The reply of "An analysis of the impacts of VOCs and NOx on the ozone formation in Guangzhou" by Y. Zou, et al

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Summary:

It is well known that fine partical (PM2.5) and ozone are two air quality headaches in China. Recently, PM2.5 has become a top topic in china due to the fact that it can be easily sensed by the public through visibility degradation. Yet for ozone, the public as well as scientists concern less as they do for PM2.5. As a matter of fact, levels of near surface ozone in the Pearl River Delta region are exceeding national air quality guideline level as frequently as that of PM2.5, ozone pollution has become a very serious problem and would be a trouble even long-lasting than PM2.5 in this area. We can foresee that ozone will be a next top topic in China. As a result, the basic analysis on the characteristics of one year of observational data of VOCs, NOx and ozone at a suburban site in Guangzhou in this manuscript will be great significant for the further research of ozone pollution in this area. The features of this manuscript were listed as follows:

(1) The data itself of VOCs, NOx and ozone for one year is valuable for the basic and further research of ozone pollution in this area where the high ozone events usually occur. You can see the specific reason for this in the reply to the QA/QC of VOC measurements below. We reveal the characteristics of VOCs, NOx and ozone by using long time series data, which will make up the research of ozone pollution in this area and get people to know about ozone pollution situation in this area for a long period of time.

(2) The sampling site we choose is very appropriate for the research on ozone pollution in this area. You can see the specific reasons for this in the reply to the sampling site selection below. In brief, firstly, it is the regional central station of the observation network for atmospheric composition in Pearl River Delta; what's more, it is in suburban site of Guangzhou City where the high ozone events usually occur; furthermore, air was sufficiently homogenized from various sources at the surface at this sampling site; finally, typical air pollution processes can be seen at this sampling site.

(3) Apart from the basic characteristics of VOCs, NOx and ozone we reveal, the conclusion that the ozone formation is more likely to be NOx-limited in high ozone concentration or when the high ozone events occur is one of the

highlights in this paper, though the methods we use for supporting this idea are only based on the observational data. However, this idea has also been confirmed by the model in recent published paper (Li et al.,2013).

Regarding the methods we use in this paper, we have to state as follows:

(1) We use one year observational data to analyze the basic characteristics of VOCs, NOx and ozone, which gives a comprehensive understanding of ozone pollution in this area. Though simulation will be a help for further research, the simulation by model for one year will be a huge task for us in a short time. As a result, our topic in revised manuscript is more appropriate and targeted, which specifically point out that we only use one year observational data to analyze the very basic characteristics of ozone and its precursors.

(2) Regarding the VOC/NOx ratio approach, several improvements in our manuscript have been made for this.

Firstly, we claim that the actual VOC/NOx ratio at which ozone production is VOC-limited or NOx-limited will depend on specific conditions within a given area, so that the use of a single ratio（8）is only approximate to be referred if detailed photochemical modeling is not available in revised manuscript (page9, line30-33).

Secondly, we don't use the VOC/NOx ratio (8:1) as a strict definition to judge the ozone formation regime, on the contrary, we used a more speculative description with respect to this. It is fare to say the ozone formation is more likely to be NOx-limited under the condition that VOC/NOx ratio is much higher than value (8); while the ozone formation is more likely to be VOC-limited under the condition that VOC/NOx ratio is much lower than value (8)(page9, line34-37).

Finally, the expressions for the description of ozone formation regime have been modified, the expressions like "is likely to be" have been used for the description.

Reply to Report #1

1. The VOC/NOx ratio approach

The reviewer appreciated the effort of the authors on the revisions of the manuscript according to the reviewers' comments. However, I am still not convinced by the revised manuscript. As stated in my previous comments, VOC/NOx can only give rough idea about VOC or NOx limited. Other methods/models must be used to confirm the traditional method. The limitations of the VOC to NOx ratio approach have already been well addressed by the U.S. scientists in the report (NESCAUM (1995): Preview of the 1994 ozone precursor concentrations in the northeastern U.S. 5/1/94 draft report; prepared by the Ambient Monitoring and Assessment Committee of

the Northeast States for Coordinated Air Use Management, Boston, MA). In brief, 1) the measured absolute concentrations of precursors at the site are determined by local emissions and transport from upwind locations. It will ultimately be critical to distinguish between ozone contributions from local precursor emissions, from transported ozone formed in upwind locations, and from in-situ ozone production from transported upwind precursors.
Reply: Considering the wind speed varies at around1.4ms^{-1} in different seasons as we show in table 1 in revised manuscript, we think that horizontal transport effect is very small. We mention this in revised manuscript (page6, line29-30).

2) It is questionable about which species should be included in a calculation of "total VOCs" and "total NOx". The VOC/NOx ratio can be very different if you chose different VOC species to make total VOCs, leading to VOC/NOx variable. Traditional NOx measurements include NO + variable combination of NO2 and some other reactive nitrogen species (NOy).

Reply: The VOCs species are the same as target volatile organic compounds of the EPA PAMS (Photochemical Assessment Monitoring Stations). NO_2 is measured by using a molybdenum converter, it's true that NOx may include some oxidized reactive nitrogen that is converted by the molybdenum, and thus that the stated mixing ratios are upper limits to the actual NOx. As a result, the specification for the type of NO_2 converter on NOx instrument has been added in the revised manuscript (page 5, line5-9) and we also have stated in the revised manuscript (page 9, line36-38)that the actual VOC/NOx ratio would possibly be larger than shown due to the fact that a molybdenum converter is used for NOx measurement when using the VOC/NOx method to judge the ozone formation regime.

3) The simple ratio of the two disregards the composition and reactivity of individual hydrocarbon and nitrogen compounds. During a multi-day episode, concentrations of TNMHCs may build to high concentrations under a stagnating high pressure system. However, without fresh injections of VOCs, the most reactive compounds will become depleted, leaving high VOC levels composed of less reactive species with little potential for ozone production. Sillman has already established equations by considering the reactivity of VOCs.

Reply: You can see the Fig.2 in revised manuscript which 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 at the sampling site.

4) The VOC/NOx ratio approach focuses exclusively on the 6 to 9 AM time frame, while this manuscript calculated the ratios at all hours of a day. Also, reactive nitrogen compounds like PAN, HONO and nitric acid exhibit diurnal patterns which differ from those of NO and NO2.

Reply: It's true that VOC/NOx ratio approach usually focuses on the 6 to 9 AM time. However, VOC/NOx ratio approach has also been used in all day in recent published paper [Han et al., 2013].In this paper we have analyzed the diurnal patterns of NOx, but not yet for PAN, HONO and nitric acid.

Although the authors emphasized that the measured ozone isopleths were used and confirmed by the measured VOC/NOx ratios, both are basically the same and a kind of self-confirmation. The conclusion is dangerous only based on the measured VOC/NOx ratios which have a number of limitations described above and are not confirmed by other methods and models. Therefore, if NOx limited result is true, you can say this is one of the highlights in this paper. If the result is not reliable, this paper will significantly mislead the readers.

Reply: The characteristics of one year of VOCs, NOx and ozone which give a comprehensive understanding of ozone pollution in this area are the main content in our paper. As for the ozone formation regime, we have stated that one year simulation will be a huge task in a short time.

Also, we don't use the VOC/NOx ratio (8:1) as a strict definition to judge the ozone formation regime. On the contrary, we use a relatively speculative description with respect to this as we talked before.

The expressions for the description of ozone formation regime have been revised. The expressions like "is likely to be" have been used for the description.

In addition, though other studies may use the VOC/NOx ratio approach to roughly estimate the sensitivity of VOCs or NOx, all these studies also used other methods and models to verify the traditional method. But in this manuscript, the authors exclusively relied on this traditional method.

Reply: We have stated that one year simulation will be a huge task in a short time. Other studies that used models are case studies analysis in a short period of time.

The conclusions we make in this paper are mainly based on

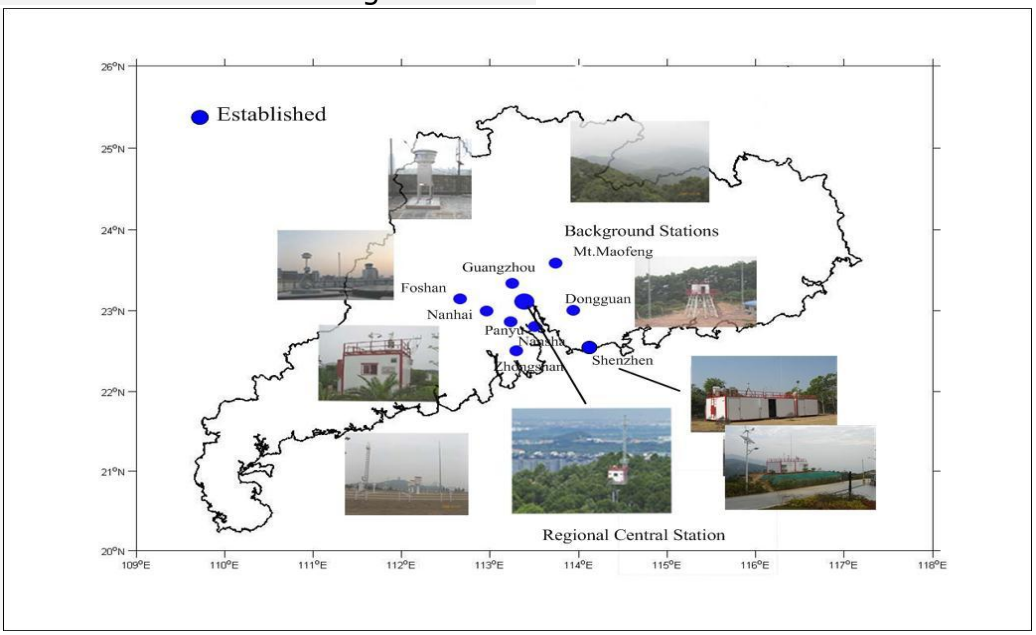
observational data analysis which are actual facts. We don't exclusively rely on traditional method.

2. Sampling site selection

The statement of "The site has been demonstrated by many experts…." does not make sense at all. Who are the experts? Please give references recognized by the national/international experts.

Reply: The sampling site we choose is appropriate for the ozone pollution research in Guangzhou City, there are several main reasons accounting for this.

To begin with, the sampling site is not only the CMA (China Meteorological Administration) site, but also the regional central station of the observation network for atmospheric composition in Pearl River Delta which is showed in the figure below.



Secondly, more specifically, the high ozone events frequently occur in suburban area of Guangzhou City. We can distinctly remember that as early as in October in 1995, ozone concentration exceeded 100μg·m^{-3} in the suburban area of Guangzhou City [Zhang et al., 1999]. As a result, the sampling site we choose in suburban area of Guangzhou City would be appropriate and targeted for the research on high ozone pollution in this area.

Thirdly, at this sampling site, you can see 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 sources at the surface (Fig.2 in revised manuscript).

Finally, you can see the typical air pollution processes in

different seasons and under different weather conditions at this sampling site. 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 (Fig.1 in revised manuscript). The site has really been demonstrated and well known by some Chinese experts.

3. QA/AC of VOC measurements

My question was not fully answered. QA/QC includes internal and external calibration. Since the authors claimed that this is the first time to measure VOCs online in the region, and the online measurement method is not the same as other online instruments, validation of the results in the study is important. Have you conducted any inter-comparison with other recognized groups nationally/internationally? In other words, how could readers trust your measurement data? As a matter of fact, I am not 100% confident with the VOC online data, based on the authors' reply to the specific comment 4) below.

Reply: We have claimed that NOx and ozone have been included in the routine observation since the year of 2006, after that time, a greater amount of systematic long-term observation data on atmospheric ozone and NOx has become available. By comparison, however, VOC is not included in the scope of daily observations and there are few monitoring stations that equipped with the VOC on-line monitoring instruments, you just get access to it involving short-term intensive observations or non-continuous long term observations. It seems that the start of VOCs monitoring in China is far behind that of some foreign countries.

To be frank, we have not conducted comparison with other recognized VOC online instruments due to the fact that there are few online VOC instruments in Pearl River Delta region. We firmly believe that with the great attention to the VOC, it will be included in the scope of daily observations in the near future. At that time, more monitoring stations will be equipped with VOCs online instruments, and we hope to conduct comparison soon.

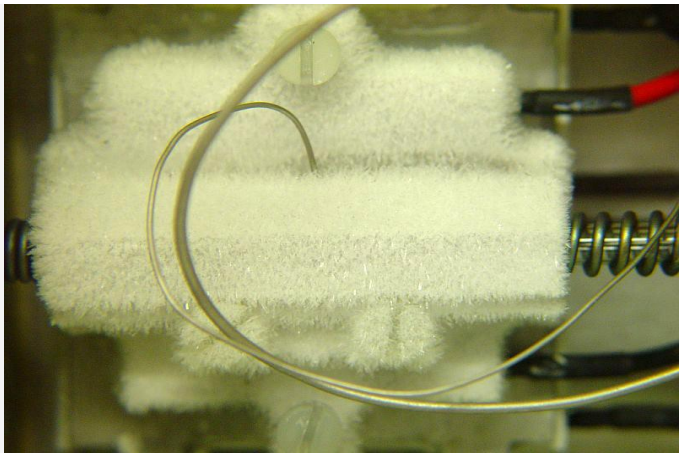
At this stage, all we should do is to strictly follow the manual and do QA/QC well, so as to ensure the VOC data correct. The detailed QA/QC description is in the manuscript (page 5,line31-40).

My another question on the separation efficiency of low carbon number VOC species at 13C was not answered. Although at 13C the

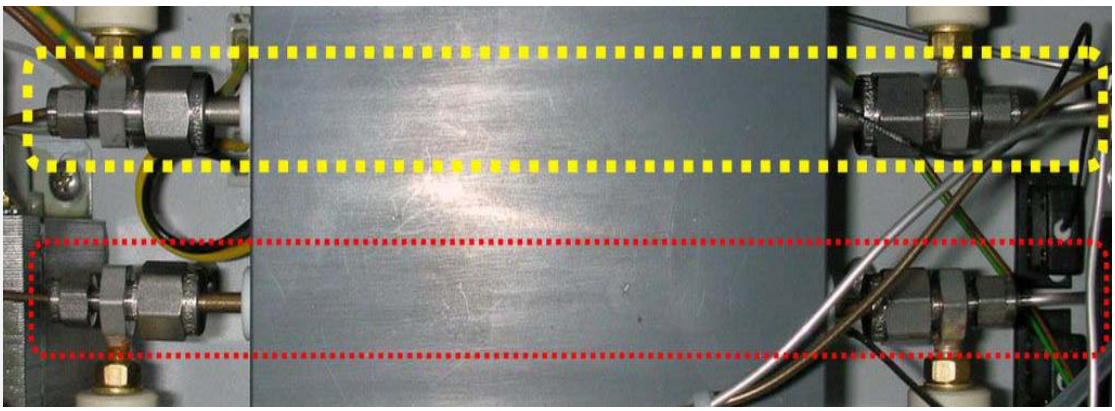
instrument can separate C2 and C3 VOCs, it can only be achieved by series connection of two columns i.e. DB-1 and plot-Q. If only one column i.e. DB-1 was used, the C2 and C3 VOCs could not be separated at such temperature. Our experience is that it is difficult to well separate C2 such as ethene from ethyne for such kind of two-analyzer instrument.

Even if the pre-concentration temperature was negative, we still need two columns in series. Otherwise the separation efficiency was poor.

Reply: Generally speaking, low carbon compounds (C_2 and C_3) have a low penetration volume and the capillary column is so thin that the the sample volume and adsorption column volume need to be small. We can increase the adsorption material, but it seems to be contradicted against that we talked before. We can also lower the enrichment temperature, which will lead to the condensation of enrichment tube, as the figure show below.



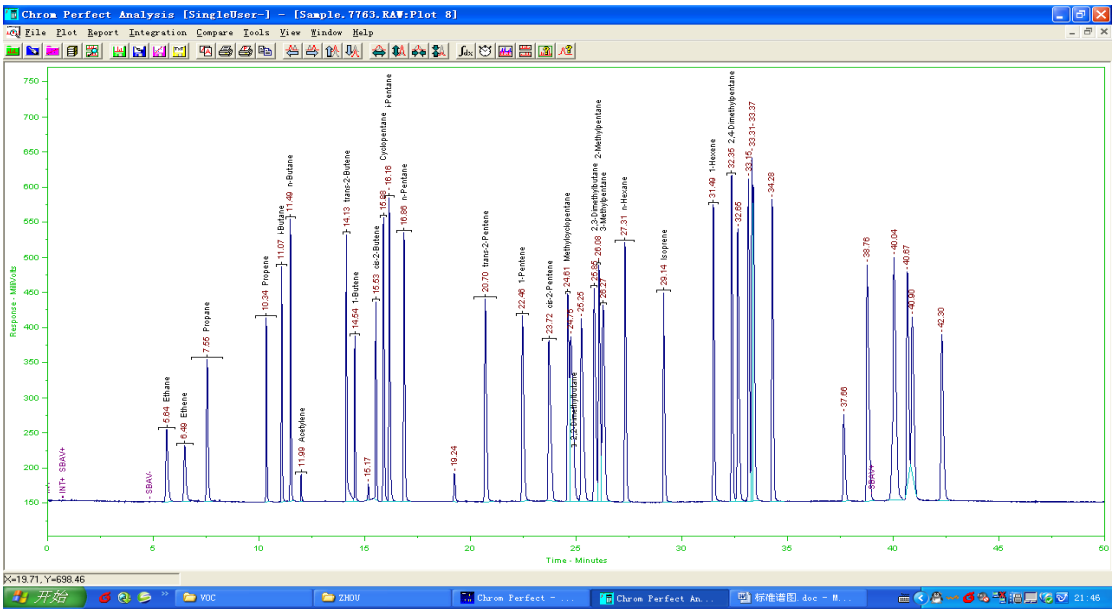
In order to overcome this, two-stage enrichment is needed as the figure show below. The first stage enrichment tube is big and the second enrichment stage tube is small, so as to coordinate the low penetration volume and the requirement of capillary.



As for the separation of C_2 and C_3 VOCs, a Al_2O_3/Na_2SO_4 plot

column and a back flushing column (carbowax) are connected to do it. I don't know whether the description about the instrument in revised manuscript has all been covered. Frankly, we learn this instrument from the manual or the engineers in domestic agent company, much more information is needed from the engineers in AMA company, so as to get the comprehensive understanding of this instrument.

Luckily, C_2 and C_3 VOCs, especially the ethene and ethyne, are well separated in this instrument as you can see in figure below.



4. Statistical analysis was still not conducted

Though the authors replied that they have added the statistical analysis in the manuscript, they actually did not. I doubt they even did not understand my question about statistical analysis.
General Comments:

Reply: We really make some statistical analysis as shown in Fig.1-Fig.11, and corresponding analysis descriptions in paper. Though we do not completely understand the meaning of statistical analysis as reviewer's view, we think sometimes the fact of data itself also can be a simplest way with regard to statistical analysis.

Reply to Report #2

This is a valuable contribution showing the seasonal and diurnal variation of ozone, NOx, VOCs and VOC reactivity at a polluted site downwind of a major Chinese urban and industrial area. The interpretation of some aspects of the paper, especially with regard to VOC and NOx limitations and how they are derived, and the role of

transport in determining ozone concentrations, needs to be further improved prior to final publication. Please follow specific recommendations outlined below.

Reply: We thank referee for good and helpful assessment. We attach great importance on the interpretation of some aspects as the referee stated in general comment and make major revisions. Our replies to the reviewer comments are listed below.

Specific Comments:

Title: The new title is a step in the right direction. The original reviewer's comments suggest that the main value in this work is the reporting of the VOC, NOx and O3 data itself, while the analysis of photochemistry is somewhat more difficult to interpret. Thus, a title more along the lines of "One year of observational data of VOCs, NOx and O3 at a suburban site in Guagnzhou, China" would be more appropriate.

Reply: We agree with the reviewer suggestion. The highlight in this manuscript is that we use one year of VOC, NOx and O_3 data itself to analyze their characteristics in Guangzhou City, which few people do and would be a good material for further O_3 research in this densely populated region with active industries. We admit that the photochemistry is somewhat more difficult to interpret, so we use characteristics instead. Thus the title "Characteristics of one year of observational data of VOCs, NOx and O_3 at a suburban site in Guangzhou, China" would be more appropriate.

Page 3, line 19: "ozone isopleth diagrams" (no s on the end of isopleth). Search on "isopleths" throughout the manuscript and change to "isopleth".

Reply: We have already searched "isopleths" throughout the manuscript and changed to "isopleth".

Page 3, line 22: The Dodge 1977 reference is a conference proceeding and not easy to find. It is cited as the key support for the 8:1 ratio of VOC to NOx below which O3 production is VOC limited. The authors should make two changes here.
1) Use the following citation, which is much more easily accessed than Dodge 1977.

Seinfeld, J. H. (1989), Urban Air Pollution: State of the Science, Science, 243, 745-752.

The ozone isopleth diagram in this paper is roughly consistent with the stated 8:1 VOC to NOx ratio, so long as the VOC is quoted in parts per million (or parts per billion) of carbon rather than as a direct mixing ratio.

2) Include a statement that the actual VOC to NOx ratio at which O3 production is VOC limited will depend on specific conditions within a given area, so that the use of a single ratio (such as 8:1) is only approximate, to be used if detailed photochemical modeling is not available.

Reply: We have cited the reference (Seinfeld,1989) that the referee recommend instead of the reference(Dodge,1977) for the judgement of O_3 production regime by 8:1 ratio of VOC to NOx.

Before we use the single ratio (8:1) to judge the O_3 formation regime, the statement "The actual VOC/NOx ratio at which ozone production…if detailed photochemical modeling is not available" has been added in new manuscript (page9, line31-33).

Besides, we don't use the VOC/NOx ratio (8:1) as a strict definition to judge the O_3 formation regime. On the contrary, we use a relatively speculative description with respect to this. It is fare to say the ozone formation is more likely to be NOx-limited under the condition that VOC/NOx ratio is much higher than value (8); while the ozone formation is more likely to be VOC-limited under the condition that VOC/NOx ratio is much lower than value (8)(page9, line34-37).

Page 3, line 38: Replace "characterizations" with "characteristics."

Reply: "characterizations" has been replaced with "characteristics" in revised manuscript (page3, line38).

Page 3. Line 39-41: The sentence on observational ozone isopleth diagrams may need to be removed. See comments below.

Reply: see the reply below

Page 4, line 1: replace "regime" with "regimes"

Reply: "regime" has been replaced with "regimes" in revised manuscript (page 3, line44).

Page 4, line 41-43: How is NO2 measured in the NOx system? Is it by photolytic conversion to NO, or by using a molybdenum converter?

If molybdenum, the actual NOx may be too large. See further comments below. At this point in the paper, please add specification for the type of NO2 converter on the NOx instrument.

Reply: NO_2 was measured in the NOx system by using a molybdenum converter, specification for the type of NO2 converter on the NOx instrument has been added in revised manuscript (page 5, line4-7).

Page 5, line 45: The quoted NOx concentrations in Table 3 and shown in Figure 4 are very large. If the converter used on the NOx instrument is heated molybdenum, then a statement should be included at this point that the NOx may include some oxidized reactive nitrogen that is converted by the molybdenum, and thus that the stated mixing ratios are upper limits to the actual NOx.

Reply: Like I say before, NO_2 was measured by using a molybdenum converter, it's true that NOx may include some oxidized reactive nitrogen that is converted by the molybdenum, and thus that the stated mixing ratios are upper limits to the actual NOx. As a result, after talking about the characteristics of NOx, the statement has been noted in revised manuscript (page6, line19-20).

Page 6, line 5: the word photochemical is used twice. Eliminate the first one.

Reply: The first word "photochemical" has been eliminated.

Page 6, line 8: Suggest replacing "variation trend" with "derivative with respect to time". On line 11, replace "growth of variation" with "derivative."

Reply: "variation trend" has been replaced with "derivative with respect to time" in revised manuscript (page6, line22-23). "growth of variation" has been replaced with "derivative" in revised manuscript (page6, line26).

Page 6, lines 10-22: There is no discussion of the role of transport in the interpretation of Figure 5. The morning rise in ozone, for example, is as likely to arise from the breakup of the nocturnal boundary layer during morning hours as from chemical production of ozone. The authors should consider if transport of ozone rich or ozone poor air to this location could influence the derivatives. At a minimum, they need to state that the assumption is that ozone is uniform vertically and horizontally if they are to interpret the diurnal variation in the ozone derivative as being due to chemistry alone. Much better, however, would be to include some discussion

of the possible role of transport, especially vertical transport, since breakup of the nocturnal boundary layer leads to growth in surface level ozone even without significant chemical production in many locations.

Also, the authors should have sufficient data to analyze this on a seasonal basis, rather than an average for the entire year, since the preceding figure shows that the diurnal variation of ozone depends on season. They should either add additional figures for different seasons to figure 5, or add a sentence to the text explaining the choice of a single plot.

Reply: Like the referee state that there is no discussion of the role of transport factor when analyzing the derivatives with respect to time of ozone in our original manuscript. As a result, the discussion about the transport has been added. Considering the wind speed varies at around1.4ms^{-1} in different seasons as we show in table 1, we think that horizontal transport effect is very small with respect to the influence of ozone derivatives in revised manuscript (page6, line29-30). Moreover, some possible role of vertical transport has been included in discussion. The sentence "the breakup of the nocturnal boundary layer" has been added to explain the phenomenon that the derivative variation of ozone was positive in the morning in revised manuscript (page6, line36-37).

Besides, the figure of the derivatives with respect to time of ozone in the entire year has been changed to that in different seasons in Fig.5 in revised manuscript. The relevant description of Fig.5 has been modified in revised manuscript (page6, line31-39).

Finally, due to the fact that the ozone may from the breakup of the nocturnal boundary layer during morning hours, as a result, we use $\triangle O_3$ instead of ozone to eliminate this effect when we analyze the relationship among VOCs, NOx and ozone.

Page 6, Equation 3: The description is not clear, especially the quantity u¬_ozone. This is the "molecular mass of species J in the ozone", where the index J refers to a VOC. Also it appears from the description that the MIR factors are taken from a table or otherwise looked up from the Carter (1994) reference. If so, please make this description clearer. Also note that MIR determined in one location may be different in another, so that the application of MIRs modeled in a different city would be only approximate correct in Guangzhou.

Reply: The description of u_j and u_{ozone} has been made clearly in revised manuscript (page7, line12-13). Actually, MIR factors are looked up from the reference (Carter,1994), which has been added in revised manuscript

(page7, line14-15). Considering the MIR determined in one location may be different in another, the sentence " the application of MIR in a different city would be approximately correct in Guangzhou" has been added in revised manuscript (page8, line10-11).

Page 6, lines 28-29: Remove sentence fragment "on ozone formation"

Reply: The sentence fragment "on ozone formation" has been removed.

Page 7, line 15: Replace "most important categories of the atmosphere" with "highest mixing ratio"

Reply: "most important categories of the atmosphere" has been replaced with "highest mixing ratio" in revised manuscript (page7, line33).

Page 7, line 17: "Alkane content is high"

Reply: The sentence has been changed to "Alkane content is high" in revised manuscript (page7, line35).

Page 7, line 40: Dong Guan should be indicated on the map in figure 1 if it is to be cited here.

Reply: Dongguan City has been cited by the circle on the map in figure 1 in revised manuscript.

Page 7, lines 44-45: Add ", respectively." After "OH activity and MIR". The following sentence does not make sense and should be revised. This reads like a policy recommendation for the types of vegetation that should be grown around the site, but is this something that could really be controlled? Better would be a simple statement of the facts, such as what type of vegetation surrounds the site (e.g., forest vs grassland) and if there is any significant variation in the vegetation around the site that would lead to variations in isoprene concentration with wind direction.

Reply: "respectively" has been added after "OH activity and MIR" in revised manuscript (page8, line20).

The following sentence has been changed to "the isoprene emissions need to be considered with respect to the control of ozone in Guangzhou" in revised manuscript (page8, line20-21).

Page 8, section 3.3 and figure 7: This new figure showing an ozone isopleth based on observational data is unconventional and likely out of place in this analysis. The addition of this figure seems to take the paper in a new direction, different from the original submission. It is also not common to present observationally based ozone isopleths. Normally these are generated only by models, since they are intended to represent chemical processes only and not transport. The figures do not lead the reader to any very obvious conclusion either, since they do not show the common transition between VOC and NOx limited regimes, showing instead several local maxima for ozone formation. Inclusion of this figure is not appropriate, especially as an addition to the paper after the first stage of review. Also, while figure 8 shows NOx and VOCs to be correlated in different seasons, it is not clear why this correlation supports the notion that ozone production is NOx limited, unless it is being used to derive the slope of VOC:NOx. In that case, the authors should include fits on this figure, show the slopes explicity, and including in the discussion.

Reply: An ozone isopleth based on observational data in our original manuscript may mislead the readers, as you say that these are generated only by models, since they are intended to represent chemical processes only and not transport. As a matter of fact, we use this figure to analyze the relationship among VOCs, NOx and the increase amount of ozone. As a result, we changed "ozone isopleth diagrams" to "the relationship among VOCs, NOx and ozone" throughout the manuscript.

Considering the importance of this figure to reveal the relationship among VOCs, NOx and ozone, and the result can match very well with that by VOC/NOx ratio, we hope to remain this figure. However, it's quite OK if this figure should be cancelled.

As we say that in our manuscript, the ozone formation regime in which limited is decided by VOCs concentrations in Fig.7 in revised manuscript. NOx and VOCs to be correlated in different seasons in Fig.8 in revised manuscript show how many days in different seasons are in the regime NOx-limited in Fig7. In order to make this clearly, ⅰ, ⅱ and ⅲ have been added in Fig. 8 and Fig. 8in revised manuscript.

Page 9, line 10: See comments above regarding the Dodge reference and the citation of a single number for the VOC:NOx ratio. Text here also seems to be a repeat of the introduction, and is thus redundant.

Reply: Considering the text here seems to be a repeat of the introduction, the content has been cancel in revised manuscript. Some appropriate

caveats have been added in revised manuscript (page9, line30-38) to remind readers when using the VOC:NOx ratio here to judge the ozone formation.

Page 9, line 19 and discussion of VOC:NOx ratio. A dashed line should appear at the stated ratio of 8 in Figure 9 to aid the reader in visualizing how the diurnal variation in this ratio changes with season. Also, the text here should include the caveat that the NOx is an upper limit to actual NOx if a molybdenum converter was used for NOx measurement. If that is it the case, the VOC:NOx ratio would possibly be larger than shown, and the authors should include appropriate caveats to this discussion if that is the case.

Reply: A line at VOC:NOx = 8 has been added in Fig.10 in revised manuscript to aid the reader in visualizing how the diurnal variation in this ratio changes with season.

Besides, for the reason that NO_2 was measured by molybdenum converter, appropriate caveats that the VOC:NOx ratio would possibly be larger than shown have been added in revised manuscript (page9, line36-38).

Page 9, line 43. New paragraph beginning with "In order to"

Reply: Considering the sentence in revised manuscript (page10, line20-21) is related with the sentence"In order to…",new paragraph is begin with "The high-concentration ozone is seriously harmful to human health,…"

Page 10, line 3: State how many days there were with ozone in excess of 93 ppbv. Also, add a line at VOC:NOx = 8 to Figure 10.

Reply: 36 days with ozone in excess of 93 ppbv has been stated in revised manuscript (page10, line23). Also, a line at VOC:NOx = 8 has been added in Fig.11 in revised manuscript.

Page 10, lines 16-24: Include transport in this discussion, see comments above.

Reply: Considering the text here seems to be a repeat of the discussion and needs to be concise in conclusion, most of the content have been cancelled and just reserve a sentence "The concentration trend of ozone begins to show a positive derivative variation at 8:00LT due to the breakup of the nocturnal boundary layer, high OH radicals and a strong" in revised manuscript (page10, line43-44).

Page 10, lines 32-36: Modify as needed after removing figure 7.

Reply: The description of this figure has been modified in revised

manuscript (page11, line9-16) though it has not been removed yet.

Reference

Han,S.Q.,Zhang,M.,Zhao,C.S.,Lu,X.Q.,Ran,L.,Han,M.,Li,P.Y.,Li,X.J.:Differences in ozone photochemical characteristics between the megacity Tianjin and its rural surroundings, Atmospheric Environment,79，209-216,2013.

Li, Y., Lau, K. H., Fung, C. H., 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.

Zhang, Y.H.et al:The traffic emission and its impact on air quality in Guangzhou area [J]. Environmental Sciences ,1999,11,355-360.