by NO titration but also low OH radicals. How could “NO_2/NO ratio subsequently reaches its maximum by further photochemical reaction (eq.2)”? The diurnal patterns of NO_2/NO are related to both primary emissions such as vehicles which can emit NO_2 as well, and secondary formation via photochemical reactions. The discussion here shows the lack of basic atmospheric chemistry knowledge.

We agree with the reviewer’s view.

“the O_3 concentration is also very low at this time because of titration of O_3” in the original manuscript need to be changed to “the O_3 concentration is also very low at this time because of low OH radicals”. “the NO_2/NO ratio subsequently reaches its maximum by further photochemical reaction（eq.2）” in the original manuscript need to be changed to “the NO_2/NO ratio subsequently reaches its maximum not only by the primary emissions such as vehicles in rush hour ,but also by the secondary formation via photochemical reactions such as eq.2”.

However, according to the other reviewer suggestion, section 3.2(original manuscript) have been omitted in revised manuscript.

12) Section 3.3 Impact of VOCs on ozone formation potential: To assess

the reactivity and the contribution to photochemical O_3 formation of individual VOC, a propylene-equivalent concentration method proposed by Chameides et al. (1992) and a maximum incremental reactivity (MIR) method proposed by Carter (1994) are used in this study. The MIR method is based on a scenario in which O_3 formation is derived under optimum conditions, such as high actinic flux and a scenario with NMHC/NOx ratios, which yield a maximum O_3 formation, whereas the propylene-equivalent concentration method simplifies the estimation by solely taking into account the OH reaction rate coefficients and concentrations of a

NMHC. However, there is no unique relationship between the competitive reaction rates of a set of organic compounds with hydroxyl radicals and their ability to produce O_3 in atmosphere because the latter depends on the subsequent reaction mechanisms of the products of the OH radical attack. Both methods are used to assess the OFPs simply by summing up the products of measured NMHC amounts and their corresponding MIR and k_{OH} factors, neither of which considers actual meteorology and transport influence. The OFPs and reactivities assessed by these two methods are not meant to represent actual O_3 concentrations in that area, because it will also be affected by meteorology and transport factors. As such, more comprehensive methodologies are necessary to study the impact of VOCs on the ozone

formation, i.e. numerical models available nowadays to simulate O_3 pollution in the atmosphere from the level of box models like observation-based model (OBM), and photochemical trajectory model (PTM-MCM) to three-dimensional chemistry and transport models such as theWeather Research and Forecasting-Chemistry mode (WRF-Chem), and the U.S. Environmental Protection Agency's Community Multi-scale Air Quality (CMAQ), because one of the most important components in these AQS models is the chemical mechanisms that describe the formation of O_3 from VOCs and NOx.

We totally agree with the reviewer's view. More comprehensive methodologies are necessary to study the impact of VOCs on the ozone formation, Ozone research should also consider meteorology and transport factors which are very important, further investigations based on numerical model are needed in the future to obtain more detailed and robust conclusions. Due to limited time and huge workload, at present, the manuscript just gives out some observational results which have some valuable findings to further research for the reason that the dataset about the ozone-NOx-VOCs triad, particularly long-term online data of VOCs that are very scarce in Pearl River Delta region. There are still a lot of things to do, we will try in the future.

Some changes in revised manuscript have been made. "by one year observational data " has been added in new title and the sentence "It should be noted that…are necessary to analyze the formation of ozone from VOCs and NOx" has been add in revised manuscript (page11,line2-8).

13) It is dangerous to use VOC/NOx ratio to judge VOC-limited or NOx-limited regimes, as stated in "General Comments".

We agree with the reviewer's view. Instead of using VOC/NOx ratio to judge VOC-limited or NOx-limited regimes, we used the ozone isopleths diagram by observational data to judge the ozone formation regime , and drew a conclusion that the peak ozone during high-concentration ozone events is found to be NOx-limited, which was very similar to the discovery in recent published paper(Li, Y., Lau, K. H., Fung, C. H., 5 Zheng, J. Y., and Liu, S. C.: Importance of NOx control for peak ozone reduction in the Pearl River Delta region, J. Geophys. Res., 118, 9428–9443, 2013.

) , in whcih Li used an emission processing model, a meteorological model, and a chemical transport model (CTM) in the Pearl River Delta to indicate the importance of NOx control for peak ozone reduction[Li et al., 2013]. Considering the fact that the VOC/NOx ratio method is a very traditional method and is also used in some recent published papers (i.e. Ran, L., Zhao, C. S., Geng, F. H., Tie, X. X., Xu, T., Li, P., Guang, Q. Z., Qiong, Y., Xu, J. M., and Guenther, A.: Ozone photochemical production in urban Shanghai, China: analysis based on ground level observations, J. Geophys. Res.,114,doi:10.1029/2008JD010752,2009;Ran,L.,Zhao,C.S.,Xu,W.Y.,Lu,X.

Q.,Han,M.,Lin,W.L.,Yan,P.,Xu,X.B.,Deng,Z.Z.,Ma,N.,Liu,P.F.,Yu,J.,Liang,W.D., and Chen, L.L.:VOC reactivity and its effect on ozone production during the HaChi summer campaign, Atmos. Chem. Phys., 11,4657–4667, doi:10.5194/acp-11-4657-2011, 2011.). We also used this method only to further confirm the conclusion we made by ozone isopleths diagram.

The analysis of ozone isopleths diagram by observational data has been added in revised manuscript (page8, line 5-43).

Referee #2 comment

General comment

1. In the “Results and Discussion” part, sections 3.1 and 3.3 are much more objective and reasonable when compared to sections 3.2 and 3.4. Section 3.2 is relatively weak in linking NO2/NO with ozone formation. In fact there is no steady-state cycle as claimed by the authors: ozone is changing with drastic diurnal/seasonal vibrations. As mentioned by the authors, in the real atmosphere ozone formation is too complicated to be merely dependent on the ratio of NO2/NO. The causal relationship between then is It is far more complicated as termed as a steady circle described by equations 2-4. I would rather this section removed from the manuscript. For section 3.4, we must bear in mind that control strategies are targeted on emission sources. The emissions of NOx and VOCs in a region are relatively stable day after day, yet mixing ratios of NOx and VOCs, as well as their ratios, may change greatly due to transport and chemical processes. Therefore cautions should be taken when trying to say something about emission control strategies based only on observed data without modeling approaches starting with emission inventories. Additionally, using VOC/NOx ratio of 8:1 to is a simplified approach long ago and thus applying it to the PRD is under question. Nonetheless, with the ozone-NOx-VOCs triad dataset, the authors already calculated hourly ozone increase in section 3.1; they

can investigate the sensitivity of NOx and VOCs on local ozone production. Also it is quite good to single out high-ozone episodes.

We agree with the reviewer's view. The content of sections 3.2 in original manuscript has been omitted and the content of section 3.4 in original manuscript has been revised. O_3 isopleths diagram by observational has been mainly used to analyze the ozone formation regime. Regarding the VOC/NOx ratio method, considering the fact that the VOC/NOx ratio method is a very traditional method and is also used in some recent published papers(i.e. Ran, L., Zhao, C. S., Geng, F. H., Tie, X. X., Xu, T., Li, P., Guang, Q. Z., Qiong, Y., Xu, J. M., and Guenther, A.: Ozone photochemical production in urban Shanghai, China: analysis based on ground level observations, J. Geophys. Res.,114,doi:10.1029/2008JD010752,2009;Ran,L.,Zhao,C.S.,Xu,W.Y.,Lu,X. Q.,Han,M.,Lin,W.L.,Yan,P.,Xu,X.B.,Deng,Z.Z.,Ma,N.,Liu,P.F.,Yu,J.,Liang,W.D., and Chen, L.L.:VOC reactivity and its effect on ozone production during the HaChi summer campaign, Atmos. Chem. Phys., 11,4657–4667, doi:10.5194/acp-11-4657-2011, 2011.), we still used it only to confirm the conclusion we made by O_3 isopleths diagram. We don't used it as a main method to judge ozone formation regime because of the fact that it is a simplified approach long ago and thus applying it to the PRD is under question.

2. Section 3.3: it is scientifically sound to calculated

propylene-equivalent concentration or MIR to say something about OFP of VOCs; at the present state of knowledge, few would agree that carbon number concentrations in ppbC or mixing ratios in ppbv can served as a measure of OFPs. It is a kind of common sense. So the authors should just show their results calculated propylene-equivalent concentrations or MIRs, and avoid unnecessary discussion (a long passage) on whether ppbC or ppbv is reasonable.

We agree with the reviewer’s view.

Carbon number concentrations in ppbc can’t served as a measure of OFPs, the sentence has been changed to “VOCs have two main factors for ozone formation potential: kinetic activity and mechanism activity” in revised manuscript(page6,line27-28). The long discussion about ppbc or ppbv has been omit and replaced by one simple sentence" As viewed from the volume mixing ratio concentration (ppbv) and carbon concentration (ppbc)…and alkenes have the lowest proportion, at 17% and 11% respectively” in revised manuscript (page7, line5-8), in order to indicate that VOCs concentrations do not correspond to their ozone formation when compared with their chemical reactivity.

3. Conclusions: this part should be consistent with and strongly supported by the results and discussions in the section 3. You can figure out major findings specific to this study and avoid saying general rules.

We agree with the reviewer’s view.

The sentence “The diurnal concentration of the ozone…which reaches their maximum around rush hour” has been omitted. The major findings in revised manuscript (page10, line 32-45 and page11, line 1) have been mainly figured out. In addition, shortcomings and improvement have been also pointed out in conclusion in revise manuscript (page11, line2-8)

Specific comments

1）English: Although I am not native English speaker, I can find errors in grammar but I would go to details one by one. I do suggest that English writing of this manuscript should be improved, better with the help of a native English speaker.

We agree with the reviewer’s view. Written English has been improved in revised manuscript with the help of a native English speaker.

You can see the revision by track changes in Word in marked-up manuscript.

2）QA/QC: Better add some words about QA/QC.

We agree with the reviewer’s view.

The description about QA/QC has been added in revised manuscript(page5, line 21-30), and the standard curve and detection line of VOCs species have been also added in Table 2 in revised manuscript.

3）Chemical reaction equations: some equations (like 2-4, 7-9), if they are common in text books and not further referred to in the discussion,

can be omitted.

We agree with the reviewer’s view.

Equations (2-4 and 7-11) have been omitted in revised manuscript.

4）The title: the manuscript has many interesting aspects, but impacts of VOCs and NOx on the ozone formation are probably not the strongest. If possible, consider a title best cover the contents after revision.

We agree with the reviewer’s view.

Considering the contents in revised manuscript, the title has been changed to “Relationship of VOCs and NOx to photochemical ozone production by one year observational data

~~An~~Relationship of ~~analysis of the impacts of~~ VOCs and NO_x to photochemical ozone production ~~on the ozone formation~~by one year observational data in Guangzhou, China

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Abstract

In this study, online monitoring instruments were used to monitor the ozone, NO_x and VOCs ~~at~~ from the Guangzhou Panyu Atmospheric Composition Station (GPACS) of the China Meteorological Administration from June 2011 to May 2012, so as to obtain their characterizations and relationships of VOCs and NOx to photochemical ozone production. The results show that during the observation period, the seasonal variation of ozone concentration was lower in spring and winter, while being higher in summer and autumn, which is contrary that of the VOCs and NOx. Aromatics ~~and alkenes~~ are the largest components for ozone formation potential, among which ~~aromatic~~ toluene, m-xylene, p-xylene and 1,3,5-trimethylbenzene are the most important components, with a total contribution of ~~about~~ approximately 31.6% to ozone formation potential. The peak ozone during high-concentration ozone events is found to be NOx-limited by measured O_3 isopleths diagram and further confirmed by measured VOC/NOx, which provides the ozone control strategy which involves, in addition to the control of VOCs emissions, increased emphasis on reducing NOx emissions, to achieve the purpose of controlling high-concentration ozone. ~~Through the analysis on local ozone control by the VOC/NOx ratio, it was found that when the ozone concentration reached a peak in the summer and autumn in which high concentrations of ozone were prone~~

~~to occur, ozone generation was NO_x limited, thus NO_x emissions must be controlled to regulate the occurrence of high-concentration ozone events. In the spring and winter, ozone generation was always VOCs controlled. Due to the relatively low ozone concentration, although NO_x emissions could be controlled to increase ozone concentration, high-concentration ozone events would not occur. Therefore, for the control of ozone in Guangzhou, in addition to the control of VOCs emissions, more attention must be paid to reducing NO_x emissions, so as to achieve the purpose of controlling high-concentration~~

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~~ozone.~~

1 Introduction

Along with its rapid economic development and urbanization, the Pearl River Delta has become one of the most serious pollution areas in China (Chan et al., 2008). Different from the air pollution situations of Beijing, Tianjin, Hebei and the Yangtze River Delta region, which involve particulate matters as the main pollutants (Wang et al., 2012; Zhao et al., 2011), due to ~~the~~ its unique geographical location and climate, as well as the rapid increase in the emissions of VOCs and NO_x ($NO+NO_2$) as ozone precursors caused by industrial activities and the growing number of motor vehicles, in the Pearl River Delta high-concentration ozone events occur frequently and have become very prominent air pollution problems (Wang et al., 2009). Tropospheric ozone is the secondary pollutant generated by photochemical reactions of VOCs and NO_x under light conditions (Sillman, 1995). However, VOCs and NO_x have no linear relationship with ozone formation, and their impacts on ozone formation can be described by VOC and NO_x ~~control areas~~limited regime (Zhang et al., 2004; Tie et al., 2007; Geng et al., 2008). A large amount of research has been conducted regarding ozone formation in the Pearl River Delta (Wang et al.,2005; Cheng et al.,2010;Guo et al.,2009). Many laboratory studies using smog chambers have served to clarify the gas-phase photochemical transformations of NOx and VOCs, and their roles in the formation of ozone. The maximum ozone concentrations generated from various mixtures of NOx and VOCs are often presented on ozone isopleths diagrams. The numerical simulations showed that although the specific actual situations differ, it is generally considered that when the VOC/NOx ratio is greater than 8:1, ozone formation regime is NOx-limited, while the VOC/NOx ratio is less than 8:1, ozone formation regime is VOC-limited (Dodge,1977), which many researchers have used to elucidate the characteristics of photochemical ozone production(Sillman,1999;Committee on Tropospheric Ozone Formation and Measurement,1991; Ran et al.,2009 , 2011). However, little attention has been given to ozone isopleths diagrams and VOC/NOx ratio using observational data. In addition, most previous studies performed in the Pearl River Delta region reported that the ozone is VOC-limited(Zhang et al., 2008b; Guo et al., 2009).However, few previous studies on the region's ozone formation regime have examined the possible diurnal variations in ozone formation regime.~~In 1977, Dodge used the model OZIPP (ozone isopleth plotting package) and drew an conclusion that although the specific actual situations differ, it is generally considered that when the VOC/NO_x ratio is more than 8 : 1, ozone is formed in the NO_x control area, while when the VOC/NO_x ratio is less than 8 : 1, ozone is formed in the VOCs control area (Dodge, 1977). And later this view had been adopted and applied by many re-searchers during their researches throughout the world (Sillman, 1999; Committee on Tropospheric Ozone Formation and Measurement, 1991; Ran et al., 2009). Therefore, the understanding of the ozone photochemical process can provide a scientific basis for the effective control of local ozone.~~

Currently, a greater amount of systematic long-term observation data on atmospheric ozone and NOx in the Pearl River Delta region ~~have~~ has become ~~been~~ available~~ on atmospheric ozone and NO_x in the Pearl River Delta region~~, while VOCs data which mostly involves short-term intensive observations or non-continuous long term observations ~~are~~ is not included in the scope of daily observations (Wang et al., 2004; Shao et al., 2009). Therefore, the relationship ~~between~~ among VOCs, NO_x and ozone cannot be fully revealed to discern the impacts of VOCs and NO_x on ozone formation in the Pearl River Delta region. In order to more effectively solve the problem of ozone pollution in the Pearl River Delta, VOCs, NO_x and ozone were observed throughout the period of one year at GPACS, focusing on analyzing the characterizations of VOCs, NOx and ozone. as well as ~~the impacts of NO/NO_2 ratio and~~ VOCs components ~~on~~ in ozone formation. In addition, ozone isopleths diagram using observational data is plotted to elucidate the characteristics of photochemical ozone productions, which can provide the policy of controlling the ozone in Guangzhou. Finally, the VOC/NOx ratio by observational data was also used to analyze the ozone formation regime with diurnal variation in Guangzhou, but this has only been done by a small number of scholars (Li et al., 2008). In order to reveal the occurrence of high-concentration ozone events in Guangzhou, ozone formation regime with diurnal variation are explored in four scenarios herein, i.e. spring, summer, autumn and winter. ~~a large amount of research has been conducted on ozone formation in the Pearl River Delta (Wang et al., 2005; Cheng et al., 2010; Guo et al., 2009). Previous studies have shown that ozone was generated in the VOCs control area of the Pearl River Delta region, but only a small number of scholars (Li et al., 2008) have analyzed the control areas of ozone formation with diurnal variation in the Pearl River Delta region. In order to control the occurrence of high-concentration ozone events in Guangzhou, the control areas of ozone formation with diurnal variation are explored in four scenarios herein, i.e. spring, summer, autumn and winter, thus providing a scientific basis for the control of ozone in Guangzhou.~~

This study is organized as follows. The second section describes the methodology used in this study, ~~mainly~~ also including the sampling point and observation instruments. The third section mainly analyzes the observed results, including characteristic analysis of ozone, NO_x and VOCs, as well as ~~,~~ an analysis of the contribution of VOCs components to ozone formation by using MIR and an equivalent propylene concentration method. In the final section, the ozone isopleths diagram by observational data is plotted to elucidate the characteristic of photochemical ozone production, and the VOC/NO_x ratio analysis method is also adopted to analyze ~~the control areas with~~ ozone formation regime in the seasonal diurnal variation process, in order to explore the ozone control strategies in Guangzhou.

2 Methodology

2.1 Measurements

From June 2011 to May 2012, automatic sampling and on-line monitoring were carried out on ozone, NO_x and VOCs. The sampling site was located at the moun-tain top of Dazhengang, Nancun Town, Panyu District, Guangzhou City, Guangdong Province, China with an elevation of 141 m, at the latitude of 23° 00.236′ N and longitude of 113° 21.292′ E (Fig. 1). This sampling station is located in suburban Guangzhou in which the high ozone events often occur, and is the main site of the observation network for atmospheric composition in Pearl River Delta. Fig.2 shows that, regardless of the large variation in concentration of the three types of VOCs, the relative contribution of the three groups remains fairly uniform throughout the observational time. Such uniformity implies that air was sufficiently homogenized from various point sources at the surface. The prevailing wind, wind speed and temperature at the sampling point during the different seasons are shown in Fig. 3 and Table 1. At the sampling point, northeasterly and southwesterly are the prevailing winds in spring (April, May and June), along with southwesterly in summer (June, July and August),

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southwesterly in autumn (September, October and November), and northeasterly in winter (December, January and February). In the different seasons, the average wind speed varies at around 1.4 ms^{-1}, while the average temperature undergoes more significant changes from 14.2 ℃ in winter to 29.4 ℃ in summer. Typical air pollution processes can also be seen in different seasons and under different weather conditions. When the prevailing wind is northeasterly in December, the difference between weekends and weekdays for VOCs is very typical, showing large amounts of pollutants are emitted from downtown Guangzhou City. When the prevailing wind is southwesterly in July, the difference between weekends and weekdays for VOCs is not apparent, for the reason that only small amounts of pollutants are emitted from the further suburban areas (Fig. 1). ~~This sampling station is a comprehensive site which is able to monitor the typical air pollution processes of the Pearl River Delta in different seasons and under different weather conditions (Deng et al., 2010).~~

2.2 Instrument description

The data used in this study include the hourly concentration of ozone, NO_x and VOCs during the observation period (June 2011–May 2012). The concentration of ozone gas was obtained using an EC9810B ozone analyzer produced by Ecotech Co. of Australia with the UV photometric method. The concentration of nitrogen oxides gas was collected using an EC9841B oxynitride ($NO/NO_2/NO_x$) gas analyzer produced by Ecotech with the chemiluminescence method.VOCs concentration was obtained using a GC5000 analyzer produced by AMA Co. of Germany with the GC-FID analysis method. This latter apparatus is comprised of a low-boiling- point VOC analyzer and high-boiling-point BTX analyzer, including two sets of sampling systems and two systems of separated chromatographic columns. A low-boiling- point VOC analyzer was able to conduct enriched concentration on a tube which is filled with special adsorption materials at 13 ℃, a second adsorption at 20 ℃ and desorption when the temperature was raised to 200 ℃, ~~following~~ followed by separation ~~by~~ with two-dimensional chromatographic columns. The chromatographic columns ~~comprised~~ consisted of ~~the~~ a Al_2O_3/Na_2SO_4 plot column with a diameter of 0.32 mm, film thickness of 5mm and ~~a~~ length of 60 m, as well as a back flushing column (carbowax) with a diameter of 0.32 mm, film thickness of 0.25mm and length of 30 m. A back flushing column was used to remove the moisture component and high boiling component, and two types of chromatographic column were polar columns. Through two rounds of thermal desorption, the low-boiling-point hydrocarbons could be well separated, and the detector was a flame ionization detector (FID). A BTX high-boiling-point analyzer was able to conduct precondensation of volatile organic compounds at 30℃, followed by thermal desorption, then separation on the DB-1 column to achieve optimum separation and prevent interference of related compounds. This column has a diameter of 0.32 mm, thickness of 10mm and length of 60 m. A flame ionization detector (FID) was used to detect the system. The detected target compounds were 56 types of VOCs designated by the US EPA with the time resolution of once per hour, and the standards we used were the same as those used by the EPA/USA PAMs(Photochemical Assessment Monitoring Stations)~~.~~The analytical method was described in a previous study (Zou et al., 2013). The QA/QC of online VOC measurements was performed. Before and after the observation period, we performed a zero gas check for memory effect or contamination and a span gas check with PAMs calibration gas in order to check the drift, repeatability and memory effects. We normally got standard curve which

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qualified the species by using a five point calibration method and retention time which quantified the species. The standard curve and the detection line of VOCs are listed in Table 2. You can see that correlation coefficient ranged from 0.984 to 0.999, and detection limit ranged from 0.03 to 0.09. During the observation period, we also performed a span gas check every month by using one point calibration and adjust the retention time. Finally, outliers need to be eliminated to guarantee the valid data.

3 Results and discussion

3.1 Characteristics of ozone, NO_x and VOCs

The seasonal diurnal variation characteristics of ozone, VOCs and NO_x are shown in Fig. 4 The seasonal variation characteristics of ozone are relatively apparent. The seasonal variation of ozone concentrations displays the seasonal pattern of being lower in the spring and winter and higher in the summer and autumn. Furthermore, the increase range is much larger in late spring and early summer than the other ~~times~~periods, which is mainly due to the light, temperature, other meteorological factors and emissions strength of air pollutants being different in each season ~~which is mainly due to the light, temperature and other meteorological factors being different in each season~~ (Bloomer et al., 2009, 2010). The seasonal variation in the concentration of ozone precursors is opposite to that of ozone concentration. NO_x concentration is higher in spring and winter, but lower in summer and autumn and VOCs concentration is higher in winter, but lower in summer. Average concentration of VOCs, NOx and ozone in four seasons are shown in Table 3.VOCs concentration varies from 34.60 ppbv in March to 63.57 ppbv in November; NOx concentration varies from 21.75 ppbv in August to 76.39 ppbv in March; and ozone concentration varies from 9.31 ppbv in January to 29.67 ppbv in September.The diurnal concentration variation of ozone is unimodal, reaching its maximum at 2.00 p.m., while those of the ozone precursors, i.e. VOCs and NO_x, show a bimodal variation with a peak ~~in~~ during rush hours, though variations may be not apparent among some seasons. These diurnal ~~concentration~~ concentration variations~~s~~ exhibit ~~consistent characteristics with~~ the photochemical characteristic that photochemical precursors gradually reduce and products increase accordingly~~the law of atmospheric photochemical reactions~~. In order to further understand the variation in ozone concentration and reveal its dependence on photochemical reactions, it is necessary to analyze the variation trend of ozone, shown as follows:

$$d[O_3]/dt = [O_3](t+1h)-[O_3](t) \qquad (1)$$

In the equation, $[O_3](t)$ represents the ozone concentration at time t, and $[O_3](t+1h)$ is the ozone concentration for the next hour of time t. A negative growth of variation in ozone concentration indicates that the chemical loss of ozone plays a dominant role in the variation in ozone concentration, while the contrary indicates the fact that the generation of ozone photochemical reactions plays a key role. The results show that a negative growth of ozone concentration occurs between 15:00-18:00LT and 19:00-23:00LT. The first period of time(15:00-18:00LT) is presumably due to low OH radicals and the fact that titration of ozone by emissions of NOx plays a key role. However, during the second period of time(19:00-23:00LT), there was no OH radicals and the NO titration could still consume the ozone, until the NO titration ceased, the ozone concentration remained a relatively stable during the period (0:00-7:00LT).The concentration trend of ozone shows a positive growth during the period of time（8:00-14:00LT）due to the high OH radicals and strong

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photochemical reaction. ~~The results show that a negative growth of ozone concentration occurs between 15:00–23:00 LT is presumably due to titration of ozone by emissions of NO_x and the photochemical reaction do not play a key role. The zero derivative between 00:00–07:00 LT indicates no further titration with the reduction of NO_x emission. And the transmission of ozone plays an important role on keeping a relatively stable ozone concentration during the period of time. The photochemical reaction is intense at noon, and the concentration trend of ozone shows a positive growth. The photochemical generation of ozone is greater than its chemical loss~~ (Fig. 5).

~~3.2 Relationship between NO_2/NO ratio and ozone formation~~

~~Atmospheric NO_2 and NO are involved in photochemical reactions, including the following:~~

~~O_3 +NO!NO_2 +O_2 (2)~~

~~O(3P)+O_2 +M!O_3 +M (3)~~

~~NO_2 +hv!NO+O(3P) (4)~~

~~These three reactions are also known as the steady-state responses, and the relationship among the three is called photo stationary state relationship. The relationship between NO_2/NO and ozone in each season is shown in Fig. 5. At around 08:00 LT in the summer, autumn and winter, NO_2/NO ratio is very low due to the fact that NO is emitted from vehicle emission and the solar radiation is very weak. And the ozone concentration is also very low at this time because of titration of ozone. After that, with the strengthen of solar radiation, the ozone concentration begins to accumulate for the photolysis of NO_2 and increases with NO_2/NO ratio rising. At around 15:00 LT, the ozone concentration reaches its maximum. NO2/NO ratio subsequently reaches its maximum by further photochemical reaction (Eq. 2). At around 19:00 LT, with the increase in NO emissions, the NO_2/NO ratio is reduced accordingly. This variation is not apparent in the spring, which may be due to meteorology in spring. However, in the actual atmosphere, the ozone concentration is also affected by VOCs, CO and other ozone precursors, and their high concentrations will in turn affect the steady-state cycle.~~

3.2 The effect of each VOCs category ~~Impact of VOCs~~ on ozone formation ~~potential~~

VOCs appear in various types~~.~~, and their concentrations do not correspond to their ozone formation. Different types of VOCs have different photochemical reactivities, thereby leading to different ozone formation potential. ~~Ozone control is mainly used to control~~ Controlling the species with the largest ozone formation potential~~, which~~ is the most cost-effective solution to ozone control.~~.~~ VOCs have two ~~three~~ main factors for ozone formation potential: ~~carbon-number concentration (ppbc),~~ kinetic activity and mechanism activity. ~~Therefore, it is necessary to analyze VOCs components~~ on ozone formation.~~through the three factors of ozone formation.~~ For kinetic activity, the propylene-equivalent concentration method (C_{PE} (J)) is expressed as shown below:

$$C_{PE}(J) = C_J K_{OH}(J)/K_{OH}(C_3H_6) \qquad (2)$$

In the equation, J represents a species of VOC, C_J represents the carbon-number concentration (ppbc) of this species, and K_{OH}(J) and $K_{OH}(C_3H_6)$ denote the chemical reaction rate constant in the free radical reaction of species J and propylene with OH. The reaction rate constants ~~is~~ are shown in Table 4. For the mechanism activity, the MIR factor weighting method is used with the following expression:

$$Con_{j.MIR} = MIR \times Com_{ppbv} \times u_j/u_{ozone} \qquad (3)$$

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In the equation, u_j and u_{ozone} represent the relative molecular mass of species J in the VOCs and ozone respectively, Com_{ppbv} represents the actual volume mixing ratio, the Maximum Incremental Reactivity (MIR) factors were developed by Carter (Carter et al., 1994) in model Scenarios, the MIR of each VOCs is from numerical simulations, ~~the model~~ and $Con_{j,MIR}$ is maximum-increment-activity MIR factor weighting concentration which represents the maximum ozone concentration generated by this species based on MIR. The maximum ozone concentrations of the different VOCs are used to compare their relative ozone formation potential. The MIR coefficients are shown in Table 4. Fig. 6 shows the characteristic~~s~~ of each VOCs ~~components~~ category obtained at the sampling point by using the volume mixing ratio concentration (ppbv), carbon number concentration (ppbc), propylene-equivalent concentration (ppbc), and maximum-increment activity MIR factor weighting concentration (ppbv) methods. As viewed from the volume mixing ratio concentration (ppbv) and carbon concentration (ppbc) , alkanes occupy the largest proportion, accounting for 59% and 53% of the total VOCs concentration respectively; followed by aromatics(24% and 36% respectively); and alkenes have the lowest proportion, at 17% and 11% respectively.~~hydrocarbons occupy the largest proportion, accounting for 59% of total VOCs concentration, among which low-carbon compounds (fewer than five carbon atoms) are dominant, accounting for 41.2%, followed by aromatics (24%); and alkenes have the lowest proportion, at 17%. As viewed from carbon concentration (ppbc), alkanes have the largest proportion of 53%, the aromatic proportion rises to 36%, and alkenes have the lowest proportion of 11%. It is thus shown that when using the volume mixing ratio concentration, the importance of low-carbon alkane compounds will be overestimated.~~ As viewed from the propylene-equivalent and MIR factor weighting concentrations, the alkenes and aromatics are dominant, accounting for total proportions of 73% and 83% respectively, and alkanes have the lowest proportion. Total propylene-equivalent concentration accounts for nearly half of the total carbon concentration, indicating that the activities of major VOCs ~~components~~ species are lower than propylene at the sampling point. In summary, during the monitoring period, as viewed from the volume mixing ratio and carbon number concentrations of VOCs, alkanes and aromatics are shown to be the most important ~~constituents~~ categories of the atmosphere at the sampling point. However, as viewed from ozone formation potential, aromatics and alkenes are the two species with the largest contributions. The ~~Alkanes~~ alkanes content are high, but because of ~~its~~ their low reactivity, alkanes have less contribution to the reactivity of VOCs and ozone formation potential. Although the alkenes concentrations are smaller than ~~that~~ those of the alkanes, due to ~~its~~ their high reactivity, alkenes have greater contributions to ozone than alkanes. Table 5 shows the ozone formation potential ranking of VOCs species as calculated by the propylene-equivalent concentration and MIR factor methods. It can be seen that the results of both methods are partially consistent, but some differences may also be seen. Among the top ~~10~~ ten species, eight species are exactly the same, differing only in terms of rank order. It is thus shown that both methods can be used to reflect the ozone formation potential of each VOCs species to some extent, and especially those with greater contributions to ozone formation have better consistency. However, since these two methods differ in principle, the calculated ranks of ozone formation potential are also different. The propylene-equivalent concentration method only considering kinetic activity ignores the differences in the mechanism activities of the reaction between peroxide radicals and NO,

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thus when assessing ozone formation potential, the species with faster OH reaction rate may be overestimated, such as isoprene. Although the MIR factor method considers the kinetics and mechanism activity, due to the fact that the MIR factor involves possible uncertainty and ~~the~~ lack of MIR data for some species, the MIR factor method cannot become a reliable assessment approach of ozone formation potential. In summary, aromatics are the species with the highest reactivity at the sample point, followed by alkenes. ~~Aromatics have a high carbon concentration in the ambient atmosphere with high activity, in which toluene~~Toluene, m-xylene, p-xylene and 1,3,5-trimethylbenzene with higher reactivity have ~~are the most important, with~~ a total contribution to ozone formation potential of about 31.61 %. These ~~substances~~ species are mainly sourced from large factories and industrial activities (Liu et al., 2008a). As an industrial city, ~~Dong guan is located in the eastern part of the sampling point, where EN wind is the prevailing in the autumn and winter at the sampling points.~~ Dong guan is presumed to have some contributions to ~~VOCs~~ these species at sampling points in the autumn and winter, due to the fact that it is located in the eastern part of the sampling site and northeasterly is the prevailing in the autumn and winter at the sampling site. Moreover, isoprene has no high concentration, but ranks at ~~no. 1~~first and third ~~and 3~~ in terms of OH activity and MIR. Therefore, the choice of green plant species must consider the isoprene emissions of plants in the greening process at the sampling point.

3.3 ~~Sensitive areas of ozone~~ Ozone formation regime

~~As mentioned in Sect. 3.2, if only steady-state reaction occurs in the atmosphere, no net formation of ozone exists, but in the actual atmosphere, ozone formation is also affected by VOCs and other precursors.~~

~~$OH+RH!R+H_2O$ (7)~~

~~$R+O_2+M!RO_2+M$ (8)~~

~~$RO_2+NO!RO+NO_2$ (9)~~

~~$RO+O_2!R_0CHO+HO_2$ (10)~~

~~$HO_2+NO!OH+NO_2$ (11)~~

~~NO_2 produced by Eqs. (9) and (11) can generate ozone, and the radical regenerated by Eqs. (10) and (11) can excite a cycle. In the formation of the tropospheric ozone, the reaction of VOCs and NO_x with free radicals plays an important role. It can be seen that the ozone formation relies on the VOC/NO_x ratio.~~ VOCs and NO_x have a non-linear relationship with the formation of the ozone as a secondary photochemical product, and their impacts on the ozone formation can be described by the VOCs and NOx control areas. The peak ozone concentrations generated from various initial concentrations of NOx and VOCs are usually presented as an O_3 isopleth diagram, in which initial mixture compositions giving rise to the same peak O_3 concentrations are connected by the appropriate isopleth. O_3 isopleth diagrams can be generated for different VOCs and NOx mixtures and for different levels of solar intensity from modeling studies using the validated chemical mechanisms (Dodge, 1977).To elucidate the photochemical potential to produce ozone in Guangzhou City, observational data selected by meteorological conditions are used to plot the O_3 isopleths diagrams. Different from the numerical simulations, the observational O_3 isopleths diagrams include all processes, such as transport, deposition and mixing, in addition to chemical reactions that control the ozone concentration. Accordingly, we selected the days when the sum of the hourly solar radiation data from sunrise to 18:00 exceeds the annual average, so as to reduce the influence

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of irregular solar intensity, and when the average wind speed data from sunrise to 18:00 is ＜ 3ms^{-1}, so as to reduce the influence of transport. For the NOx and VOCs concentrations to generate the O_3 isopleths diagrams, the average concentrations of VOCs and NOx in the daytime(6:00-9:00)are used, and the amount of ozone increase (△O_3)is defined as the difference between the maximum value in (10:00-18:00) and the average value in the daytime (6:00-9:00)(Fig.7, left panel), the 8h O_3max is defined as the maximum ozone value during the time between 10:00-18:00(Fig.7, right panel). Fig.7 shows that when the VOCs concentration is between 0ppbc and 250ppbc, the ozone formation regime is VOC-limited, thus reducing the emissions of VOCs may reduce ozone formation; when the VOCs concentration is between 250ppbc and 600ppbc, the ozone formation regime is under NOx-limited and reduction of the emissions of NOx may reduce ozone formation; and when the VOCs concentration is above 600ppbc, the ozone formation regime is the (VOC and NOx)-limited regime, and reducing the VOCs and NOx together may reduce ozone formation. Ozone formation regime by VOCs concentrations may be decided by the composition of VOCs. Assuming that more active organic carbons are included in the VOCs composition, they are reacted with OH radicals more active than other hydrocarbons, and the chain propagating reaction ($OH+RH \rightarrow R+H_2O$) would be more dominant than the chain terminating reaction ($OH+NO_2(+M) \rightarrow HNO_3(+M)$). We select the day(2011.8.12) represented by A point and the day (2011.11.5) represented by B point in Fig.7(left panel）.Alkanes, alkenes and aromatics are accounting for 50%,18% and 32% of the total VOCs respectively on the day(2011.8.12), while alkanes, alkenes and aromatics are accounting for 58%,17% and 25% of the total VOCs respectively on the day(2011.11.5). Thus more active organic carbons are included in the VOCs composition on the day (2011.8.12). As a result, you can see lower VOCs concentration on the day (2011.8.12)can produce the same △O_3 as the day(2011.11.5) with higher VOCs concentration, though other factors like meteorology should be taken into account. The high △O_3 and 8h O_3max usually occur in the NOx-limited regime, which indicates that NO$_x$ emissions must be controlled to regulate the occurrence of high-concentration ozone events. Fig.8 shows the scatters between VOCs and NOx selected by meteorological conditions in different seasons, most of the scatters under NOx-limited and (VOC and NOx)-limited regimes correspond to summer and autumn, in which the high ozone episodes usually occur, strengthening the result that when the ozone concentration is very high, the ozone formation regime is NOx-limited. NOx emission control was of importance for peak ozone reduction in Guangzhou City.

In the formation of the tropospheric ozone, the reaction of VOCs and NO$_x$ with free radicals plays an important role and the ozone formation relies on VOC/NO$_x$ ratio. The numerical simulations showed that although the specific actual situations differ, it is generally considered that when the VOC/NOx ratio is greater than 8:1, the ozone formation regime is NOx-limited, and when the VOC/NOx ratio is less than 8:1, the ozone formation regime is VOC-limited (Dodge, 1977). This has been adopted and applied by many researchers during their researches throughout the world (Sillman, 1999; Committee on Tropospheric Ozone Formation and Measurement, 1991; Ran et al., 2009, 2011). In order to further prove the point we made earlier, the VOCs/NOx ratio (8) was used to judge the ozone formation regime, as it should provide a rough idea as to whether it is a NOx-sensitive or VOC-sensitive environment. ~~In 1977, Dodge used the model OZIPP (ozone isopleth plotting package) and~~

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~~drew an conclusion that although the specific actual situations differ, it is generally considered that when the VOC/NO_x ratio is more than 8 : 1, ozone is formed in the NO_x control area, while when the VOC/NO_x ratio is less than 8 : 1, ozone is formed in the VOCs control area (Dodge, 1977). And later this view had been adopted and applied by many researchers during their researches throughout the world (Sillman,1999; Committee on Tropospheric Ozone Formation and Measurement, 1991; Ran et al., 2009). We also use this VOCs/NO_x ratio value (8) to research the ozone formation~~

~~in Guangzhou for the reason that the VOC/NO_x ratio has not yet been confirm in Guangzhou to judge whether the ozone is formed in the VOCs control area and NO_x control area.~~Most previous studies in the PRD region reported that the ozone was VOC-limited(Zhang et al., 2008b; Guo et al., 2009). However, few previous studies ~~on the~~ regarding the region's ozone formation regime have examined the possible diurnal variations in ozone formation regime. An analysis was carried out on the diurnal variation of seasonal ozone concentration and the VOC/NO_x ratio during the monitoring period (Fig. 9). It was found that high-concentration ozone events are prone to occur in the summer and autumn. According to the traditional theory,~~In~~ in the morning (7:00 to 08:00 LT), the VOC/NO_x ratio is less than 8, ~~and~~ the ozone ~~is formed~~formation regime is likely to be ~~in the VOCs~~ VOC-limited ~~control area~~regime, ~~leading to~~and a decline in VOCs concentration would~~, which~~ help~~s~~ to further reduce the ozone concentration. However, when the ozone concentration reaches a peak at noon, the VOC/NO_x ratio is greater than 8, and the ozone formation regime is likely to be ~~formed in the~~ NO_x-limited~~ control area~~. The ozone formation regime can shift from VOC-limited in early the morning to NOx-limited at noon. The NO_x emissions must be controlled to achieve the purpose of controlling high-concentration ozone events, which is similar to the research findings ~~of~~ in the Pearl River Delta (Li et al., 2013). In the spring and winter, the VOC/NO_x ratio is always less than 8, and ozone formation regime is likely to be ~~generated in the~~ VOC-limited ~~s~~ ~~control area~~ for a long period of time. Since the ozone concentration is relatively low in these two seasons, although the control of NO_x emissions can increase the ozone concentration, no high-concentration ozone event will occur. Therefore, for the control of the local ozone, in addition to VOCs control, the control of NO_x concentration will further reduce high ozone concentration to prevent the occurrence of high-concentration ozone events~~.~~, which to some extent may prove the point that we showed before. Considering the impact of VOCs to ozone formation is more relevant to the reactivity of individual VOC species rather than to the amount of VOCs, the VOC(reactivity)/NOx ratio was used to analyze ozone formation(Fig.9), the VOC(reactivity)/NOx ratio(PE or MIR) was shown to be consistent with the VOC(ppbc)/NOx ratio may due to the fact that regardless of the large variation in concentration of the three types of VOCs, the relative contribution of the three groups remains fairly uniform throughout the observational time(Fig.2). —The high-concentration ozone is seriously harmful to human health, thus many regulators are focusing on reducing emissions at peak ozone forming hours (Castellanos et al., 2009). In order to further study the relationship of VOCs and NOx to the photochemical ozone production ~~ozone control strategies~~ under the conditions of high-concentration ozone, the days with high-concentration ozone were selected for analysis in the monitoring period; ~~the~~ days with high-concentration ozone refers to the days with an hourly ozone value higher than 93 ppbv. It may be seen in Fig. 10 that under the conditions of high-concentration ozone at

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noon, the control of NO_x concentration may transiently reduce the peak of high-concentration ozone. However, when the ozone concentration is relatively low in the morning and at night, the control of the NO_x concentration may transiently increase the ozone concentration. Therefore, when high-concentration ozone events occur, more attention must be paid to controlling NO_x emissions, so as to achieve the purpose of controlling high-concentration ozone events.

4 Conclusions

One-year (from June 2011 to May 2012) consecutive observation was carried out on the near-surface ozone and its precursors VOCs and NO_x at GPACS, which is located in suburban Guangzhou where the high ozone events often occur. Observation-based analysis has been performed to investigate the relationship of VOCs and NOx on photochemical ozone production in this highly populated region.

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~~and the seasonal and diurnal variations were characterized. The results indicate that seasonal variation in the~~ The ozone concentration is significantly shown as being lower in the spring and winter and higher in the summer and autumn, while the precursors VOCs and NO_x display the opposite seasonal variation against the ozone.~~–~~ ~~The diurnal concentration variation of the ozone shows a unimodal variation, which reaches its maximum at 14:00 LT, while that of the ozone precursors VOCs and NO_x display a bimodal variation, which reach their maximum around rush hour. A negative growth of ozone concentration occurs between 15:00-23:00 LT is presumably due to titration of ozone by emissions of NO_x and the photochemical reaction do not play a key role.~~ A negative growth of ozone concentration occurs between 15:00-18:00LT and 19:00-23:00LT. The first period of time (15:00-18:00LT) is presumably due to low OH radicals and the fact that titration of ozone by emissions of NOx plays a key role, while the second period of time is due to the fact that there was no OH radicals and NO titration could still consume the ozone .The photochemical reaction is intensive at noon, so that the variation trend of the ozone concentration shows a positive growth, and the ~~–~~photochemical formation of the ozone is larger than its chemical loss.

~~Through analyzing the relationship between NO_2/NO ratio and ozone concentration, it is found that at around 09:00 LT in the summer, autumn and winter, both the ozone concentration and NO_2/NO ratio begin to increase, and the NO_2/NO ratio reaches its maximum after the peak of ozone concentration. In the spring, the NO_2/NO ratio performs differently from the other three seasons, which may be due to the spring weather factors. Through analyzing the impacts of the VOCs components on ozone formation, it is revealed that, as~~ In terms of ~~viewed from the~~ volume mixing ratio concentration and carbon number of VOCs, alkanes and aromatics are the most important atmospheric ~~constituents~~ categories at the sampling ~~point~~site. As viewed from ozone formation potential, aromatics ~~and alkenes~~ are the ~~two~~ species with the largest contributions. Among these, toluene, m-xylene, p-xylene and 1,3,5-trimethylbenzene are the most important, with a total contribution to ozone formation potential of about 31.6 %. It should be noted that the concentration of isoprene emitted by plants is not high, but has a very large contribution to the ozone.

The ozone isopleths diagrams by measured data are employed to determine the ozone formation regime. When the VOCs concentration is between 0ppbc and 250ppbc, the ozone formation regime is VOC-limited; when the VOCs concentration is between 250ppbc and 600ppbc, the ozone formation regime is NOx-limited; and when the VOCs concentration is above 600ppbc, the ozone formation regime is (VOC and NOx)-limited regime. The high △O_3 and 8h O_3max usually occur in NOx-limited which indicated that NO_x emissions must be controlled to regulate the occurrence of high-concentration ozone events in summer and autumn. This phenomenon is further confirmed by the measured VOCs/NOx, which shows that the ozone formation regime can shift from VOC-limited in early the morning to NOx-limited at noon in the summer and autumn, and the NO_x emissions must be controlled to achieve the purpose of controlling high-concentration ozone events; however, in the spring and winter, the ozone formation regime is VOC-limited for a long period of time. ~~Through analyzing the diurnal variation law of seasonal ozone concentration and the VOC/NO_x ratio, it is found that high-concentration ozone events are prone to occur in the summer and autumn. In the morning (07:00 to 08:00 LT), ozone is formed in the VOCs control area, and the reduction of VOCs concentration helps to further reduce the ozone concentration. However, when the ozone concentration reaches its peak at noon, the ozone is formed in the NO_x control area. The NO_x emissions must be controlled to achieve the purpose of controlling high-concentration ozone events. However, in the spring and winter, ozone is generated in the VOCs control area for a long period of time. Due to the fact that~~ Since the ozone concentration is relatively low in these two seasons, although the control of the NO_x emissions can increase the ozone concentration, no high-concentration ozone event will occur. It should be noted that the results are presented above only by observational data, and further investigations based on numerical model are needed in the future to obtain more detailed and robust conclusions. Numerical models currently available for simulating ozone pollution in the atmosphere, such as observation-based model (OBM), Weather Research and Forecasting-Chemistry mode (WRF-Chem) and U.S. Environmental Protection Agency's Community Multi-scale Air Quality (CMAQ), are necessary to analyze the formation of ozone from VOCs and NOx.~~Through further analysis of the days with high-concentration ozone, it is found that when high-concentration ozone events occur, more attention must be paid to controlling NO_x emissions.~~

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Table 1. The wind speed and temperature in four seasons (from June 2011 to May 2012) at GPACS.

		Minimum	Maximum	Mean value	Median
Spring	Windspeed/ms^{-1}	0	5.4	1.3	1.2
	Temperature/℃	9.4	35.5	22.6	22.9
Summer	Windspeed/ms^{-1}	0	6.0	1.4	1.2
	Temperature/℃	23.9	37.1	29.4	28.8
Autumn	Windspeed/ms^{-1}	0	5.7	1.5	1.4
	Temperature/℃	16.2	35.3	25.2	25.2
Winter	Windspeed/ms^{-1}	0	6.3	1.5	1.4
	Temperature/℃	4.7	26.9	14.2	14.1

Table 2. The standard curve and detection line of VOC species

Target compound	Standard curve	correlation coefficient	Detection limit (ppbv)
Ethylene	y=1.0188x+0.2659	0.997	0.07
Acetylene	y=1.0409x+0.1756	0.998	0.08
Ethane	y=1.0162x+0.2891	0.997	0.08
Propylene	y=0.9959x+0.1506	0.999	0.07
Propane	y=0.9824x+0.2082	0.998	0.09
Isobutane	y=0.9753x+0.3785	0.994	0.05
1-Butene	y=0.9587x+0.3641	0.994	0.06
n-Butane	y=0.9776x+0.3718	0.994	0.05
t-2-Butene	y=0.9746x+0.2747	0.997	0.05
c-2-Butene	y = 0.9834x+0.1606	0.999	0.06
Isopentane	y=0.9753x+0.2135	0.998	0.07
1-Pentene	y = 0.919x+0.1626	0.998	0.05
n-Pentane	y = 0.9557x+0.2038	0.984	0.07
Isoprene	y=1.0304x+0.1653	0.998	0.07
trans-2-pentene	y=0.9753x+0.2135	0.998	0.07
cis-2-pentene	y = 0.9557x+0.2038	0.984	0.07
2,2-Dimethylbutane	y=0.9731x+0.1971	0.998	0.07
Cyclopentane	y=0.9993x+0.1412	0.997	0.06
2,3-Dimethylbutane	y = 0.919x+0.1626	0.999	0.07
2-Methylpentane	y = 0.9557x+0.2038	0.984	0.07
3-Methylpentane	y=0.9753x+0.2135	0.998	0.07
2-Methyl-1-Pentene	y=0.9700x+0.3300	0.995	0.05
n-Hexane	y=0.9915x+0.2626	0.997	0.06
Methylcyclopentane	y = 0.9749x+0.1832	0.999	0.07
2,4-Dimethylpentane	y=0.9993x+0.1412	0.999	0.05
Benzene	y=0.9753x+0.2835	0.997	0.06
Cyclohexane	y=0.9841x+0.2744	0.997	0.07
2-methylhexane	y=0.9744x+0.2979	0.996	0.05
2,3-dimethylpentane	y=0.9779x+0.2953	0.997	0.05
3-methylhexane	y=0.9735x+0.3374	0.995	0.05
2,2,4-trimethylpentane	y=0.9696x+0.3947	0.994	0.05
n-Heptane	y=0.9678x+0.3635	0.994	0.05
Methylcyclohexane	y=0.9819x+0.3629	0.995	0.05
2,3,4-trimethylpentane	y=0.9691x+0.3994	0.994	0.04
Toluene	y=0.9696x+0.3397	0.995	0.05
2-methylheptane	y=0.9603x+0.4835	0.990	0.04
3-methylheptane	y=0.9625x+0.4550	0.991	0.04
n-Octane	y=0.9524x+0.5082	0.989	0.04
Ethylbenzene	y=0.9629x+0.4253	0.992	0.04
m&p-Xylenes	y=0.9541x+0.5844	0.986	0.03

Styrene	y=0.9524x+0.4132	0.991	0.04
o-Xylene	y=0.9515x+0.4926	0.989	0.04
n-Nonane	y = 0.9878x+0.1635	0.998	0.04
Isopropylbenzene	y=0.9418x+0.5162	0.986	0.04
n-Propylbenzene	y=0.9426x+0.5468	0.986	0.04
m-Ethyltoluene	y = 0.9532x+0.4838	0.989	0.04
p-Ethyltoluene	y = 0.9554x+0.3953	0.992	0.04
1,3,5-Trimethylbenzene	y = 0.951x+0.4724	0.989	0.04
o-Ethyltoluene	y = 0.9784x+0.0956	0.999	0.04
1,2,4-trimethylbenzene	y = 0.9563x+0.4509	0.991	0.03
n-Decane	y = 0.9651x+0.3068	0.995	0.04
1,2,3-trimethylbenzene	y = 0.9537x+0.3191	0.993	0.04
m-Diethylbenzene	y = 0.9541x+0.4494	0.991	0.04
p-Diethylbenzene	y = 0.9607x+0.3788	0.993	0.04
n-Undecane	y = 0.9519x+0.3329	0.992	0.04

Table 3. Daily average of VOCs and its constituents, NOx and ozone in four seasons（from June 2011 to May 2012）at GPACS

		Alkanes/ ppbv	Alkenes/ ppbv	Aromatics /ppbv	VOCs/ ppbv	NOx/ ppbv	O_3/ ppbv
Spring	March	20.84	5.26	8.50	34.60	76.39	12.46
	April	25.11	5.86	11.33	42.30	35.17	16.02
	May	21.45	5.47	10.94	37.86	25.29	24.55
Summer	June	19.74	6.62	14.23	40.60	24.40	24.26
	July	20.07	6.72	12.90	39.69	24.70	24.26
	August	22.36	9.12	9.99	41.46	21.75	28.26
Autumn	September	20.82	7.80	8.95	37.57	25.18	29.67
	October	22.26	5.63	8.89	36.78	26.59	25.34
	November	39.16	10.24	14.16	63.57	39.98	21.78
Winter	December	33.61	8.47	5.97	48.05	39.14	20.37
	January	32.13	7.96	7.54	47.63	34.82	9.31
	February	-	-	-	-	52.69	9.97

Table 4. Photochemical properties of VOCs and their average mixing ratios at GPACS from June 2011 to May 2012.

Compound	MIR[a]	$K^{b}_{OH}\times10^{12}$	Mixing ratio（ppbv）	Mixing ratio（ppbc）
Alkanes				
Ethane	0.25	0.27	3.66	7.31
Propane	0.46	1.15	4.34	13.02
i-Butane	1.18	2.34	2.67	10.68
n-Butane	1.08	2.54	3.07	12.28
Cyclopentane	2.24	5.16	0.15	0.77
i-Pentane	1.36	3.9	1.72	8.61
n-Pentane	1.22	3.94	1.37	6.86
Methylcyclopentane	1.46	5.1	0.32	1.94
2,3-Dimethylbutane	1.07	6.3	0.13	0.76
2-Methylpentane	1.4	5.6	0.88	5.29
3-Methylpentane	1.69	5.7	0.75	4.51
n-Hexane	1.14	5.6	1.43	8.56
2,4-Dimethylpentane	1.11	5.7	0.37	0.41
Cyclohexane	1.14	7.49	1.65	9.90
2-Methylhexane	1.09	6.9	0.58	4.04
2,3-Dimethylpentane	1.25	5.1	0.26	1.82
3-Methylhexane	1.5	5.1	0.52	3.66
2,2,4-Trimethylpentane	1.2	3.68	0.22	1.79
n-Heptane	0.97	7.15	0.32	2.24
Methylcyclohexane	1.56	10.4	0.26	1.81
2,3,4-Trimethylpentane	0.97	7	0.12	0.96
2-Methylheptane	1.12	8.3	0.08	0.66
3-Methylheptane	0.8	8.6	0.08	0.68
n-Octane	0.68	8.68	0.19	1.54
n-Nonane	0.59	10.2	0.35	3.18
n-Decane	0.52	11.6	0.03	0.29
n-Undecane	0.47	13.2	0.17	1.92
n-Dodecane	0.38	14.2	0.14	1.65
Alkenes				
Ethene	7.4	8.5	2.99	5.97
Propene	11.57	26.3	1.32	3.96
trans-2-Butene	15.2	64	0.28	1.14
1-Butene	9.57	31.4	0.44	1.77
cis-2-Butene	14.26	56.4	0.22	0.86
trans-2-Pentene	10.47	67	0.03	0.15
1-Pentene	7.07	31.4	0.05	0.23
cis-2-Pentene	10.28	65	0.19	0.97
Isoprene	10.48	101	1.14	5.72
1-Hexene	—	—	0.67	3.99

Aromatics				
Toluene	3.93	5.96	4.59	32.10
Ethylbenzene	2.96	6.96	1.48	11.81
m,p-Xylene	8.54	20.5	1.41	11.24
Styrene	1.66	58	0.41	3.25
o-Xylene	7.58	13.6	0.66	5.28
i-Propylbenzene	2.45	6.6	0.10	0.86
n-Propylbenzene	1.96	5.7	0.23	2.05
m-Ethyltoluene	7.39	18.6	0.25	2.22
p-Ethyltoluene	4.39	11.8	0.21	1.89
1,3,5-Trimethylbenzene	11.75	56.7	0.21	1.86
o-Ethyltoluene	5.54	11.9	0.27	2.47
1,2,4-Trimethylbenzene	8.83	32.5	0.21	1.92
1,2,3-Trimethylbenzene	11.94	32.7	0.15	1.32
m-Diethylbenzene	7.08	15	0.12	1.25
p-Diethylbenzen	4.39	10	0.11	1.05

MIR[a] denotes maximum incremental reactivity（Carter, et al., 1994)

k^{b}_{OH} denotes rate constant of VOCs react with hydroxyl radicals at 298K,(Atkinson and Arey,2003)

Table 5. Top 10 VOCs species at GPACS based on the Propy-Equiv and MIR scales from June 2011 to May 2012.

OH Reactivity Rank		MIR Rank	
Compound	Percentage（%）	Compound	Percentage（%）
Isoprene	19.97	Toluene	16.26
m,p-Xylene	7.97	m,p-Xylene	12.48
Toluene	6.62	Isoprene	7.99
Styrene	6.51	Propene	6.30
1,3,5-Trimethylbenzene	3.82	Ethene	6.07
Propene	3.60	o-Xylene	5.21
Ethylbenzene	2.85	Ethylbenzene	4.54
Cyclohexane	2.56	1,3,5-Trimethylbenzene	2.87
trans-2-Butene	2.51	trans-2-Butene	2.37
o-Xylene	2.48	1,2,4-Trimethylbenzene	2.22

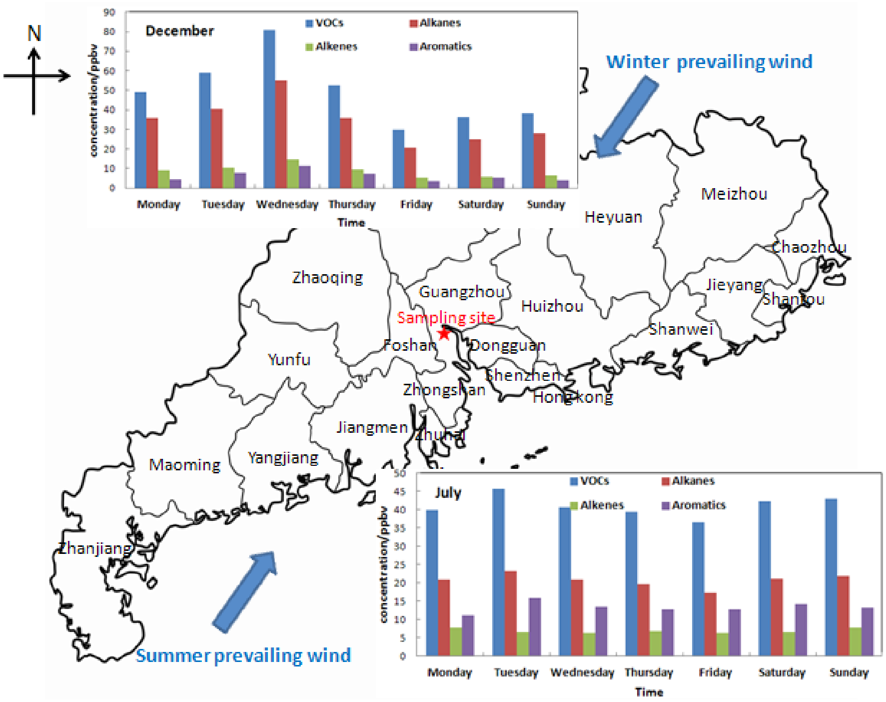


Figure 1. The location of observation site at GPACS and its surrounding area, the pentagram represents the sampling site. The VOCs concentration in July when the summer prevailing wind is southwesterly and in December when the winter prevailing wind is northeasterly is showed in the map.

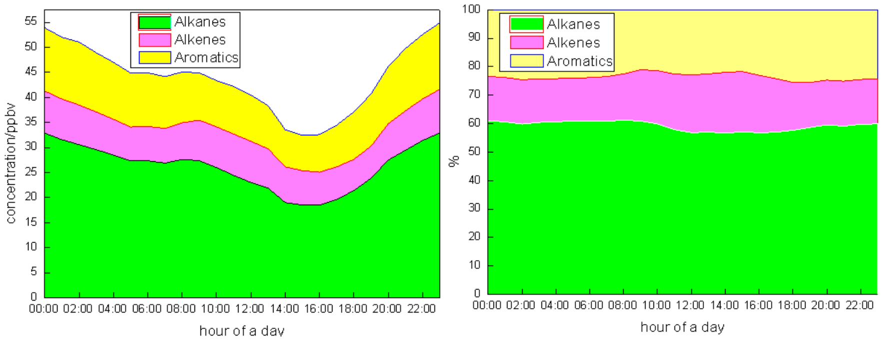
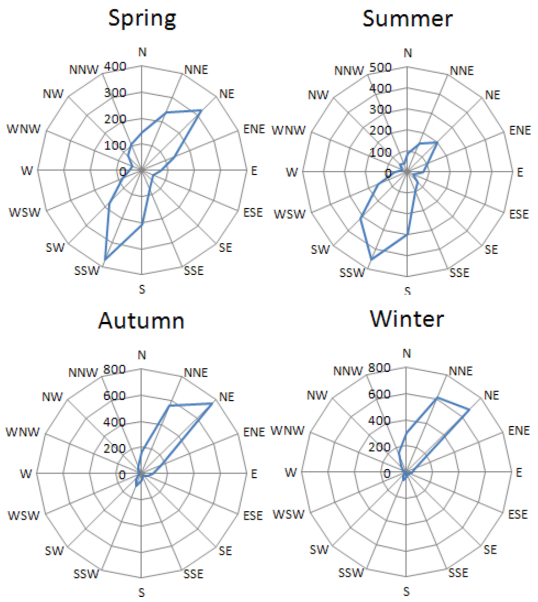


Figure 2. Daily cycle of hourly averaged concentration of three categories of VOCs in ppbv and in % of total (from June 2011 to May 2012) at GPACS



Spring

Summer

Autumn

Winter

Fig 3. The frequency of wind direction plotted by wind rose for four seasons（from June 2011 to May 2012）at GPACS

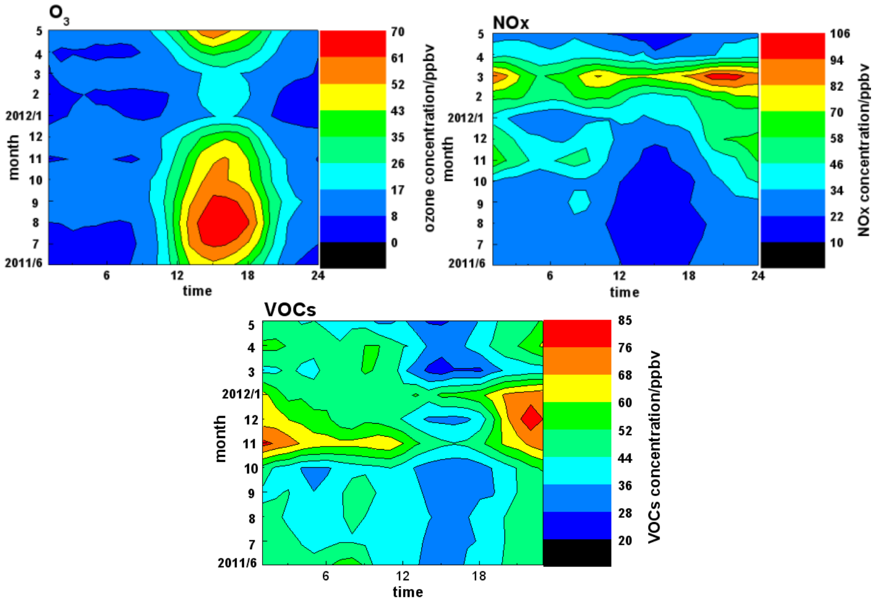


Fig 4. The diurnal variations of ozone, NOx and VOCs in months（from June 2011 to May 2012）at GPACS.

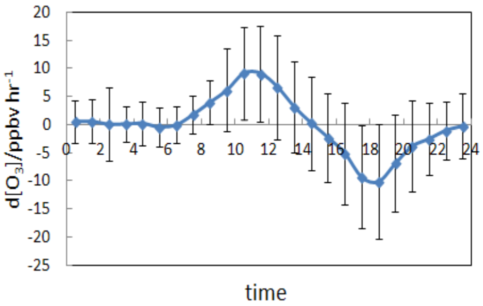


Fig 5. Average diurnal trends in ozone from June 2011 to May 2012 at GPACS. Colored marker represents hourly mean value. The black line gives the standard deviation.

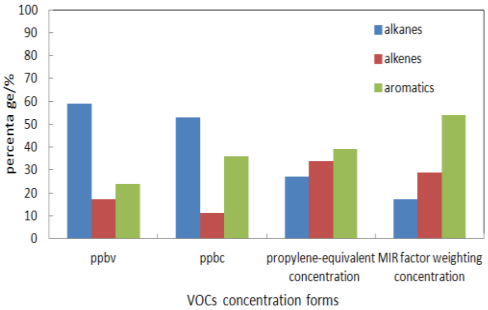


Fig 6. Average fractions of each category based on volume mixing ratio (ppbv), carbon-atom-based concentration (ppbc), OH-reactivity-based Propy-Equiv concentration (ppbc), and MIR factor weighting concentration(ppbv). Fractions of each VOCs category（alkanes, alkenes and aromatics）plotted by bar based on four methods (ppbv, ppbc, propylene-equivalent concentration and MIR factor weighting concentration) from June 2011 to May 2012 at GPACS.

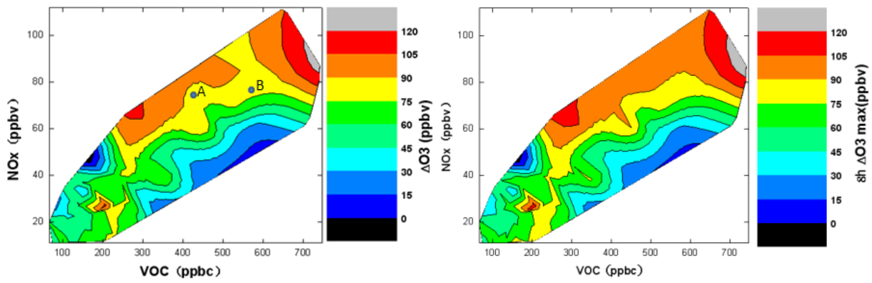


Fig 7. O_3 isopleth diagrams plotted by observational data from June 2011 to May 2012 about the amount of O_3 increase(△O_3)（left panel）and 8h O_3max（right panel）. The observational data are selected by the days when the sum of the solar radiation from sunrise to 18:00 exceeds the annual average and when the average wind speed from sunrise to 18:00＜$3ms^{-1}$. The average concentrations of VOCs and NOx in the daytime (6:00-9:00) are used, and the amount of O_3 increase(△O_3)is defined as the difference between the maximum value in (10:00-18:00) and the average value in the early morning (6:00-9:00), the 8h O_3max is defined as the maximum during the time between 10:00-18:00.A point represents the day (2011.8.12) and B point represents the day (2011.11.5).

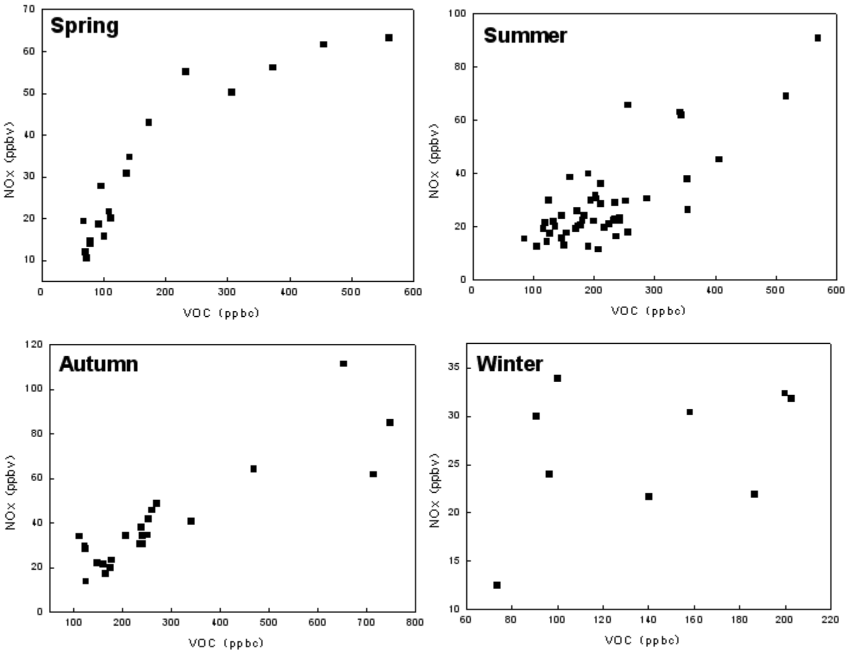


Fig 8. The scatter diagram between VOCs and NOx by observational data from June 2011 to May 2012 selected by the days when the sum of the solar radiation from sunrise to 18:00 exceeds the annual average and when the average wind speed from sunrise to 18:00＜3ms^{-1}.

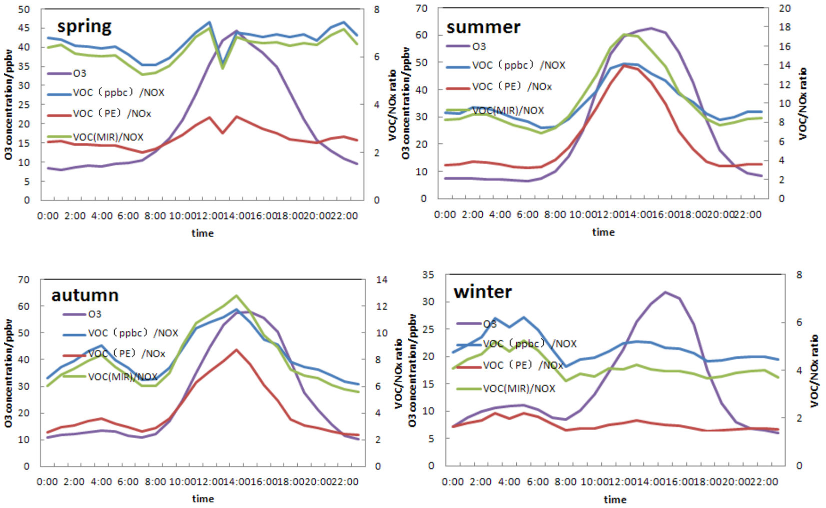


Figure 9. The variation patterns of VOC/NOx ratio and ozone concentration at four seasons（from June2011 to May 2012）at GPACS. Three forms of VOC（ppbc, PE and MIR）is presented by blue, red and green respectively and colored markers represent hourly mean value.

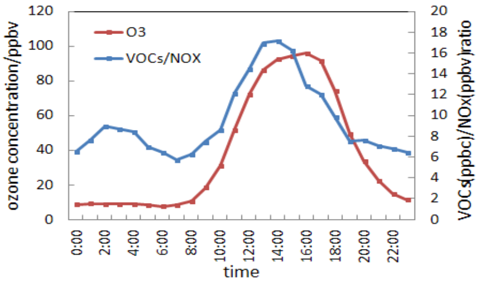


Fig 10. The variation patterns of VOC/NOx ratio and ozone concentration at high ozone episode at GPACS. Colored markers represent hourly mean value. High ozone episode refers to the days with an hourly ozone value higher than 93ppbv.