Co-Editor's comments

Here I have a question on the use of a phrase in the Abstract (Page 1, line 20). What do you mean by "natural pollutants"? Please give a specification or correction.

5 <u>REPLY:</u>

Corrected to "species emitted from natural sources".

Referee #1's comments

10

1. It is difficult to get the point from the title of this paper. What does the "Characterization of local and regional sources" mean? It is not clear though one finish reading the paper.

REPLY:

The title has been changed to "Differentiating local and regional sources of Chinese urban air pollution based on effect of Spring Festival", which may make the idea of this paper clearer.

2. Page 1 Line 22-23: "More detailed analysis----- reduce urban $PM_{2.5}$ levels in China". Are you sure that the results from this paper can be used to all China? The air pollution problems are different in various regions in China. So the results from Shenzhen cannot represent the normal situation in other regions.

20 <u>REPLY:</u>

To be more rigorous, this sentence is changed to "More detailed analysis of the Spring Festival effect reveals an urgent need to reduce emissions of SO_2 and VOCs on a regional scale rather than on an urban scale to reduce urban $PM_{2.5}$ in Shenzhen, which can also produce some use for reference for other megacities in China."

25 3. Introduction: The previous studies are not enough. More references should be added.

REPLY:

We have rephrased the introduction part, with more details and references added as below (see the red words):

"The rapid economic development and urbanization of China over the recent decades has brought with it the consequence of severe atmospheric pollution, especially in the key economically developed regions, such as the Beijing–Tianjin–Hebei region

- 30 (Sun et al., 2013, 2015; Guo et al., 2014), the Yangtze River Delta (Huang et al., 2013), and the Pearl River Delta (PRD), as well as their densely populated megacities (Hagler et al., 2006; Zhang et al., 2008; He et al., 2011). Great efforts have been made to determine the sources and formation mechanisms of fine particles (PM_{2.5}) in these region. Previous studies indicate that PM_{2.5} forms from primary fine particles and through secondary formation from gaseous precursors (Zhang et al., 2008; Zheng et al., 2009; Huang et al., 2014), and the sources of local production and regional transport are both important (Huang et al., 2014).
- 35 et al., 2014; Huang et al., 2006, 2011; Li et al., 2015).

The causes of air pollution in urban atmosphere in China are particularly complicated, and bring great challenges to management strategies for protecting human health (Parrish and Zhu, 2009). To explore the causes of urban air pollution in China, previous studies have focused on monitoring and comparing the reduction in emissions during special events, such as

- 40 the 2008 Beijing Olympic Games (Huang et al., 2010), the 2010 Guangzhou Asian Games (Xu et al., 2013), the 2014 Asia Pacific Economic Cooperation conference (APEC) (Chen et al., 2015; Sun et al., 2016; Zhang et al., 2016) and the 2015 China victory day parade (Zhao et al., 2016). During such events, the air quality improved remarkable because of short-term limitations on traffic and industrial activity (Huang et al., 2010; Wang et al., 2010; Xu et al., 2013; Zhang et al., 2016). However, these limitations were temporary, non-repeatable measures, so the reported emission reductions cannot be verified. Actually,
- 45 a spontaneous reduction in emissions occurs every year in China during the Spring Festival (SF), which is the single most important holiday in China. During the week-long holiday (in January or February every year), the urban emission patterns depart significantly from the usual patterns: traffic decreases in the mega cities because most people are not working, and most of the industries, stores, and production sites are closed in the city except for the utilities and industries (e.g., power plants) that cannot be shut down (Qin et al., 2004; Feng et al., 2012; Shi et al., 2014). Tan et al. (2009) reported that the concentrations
- 50 of NOx, CO, NMHC, SO₂, and PM₁₀ were lower in the SF periods than in the non-Spring Festival (NSF) periods in the

metropolitan area of Taipei over 1994-2006, while the variation of O_3 was in a reversed trend. Jiang et al. (2015) found that the ambient concentrations of VOCs had a sharp decline by ~60% during the SF in Shijiazhuang.

This study focuses on Shenzhen as an example to evaluate the effect on urban air pollution of the SF. Shenzhen is in the eastern

- 5 Pearl River Delta (PRD) and is the fourth largest economic center in China, with a total residential population of over 10 million and a fleet of civilian vehicles of more than 3.1 million (Shenzhen Yearbook of Statistics, 2015). Known as the country's city of most floating population, Shenzhen owns 7.4 million immigrants in 2014, which accounts 70% of the city's total population (Shenzhen Yearbook of Statistics, 2015). During the SF period, over 50% of the residents are used to travel back to their hometowns (http://sz.gov.cn). It is reported that the traffic flow during the SF in 2016 (Feb 7–13) was only the
- 10 half before the SF period (<u>http://sz.gov.cn</u>). Additionally, industrial activities are almost totally suspended in Shenzhen during the SF period. To characterize the air quality during such extreme reductions of anthropogenic activities during the SF period in Shenzhen, various air pollutants in Shenzhen urban areas were comprehensively and systematically monitored in real time in winter for three consecutive years (2014–2016). The annual SF thus provides an excellent spontaneous control experiment for local emissions, which could provide unique and valuable information regarding the sources of Chinese urban air pollution."
- 15

New references:

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- 25 Hagler, G. S., Bergin, M. H., Salmon, L. G., Yu, J. Z., Wan, E. C. H., Zheng, M., Zeng, L. M., Kiang, C. S., Zhang, Y. H., Lau, A. K. H., and Schauer, J. J.: Source areas and chemical composition of fine particulate matter in the Pearl River Delta region of China, Atmos. Environ., 40, 3802-3815, doi:10.1016/j.atmosenv.2006.02.032, 2006.
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4. Page 3 Line 47 and Line 52: Shenzhen is a megacity in South China. In Spring Festival, over 50% of the residents are used to travel back to their hometown. But in other small or medium city, the situation are total opposite. The representativeness should be considered.

REPLY:

5 Yes, the SF effect is a feature for Shenzhen rather than other cities, which is the reason why we selected Shenzhen as the area for this unique study. We have rephrased the few sentences to make it clearer that the SF study is special for Shenzhen.

5. Page 15 Line 289-290: It is very important that the concentration ratio VOC/NOx plays a role in controlling O_3 concentration. This result is very useful to make sure the control strategy of O_3 . More discussions should be added.

10 <u>**REPLY:</u>**</u>

Following the editor's requirement, this comment will be addressed after the open discussion of the current version of the paper.

6. Page 16 Fig.3V: It is interesting that the super fine particle did not decrease due to the Spring Festival. The emission sources

15 and formation process of these super fine particle are important to the controlling the air pollution problem. More discussion should be emphasized.

REPLY:

Following the editor's requirement, this comment will be addressed after the open discussion of the current version of the paper.

20

7. Page 17 Line 319-320: It seems that the SF period, the regional photochemical production is not weakened. The reason should be discussed more.

REPLY:

Following the editor's requirement, this comment will be addressed after the open discussion of the current version of the paper.

Referee #2's comments No detailed comments.

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Referee #2's comments

General comments:

Large reduction in emissions of anthropogenic pollutants in a mega city during the week-long holiday gives an opportunity to investigate how the urban air quality reacts to reductions in emission. This study conducted a systematical examination of the

- 5 "Spring Festival effect" over three consecutive winters in Shenzhen with a population of greater than ten million, and the difference in the concentrations of various air pollutants between the Spring Festival (SF) and non-Spring Festival (NSF) periods was exploited to indicate that the origins of pollutants are primarily local or regional.
- Although "holiday effect" has been discussed in a large number of studies in recent decades, the rich and comprehensive dataset provided in this study is informative and helpful for understanding of sources of a large array of species with considerable differences in properties. The authors clearly show their own contribution in the study of Spring Festival effect. In the present form, the authors focus on exploiting the percent change in the concentrations of various air pollutants to differentiate contribution from local and regional sources. The value of this paper could be further enhanced if the authors can make more in-depth discussion on the species (e.g., PM_{0.8–2.5} and O₃), which had a small difference between the SF and NSF
- 15 periods. It is interesting to know that these species revealed only a small difference when traffic flow dropped by \sim 50% and the industrial plants were almost entirely shut down. It is well known that PM has numerous and complex constituents contributed from diversified sources (primary and secondary, anthropogenic and natural), and O₃ is a secondary photochemical product with nonlinear relation with its precursors NOx and VOCs (anthropogenic and natural). I encourage the author to strengthen the link between their observation results and the possible causes (composition, property, sources, transport,
- 20 physical and chemical processing, meteorology, etc.). In general, the manuscript was well written and organized. The subject of the paper is well within the scope of ACP. The paper is suitable for publication provided the general comments and following points are addressed.

REPLY:

25 We have looked for new useful evidence to explain the small decrease of SO_2 and $PM_{0.8-2.5}$ in Group SD, and have given new information as below in section 3.1:

"On the other hand, a piece of evidence for the regional origin of SO_2 is from the newly established 356 m meteorological and environmental monitoring iron tower in Shenzhen. The ambient SO_2 concentrations were similar at the highest platform

- 30 (ave.=7.4 ppbv@325 m) and the lowest platform (ave.=7.2 ppbv@60 m) during January–February, 2017, indicating that SO₂ was already well mixed in the atmosphere and the local contributions should be minor. In contrast, the concentrations of NOx, which belongs to Group LD, had a 56% higher concentration at the lowest platform than at the highest platform (Zhuang, 2017). The small decrease of SO₂ is thus a reasonable result of the stable emissions during the SF periods and the primarily regional origin."
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"In terms of chemical composition of $PM_{0.8-2.5}$, implications can be found in our previous size distribution measurement of aerosol chemical composition, using a ten-stage micro orifice uniform deposit impactor (MOUDI), during the fall to winter in Shenzhen (Lan et al., 2011). The results clearly indicate that smaller fine particles (e.g., 0.18–0.56 µm) contains relatively more BC (BC/SO₄^{2–}=0.83), while larger fine particles (e.g., 1.0–1.8 µm) contained a higher proportion of SO₄^{2–} (BC/SO₄^{2–}=0.17). The SO₄^{2–} in PM_{2.5} in Shenzhen has been well proved to be mostly a regional pollutant, with similar concentrations at various sites including both urban and rural sites (Huang et al., 2014). Therefore, the very small decrease of PM_{0.8–2.5} during

SF should be closely related to its enrichment of secondary regional species like SO₄²⁻."

As to the unique variation of O₃, it is clearly related to the nonlinear relation with its precursors NOx and VOCs, as stated by

45 this reviewer. The other reviewer also pointed out that, based on limited VOCs measured, we cannot achieve a conclusion that whether the O_3 formation is VOCs-sensitive or NOx sensitive. Therefore, in the revised manuscript, we only pointed out the idea as below in section 3.2:

"... As a result, although the reduction in emissions of urban anthropogenic sources leads to a large decline of NOx and VOCs, this reduction does not mitigate the average ambient O_3 concentration, which implies that the concentration ratio VOCs/NOx play an important role in controlling O₃ concentration."

5 Specific comments:

1. Page 7 Lines 137-139: 2016. Are "all fragments" of m/z 44 and m/z 57 measured by AMS are the tracers of oxygenated organic aerosol and primary hydrocarbon organic aerosol, respectively? Or "most of fragments" are?

REPLY:

We have corrected in the revised manuscript as below:

"Most of fragments of m/z 44 and m/z 57 are the tracer of oxygenated organic aerosol and the tracer of primary hydrocarbon 10 organic aerosol (Zhang et al., 2005), respectively, which are measured by AMS."

2. Page 11 Lines 212-213: This sentence is confusing to me. In addition to emissions and sinks, the concentration of air pollutants is also dominated by meteorological conditions, especially PBL and wind field. In Table 1, meteorological conditions

15 in NSFT and NSFM are not much different (similar wind speed and no precipitation), and it may be the major reason for the small difference in the concentrations of most air pollutants between the two periods. It is not suitable to conclude that meteorology has only a small impact on their concentrations. Please provide a more appropriate interpretation.

REPLY:

To be more rigorous, this sentence is changed to:

"The decreasing ratios of various species during SF when compared with the NSFT and NSFM periods are similar, which 20 suggests that the meteorological variations might not be the dominant reason for the species decreasing during SF."

3. Page 15 Lines 282-283: "emissions are greater on holidays than on non-holidays" and "In addition, emissions were higher during the 2008 Beijing Olympic Games" Do the authors mean "emissions of O₃"? If so, I suggest using the word "concentrations" instead of "emissions".

REPLY:

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We have corrected in the revised manuscript.

4. Page 15 Lines 287 and 288: VOC/NOx ratio gives an important idea that it tends towards a NOx-sensitive or VOC-sensitive 30 environment. However, VOCs are a very 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 total reactivities of VOC species rather than to the total amount of VOCs. Furthermore, the VOCs reported in the study (Table S1, measured by PTR-MS) include only a total of 13 masses. TVOC/NOx ratio in the study should be carefully used to explain its effect on the ozone level due to above-mentioned concerns.

35 **REPLY:**

We agree that based on limited VOCs measurements, it is not reasonable to get the conclusions that whether the O_3 formation is NOx-sensitive or VOCs-sensitive. Therefore, in the revised manuscript, we only state as below:

"As a result, although the reduction in emissions of urban anthropogenic sources leads to a significant decline of NOx and VOCs, this reduction does not mitigate the average ambient O_3 concentration, which implies that the concentration ratio VOC/NOx plays an important role in controlling O₃ concentration."

5. Page 15 Lines 288 and 289: Do the authors mean the chemical regime at noon during the SF period was NOx-sensitive? If so, the authors should provide a clearer explanation to support the statement.

REPLY:

45 Following the reply to the above question, we are not making the conclusion about whether the O₃ formation is NOx-sensitive or VOCs-sensitive.

Referee #3's comments

General comments:

- The paper presents an assessment of the effect of the Chinese Spring Festival on urban air quality in a southern China city.
 Various trace gases and aerosols were measured over three consecutive winters (2014-2016), including both the Spring Festival (SF) and non-Spring Festival (non-SF) periods, at an urban site of Shenzhen city. By comparing the concentrations of these pollutants in different periods, the authors show that the decreases for some pollutants are significant (by 50%-80%) in the SF with respect to the non-SF while the decreases of others pollutants are smaller. They suggest that such differences in the reduction extent of pollutant concentrations be used to judge their sources, i.e., predominantly from local emissions or from
- 10 regional transport. This study, together with a valuable dataset, should be a welcome addition to the literatures on the holiday effects on air quality. The manuscript can be accepted for publication after the following issues have been well addressed.

As the main purpose of the study is to distinguish the sources of urban pollution between the local emissions and regional transport, the local and regional pollution sources should have been clearly defined. It would be great if the authors could

15 provide a map showing the geographical distributions of emissions rates of major air pollutants in Shenzhen city and its surrounding areas during wintertime. It is also suggested that if possible, the geographical extent of pollution reduction during the SF in relative to the non-SF period be identified, perhaps by using population density or satellite product.

The study identifies the primary source of each pollutant, i.e. the local or regional origin, using the reduction extent of a

20 pollutant (in relative percent) from the non-SF to SF period. This methodology is fine for primary pollutants (such as NOx and BC), and it may also work for some secondary pollutants (perhaps SO_4^{2-}); but it might not entirely applicable to O_3 since ozone production changes non-linearly with an increase (or a decrease) of NOx. A stronger evidence is needed before a conclusion on the origin of ozone is given in the manuscript.

<u>REPLY:</u>

25 As to the definition of the local and regional pollution sources, please see our reply to your specific comment #14. In the revised manuscript, we have tried to define them as below:

"Apparently, the dominant sources for most of these pollutants are primarily local emissions in the urban scale, such as combustion sources for BC, m/z 57, and NOx..."; "The species in this group are either typical regional air pollutants mostly from beyond the urban scale, such as CO, which has a long lifetime..."

30

As to a map showing the geographical distributions of emissions rates of major air pollutants and the geographical extent of pollution reduction during the SF, they need a lot of supporting data sources, which are not easily available, and such work could be much beyond the scope of this paper. Alternatively, we have cited a paper of emission inventory in PRD (Zheng et al., 2009b) in section 2.1 to describe the relative location of the sampling site in terms of pollutant emissions in PRD, as below:

- 35 "A highly resolved temporal and spatial emission inventory for PRD indicates that the sampling area is characterized by lower SO₂ emissions but higher NOx and VOCs emissions in comparison with other areas in PRD (Zheng et al., 2009b)." As to the conclusion on the origin of ozone, we agree on your specific comment #12 that based on limited VOCs measurements, it is not reasonable to get the conclusions that whether the O₃ formation is NOx-sensitive or VOCs-sensitive. Therefore, in the revised manuscript, we only state as below:
- 40 "As a result, although the reduction in emissions of urban anthropogenic sources leads to a significant decline of NOx and VOCs, this reduction does not mitigate the average ambient O₃ concentration, which implies that the concentration ratio VOC/NOx plays an important role in controlling O₃ concentration."

Specific comments:

45 1. Line 12 and Line 49-53: During the SF, the power plants are generally not shutdown in the megacities of China. Are there any power plants in Shenzhen? Where the industrial area of Shenzhen located in reference to the measurement site? Are the wind roses of various pollutants in the SF different from those in the non-SF period?

REPLY:

There are few power plants in Shenzhen. We now cite a paper (Zheng et al., 2009b) in section 2.1 to describe the relative location of the sampling site in terms of pollutant emissions in PRD, as below:

"A highly resolved temporal and spatial emission inventory for PRD indicates that the sampling area is characterized by lower SO₂ emissions but higher NOx and VOCs emissions in comparison with other areas in PRD (Zheng et al., 2009b)." Since the data points on each wind direction are limited, wind rose analysis may not be a solid evidence. However, the analysis

of relationship between pollutant concentrations and wind speeds during SF and NSF in section 3.3 can already well reveal that Group LD was highly influenced by wind speed.

5

2. Line 19-21: Here it might not be suitable to say "decreasing of regional pollutants" since there is an increase of O_3 by 6%. **REPLY:**

We rephrased the sentences by "The concentration variation of species mostly from regional or natural sources, however, is found to be much less, such as for bulk PM₂₅." 10

3. Line 47: It might not be fully suitable to say so. The reported emission reductions could be verified by comparisons of different approaches, e.g., ground measurements, satellite observations, and model simulations with different emission inventories.

15 **REPLY:**

"...so the reported emission reductions cannot be verified" changed to "...so the air quality monitoring campaigns cannot be repeated."

4. Line 77-79: Figure S1 provides only geographical position of measurement site. How far away from the main traffic roads the site is? How about regional distributions of pollutants' emissions?

REPLY:

20

We have provided the relevant information in the revised text as below:

"PKUSZ is located in the western urban area of Shenzhen, and there are no significant anthropogenic pollution sources nearby except a local road ~100 m far from the sampling site. A highly resolved temporal and spatial emission inventory for PRD indicates that the sampling area is characterized by lower SO₂ emissions but higher NOx and VOCs emissions in comparison

25 with other areas in PRD (Zheng et al., 2009b)."

5. Line 135: Figures S3-S5 provide more detailed information and can be moved into the formal part of the manuscript. **REPLY:**

30 After careful consideration, we still believe that Figures S3-S5 are too large to be moved into the main text. Therefore, supporting information could be a better choice when considering that ACP is freely available on the internet.

6. L174: CO is NOT a typical SECONDARY regional air pollutant as most of CO in the urban and polluted areas are mostly probably to be primarily emitted.

35 **REPLY:**

It is a typo. "secondary" is now deleted.

7. L183-184, L252-253, L261-267, L309-312 and L337-340: According to the study, isoprene and DMS measured in Shenzhen have anthropogenic sources. But they are repeatly described as "natural" gases; on the other hand, sometimes they are classified

40 as "pollutants". These vague expressions should be corrected.

REPLY:

We have checked all the manuscript and rephrased the words to say that they are "mainly emitted by natural sources"

8. Line 191-192: It should noted that there is an increase of O_3 to a small extent.

45 **REPLY:**

We have rephrased the sentences as below:

"The group of pollutants with smallest decrease in concentration (hereinafter called "SD") includes SO₂, $PM_{0.8-2.5}$, and O_3 (8h) in the case of comparison with NSFM. The magnitude of the average percent change is less than 20% relative to the two NSF periods. It is interesting to note that there was even concentration increase in other O₃-related cases."

9. L195-202: Are there any power plants in Shenzhen and nearby areas? A plot of the regional emission distributions of SO_2 would be helpful for the reader to follow the discussion here. It would also be great if the wind rose or trajectory analysis result could be given.

REPLY:

5 There are few power plants in Shenzhen. We now cite a paper (Zheng et al., 2009b) in section 2.1 to describe the relative location of the sampling site in terms of pollutant emissions in PRD, as below:

"A highly resolved temporal and spatial emission inventory for PRD indicates that the sampling area is characterized by lower SO₂ emissions but higher NOx and VOCs emissions in comparison with other areas in PRD (Zheng et al., 2009b)."

- Since the data points on each wind direction are limited, wind rose analysis may not be a solid evidence. However, the analysis
- 10 of relationship between pollutant concentrations and wind speeds during SF and NSF in section 3.3 can already well reveal that Group LD was highly influenced by wind speed.

10. L212-215 and L300-301: The sentence "meteorology has only a small impact on their concentrations" is misleading. Note that only for the period average values are the result consistent.

15 <u>REPLY:</u>

To be more rigorous, this sentence is changed to:

"The decreasing ratios of various species during SF when compared with the NSFT and NSFM periods are similar, which suggests that the meteorological variations might not be the dominant reason for the species decreasing during SF."

20 11. L231, Figure 2: Ticks for 10 nm and 1000 nm could be given.

REPLY:

Our instrument (SMPS) determined the particle number size distribution in the size range of 15-615 nm.

12. L288-289: In-depth analysis should be performed if you insist that the lack of NOx at noon during the SF period hinders

25 the generation of O₃. Figure 3B shows that the levels of NOx in the SF and NSFM at noon are comparable. It seems that the difference in VOCs might play an important role.

REPLY:

We agree that based on limited VOCs measurements, it is not reasonable to get the conclusions that whether the O_3 formation is NOx-sensitive or VOCs-sensitive. Therefore, in the revised manuscript, we only state as below:

30 "As a result, although the reduction in emissions of urban anthropogenic sources leads to a significant decline of NOx and VOCs, this reduction does not mitigate the average ambient O_3 concentration, which implies that the concentration ratio VOC/NOx plays an important role in controlling O_3 concentration."

13. L300: What are the wind fields look like? It might be more appropriate to say the wind field patterns are the same.

35 <u>REPLY:</u>

The wind rose plots can be seen in Figure S2. We take this suggestion to use "wind field patterns"

14. L368-370: The concept of regional air pollutants is unclear. How are they defined? Even for NOx, it can also result in regional pollution.

40 <u>**REPLY:</u>**</u>

In this study, we studied urban air quality and urban emissions, and thus regional pollutants refer to species from outside the urban areas. Yes, NOx can also be from regional transport. However, based on our results, NOx is found to be mostly from local urban emissions. In the revised text, we have added the words like "air pollutants mostly from regional or natural sources" to be more rigorous.

Co-editor's comments:

Please consider the suggestion from the referee carefully and make necessary revisions and/or specific response. Alternatively, you may also consider using satellite data, e.g., OMI NO2, OMI SO2 and nighttime lights, to show the regional distributions of pollution in the investigated city and its surrounding areas.

5 <u>REPLY:</u>

Please see the reply to the referee. We have used the map of nightlights.

Referee#2's comments

- 10 The revised manuscript does improve to some degree with ambiguous expressions corrected. Whiles the main purpose of this study is to distinguish the sources of urban pollution between the local emissions and regional transport, measurements were made only at an urban site. Therefore, I think the geographical distributions of emissions can be shown as compensation. There are some global and regional emission inventories with high resolution (0.5 degree by 0.5 degree) available, for example, the GEIA-ACCENT emission data (http://accent.aero.jussieu.fr/index.php), the Regional Emission inventory in ASia (REAS)
- 15 Data (https://www.nies.go.jp/REAS/), and the MEIC dataset from the Chinese research group. It might be true that none of these emission inventories provide information on the emission reduction during the festival. But a seasonal or annual average distribution of "normal" emissions will also be helpful for understanding the observational results. REPLY:

We have created a new Figure S1 to clearly indicate the regional pollution distribution of PRD and the location of the sampling

20 site, as below. In Line 79, we have also added this sentence "Figure S1 shows that the sampling area had a middle-level aerosol pollution during the winter in comparison with other areas in PRD and further areas."

Figure S1 The locations of Shenzhen and its sampling site. The upper map is part of the global maps of Earth at night from NASA (https://www.nasa.gov/feature/goddard/2017/new-night-lights-maps-open-up-possible-real-time-applications), which

25 indicates that PRD is one of the most developed regions in China. The lower map is the surface extinction coefficient (SEC) of dry aerosol in southern China in winter (using the monthly average in February, 2015 as the example) from the Institute for the Kong University of Science and Technology the Environment, Hong (http://envf.ust.hk/itfsi/index.py?where=Home/SAMap&id=premap), which presents the general spatial distribution of aerosol pollution, as well as the locations of Shenzhen and its sampling site.





Differentiating local and regional sources of Chinese urban air pollution based on effect of Spring Festival

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Abstract: The emission of pollutants is extremely reduced during the annual Chinese Spring Festival (SF) in Shenzhen, China. During the SF, traffic flow drops by ~50% and the industrial plants are almost entirely shut down in Shenzhen. To characterize the variation in ambient air pollutants due to the "Spring Festival effect", various gaseous and particulate pollutants were
measured in real time in urban Shenzhen over three consecutive winters (2014–2016). The results indicate that the concentrations of NOx, volatile organic compounds (VOCs), black carbon (BC), primary organic aerosols, chloride, and nitrate in submicron aerosols decrease by 50%–80% during the SF period relative to the non-Spring Festival periods, regardless of meteorological conditions, which suggests that these pollutants are mostly emitted or secondarily formed from urban local emissions. The concentration variation of species mostly from regional or natural sources, however, is found to be much less,

such as for bulk $PM_{2.5}$. More detailed analysis of the Spring Festival effect reveals an urgent need to reduce emissions of SO_2 and VOCs on a regional scale rather than on an urban scale to reduce urban $PM_{2.5}$ in Shenzhen, which can also produce some use for reference for other megacities in China.

1 Introduction

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The rapid economic development and urbanization of China over the recent decades has brought with it the consequence of

- 20 severe atmospheric pollution, especially in the key economically developed regions, such as the Beijing–Tianjin–Hebei region (Sun et al., 2013, 2015; Guo et al., 2014), the Yangtze River Delta (Huang et al., 2013), and the Pearl River Delta (PRD), as well as their densely populated megacities (Hagler et al., 2006; Zhang et al., 2008; He et al., 2011). Great efforts have been made to determine the sources and formation mechanisms of fine particles (PM_{2.5}) in these region. Previous studies indicate that PM_{2.5} forms from primary fine particles and through secondary formation from gaseous precursors (Zhang et al., 2008;
- 25 Zheng et al., 2009a; Huang et al., 2014), and the sources of local production and regional transport are both important (Huang et al., 2014; Huang et al., 2006, 2011; Li et al., 2015).

The causes of air pollution in urban atmosphere in China are particularly complicated, and bring great challenges to management strategies for protecting human health (Parrish and Zhu, 2009). To explore the causes of urban air pollution in China, previous studies have focused on monitoring and comparing the reduction in emissions during special events, such as the 2008 Beijing Olympic Games (Huang et al., 2010), the 2010 Guangzhou Asian Games (Xu et al., 2013), the 2014 Asia

Pacific Economic Cooperation conference (APEC) (Chen et al., 2015; Sun et al., 2016; Zhang et al., 2016) and the 2015 China victory day parade (Zhao et al., 2016). During such events, the air quality improved remarkable because of short-term limitations on traffic and industrial activity (Huang et al., 2010; Wang et al., 2010; Xu et al., 2013; Sun et al., 2016; Zhao et al., 2016). However, these limitations were temporary, non-repeatable measures, so the air quality monitoring campaigns

- 5 cannot be repeated. Actually, a spontaneous reduction in emissions occurs every year in China during the Spring Festival (SF), which is the single most important holiday in China. During the week-long holiday (in January or February every year), the urban emission patterns depart significantly from the usual patterns: traffic decreases in the mega cities because most people are not working, and most of the industries, stores, and production sites are closed in the city except for the infrastructure (e.g., power plants) that cannot be shut down (Qin et al., 2004; Feng et al., 2012; Shi et al., 2014). Tan et al. (2009) reported that the
- 10 concentrations of NOx, CO, NMHC, SO₂, and PM₁₀ were lower in the SF periods than in the non-Spring Festival (NSF) periods in the metropolitan area of Taipei over 1994-2006, while the variation of O_3 was in a reversed trend. Jiang et al. (2015) found that the ambient concentrations of VOCs had a sharp decline by ~60% during the SF in Shijiazhuang.

This study focuses on Shenzhen as a special example to evaluate the effect on urban air pollution of the SF. Shenzhen is in the eastern Pearl River Delta (PRD) and is the fourth largest economic center in China, with a total residential population of

- 15 over 10 million and a fleet of civilian vehicles of more than 3.1 million (Shenzhen Yearbook of Statistics, 2015). Known as the country's city of most floating population, Shenzhen owns 7.4 million immigrants in 2014, which accounts 70% of the city's total population (Shenzhen Yearbook of Statistics, 2015). During the SF period, over 50% of the residents in Shenzhen are used to travel back to their hometowns (<u>http://sz.gov.cn</u>). It is reported that the traffic flow in Shenzhen during the SF of 2016 (Feb 7–13) was only the half before the SF period (<u>http://sz.gov.cn</u>). Additionally, industrial activities are almost totally
- 20 suspended in Shenzhen during the SF period. To characterize the air quality during such extreme reductions of anthropogenic activities during the SF period in Shenzhen, various air pollutants in Shenzhen urban areas were comprehensively and systematically monitored in real time in winter for three consecutive years (2014–2016). The annual SF in Shenzhen thus provides an excellent spontaneous control experiment for local emissions, which could provide unique and valuable information regarding the sources of urban air pollution.

25 2 Experimental methods

2.1 Monitoring sites and meteorological conditions

The monitoring site (22°36'N, 113°54'E) was on the roof (20 m above ground level) of an academic building on the campus of Peking University Shenzhen Graduate School (PKUSZ) (Figure S1). PKUSZ is located in the western urban area of Shenzhen, and there are no significant anthropogenic pollution sources nearby except a local road ~100 m far from the sampling

30 site. Figure S1 shows that the sampling area had a middle-level aerosol pollution during the winter in comparison with other areas in PRD and further areas. A highly resolved temporal and spatial emission inventory for PRD indicates that the sampling area is characterized by lower SO₂ emissions but higher NOx and VOCs emissions in comparison with other areas in PRD (Zheng et al., 2009b). The sampling schedule ran roughly from late January to early March over 2014–2016, which includes the official SF holiday period and the prior and following periods. Our definition of the SF period follows that of the statutory public holiday calendar in China, and it is continuous seven days in each year. While the seven days immediately before or

- 5 after the holidays are actually the transition periods between the holidays and normal days (called the Tran. periods hereafter), when people begin to move from the city (or their hometowns) to their hometowns (or the city), the typical non-spring festival (NSF) periods are better defined as the 7–14 days close to the SF period (called the NSFT period hereafter, where T indicates time similar). The specific dates and the average meteorological parameters are listed in Table 1, and Figure S2 shows wind rose plots. The data in Table 1 show that the meteorology differs among the SF, NSFT, and Tran. periods. To control for the
- 10 influence of meteorology on the evaluation of emissions, we selected another 7-day period each year when the meteorology is similar to that of the SF period (called the NSFM period hereafter, where M indicates meteorology similar); the detailed parameters are listed in Table 1 and Figure S2. The meteorological data for the SF period are fairly similar to those of the NSFM period, suggesting similar meteorological conditions.

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Table 1. Summary of meteorological conditions at sampling site during the SF, NSFT, NSFM and Tran. periods of 2014-
2016.

		SF	Tran.	NSFT	NSFM
Data period	2014	Jan 31–Feb 6	Feb 7–Feb 13	Feb 14–Feb 20	Feb 20–Feb 26
	2015	Feb 18–Feb 24	Feb 11–Feb17	Feb 4–Feb10	Jan 24–Jan 30
	2016	Feb 7–Feb 13	Feb 14–Feb 20	Feb 21–Feb 27	Feb 27–Mar 4
Meteorological parameters	Temperature (°C)	19.0±4.7	14.1±5.3	14.1±4.0	18.1±3.8
	RH (%)	68.1 ± 17.8	69.3±18.4	64.9±16.7	67.4±14.7
	Wind speed (m s ⁻¹)	0.88 ± 0.57	0.81±0.49	0.83±0.48	0.86±0.55
	Dominant wind direction	NW	NW and NE	NW and NE	NW
	Precipitation (mm)	0	0	0	0
	UVA (W m ⁻²)	5.4±8.5	2.5±4.3	3.8±6.7	5.0±8.0
	UVB (W m ⁻²)	0.24±0.40	0.11±0.25	0.16±0.32	0.22±0.38

2.2 Instrumentation

For the ambient sampling in this study, the measuring instruments were placed in a room on the top floor of a four-story teaching building at PKUSZ. A high-sensitivity proton transfer reaction mass spectrometer (PTR–MS) (Ionicon Analytik GmbH, Austria) was used to measure the selected volatile organic compounds (VOCs). The PTR–MS measured a total of 25 masses in the selected ion mode at a time resolution of 30 s. Background checks were done for 30 of every 300 scan cycles with an activated charcoal trap at 360 °C, which can remove VOCs from the ambient air without changing water content. The VOCs reported here (Table S1) may be broadly classified into three categories: oxygenated VOCs [OVOCs: methanol, acetone,

10 methyl ethyl ketone (MEK), acetaldehyde, and acetic acid], aromatics (benzene, toluene, styrene, C8 and C9 aromatics), and three types of tracers [isoprene, acetonitrile, and dimethyl sulfide (DMS)]. The PTR–MS was calibrated every 5 to 7 days by using a TO15 mixture standard (Air Environmental Inc., US) and permeation tubes (Valco Instruments Co. Inc., US) (de Gouw

and Warneke, 2007).

An aerodyne high-resolution time-of-flight aerosol mass spectrometer (HR–ToF–AMS) (Aerodyne Research, US) was deployed to measure non-refractory PM_1 (NR-PM₁) (Canagaratna et al., 2007) in the period 2014–2015 with a time resolution of 4 min. An aerosol chemical speciation monitor (ACSM) (Aerodyne Research, US) was used in 2016 with a dynamic

- 5 resolution of 10 min. The detailed description of the ACSM is available in the recent review (Ng et al., 2011). The HR-ToF-AMS and ACSM were calibrated every month following the standard protocols (Ng et al., 2011; Jayne et al., 2000). An aethalometer (AE–31) (Magee, US) was used for simultaneous detection of refractory black carbon (BC) with a time resolution of 5 min. In addition, a Scan Mobility Particle Sizer (TSI Inc., US) system was used to determine the particle number size distribution in the size range 15–615 nm (Stokes diameter) with a time resolution of 5 min. The stokes diameters of 15–
- 10 615 nm is converted to aerodynamic diameters of 22–800 nm, and then $PM_{0.8}$ mass concentration can be calculated with the particle density assumed according to the AMS measurement results of species.

To measure the PM_{2.5} mass concentration, we used a Thermo Scientific TEOM 1405–D monitor. The trace-gas instruments included a 43i sulfur dioxide (SO₂) analyzer, a 42i nitric oxide (NO)–nitrogen dioxide (NO₂)–nitrogen oxide (NOx) analyzer, a 49i ozone (O₃) analyzer, and a 48i carbon monoxide (CO) analyzer (Thermo Scientific, US). A meteorological station, also

15 located on the roof of the same building, measured the main meteorological parameters, such as temperature, relative humidity, and wind speed (see Table 1).

3 Results and Discussion

3.1 The NSF-SF differences for major air pollutants

The results of observations from 2014 to 2016 appear in Figures S3–S5. Figure 1 shows the averaged percent changes in the
concentrations of major air pollutants of the SF periods relative to the two NSF periods and Tran. period over 2014–2016.
Most of fragments of m/z 44 and m/z 57 are the tracer of oxygenated organic aerosol and the tracer of primary hydrocarbon organic aerosol (Zhang et al., 2005), respectively, which are measured by AMS. The notation O₃–8h refers to the average maximum O₃ concentration over a continuous diurnal 8 h and PM_{0.8–2.5} refers to the difference between the concentrations of PM_{2.5} and PM_{0.8}.

- We can divide these air pollutants into three classes based on their percent changes: The group with the largest drop (hereinafter called "LD") in concentration includes the aromatics (-50% to -88% for the various species, see Figure S6), OVOCs (-40% to -85% for the various species, see Figure S6), NOx, chloride (Chl), nitrate (NO₃⁻), BC, and m/z 57. The concentrations of these pollutants all decrease by over 50% during the SF period compared with both the NSF periods. Apparently, the dominant sources for most of these pollutants are primarily local emissions in the urban scale, such as combustion sources for BC, m/z 57, and NOx (Zhang et al., 2005; Kuhlbusch et al., 1998; Lan et al., 2011), and vehicle,
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industrial and solvent use for aromatics (Liu et al., 2008). As detailed in the following section, the diurnal patterns and

relationships with respect to wind speed further confirm the sources of these pollutants. The dramatic decrease in the ambient concentrations of these species is consistent with reduction in local anthropogenic activities in Shenzhen during the SF period. The SF causes a 50% decrease in urban traffic and temporarily closing of almost all local industrial plants. The nitrate and chloride measured by AMS or ACSM are actually ammonium nitrate (NH₄NO₃) and ammonium chloride (NH₄Cl), which are

- 5 typical secondary air pollutants. These are thought to form via reversible phase equilibria with gaseous ammonia (NH₃), nitric acid (HNO₃), and hydrochloric acid (HCl) (He et al., 2011; Huang et al., 2011; Zhang et al., 2007). Typically, the formation of NH₄NO₃ from NOx and the reaction between HCl and NH₃ occur quickly in the atmosphere (Stelson and Seinfeld, 1982; Baek et al., 2004), suggesting that the concentrations of NO₃⁻ and Chl in winter in Shenzhen depend largely on the emission of precursors such as HCl and NOx. Therefore, the significant decline in the ambient concentrations of NO₃⁻ and Chl during the
- 10 SF period and indicates that their precursors also have local origins, similar to the case for primary pollutants (this is also supported by the discussion in the following sections). The huge decline in the ambient concentration of OVOCs during the SF period shows that the source of these pollutants is (i) mainly from local emissions, including vehicle and industrial emissions (Schauer et al., 1999; Singh et al., 2001) and (ii) from secondary reactions involving local primary VOCs (Liu et al., 2015). Thus, in the LD group, the significant reduction in local sources of pollutants strongly impacts the concentration of air
- 15 pollutants.

The pollutants in the next group undergo a medium drop in concentration during the SF period (hereinafter called "MD"). These are $PM_{2.5}$, $NR-PM_1$, $PM_{0.8}$, organic aerosol, m/z 44, sulfate (SO_4^{2-}), ammonium (NH_4^+), isoprene, acetonitrile, DMS, and carbon monoxide (CO), and their percent change varies from -20% to -55% when comparing the SF periods to the NSFT and NSFM periods. The species in this group are either typical regional air pollutants mostly from beyond the urban scale,

- **20** such as CO, which has a long lifetime and is a tracer for combustion sources, acetonitrile from rural biomass burning (de Gouw et al., 2003; Le Breton et al., 2013), m/z 44 representing secondary organic aerosols, SO_4^{2-} from SO_2 oxidation (He et al., 2011; Huang et al., 2011), or typical tracers mainly emitted by natural sources, such as isoprene from vegetation (Guenther et al., 1995) and DMS from marine source (Dacey and Wakeham, 1986). In winter, the northeastern monsoon prevails in the PRD and transports significant amounts of various air pollutants from the northern inland, increasing air pollution of the PRD to the
- 25 highest levels through the year (Huang et al., 2014). In particular, the small drop in CO concentration during the SF period puts it in this group and indicates that the contribution to regional air pollution does not decrease significantly during the SF period. Note that, the significant declines of the concentrations of isoprene and DMS imply that they have anthropogenic sources, which will be supported in the following sections. The other air pollutants in this group are the reflection of the overall effect of the reduction of relevant air pollutants: OA is the whole of the two types of organic aerosol represented by m/z 44
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and m/z 57, NH_4^+ is represented by SO_4^{2-} , NO_3^- and Chl, and $NR-PM_1$ is the sum of all species measured by AMS or ACSM (their average chemical compositions during different periods are shown in Figure S3–S5).

The group of pollutants with smallest decrease in concentration (hereinafter called "SD") includes SO₂ and PM_{0.8–2.5}, and O₃ (8h) in the case of comparison with NSFM. The magnitude of the average percent change is less than 20% relative to the two NSF periods. It is interesting to note that there was even concentration increase in other O₃–related cases. The average

concentration of SO₂ was only 2.8 ppbv in Shenzhen in 2015 (<u>http://www.szhec.gov.cn/</u>), which is much lower than that in Beijing (4.7 ppbv) and elsewhere in China (<u>http://www.zhb.gov.cn/</u>). This result is partly attributed to the negligible coal consumption in Shenzhen, which instead relies mainly on natural gas and liquefied petroleum gas (Shenzhen Yearbook of Statistics, 2015). The emission inventory indicates that power plants and international marine container vessels are the

- 5 dominant source of SO₂ in Shenzhen (Wang et al., 2009; Zheng et al., 2009b). According to official statistics, the Shenzhen port piloted 401, 568, and 521 ships during the SF period in the years 2014–2016, respectively, which is quite similar to numbers for the NSF periods (<u>http://www.pilot.com.cn</u>). As infrastructure, power plants are not fully shut down during SF. On the other hand, a piece of evidence for the regional origin of SO₂ is from the newly established 356 m meteorological and environmental monitoring iron tower in Shenzhen. The ambient SO₂ concentrations were similar at the highest platform
- 10 (ave.=7.4 ppbv@325 m) and the lowest platform (ave.=7.2 ppbv@60 m) during January–February, 2017, indicating that SO₂ was already well mixed in the atmosphere and the local contributions should be minor. In contrast, the concentrations of NOx, which belongs to Group LD, had a 56% higher concentration at the lowest platform than at the highest platform (Zhuang, 2017). The small decrease of SO₂ is thus a reasonable result of the stable emissions during the SF periods and the primarily regional origin. The small decline of PM_{0.8-2.5} during the SF period suggests that the reduction of more aged particles of lager
- 15 sizes in PM_{2.5} is much lower than fresher particles of smaller size. This can be also confirmed by particle number concentration (PNC) measurement by SMPS, as shown in Figure 2. The largest difference of the PNC between the SF and NSFM periods exists mainly in a smaller size range (20–40 nm), which is recognized as the nucleation mode or second Aitken mode that represents fresh combustion emission (Ferin et al., 1990). In terms of chemical composition of PM_{0.8–2.5}, implications can be found in our previous size distribution measurement of aerosol chemical composition, using a ten-stage micro orifice uniform
- 20 deposit impactor (MOUDI), during the fall to winter in Shenzhen (Lan et al., 2011). The results clearly indicate that smaller fine particles (e.g., 0.18–0.56 μ m) contains relatively more BC (BC/SO₄²⁻=0.83), while larger fine particles (e.g., 1.0–1.8 μ m) contained a higher proportion of SO₄²⁻ (BC/SO₄²⁻=0.17). The SO₄²⁻ in PM_{2.5} in Shenzhen has been well proved to be mostly a regional pollutant, with similar concentrations at various sites including both urban and rural sites (Huang et al., 2014). Therefore, the very small decrease of PM_{0.8–2.5} during SF should be closely related to its enrichment of secondary regional
- species like SO_4^{2-} . Contrary to other pollutants, the concentrations of O₃, present small increasing during the SF period (except a little decline when comparing O₃–8h with the NSFM period), which could be attributed to the different drop rates for O₃ precursor species, i.e. NOx and VOCs (Qin et al., 2004), and will be discussed in more detail in section 3.2.

The decreasing ratios of various species during SF when compared with the NSFT and NSFM periods are similar, which suggests that the meteorological variations might not be the dominant reason for the species decreasing during SF. This means

30 that the strong decrease in the concentrations of air pollutants in group LD and MD is mainly due to the abatement of local sources. The larger decline in the SF period when compared to NSFT than to NSFM is associated with the lower temperature and stronger winds from the polluted northwest inland of the PRD during the NSFT period. In addition, the effect of the SF on the concentrations of the various species is almost identical each year (see Figure S7), which further confirms that the pollutant concentrations are determined primarily by the activity of the sources. In Figure 1, the percent changes of pollutants of the SF

periods relative to the Tran. periods are also presented, and it is found that the three-group classification defined above is also applicable, while the decrease levels are lower. For example, the average decrease percent of Group LD for the Tran. period case is 61%, while those for the NSFT and NSFM cases are 71% and 63%, respectively. This result is consistent with the fact that the SF travel of people occurred mostly during the seven days before and after the SF holidays (<u>http://sz.gov.cn</u>), and thus the if the travele of the travele o

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the city became much emptier even in the Tran. periods. In order to make a deeper and valid comparison for revealing the SF effect, the following discussion will only take the NSFM periods and SF periods for comparative analysis due to their more similar meteorology.



Figure 1. Percent change in concentrations of major air pollutants during the SF period relative to (a) Tran., (b) NSFT and (c)10 NSFM periods averaged over 2014–2016.



Figure 2. Distribution of particle number concentration in the 15–615 nm size range during the SF and NSFM periods.

3.2 The diurnal variation of major air pollutants

As shown in Figure 3, the diurnal cycles of all LD pollutants (except for the OVOCs) reveal significant peaks in concentration

- 5 around 8–9 am in the NSFM period, which is attributed to the low planetary boundary layer (PBL) in the morning and local rush hour traffic emissions. The evening rush hour peak, however, is not apparent for all the species, which is attributed to the higher ambient temperature and thus the higher PBL at that time than in the morning. During the SF period, the concentrations of all pollutants are far lower over the entire day. In particular, the rush-hour peaks become much smaller or disappear altogether, which is consistent with the large reduction in local vehicle emissions during the SF period. Although the sources
- of Chl remained uncertain in previous studies (Huang et al., 2011; Aiken et al., 2008), the maximal reduction (80%) in this pollutant during the morning rush hour during the SF period implies that local traffic emissions account for a significantly fraction of this pollutant in Shenzhen (Figure 3E). Contrary to other species in this group, the concentration of OVOCs is high in the daytime and peaks in the morning after the morning rush hour time during the NSFM period (Figure 3D), suggesting that photochemical production and/or daytime industrial activities may be important sources of OVOCs. The concentrations of different aromatics and OVOCs usually follow similar diurnal variations (Figure S8).

The diurnal variations of the MD pollutants are relatively smooth except for two VOCs mainly from natural sources (isoprene and DMS; see Figures 3L and 3M), which indicates that these pollutants predominantly come from regional sources and are dispersed more uniformly over a larger scale. The apparent difference of the diurnal variations of those anthropogenic air pollutants between the SF and NSFM periods also exists in the rush hours (except for acetonitrile; Figure 3J), however, the

20 reduction in local sources has a relatively weak effect on the overall concentrations of these pollutants. Acetonitrile, which is a tracer of biomass burning, is more concentrated during the daytime and its peak concentration occurs after the rush hours during the NSFM period (Figure 3J), which is similar to the result obtained for OVOCs and may be attributed to the influence of daytime anthropogenic activities, for example, industrial biomass boilers. Isoprene is primarily emitted by vegetation as a function of light and temperature, so the concentration of this pollutant goes through a broad peak that spans the daytime hours during both the NSFM and SF periods. The percent change in isoprene concentration between the SF and NSFM periods is approximately –40% (Figure 3M), despite the NSFM and SF periods having similar temperature and solar radiation, which

5 implies that the contribution of anthropogenic sources to isoprene cannot be overlooked in Shenzhen. Many studies have reported isoprene from vehicle exhaust, especially in cold seasons (Barletta et al., 2005; Borbon et al., 2001). DMS is reported to be a marine tracer (Dacey et al., 1986), its peak concentration occurs in the morning during both the NSFM and SF periods (Figure 3L), which is presumably related to the minimal PBL. The concentration of DMS decreases by 30%–50% during the SF period, which reflects the reduced DMS emissions from anthropogenic sources. As reported in the literature, industrial activities can make significant emissions of DMS (Schafer et al., 2010).

The diurnal variations of $PM_{0.8-2.5}$, SO_2 and O_3 demonstrated more similar concentrations and trends in the SF and NSFM periods, respectively (Figure 3T–3V). For $PM_{0.8-2.5}$, a small difference is found in the afternoon, which is supposed to be a result of more aged larger particles formed through stronger photochemical reactions during the NSFM period. Though, slight differences appear in SO_2 concentration, mainly during the nighttime when the PBL is low. These data suggest a minor role of

- 15 local near-ground SO₂ sources, such as vehicles. Although the daytime peak concentration of O₃ during the NSFM period is slightly greater than that during the SF period, this trend reverses from the evening to the midmorning hours. Similar phenomena have also been observed in other emission-reduction studies of urban areas (i.e., O₃ concentrations are greater on holidays than on non-holidays) (Qin et al., 2004; Tan et al., 2009). In addition, O₃ concentrations were higher during the 2008 Beijing Olympic Games (Chou et al., 2011), during which strict controls were imposed. The lower peak concentration of O₃
- 20 in the afternoon (13:00-16:00 LT) during SF suggests that the large reduction on precursors can also help mitigate the daytime O_3 concentration. However, the O_3 concentration at night during SF was higher than that during NSFM, which could be attributed to the oxidation reaction with NO of higher concentrations during NSFM, producing a titration effect and thus destroying O_3 (Qin et al., 2004; Tan et al., 2009). As a result, although the reduction in emissions of urban anthropogenic sources leads to a large decline of NOx and VOCs, this reduction does not mitigate the average ambient O_3 concentration,
- 25 which implies that the concentration ratio VOCs/NOx play an important role in controlling O₃ concentration.





3.3 Influence of wind on observed air pollutants

- 5 Wind plays a crucial role in the dilution and transport of air pollution. The wind field patterns are quite similar between the SF and NSFM periods (Figure S2). In general, the concentrations of LD air pollutants depend strongly on wind speed during the NSFM period, whereas this dependence becomes much weaker during the SF period (Figure 4). The difference in the concentration of LD air pollutants (including various aromatics and OVOCs, see Figure S9) between the NSFM and SF periods is maximal (50%–80%) under conditions of low wind speeds (<1 m/s) because local pollution can more easily accumulate</p>
- 10 under these conditions. These results confirm that the concentration of air pollutants mainly from local sources is strongly reduced during in the SF period.

Compared with the LD pollutants, the concentrations of CO, SO_4^{2-} , m/z 44, isoprene, DMS, and acetonitrile do not vary significantly with wind speed during the NSFM period, providing further evidence that these pollutants primarily come from regional or natural sources and are consequently more evenly distributed in the atmosphere.

In the Group SD, SO₂ is generally little influenced by wind speed during the SF period, while some higher concentrations
appeared under low wind speeds during the NSFM period, indicating again small contribution of urban local sources to SO₂. The fluctuation of PM_{0.8-2.5} both in the SF and NSFM periods does not reveal a clear relationship with wind speed, suggesting again it is not a typical locally emitted air pollutant. The variations of O₃--8h display the opposite trend to other air pollutants both in the SF and NSFM periods, growing smoothly as wind speed increases, which could be possibly attributed to more regional transport and/or the higher VOCs/NOx ratio under high wind speeds (Figure 4H). Note that, when the proportion of regional transport relative to local emission becomes bigger under higher wind speeds, the concentrations of NO₃⁻, SO₄²⁻, m/z 44, PM_{0.8-2.5}, and O₃--8h are even slightly higher in the SF period than in the NSFM period, implying that regional photochemical production during the SF period is not weakened.



Figure 4. Concentrations of major air pollutants as a function of wind speed during the SF and NSFM periods.

3.4 Emission ratio analysis

pollutants have an anthropogenic source during the NSFM period.

Several groups of special correlations were applied to analyze the source characteristics of air pollutants in Figure 5. CO and BC are both products of incomplete combustion (Subramanian et al., 2010), but gaseous CO can travel farther

- because of its longer atmospheric lifetime (approximately a month for CO vs a week for BC) (Khalil et al., 1990; Ogren et al., 1983). As shown in Figure 5A, the correlation coefficient and slope between BC and CO during the NSFM period (r² = 0.56, slope = 13.9) is greater than during the SF period (r² = 0.31, slope = 3.9), suggesting that local combustion sources make a much greater contribution during the NSFM period, but decline significantly during the SF period (He et al., 2011). The concentrations of isoprene and DMS, are not correlated with CO during the SF, whereas their
 correlation with CO is non-negligible during the NSFM period (Figures 5B and 5C), suggesting again that these
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The toluene/benzene ratio can be used to estimate the contribution of traffic emissions (Schneider et al., 2005). Generally, a value of 1.2–3 is found to be characteristic of vehicular emission in many urban areas (Nelson et al., 1984; Wang et al., 2002; Araizaga et al., 2013). The lower ratio of toluene to benzene (ave.=2.6) in the SF period suggests that

15 the dominant source is vehicle emission. This ratio in the NSFM period, however, is much higher (ave.=7.7), indicating more complicated sources of VOCs like huge amount of toluene solvent usage in industrial activities in PRD (Barletta et al., 2005, 2008; Chan et al., 2006). This finding is well consistent with the temporary closure of industrial plants in the SF period, which leads to little toluene emission.



Figure 5. Correlation between air pollutants (A) BC and CO (B) isoprene and CO, (C) DMS and CO, and (D) toluene and benzene during the SF (blue circles) and the NSFM (red circles) periods.

3.5 Conclusions

- 5 This study uses the SF in Shenzhen to investigate how the urban air quality reacts to significant, temporary reductions in emission. During the winters of 2014 to 2016, the air quality was observed continuously at Peking University Shenzhen Graduate School, from which we obtained the percent change in the concentrations of various air pollutants during the SF periods with respect to the comparable NSF periods. The analysis of these data shows that, despite meteorological variations, the Spring Festival clearly and consistently influences the urban concentrations of various air pollutants.
- 10 The air pollutants can be divided into three groups: the large-decrease (LD) pollutants are those with a percent change in concentration of -50% to -80% during the SF period and include aromatics, NOx, m/z 57, OVOCs, Chl, BC, and NO₃⁻. These results are consistent with the variation in urban emission sources during the SF, suggesting that these pollutants are mostly directly locally emitted or formed from secondary reactions between locally emitted pollutants. The medium-decrease (MD) pollutants are PM_{2.5}, NR–PM₁, PM_{0.8}, organic aerosol, m/z 44, SO₄²⁻, NH₄⁺, isoprene, acetonitrile, DMS, and CO; the

concentrations of these pollutants decrease by 20% to 55% during the SF, which indicates that the extreme reduction in urban emissions during the SF period has limited effect on air pollutants mostly from regional or natural sources. Finally, the slight-decrease (SD) pollutants include SO₂, PM_{0.8–2.5}, and O₃. The average percent change in the concentrations of these pollutants during the SF period is less than 20%, which indicates that a significant reduction in urban emissions does not significantly affect their concentration. Of particular interest is the origin of PM_{0.8–2.5}, which is almost completely regional.

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The results of this study show that the extreme reductions in urban emissions of Shenzhen only affects the concentration of smaller fresh particles, such as $PM_{0.8}$, whereas the reduction of $PM_{2.5}$ is only slightly affected because of the weak influence on aged, larger particles such as $PM_{0.8-2.5}$. The concentrations of SO_4^{2-} and secondary organic aerosols are hardly affected by local reductions in emissions. Therefore, reducing the emissions of SO_2 and VOCs on a regional scale is critical for reducing

10 their concentrations and achieving the goal of reducing concentrations of $PM_{2.5}$, at least for South China. On the other hand, O₃ has recently become an increasingly important air pollutant in China, especially in the PRD. However, the large reduction of O₃ precursors (NOx and VOCs) during the SF period only lead to small variation of O₃ concentrations. Consequently, further investigations are required to control not only the emissions of VOCs and NOx but also their concentration ratio.

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20