Interactive comment on “An analysis of the impacts of VOCs and NOx on the ozone formation in Guangzhou”

by Y. Zou, et al

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We thank Referee #1 for his good and very helpful assessment. Following the reviewers advice we elaborate some specific points, which strengthen the findings of our paper. Our reply to the reviewer comments is listed in detail below.

As author’s views, this manuscript has at least included three strong points: (1)The control areas of ozone formation with diurnal variation have been revealed, which seldom scholars do in Pearl River Delta（PRD）region. Although we made the conclusion referring traditional method (in fact the method is also referred in some recent published papers, i.e. Ran, L., C. Zhao, F. Geng, X. Tie, X. Tang, L. Peng, G. Zhou, Q. Yu, J. Xu, and A. Guenther (2009), Ozone photochemical production in urban Shanghai, China: Analysis based on ground level observations, J. Geophys. Res., 114, D15301, doi:10.1029/2008JD010752.), we are amazed to find that when the O_3 concentration is very high, the O_3 is formed in NOx control area, which is a new discovery, for most previous studies in PRD region reported that O_3 formation was VOC-limited. The observed VOC/NOx ratio is much higher than the classic referring ratio when the O_3 concentration is very high, the ozone formation has a high potential in NOx-limited regimes. In other words, our measurement result is consistent with the classical understanding in some extent. What' more, we used the O_3 isopleth diagrams by observational data which also convinced us of the conclusion that the high O3 concentration is formed in NOx sensitive. At last, the high O_3 concentration is formed in NOx sensitive in PRD region which is also revealed by recent published paper(i.e 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.).(2) Comparing with the previous studies on photochemistry in PRD region, the continuous online data of VOCs has been used, which has a strong lead in PRD region with the reason that VOCs monitoring has not been a routine observation and most of the VOCs monitoring were off-lined before. (3) Many studies using numerical simulations to analyze the impact of VOCs and NOx on the O_3 formation in PRD region. However, little attention has been given to the O_3 isopleth diagram and initial VOCs and NOx concentration to produce O_3 using observational data. To elucidate the control areas of O_3 formation and the initial VOCs and NOx concentration to produce O_3, yearly observational data selected by meteorological conditions (low wind, the airmass in stagnation to exclude the impact of airflow transportation on ozone) are used to plot the O_3 isopleth diagrams, which has been analyzed in the revised manuscript.

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.

Although VOC/NOx ratio only give a rough idea as to whether it is a NOx-sensitive or VOC-sensitive environment, we do used this traditional method to make a new discovery that when the O_3 concentration is very high, the ozone is formed in NOx control area in Guangzhou city. We used VOC/NOx ratio to give a general idea about general characteristics of photochemistry in Guangzhou city, in order to give a more detail about this, O_3 isopleth diagram by yearly observational data selected by meteorological condition has been plotted (in attached Fig.1) and analyzed in revised manuscript, a case in point is that you can see when the VOCs concentration is between 250ppbc and 600ppbc,the O_3

formation is under NOx-limited regime，increasing the emissions of VOCs could reduce O_3 formation. Attached Fig.2 shows that the dots in different seasons by meteorological condition. We find that high $\triangle O_3$ is under NOx-limited regime and VOC / NOx-limited regimes, and most of the dots under these regimes are in summer and autumn, which strengthen the finding that when the O_3 concentration is very high（i.e. summer and autumn）, the O_3 is formed in NOx control area.

As for the truth that the impact of VOCs to ozone formation is more relevant to the reactivity of individual VOC species rather than to the amount of VOCs, VOC(reactivity)/NOx ratio was used to analyze ozone formation(attached Fig.3) in revised manuscript. Furthermore, the true is that we have already considered the reactivity of individual VOC species in 3.3 in original manuscript, we find that aromatics have the most reactivity in VOCs species and we also rank the top ten VOCs species in reactivity by the traditional method（i.e. MIR and propylene-equivalent concentration）.At last, considering the O_3 isopleth diagram may be decided by the composition of VOCs, we find that more high reactivity VOC species are included in VOC composition, they are reacted with OH radicals more active than other VOCs, thus lower VOCs concentration can produce O_3 under the same condition. For example, we choose the days when the NOx and $\triangle O_3$ are nearly the same in O_3 isopleth diagram, you found that the lower VOCs concentration is corresponding to the more higher reactivity VOCs species.

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 O_3 episodes often occur in suburban Guangzhou, so choosing this suburban site to do some researches about ozone problems is targeted.

Secondly, the site 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, which can be good representative of atmospheric composition with the uniform mixing in Pearl River delta. You can see in attached figure 4, 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 from the map(attached Fig.5) that when the prevailing wind is NE in December, the weekend effect of VOCs is very typical showing a lot of pollutants emitted from the downtown Guangzhou city. However, when the prevailing wind is SW in July, the weekend effect of VOCs is not apparent for the reason that few pollutants emitted from the further suburban areas. So you can see two different typical air pollution processes in this site.

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

Actually, QA/QC of online VOC measurements have been done. we run validation or /and calibration with zero gas and span gas every month.

Firstly, a validation is a run with zero gas and /or a span gas in order to check the drift, repeatability and/or memory effects. The run is treated as a regular sample, i.e. no new calibration data will be produced.

Secondly, check types

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

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

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

Thirdly, we can define two level on the software for the checks，

（1） Warning level:

You get a message if it is reached but the program will continue. Calibration is needed. We will run calibration, check or/and adjust retention time windows, update retention times and responses.

（2）Error level:

You get a message and the program will stop because the system must have a problem which should be fixed first.

At last, we normally run calibration every month, the standard curve and the detection line of VOCs are in attached table 1.

Specific comments

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

The map has been changed. The surrounding cities are showed in the map. The VOCs concentrations in July when the summer prevailing wind is SW and in December when the winter prevailing wind is NE are also showed in the map.

2) Page 5 lines 10-12: why?

As I stated in general comment 2 that 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, which can be good representative of atmospheric composition with the uniform mixing in Pearl River delta and you can monitor the typical air pollution processes in different seasons and under different weather conditions.

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 (Attached Fig.7).

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.

(f) 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).

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 (Attached Fig.8), the analyzer enriched the VOCs by absorbents, lower temperature is corresponding to more VOCs enriched by absorbents, but when the temperature is below 0 ℃ , which would make the tube condensed(Attached Fig.9).So we choose 13℃ to enrich VOCs by adsorption materials.

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. In original manuscript, the description "which is mainly due to the light, temperature and other meteorological factors being different in each season" 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".

6) Lines 16-24, page 6: no statistical analysis was conducted for all

the comparisons. Are they really statistically different?

Statistical analysis has been conducted for all the comparisons. Average VOCs, NOx and O_3 in four seasons are showed in attached table 2.VOCs concentration is varied from 34.60ppbv in March to 63.57ppbv in November, NOx concentration is varied from 21.75ppbv in August to 76.39 in March, O_3 concentration is varied from 9.31ppbv in January to 29.67 in September. They are really statistically different.

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

Attached Fig 6 shows the average diurnal variations of VOCs, NOx and O3 in four seasons， you can see this pattern in one year though different seasons may display a little bit different.

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 low 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”.

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. Line10-19, page7 has been changed to “the results show that a negative growth of O3 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 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 NO titration could still consume O_3, until the NO titration stops, the O_3 concentration keeps a relatively stable during the period (0:00-7:00LT). the concentration trend of O_3 shows a positive growth due to the high OH radicals and strong photochemical reaction”.

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

Thanks reviewer to point out our carelessness. The titile of Fig.5（original manuscript） has been changed to “diurnal variations of NO_2/NO and O_3”

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 atmosphericchemistry 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”has been 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）” has been 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”.

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. Due to limited time and huge workload, at present, the manuscript just give out some observational results which have some valuable findings we think. There are still a lot to do, we will try in the future.

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 in some extent. So we also using VOC(reactivity)/NOx ratio to analyze ozone formation(attached Fig.3) in revised manuscript. But using VOC/NOx ratio could broadly judge VOC-limited or NOx-limited regimes by referring the classic method in our dataset, which is because the observed VOC/NOx ratio is much higher than the classic referring ratio when the O_3 concentration is very high, the ozone formation has a high potential in NOx-limited regimes as data shown.O_3 isopleth diagram has been used by observational data, which reveals the initial VOCs and NOx concentration to the O_3 formation and judges whether the O_3 formation is in VOC limited or NOx limited regime. In a word, we try to use more methods to judge the O_3 formation in Guangzhou area.

Table 1.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 2. Daily average of VOCs and its constituents, NOx and O_3 in four seasons（from June 2011 to May 2012）at GPACS

		Alkanes/ ppbv	Alkenes /ppbv	Aromatics /ppbv	VOCs/ppbv	NOx/ppbv	O3/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	19.53
	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	38.98	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

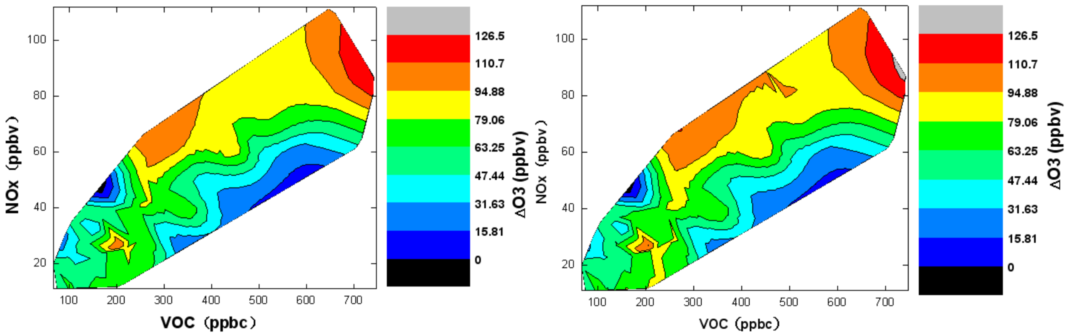


Fig1. O3 isopleth diagrams plotted by observational data from June 2011 to May 2012 about the amount of O3 increase(△O3)（left panel）and 8h O3max（right panel）. The observational data are selected by the days when the sum of the solar radiation from sunrise to 18:00 exceeds the annual average and when the average wind speed from sunrise to 18:00＜3ms^{-1}. The maximum concentrations of VOCs and NOX in the early morning (6:00-9:00) are used, and the amount of O3 increase(△O3)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 O3max is defined as the maximum during the time between 10:00-18:00.

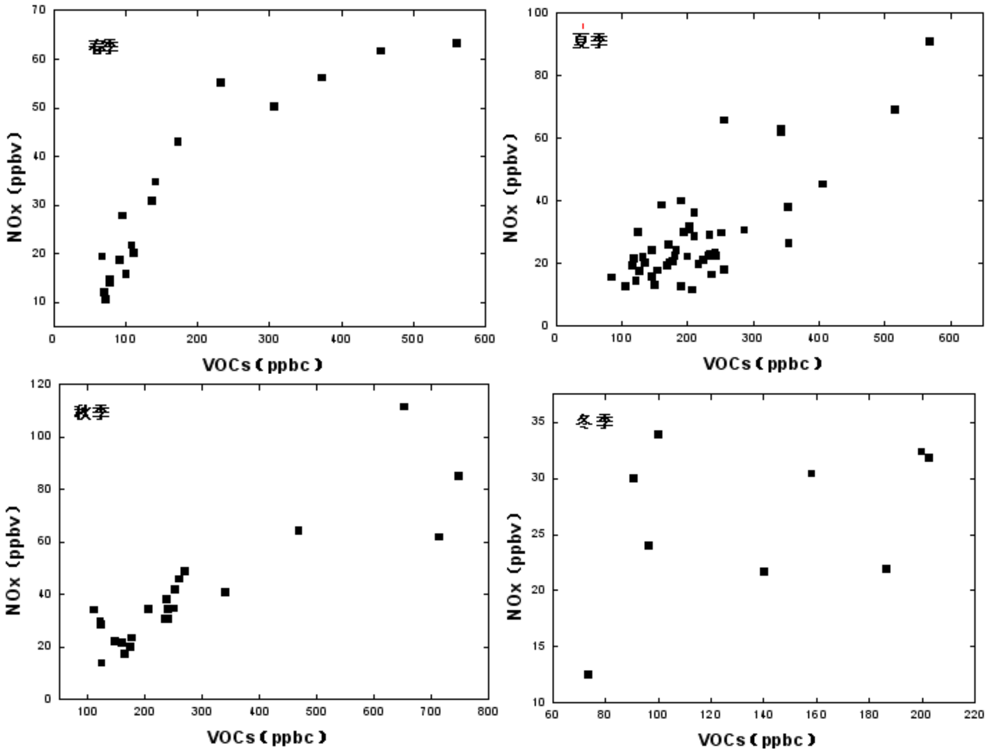


Fig2. The scatter diagram between VOCs and NOX by observational data from June 2011 to May 2012 selected by the days when the sum of the solar radiation from sunrise to 18:00 exceeds the annual average and when the average wind speed from sunrise to 18:00＜3ms^{-1}.

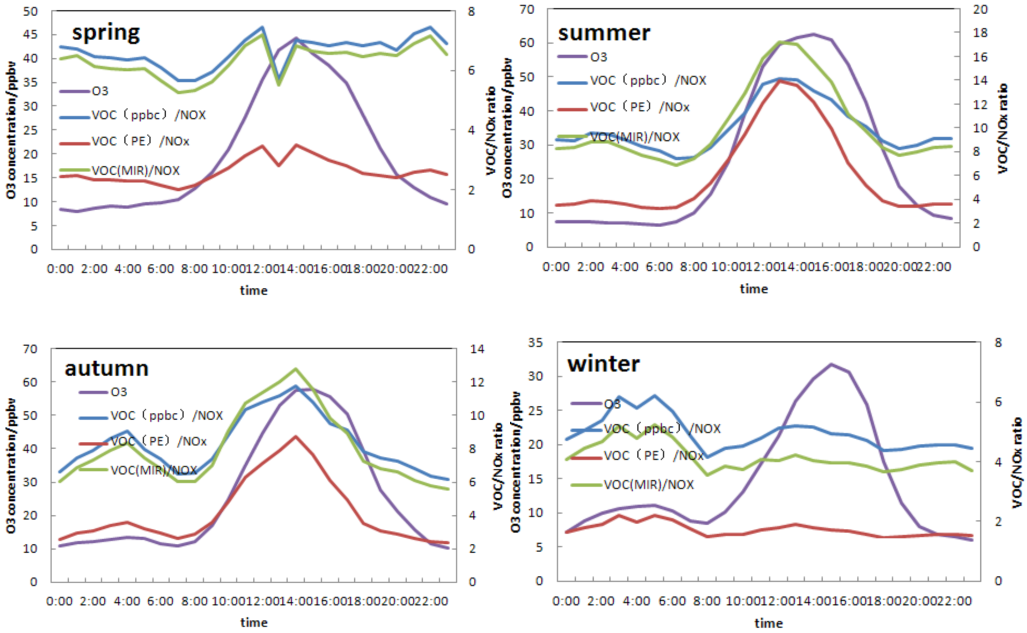


Figure 3. The variation patterns of VOC/NOx ratio and O3 concentration at four seasons（from June2011 to May 2012）at GPACS. Three forms of VOC（ppbc, PE and MIR）is presented by blue, red and green respectively and colored markers represent hourly mean value.

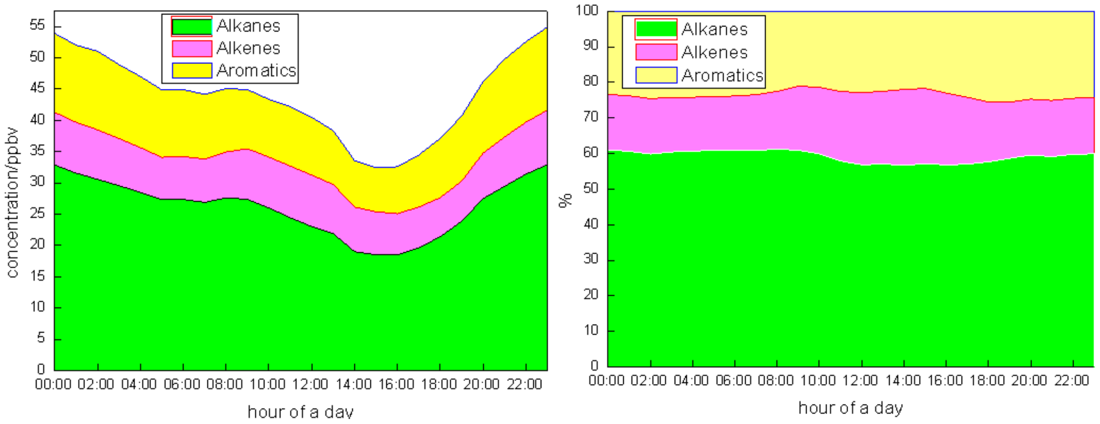


Figure 4.Daily cycle of hourly averaged concentration of three categories of VOCs in ppbv and in % of total (from June 2011 to May 2012) at GPACS

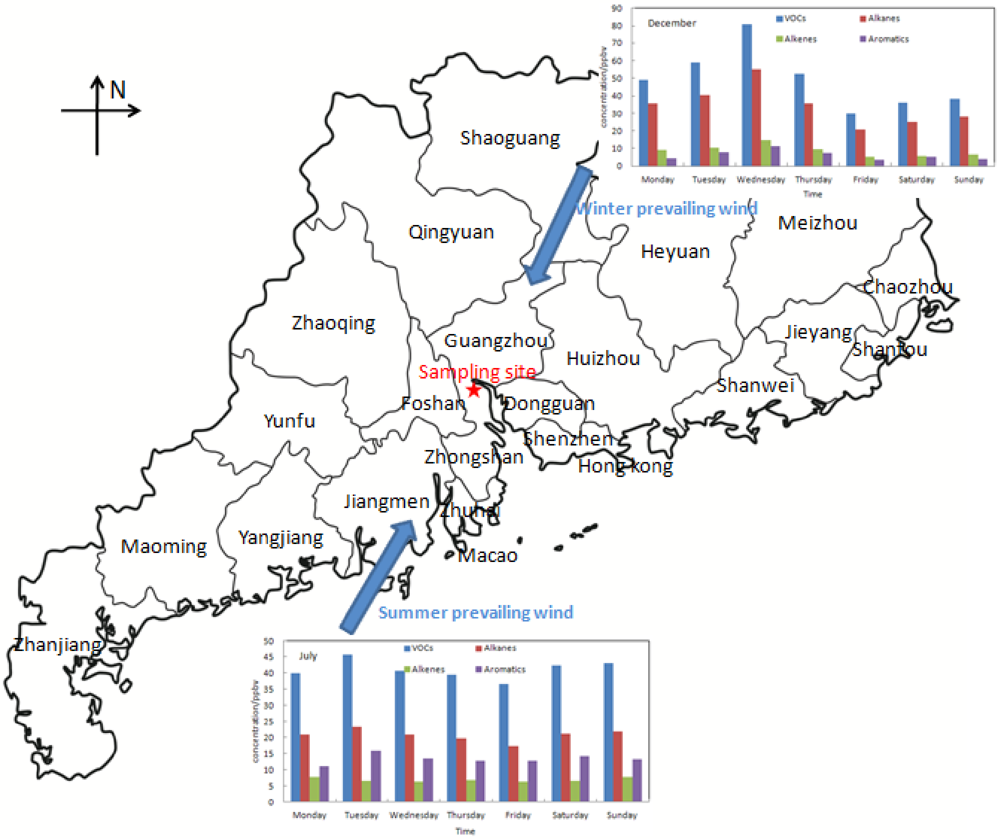


Figure 5. The location of observation site at GPACS and its surrounding area, the pentagram represents the sampling site. The VOCs concentration in July when the summer prevailing wind is SW and in December when the winter prevailing wind is NE are showed in the map.

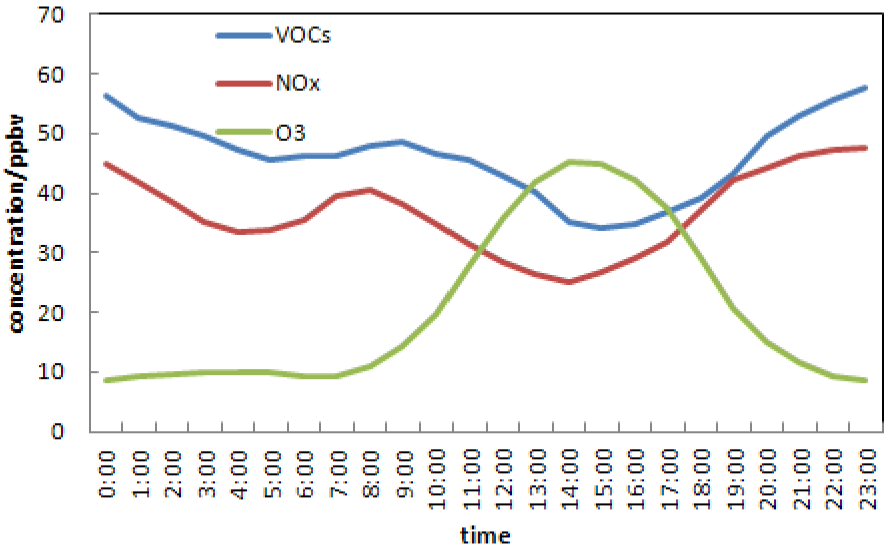


Figure 6.The diurnal variations of VOCs ,NOx and O_3 in four seasons (from June 2011 to May 2012) at GPACS. Colored markers represent hourly mean values.

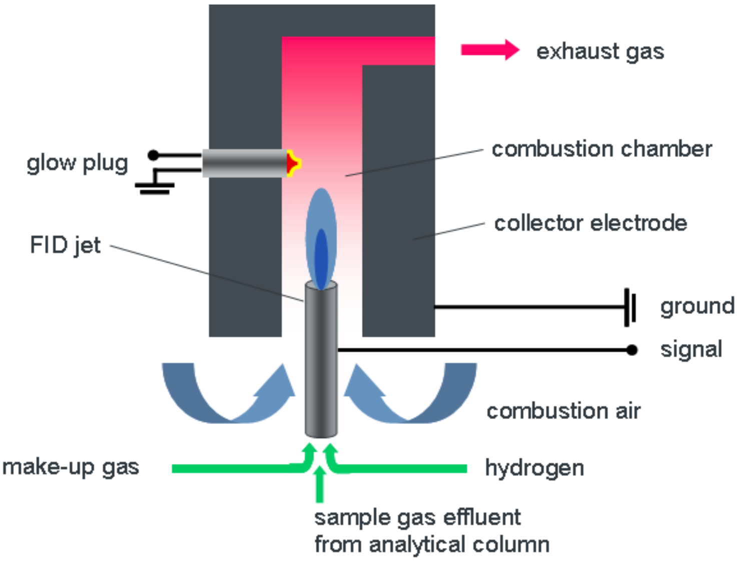
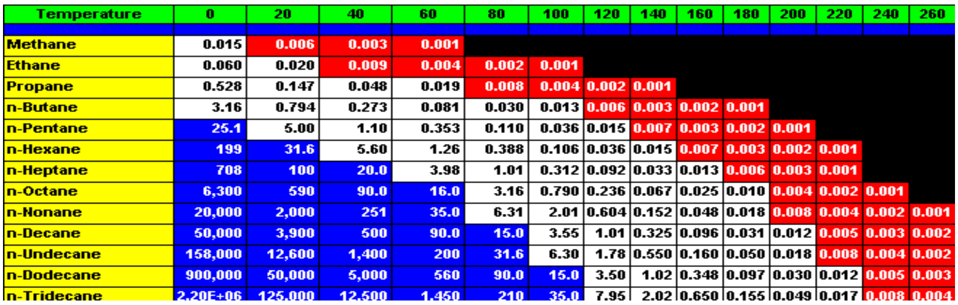


Figure 7. The design drawing of flame ionization detector



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

Fig.8 The relationships between penetration capacity and temperature by using the absorbent Tenax-TA

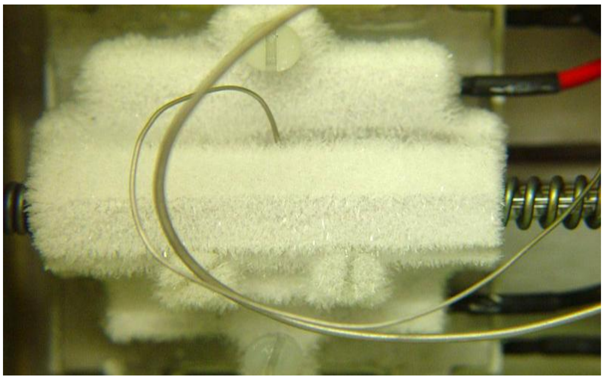


Fig.9 The scene of enriching tube freezing when the temperature is below 0