

We want to thank the reviewers for their helpful comments and suggestions which have helped to improve our manuscript. We have provided a point by point response to the comments (see below), and have modified our manuscript accordingly.

Review 1:

General Comments: The manuscript by Su et al. developed a mass closure $PM_{2.5}$ online integrated system and characterized the $PM_{2.5}$ sources and composition in Shenzhen. One of the major concerns of this study is that, apart from sharing a sampling line, what is the difference between using them separately and using the sampling system including aerosol chemical speciation monitor (Aerodyne, ACSM), Aethalometer (Magee, AE-31), automated multimetals monitor (Cooper Corporation, Xact-625), and hybrid synchronized ambient particulate real-time analyzer monitor (Thermo Scientific, SHARP-5030i)? What is the purpose and significance of establishing such a sampling system given that I already have these instruments? On the other hand, the manuscript fails to identify the new information and seems to be a report regarding sources and composition of $PM_{2.5}$ in a different location and season. Before its publication, the following comments need to be addressed.

Response: We would like to thank the reviewer for the comments. Regarding the purpose and significance of this study, we would like to make the following explanation:

First, it is difficult for online instruments to sharing a sampling line, because the flow rate and measurement principle of the instruments are different. Reducing particulate matter loss, controlling temperature and humidity during the sampling process is also important. Therefore, unlike independent sampling, we have spent a lot of effort to achieve integrated sampling using isokinetic sampling manifold.

Second, as the reviewer mentioned, we already have these instruments. However, sampling separately cannot achieve $PM_{2.5}$ mass closure and source analysis, so we tried to integrate them. The dataset obtained is comparable and more reliable.

Third, the choice of instruments in the integrated system is not involved in other studies. ACSM was integrated into the new system to measure OM and make PM_{2.5} mass closure better.

Last, it is not only a report of source analysis, we used the data of the integrated system to improve the time resolution of the source analysis results, and resolved the secondary organic aerosol (SOA) from the total PM_{2.5} mass by the usage of m/z 44 (a good tracer). This research had made a demonstration for PM_{2.5} full component monitoring and source analysis.

We explained the above content in detail and added it in the manuscript when addressed the major comments.

Major comments

1. What is the difference between the sampling system and the separate detection by separate instrument?

Response: In previous studies, separate instruments were widely used to measure the chemical composition of a certain class, but cannot achieve the quantification of all or most of PM_{2.5} mass concentration. Compared with separate instruments, in our study, the same sampling head was used to collect particles, and then divides into four monitoring instruments to monitor the corresponding components. The sampling system aimed to ensure the reliability and comparability of synchronous sampling of different instruments, reduce the different influence of loss of drainage pipes, temperature, humidity on different instruments, and output unified PM_{2.5} component data that can be directly applied to source analysis.

To illustrate this point, we made the following changes in the original manuscript:

“There are two differences between the new online integrated system and the separate online instruments. On one hand, the new online integrated system used isokinetic sampling manifold and the same sampling head to ensure the reliability and comparability of synchronous sampling among different instruments. On the other hand, ACSM was integrated into the new system to measure OM and make PM_{2.5} mass

closure better.” (Line 62-66)

2. What is the uncertainty quantification of chemical species measured by ACSM, AE31 and Xact-625? And what’s the uncertainty quantification of PM_{2.5}? What’s the error margin of PM_{2.5} mass closure? What’s the Detection Limit of each species?

Response: We thank the reviewer for this question, we added uncertainty quantification of each instruments in the supplementary material, and hoped those can give reader a better idea about the reliability of integrated systems. we also have added the table about Detection Limit to SI (in Table S1):

“Uncertainty analysis on mass concentrations of integrated system

For Xact-625, the combined uncertainty included contribution from flow (1.5%), calibration standard uncertainty (5%), long term stability (calculated from the standard deviation of hourly internal Pd reference, 1.3%), and an element-specific uncertainty associated with the spectral deconvolution calculated by instrument software for each spectrum (US-EPA,1999; Tremper et al.,2018). In our study, each of elements was calibrate individually with a reference sample, the Xact-625 LOD (Limit of detection) was calculated using HEPA field blank measurements during sampling campaign these are shown in Table S1.

The uncertainty of ACSM is similar to AMS, as described previously (Allan et al.,2003; Nga et al., 2011), the overall uncertainty includes uncertainties associated with the Q (flow), IE (Ionization Efficiencies), RIE (Relative Ionization Efficiencies), and CE (Collection Efficiency) (Middlebrook et al., 2012; Freney et al., 2019). In which, IE is the ionization, transmission, and ion detection efficiency of nitrate (typically shortened as “ionization efficiency”), 10% uncertainty. In this study, the capture vaporizer (CV) was equipped, compared with a standard vaporizer (SV), to reduce the particle bouncing effect at vaporizer and the particle bouncing effect at vaporizer and hence improves the quantitative uncertainties caused by CE (Hu et al., 2017b; Zhang et al., 2017), the uncertainty in CE is less than 30%. RIE is the ionization

efficiency of species relative to the ionization efficiency of nitrate; for ammonium and sulfate: determined in routine calibrations (10% uncertainty and 30% uncertainty, respectively); for organics: determined for various types of organics in previous laboratory experiments and literature values, an average value is used (20% uncertainty) (Bahreini et al., 2009). Q is the volumetric sample flow rate into the instrument (<0.5% uncertainty). The propagated, overall uncertainty for the total ACSM mass concentration is 20%-30%.

For AE-31 and SHARP-5030i, according to instrument manufacturer's test of instruments, the measurement accuracy is 5%, that is, the measurement error is within 5% of the measured value.

In addition, to guarantee the data quality acquired by the integrated system, relevant quality assurance and quality control (QA/QC) measures are implemented. The calibration of sampling flow rate, blank experiment and instrument calibration were performed periodically to ensure data quality according to relevant national standards. The sampling flow rate was calibrated every month to ensure the sampling flow precision was in the range of $\pm 1.5\%$. The blank experiment and instrument calibration were conducted every two months.”

“Table S1. The concentrations and detection limit of PM_{2.5} and chemical species during the sampling campaign.”

	Species	Average concentration	Standard deviation	Detection Limit
Organic ($\mu\text{g m}^{-3}$)	OM	14.1	7.4	0.3
Inorganic ions ($\mu\text{g m}^{-3}$)	SO ₄ ²⁻	8.6	3.3	0.4
	NO ₃ ⁻	1.8	1.9	0.2
	NH ₄ ⁺	3.8	1.7	0.5
	Cl ⁻	0.1	0.07	0.2
	BC	2.1	1.0	0.1
Trace elements (ng m^{-3})	Si	380.6	185.0	17.8
	K	443.9	269.1	1.17
	Ca	103.0	53.8	0.3
	Ti	14.4	8.2	0.16
	V	3.2	2.3	0.12

Cr	2.9	2.0	0.12
Mn	24.3	13.0	0.14
Fe	288.7	132.2	0.17
Co	0.03	0.1	0.14
Ni	2.9	1.3	0.1
Cu	11.3	7.7	0.079
Zn	102.2	60.9	0.067
As	5.8	4.7	0.063
Se	2.2	1.2	0.081
Mo	0.5	0.5	0.1
Cd	7.3	3.2	2.5
Sn	19.8	8.3	4.1
Sb	28.0	10.2	5.2
Ba	3.9	7.4	0.39
Hg	1.9	0.7	0.12
Pb	18.6	9.5	0.13

The integrated system has a small error margin of mass closure, which is one of the advantages of the system. We explained in the manuscript:

“The average error margin of mass closure during the observation period is about 6%, which might be due to the measurement error of the integrated instruments, particle composition, temperature and relative humidity (Su et al., 2018; Zhang et al., 2017).” (Line 227-228).

3. More needs to be listed to support source apportionment results. For example, please make clear that Chl shows dominated contribution to coal combustion factor while negligible fraction in biomass burning. Besides the high mass loading of K in factor 6, is there any other evidences to support that factor6 is related to the biomass burning? In addition, the factor related coal combustion shows 3 peaks during daytime. Please explain this.

Response: Thank you for your questions about coal and biomass burning, which reminded us to think

deeply about these two sources. Cl^- in $\text{PM}_{2.5}$ originates mainly from ammonium chloride, which is formed by the rapid combination of HCl and ammonia in the atmosphere. In China, a country with huge coal-consumption, the biggest potential source of HCl is coal burning (Yudovich and Ketris, 2006; Wang et al., 2015). Huang et al. (2018) found that the concentration distribution of Cl^- in the Pearl River Delta is consistent with the distribution of coal-fired power plants in the source list. The factor also had some mass contributions from SO_4^{2-} , NO_3^- , and EC, further confirming that it was from coal burning (Zheng et al., 2013).

Factor 6 was identified as biomass combustion not only because that K is a tracer for biomass burning, but also for the following reasons. First, the factor had a large part of mass contribution of OM, and biomass burning is a significant source of $\text{PM}_{2.5}$ and major organic carbon in China (Akagi et al. 2011). Second, the factor had a certain amount of Zn, open-air biomass burning often mixes with garbage burning in Chinese rural areas. The smoke of garbage-burning emission might contain Zn (Zou et al., 2017). Third, according to previous study about source inventory surveys, particulate matter emitted from biomass combustion usually contains a certain amount of Ca (Ma et al., 2015). Besides, as Fig.8 shown, biomass burning has a high contribution from north and south-west, which is in agreement with the distribution of fire points in Guangdong (Fig.S6), it can be clearly seen that Shenzhen surrounding areas present a high-density fire point distribution, indicating frequent occurrence of biomass burning. The activities of biomass burning often occurs during the daytime, that is the reason why biomass burning had a trend of high day concentration and low night-time (Fig.7). Therefore, we think that factor 6 can be identified as biomass combustion.

The daily variation of coal burning sources derived from Cl^- is consistent (Fig S7.), and there is a peak around 9:00 in the morning. It might be because the temperature starts to rise in the morning and the vertical air convection activity is strengthened, bringing the pollutants transmitted by overhead sources to the near ground. As for the other two peaks, we found that it was the abnormally high contribution of coal-burning around 14:00 on September 25, so there might be local source that caused the peak of the diurnal variations. The spike around 22:00 was mainly because of China's National Day on October 1, there were

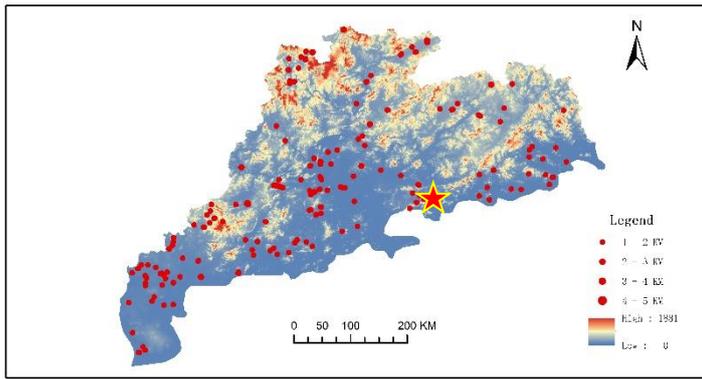
displays of fireworks from September 25 to October 1 at 3 playgrounds 10 km away from sampling site. Previous study has shown that the concentration of species (e.g. K, Ca, Cl⁻, NO₃⁻) in the PM_{2.5} would have greatly increase due to the fireworks (Tsai et al., 2012).

We also added more specifically state the sources in manuscript:

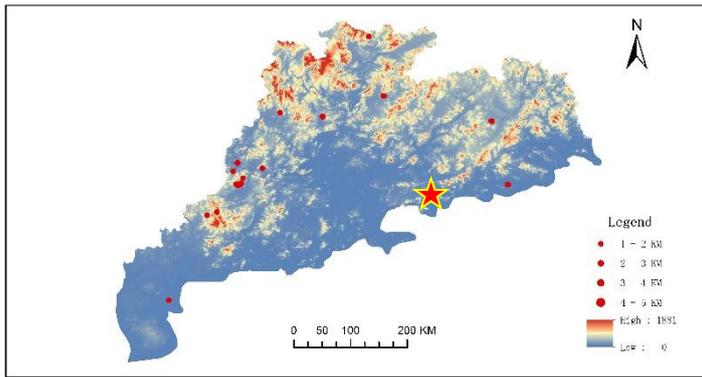
“Factor 4 was associated with coal burning due to the high EV value of Cl⁻, which is formed by the rapid combination of HCl and ammonia in the atmosphere, and the potential source of HCl is coal burning in China (Yudovich and Ketris, 2006; Wang et al., 2015), and the concentration distribution of Cl⁻ in the Pearl River Delta was consistent with the distribution of coal-fired power plants in the source list (Huang et al., 2018). This factor also had some mass contributions from SO₄²⁻, NO₃⁻, and EC, further confirming that it was from coal burning (Zheng et al.,2013).” (Line 289-293)

“Factor 6 has a high loading of K and a certain of OM and BC. K has been used as a clear tracer for biomass burning (Yamasoe et al., 2000; Sillapapiromsuk et al., 2013). Biomass burning is a significant source of PM_{2.5} and organic matter in China (Akagi et al., 2011). The Zn contained in this factor might be related to garbage-burning (Yuan et al., 2006). Besides, biomass burning has a high contribution from north and south-west (Fig. 8), which is consistent with the distribution of fire points in Guangdong (Fig.S8). The activities of biomass burning often occurs during the daytime, which consisted with the diurnal pattern of biomass burning that high day concentration and low night-time (Fig. 7).” (Line 297-302)

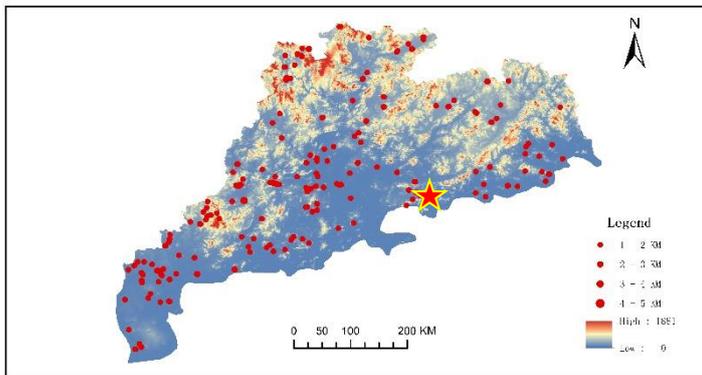
“The daily variation of coal burning and Cl⁻ was consistent (Fig S7), and there is a peak around 9:00 in the morning. It might because the temperature starts to rise in the morning and the vertical air convection activity is strengthened, bringing the pollutants transmitted by overhead sources to the near ground. The spike around 22:00 was mainly because of firework shows during September 25 to October 1. The peak around 14:00 mainly came from local sources on September 25.” (Line 361-364)



DAY



NIGHT



ALL

Figure S6. Spatial distribution of fire points in Guangdong (divided into day and night) during observation (the five-pointed star was used to represent sampling site).

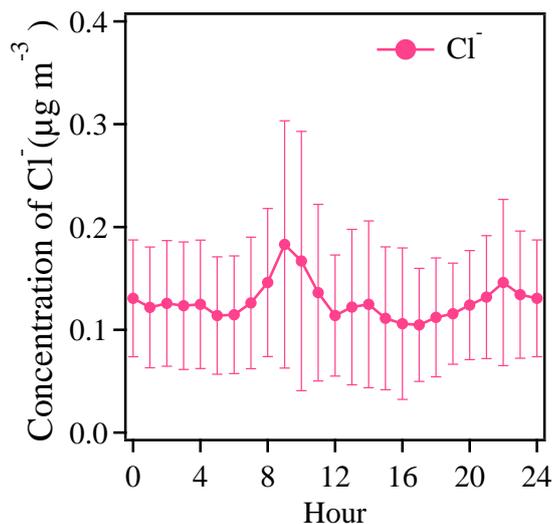


Figure S7. Diurnal variation of the Cl⁻ during the observation.

4. Although there is tight correlation between reconstructed and measured PM_{2.5}, what are the reasons caused the underestimation in 10/20 and overestimation in 10/3? Please elaborate.

Response: In the process of sampling, we tried our best to do a good job in quality control and guarantee. However, PM_{2.5} monitor instruments of different principles can be overestimated and underestimated for PM_{2.5} (Su et al., 2018; Zhang et al., 2017; Budisulistiorini et al., 2014), so are the reconstruction and measurement (Ji et al., 2018). We think it's almost inevitable, the possible reasons are as follows, the measurement error of the integrated instruments, particle composition, temperature and relative humidity and so on. In our study, the deviation between the reconstructed and measured PM_{2.5} form a normal distribution, ranging from -30% to +30%. On the whole, the correlation is tight and the slope is close to 1, which indicates that the data is relatively reasonable.

As the reviewer pointed out that the fitting problem of October 3 and October 20, we think it may be related to the temperature. The temperature on October 3 is the highest during the observation period, and at October 20, the temperature is at a relatively low level. The temperature has different effects on SHARP-5030i and integrated instruments, which results in different fitting effects to a certain extent. Of

course, there may be other reasons just as mentioned above.

We also pointed out the reasons caused the underestimation in the manuscript:

“The average error margin of mass closure during the observation period is about 6%, which might be due to the measurement error of the integrated instruments, particle composition, temperature and relative humidity (Su et al., 2018; Zhang et al., 2017). A significant mass discrepancy between reconstructed and measured PM_{2.5} appeared in some periods (Fig. 2a). For example, the underestimation on October 3 and the overestimation on October 20 occurred when the temperature was the highest and the lowest during the observation period, respectively. Therefore, it was speculated that temperature might affect the composition of PM_{2.5}, causing the mass closure to deviate.” (Line 227-232)

5. What ACSM is used in your manuscript? Q-ACSM or ToF-ACSM? Did you measure the PM₁ species in this study (based on the reference of Nga et al., 2011)? if so, how about the gap of chemical species between the PM₁ and PM_{2.5}? Please mention it here. Also, more details in concentration and composition of PM species need to be shown wherever in the main text or the supplementary.

Response: We are sorry for not describing it clearly, PM_{2.5}-Q-ACSM was used and the PM₁ species was not be measured in this study. But, the performance of PM_{2.5}-Q-ACSM have been fully evaluated in both laboratory and field studies (Hu et al., 2017a; Xu et al.,2017). The gap of chemical species between PM_{2.5}-Q-ACSM and PM₁-Q-ACSM also has been analyzed in previous study: the comparisons between the two Q-ACSMs illustrated similar temporal variations in all non-refractory (NR) species between PM₁ and PM_{2.5}($r^2>0.9$); one average, NR-PM_{1-2.5} contributed 53% of the total NR-PM_{2.5}, the ratios of [NR-PM₁]/[NR-PM_{2.5}] varied among different species. In particular, nitrate and chloride showed much higher [NR-PM₁]/[NR-PM_{2.5}] ratios compared with other species (Zhang et al.,2017).

In the manuscript, we present the time series stack diagrams of several classes of components (Fig. 2(a)) and the proportions of all components (Fig. 3), and describe them in main text (Line 214-220). In addition, we supplement the concentration and relative standard deviation of each component in SI (Table S1). To clarify this question, we have modified the description of the ACSM in the manuscript.

“PM_{2.5}-capable Q-ACSM was selected for monitoring the mass concentrations of ambient OM, SO₄²⁻, NO₃⁻, NH₄⁺, and Cl⁻ in non-refractory PM_{2.5}. The PM_{2.5}-Q-ACSM equipped with a PM_{2.5} lens and capture vaporizer (CV), and can detect approximately 90% of PM_{2.5} particles (Hu et al., 2017; Xu et al., 2017; Zhang et al., 2017)” (Line 95-97)

6. The frequency of data is negligible at PM_{2.5} > 80 μg/m³ in Fig.6. In my view point, there might be a significant uncertainty in fraction of composition when PM levels are low. The authors need to address such uncertainties in the revised manuscript.

Response: Thank you for pointing it out. During our observation period, the proportion of data that PM_{2.5}>80 μg/m³ is only 1.3%, so we combined the data that PM_{2.5} > 80 μg/m³ into the concentrations of 70-80 μg/m³. Fig. 6(b) has been revised.

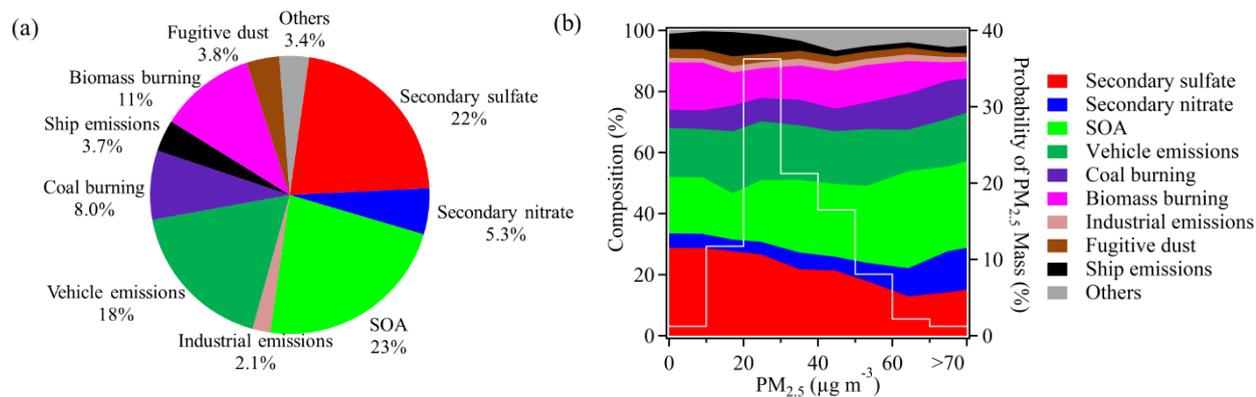


Figure 6. Average contributions of each source to PM_{2.5}(a). Variation in the proportion of sources in PM_{2.5} during the observation period. The white curve represents the occurrence probability of the PM_{2.5} concentration (b). (Line 331-335)

The uncertainties of PM_{2.5} and their compositions have been clarified in the secondary question and added into SI, when PM level were below the detection limit, we use the half detection limit (DL) instead the concentration, and their uncertainties was set as 5/6 DL when source resolution was calculated. Please see lines 171-174.

7. Line 31: “PM_{2.5} is currently a serious problem” is not suitable expression

Response: Thank you for this comment. The sentence was not clear enough and could be misunderstood.

Therefore, we changed it to: “PM_{2.5} is a long-term problem in some cities or regions.” (Line 31)

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Review 2:

This paper reports the development of an online monitoring system for PM_{2.5} composition. The unique feature for this system is the capability to measure more than 90% of PM_{2.5} mass with a high time resolution. This advance makes this system a powerful tool for understanding PM_{2.5} sources and deciding the corresponding control measures. Another novelty of this paper is the resolving of secondary organic aerosol (SOA) from the total PM_{2.5} mass by the usage of m/z 44, a good SOA tracer, in the PMF modelling. This system has been successfully applied in a megacity in China, with nine sources well identified, supporting its effectiveness and usefulness in PM_{2.5} control. Overall, I think it is a well-written paper with novelty and recommend its publication after considering the following concerns.

Response: Thank you.

Comments:

1. The author should make a clearer statement of the advantage of the new system compared to the separate instruments in the introduction part.

Response: Thanks for your comment. The statement of the new system has been added to the main text:

“There are two differences between the new online integrated system and the separate online instruments. On one hand, the new online integrated system used isokinetic sampling manifold and the same sampling head to ensure the reliability and comparability of synchronous sampling among different instruments. On the other hand, we integrated ACSM into the new system to measure OM to achieve PM_{2.5} mass closure better” (Line 62-66)

2. Line 31. “serious” might not be suitable to the current PM_{2.5} pollution status. A description of long-term problem should be better.

Response: Thank you for this comment and suggestion. we changed the sentence to: “PM_{2.5} is a long-

term problem in some cities or regions.” (Line 31)

3. Why Na was not measured? Could sea salt be a major source for PM_{2.5} in Shenzhen, a coastal city?

Response: We did not measure Na mainly for two reasons.

First, it is difficult to accurately measure the online integration of Na, Na has lighter atomic number, so the uncertainty of data measured by X-ray fluorescence method is larger. The ACSM evaporator was ~550°C, and some components such as NaNO₃, NaCl, and Mg(NO₃)₂ in the sea salt may not be detected due to the lack of gasification at this temperature. Although the instruments of ion chromatography, such as MARGA can realize Na⁺ online measurement, it is not suitable for integration due to its large volume and cumbersome operation.

Second, as the reviewer noted, sea salt represented by Na is not the main source of PM_{2.5} in Shenzhen, previous studies have shown that sea salt contributes less (1% to 3%) to PM_{2.5} (Huang et al., 2014; Huang et al., 2018).

We also pointed out it in the manuscript:

“The factor of sea salt cannot be identified in this study, because the measurement of its tracer (Na) is limited for X-ray fluorescence method and ACSM. However, the contribution of sea salt is little for Shenzhen (about 1% to 3%), and is not the main source of pollution.” (Line 310-312)

4. 2.4 Design of the data analytics platform. More details for data conversion of each instrument should be given.

Response: Thanks for your comments as it identifies a potential area for confusion of other readers. The details of data analytics platform have been clarified in the revised supplement.

“Design of the data analytics platform

The design solution of the data analytics platform was shown in Fig. S2, the data of three online instruments (ACSM, Xact-625, AE-31) were processed in same (.csv) format and saved in their respective

local computer using data transmission software, and uploaded data to a same SQL Server remote database for data management. The database was based on the dedicated server of the integrated system. The data of SHARP-5030i can be directly connected to the server. In addition, an atmospheric environment data collection and processing system had been established. The data in the SQL Server database was called to achieve unified processing and display of integrated data.

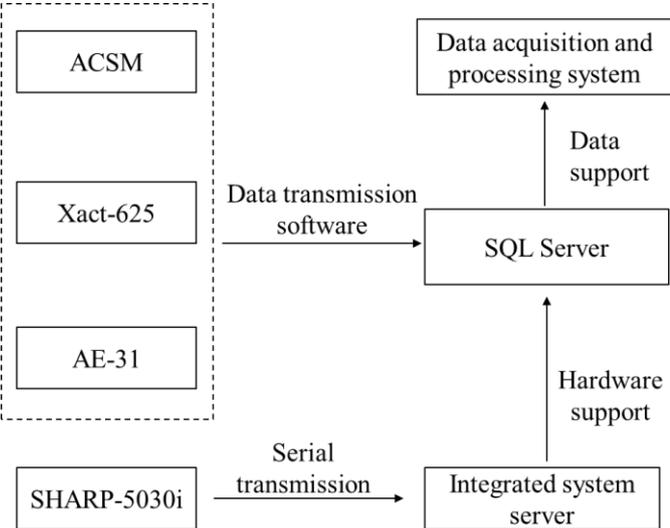


Figure S2. Design solution of data analytics platform”

5. Figure 2a. The mass closure is generally good. However, the authors should comment on some periods when a significant mass discrepancy appeared.

Response: As pointed out by the reviewer, the overall quality of the instrument is very good, with an average deviation of 6%, but the differences between reconstructed and measured are relatively large sometimes.

We further analyzed the 10/3 and 10/20, and think it may be related to the temperature. The temperature on October 3 is the highest during the observation period, and at October 20, the temperature is at a

relatively low level. The temperature has different effects on SHARP-5030i and integrated instruments, which results in different fitting effects to a certain extent. Of course, there may be other reasons, such as the measurement error of the integrated instruments, particle composition, temperature and relative humidity (Su et al., 2018; Zhang et al., 2017).

We also pointed out the reasons caused the underestimation in the manuscript:

“The average error margin of mass closure during the observation period is about 6%, which might be due to the measurement error of the integrated instruments, particle composition, temperature and relative humidity (Su et al., 2018; Zhang et al., 2017). A significant mass discrepancy between reconstructed and measured PM_{2.5} appeared in some periods (Fig. 2a). For example, the underestimation on October 3 and the overestimation on October 20 occurred when the temperature was the highest and the lowest during the observation period, respectively. Therefore, it was speculated that temperature might affect the composition of PM_{2.5}, causing the mass closure to deviate.” (Line 227-232)

6. Figure 4. The elements with low concentrations should be displayed with enlargement.

Response: We thank the reviewer for this suggestion. The figure is corrected as:

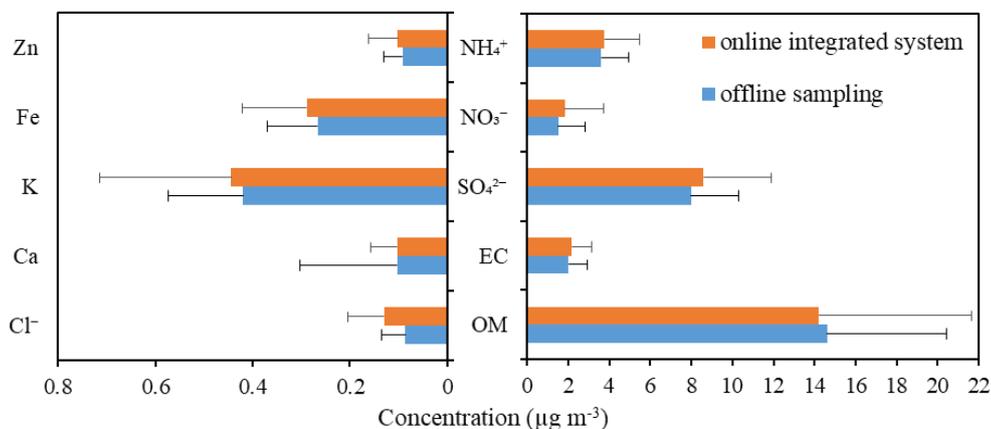


Figure 4. Concentrations of major chemical compositions of PM_{2.5} measured by online Integrated system and offline sampling. Note that the EC in the online integrated system was referred to as BC. (Line 271-

273)

7. Figure 7. There is a spike at 1:00 am for both biomass burning and fugitive dust.

Why?

Response: The spike of fugitive dust at 1:00 might be due to the influence of local sources. We carefully analyzed the time series of fugitive dust and biomass combustion sources, and found that the fugitive dust appeared a very high value at 1:00 on October 19, 25 and 28, which was significantly higher than the average dust concentration during the observation period, and made the average value of fugitive dust higher at 1:00. The tracer Ca also showed a higher value at the corresponding time, indicating that there were short-term dust emission activities. The biomass burning also appeared abnormally high value at 1:00 on October 2, relating to the firework shows on the China's National Day.

We added more specifically state the sources in manuscript:

“Analyzed with the time series of pollution sources (Fig. 5b), the results showed, the peaks around 22:00 and 1:00 of biomass burning was mainly due to the abnormally high source contribution, on the night of October 1, which is China's National Day, and there was a firework show 10 km away from the sampling site. Previous study has shown that the concentration of species (e.g. K, Ca, Cl⁻, NO₃⁻) in the PM_{2.5} would have greatly increase due to the fireworks (Tsai et al., 2012). The spike at 1:00 of fugitive dust and biomass burning mainly caused by several abnormally high values at 1:00, suggesting it might be due to the influence of local short-term activities.” (Line 355-361)

We added the standard deviation to the Fig. 7, so that readers can get more information from it.

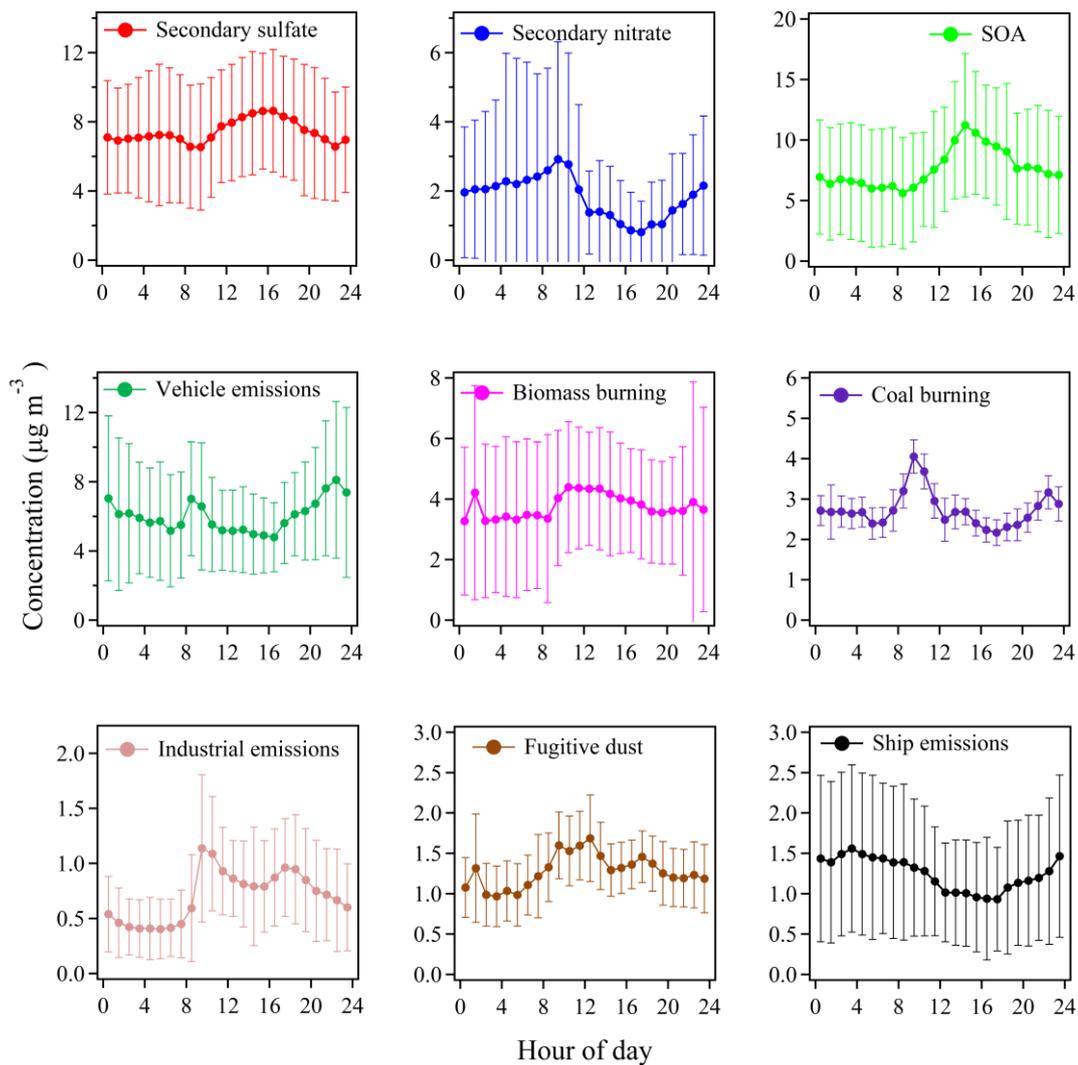


Figure 7. Diurnal variations of the nine sources resolved by ME-2. (Line 367-368)

8. Conclusions. For a technical paper, the prospects of further development of the new system should be given.

Response: We have mentioned the prospects, and added more explanation about this in the manuscript:

“The development and successful application of the online integrated system and source apportionment

method suggested that they can be used for precise regulation of PM_{2.5}.” (Line 417-418)

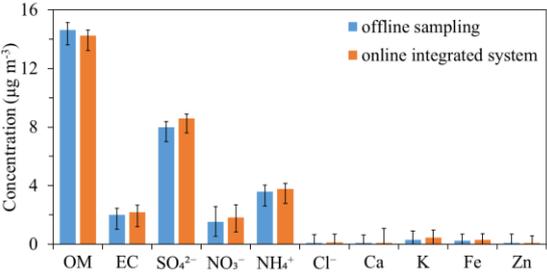
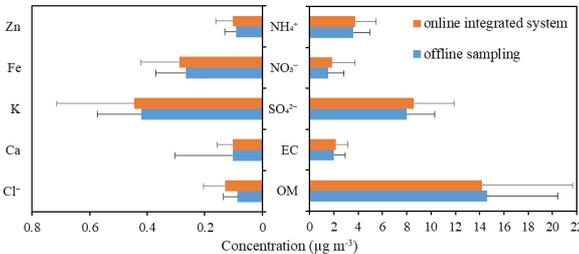
“The high time resolution source analysis of the new integrated system is helpful to study the variation of the primary and secondary sources of PM_{2.5} in the process of heavy pollution (such as fireworks), and to identify the key sources and its mechanism, then to assess the impact of different sources. The system can run stably for a long time, and provides a key scientific basis for particulate matter control of China.” (Lines 418-422)

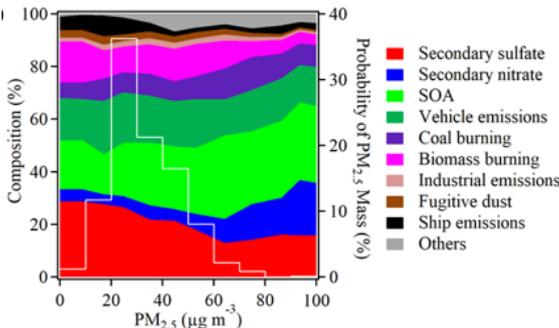
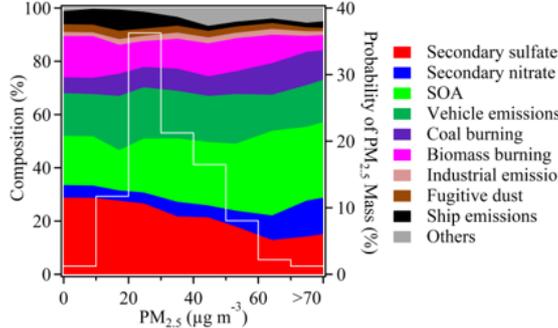
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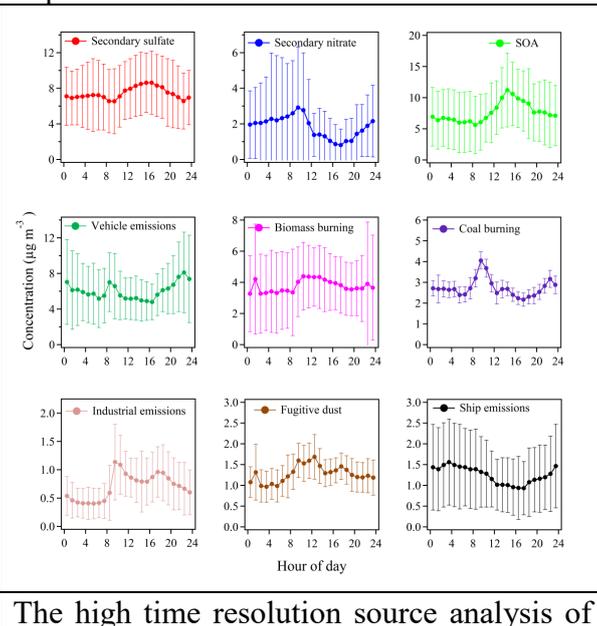
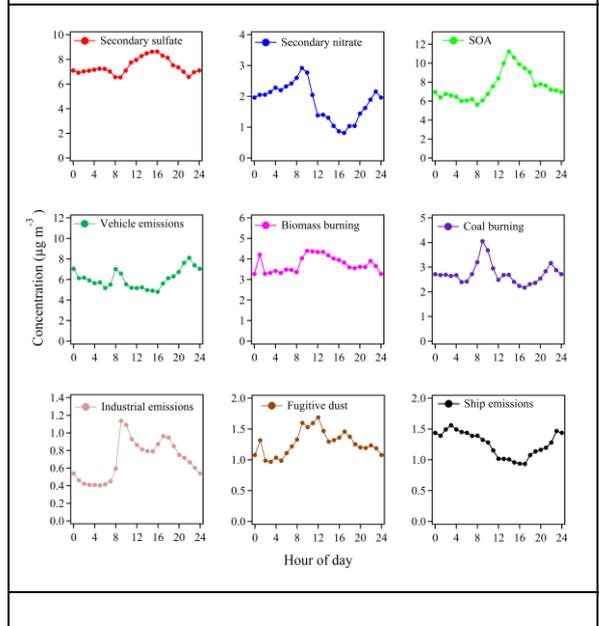
The list of all relevant changes made in the manuscript

original	modification	Line
PM _{2.5} (aerodynamic particles smaller than 2.5 microns in size) is currently a serious problem	PM _{2.5} (aerodynamic particles smaller than 2.5 microns in size) is a long-term problem in some cities or regions	31
Compared with other online instruments (e.g., AMS, semicontinuous OC/EC analyzer, ACSM, etc.), the new online integrated system could fully measure the chemical species and better achieve PM _{2.5} mass closure.	There are two differences between the new online integrated system and the separate online instruments (e.g., semi-continuous OC/EC analyser, MARGA, etc.). On one hand, the new online integrated system used isokinetic sampling manifold and the same sampling head to ensure the reliability and comparability of synchronous sampling among different instruments. On the other hand, ACSM was integrated into the new system to measure OM and make PM _{2.5} mass closure better.	62-66
The ACSM was selected for monitoring the mass concentrations of ambient organic aerosol and inorganic ions (SO ₄ ²⁻ , NO ₃ ⁻ , NH ₄ ⁺ , and Cl ⁻) because of its small volume, low cost, operational stability and high resolution (18 min) (Nga et al., 2011).	PM _{2.5} -capable Q-ACSM was selected for monitoring the mass concentrations of OM, SO ₄ ²⁻ , NO ₃ ⁻ , NH ₄ ⁺ , and Cl ⁻ in non-refractory PM _{2.5} , the PM _{2.5} -Q-ACSM equipped with a PM _{2.5} lens and capture vaporizer (CV), and can detect approximately 90% of PM _{2.5} particles (Hu et al., 2017; Xu et al., 2017; Zhang et al., 2017).	95-97
	The average error margin of mass closure during the observation period is about 6%, which might be due to the measurement error of the integrated instruments, particle composition, temperature and relative humidity (Su et al., 2018; Zhang et al., 2017). A significant mass discrepancy between reconstructed and measured PM _{2.5} appeared in some periods (Fig. 2a). For example, the underestimation on October 3 and the overestimation on October 20 occurred when the temperature was the highest and the lowest during the observation period,	227-232

	<p>respectively. Therefore, it was speculated that temperature might affect the composition of PM_{2.5}, causing the mass closure to deviate.</p>	
<p>In this study, the ACSM evaporator was ~550 °C, and some components such as NaNO₃, NaCl, and Mg(NO₃)₂ in the aged sea salt and mineral dust may not be detected due to the lack of gasification at this temperature. The low concentration of nitrate and chloride ions measured by the ACSM may be caused by the presence of sea salt or crustal particles in the collected samples. Another study also found a large difference between ACSM and MARGA when measuring chloride and nitrate (Zhang et al., 2017).</p>	<p>Another study also found a large difference between ACSM and MARGA when measuring chloride and nitrate (Zhang et al., 2017). Besides, the evaluation of PM_{2.5}-AMS also found a large difference in the measurements of Cl⁻ (Hu et al., 2017), which might be caused by the measuring principle of the instrument.</p>	<p>265-268</p>
		<p>271-273</p>
<p>Factor 4 was associated with coal burning due to the high EV value of Cl⁻, which mainly come from coal in Shenzhen, besides OM, BC, and SO₄²⁻ were typical combustion products (Li et al., 2016)</p>	<p>Factor 4 was associated with coal burning due to the high EV value of Cl⁻, which is formed by the rapid combination of HCl and ammonia in the atmosphere, and the potential source of HCl is coal burning in China (Yudovich and Ketris, 2006; Wang et al., 2015) and the concentration distribution of Cl⁻ in the Pearl River Delta was consistent with the distribution of coal-fired power plants in the source list (Huang et al., 2018), This factor also had some mass contributions from SO₄²⁻, NO₃⁻, and EC, further confirming that it was from coal burning (Zheng et al., 2013).</p>	<p>289-293</p>

<p>Factor 6, with high loading of K, was biomass burning (Yamasoe et al., 2000).</p>	<p>Factor 6 has a high loading of K and a certain of OM and BC. K has been used as a clear tracer for biomass burning (Yamasoe et al., 2000; Sillapapiromsuk et al., 2013). Biomass burning is a significant source of PM_{2.5} and organic matter in China. The Zn contained in this factor might be related to garbage-burning (Yuan et al., 2006). Besides, biomass burning has a high contribution from north and south-west (Fig. 8), which is consistent with the distribution of fire points in Guangdong (Fig.S6). The activities of biomass burning often occurs during the daytime, which consisted with the diurnal pattern of biomass burning that high day concentration and low night-time (Fig. 7).</p>	<p>297-302</p>
	<p>The factor of sea salt cannot be identified in this study, because the measurement of its tracer (Na) is limited for X-ray fluorescence method and ACSM. However, the contribution of sea salt is little for Shenzhen (about 1% to 3%), and is not the main source of pollution.</p>	<p>310-312</p>
		<p>331-335</p>
<p>The small peak at 2:00 was mostly related to the local biomass burning activities at night.</p>	<p>Analyzed with the time series of pollution sources (Fig. 5b), the results showed, the peaks around 22:00 and 1:00 of biomass burning was mainly due to the abnormally high source contribution, on the night of October 1, which is China's National Day,</p>	<p>355-364</p>

and there were displays of fireworks from September 25 to October 1 at 3 playgrounds 10 km away from sampling site. Previous study has shown that the concentration of species (e.g. K, Ca, Cl⁻, NO₃⁻) in the PM_{2.5} would have greatly increase due to the fireworks (Tsai et al., 2012). The spike at 1:00 of fugitive dust and biomass burning mainly caused by several abnormally high values at 1:00, suggesting it might be due to the influence of local short-term activities. The daily variation of coal burning and Cl⁻ was consistent (Fig. S7), and there is a peak around 9:00 in the morning. It might because the temperature starts to rise in the morning and the vertical air convection activity is strengthened, bringing the pollutants transmitted by overhead sources to the near ground. The spike around 22:00 was mainly because of firework shows during September 25 to October 1. The peak around 14:00 mainly came from local sources on September 25.



367-368

418-422

	<p>the new integrated system is helpful to study the variation of the primary and secondary sources of PM_{2.5} in the process of heavy pollution (such as fireworks), and to identify the key sources of heavy pollution and its mechanism, then to assess the impact of different sources. The system can run stably for a long time, and provides a key scientific basis for particulate matter control of China.</p>	
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Development and application of a mass closure PM_{2.5} composition online monitoring system

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Abstract. Online instruments have been widely applied for the measurement of PM_{2.5} and its chemical components; however, these instruments have a major shortcoming in terms of the lack or limited number of species in field measurements. To this end, a new mass closure PM_{2.5} online integrated system was developed and applied in this work to achieve more comprehensive information on chemical species in PM_{2.5}. For the new system, one isokinetic sampling system for PM_{2.5} was coupled with an aerosol chemical speciation monitor (Aerodyne, ACSM), an Aethalometer (Magee, AE-31), an automated multimetals monitor (Cooper Corporation, Xact-625), and a hybrid synchronized ambient particulate real-time analyzer monitor (Thermo Scientific, SHARP-5030i) to enable high-resolution temporal (1 h) measurements of organic matter, SO₄²⁻, NO₃⁻, Cl⁻, NH₄⁺, black carbon and important elements as well as PM_{2.5} mass concentrations. The new online integrated system was first deployed in Shenzhen, China to measure the PM_{2.5} composition from 25 September to 30 October 2019. Our results showed that the average PM_{2.5} concentration in this work was 33 μg m⁻³, and the measured species well-reconstructed the PM_{2.5} and almost formed a mass closure (94%). The multilinear engine (ME-2) model was employed for the comprehensive online PM_{2.5} chemical dataset to apportion the sources with predetermined constraints, in which the organic ion fragment m/z 44 in ACSM data was used as the tracer for secondary organic aerosol (SOA). Nine sources were determined and obtained reasonable time series and diurnal variations in this study, including identified SOA (23%), secondary sulfate (22%), vehicle emissions (18%), biomass burning (11%), coal burning (8.0%), secondary nitrate (5.3%), fugitive dust (3.8%), ship emissions (3.7%), and industrial emissions (2.1%). The potential source contribution function (PSCF) analysis indicated that the major source areas could be the region north of the sampling site. This is the first system in the world that can perform online measurements of PM_{2.5} components with a mass closure, thus providing a new powerful tool for PM_{2.5} long-term daily measurement and source apportionment.

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1 Introduction

30 **PM_{2.5} (aerodynamic particles smaller than 2.5 microns in size) is a long-term problem in some cities or regions** because its chemical components have strong harmful effects on visibility (Campbell et al., 2018), radiative forcing (Gao et al., 2017), human health (Puthussery, et al., 2018; Zhang et al., 2019), climate change (Glotfelty et al, 2014), and ecosystems (Diemoz et al., 2019; Amarloei et al., 2020). PM_{2.5} contains many types of components, such as trace elements, water-soluble inorganic ions, elemental carbon (EC), black carbon (BC), organic carbon (OC) or organic matter (OM), etc. (Budisulistiorini et al., 35 2014; Jayarathne et al., 2018). Accurately measuring PM_{2.5} and chemical species are essential for identifying their sources, assessing their negative effects (e.g., radiative forcing, human health, etc.), and developing effective abatement strategies (Huang et al., 2018; Hand et al., 2019).

Various online measurement techniques for PM_{2.5} and chemical species have been developed and widely applied to get their detailed chemical and physical information in recent years because of their high time resolution (1 h or less) (Vodicka et al., 40 2013; Li et al., 2017). For example, the Aerodyne Aerosol Chemical Speciation Monitor (ACSM) has been used to determine OM, inorganic aerosol constituents in PM₁ or PM_{2.5} (Budisulistiorini et al., 2014; Zhang et al., 2017). Water-soluble ions in PM_{2.5} can be determined by several online instruments using ion chromatography (IC) methods, such as Particle Into Liquid Sampler-ion chromatography (PILS-IC), the Monitor for AeRosols and GAses (MARGA), the in situ Gas and Aerosol Composition (IGAC), and ambient ion monitor (AIM, URG Corporation, USA) (Kuokka et al., 2007; Harry et al., 2007; Ellis 45 et al., 2011; Yu et al., 2018). A semi-continuous OC/EC analyzer was developed by Sunset Laboratory for the measurement of OC and EC (Vodicka et al., 2013). Trace and crust elements can be measured by an automated multi-metals monitor (Xact-625) using the X-ray fluorescence method (XRF) (Yu et al., 2019). However, a major shortcoming in these instruments is the lack or limited species from field measurements. To obtain more comprehensive information on chemical species in PM_{2.5}, some previous studies have employed several online instruments to simultaneously measure the organic carbon, element 50 carbon, important elements, and water-soluble inorganic ions in PM_{2.5} (Gao et al., 2016; Peng et al., 2016b; Wang et al., 2018; Huang et al., 2019; Liu et al., 2019). Although major species of PM_{2.5} have been measured in these research studies, the sum concentration of all the determined species was not close to the PM_{2.5} mass concentrations, which was partly because OM has not been measured (Hand et al., 2011; Wang et al., 2018). OM can be calculated by multiplying the OC concentrations by a multiplier that is an estimation of the average molecular weight per carbon weight for the organic aerosol. This multiplier has 55 been investigated in previous studies (Turpin and Lim, 2001; Boris et al., 2019; Chow et al., 2019) and is widely used to estimate OM concentrations (Chow et al., 2015). This estimation method has large uncertainty because the multiplier varies with time and location and ranges from 1.2 to 2.6 (Chow et al., 2015). Therefore, accurately characterizing the OM and other major species of PM_{2.5} is important for computing the PM_{2.5} mass closure and estimating their contribution to PM_{2.5} mass concentrations. To this end, we developed a new mass closure PM_{2.5} online integrated system, where one isokinetic sampling 60 system for PM_{2.5} is coupled with the ACSM, AE-31, Xact-625, and SHARP-5030i to enable high time resolution (1 h) measurements of organic matter, inorganic ions, black carbon, important elements, and PM_{2.5} mass concentration. **There are**

two differences between the new online integrated system and the separate online instruments (e.g., semi-continuous OC/EC analyser, MARGA, etc.). On one hand, the new online integrated system used isokinetic sampling manifold and the same sampling head to ensure the reliability and comparability of synchronous sampling among different instruments. On the other hand, ACSM was integrated into the new system to measure OM and make PM_{2.5} mass closure better. The SHARP-5030i monitor uses particle light scattering and Beta Attenuation Monitors, which are recommended for use in PM_{2.5} monitoring networks in China. Therefore, obtaining the comprehensive chemical species of PM_{2.5} measured by the SHARP-5030i monitor and apportioning the PM_{2.5} sources based on the mass closure data could be directly used to control PM_{2.5}. Researches have indicated that SOA is an important contributor of PM_{2.5} and that it originated from the oxidation of gas phase precursors (Carlton et al., 2009; Huang et al., 2018). It is currently difficult to measure SOA, and most estimates are indirect and use the OC/EC ratio, receptor models (e.g., CMB and PMF), and chemical transport models (Murphy and Pandis, 2009; Cesari et al., 2016; Al-Naiema et al., 2018). The ACSM can also measure the nucleus-mass ratios of fragmented ions, such as m/z44 (CO₂⁺), which is a good indicator for SOA (Zhu et al., 2018). We propose an improved source apportionment method using m/z44 as the prior information to introduce into the receptor model to solve the collinear problem and estimate SOA contributions to PM_{2.5} mass concentrations.

Here, the new online integrated system was deployed in Shenzhen, China in autumn for approximately one month, and its field performance was evaluated by comparing the results with other measurements of simultaneously collected data. The online receptor dataset also used to fully resolve the PM_{2.5} sources using receptor model. We used mass spectra information to constrain the SOA and successfully estimated SOA contributions to PM_{2.5}.

2 System design and integration

2.1 Objectives

Our study aimed to integrate the most reliable and stable online instruments under the current technology development level for components of PM_{2.5}. The same Cut Cyclone values could ensure the comparability of different instruments, and the sampling manifold was developed to ensure that particles enter each online monitoring instrument with minimum loss. The flowrate, pipeline turbulence and dehumidification effect need to be fully considered during the research and development of the manifold. The data analytics platform was designed to integrate and manage data automatically.

Based on the objectives above, the integrated system included three parts: sampling module, instrumentation, and data analytics platform, which was used to store data and perform analyses. The sampling module included a size-selective sampling head and a tube to deliver aerosol to the instrument. The instrumentation part included the online monitoring equipment for PM_{2.5} and its chemical components.

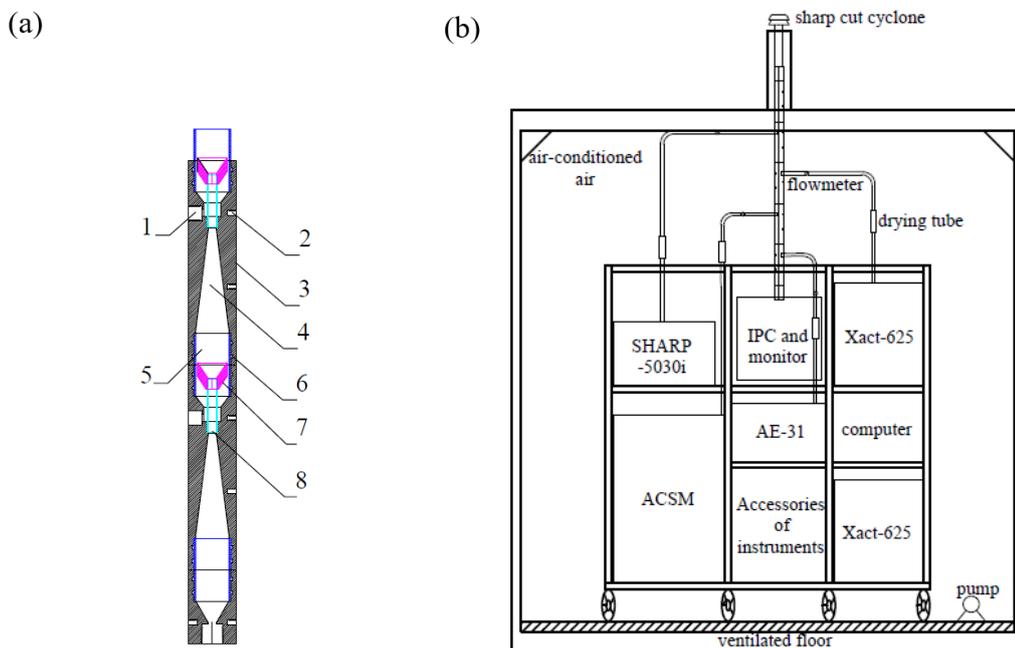
2.2 Instrument selection

To realize high temporal-resolution, precise, stabilized, and mass-closure chemical measurements of $PM_{2.5}$ concentrations, four typical online instruments were selected to integrate into the new system: ACSM, Xact-625, AE-31, and SHARP-5030i. $PM_{2.5}$ -capable Q-ACSM was selected for monitoring the mass concentrations of OM, SO_4^{2-} , NO_3^- , NH_4^+ , and Cl⁻ in non-refractory $PM_{2.5}$, the $PM_{2.5}$ -Q-ACSM equipped with a $PM_{2.5}$ lens and capture vaporizer (CV), and can detect approximately 90% of $PM_{2.5}$ particles (Hu et al., 2017; Xu et al., 2017; Zhang et al., 2017). Xact-625 was selected to obtain the hourly element concentration in $PM_{2.5}$. The quantification of 21 elements in $PM_{2.5}$, such as As, K, Co, Ti, Ca, Cr, Fe, Hg, V, Mn, Sn, Ni, Cu, Sb, Zn, Se, Mo, Cd, Ba, and Pb, was performed using nondestructive energy-dispersive X-ray fluorescence, which was certified by the United States Environmental Protection Agency IO3.3 (Ji et al., 2018). Modifications were conducted in the Xact-625 design to realize the measurement of Si, because it is a tracer of fugitive dust source (Taylor and McLennan, 1995). The BC mass concentration represented a large fraction in the atmosphere (Prasad et al., 2018), and the advanced AE-31 with 5 min temporal resolution was used for continuous monitoring of the BC mass concentration at seven wavelengths viz., 370, 470, 525, 590, 660, 880, and 950 nm. Due to strong absorption of BC aerosols at 880 nm, the mass concentrations measured at this wavelength were considered as a standard for BC measurements (Prasad et al., 2018). To monitor $PM_{2.5}$, a SHARP-5030i instrument was used. SHARP-5030i measures $PM_{2.5}$ mass concentrations based on the principles of particle light scattering (nephelometer) and beta attenuation. The monitor measures $PM_{2.5}$ mass concentrations every minute and reports hourly averages (Su et al., 2018). When the time resolution is 1 hour, the minimum detection limit is less than $0.5 \mu g m^{-3}$. (Ji et al., 2018). The quality control, uncertainty and detection limit of the instruments in the new online integrated system can be referred to SI.

2.3 Design of the rack and sampling module

The sampling module mainly involved the selection of the $PM_{2.5}$ Very Sharp Cut Cyclone (VSCC) particle size separator and the design of the particle isokinetic sampling manifold. A cyclone (sharp cut cyclone 2000-30EC, URG Inc. US) with a flow rate of 42 L per minute was selected, which was based on the total flow of the sampling instruments above. The main technical challenge in designing the sampling module was the sampling manifold, which needed to reduce turbulence due to the different flow rate of instruments. To solve this problem, a particle isokinetic sampling manifold was designed, which was equivalent to thin-walled, sharp-edged, isokinetic inlets (the velocity ratio of the velocity outside of the isokinetic inlet and the average sampling velocity in the inlet is 1) that were sampled isoaxially from vertical airflows under laminar flow conditions (Reynolds number < 2000), which is proven to sample particles with a transmission efficiency of close to 100% (Okazaki et al., 1987). As shown in Fig. 1a, the main pipe diameter was calculated according to the total flow rate of the integrated instruments and designed to be 31 mm to ensure that airflows under laminar flow conditions when it reaches the inlet of the isokinetic sampling tube. The gradual expansion angle of the gradual expansion channel in the pipeline was 7° to prevent the gas from separating from the pipe wall, and temperature, humidity and flow sensors were equipped on sample tubes to monitor the gas state. The

sampling flow of the sample tube was large to meet the needs of integration. After the test, the relative to standard deviation of the mass concentration among each instrument was within 5%. To integrate the instruments, a rack was designed according to the size of integrated instruments, on which aluminum plates were laid to form a platform for placing the instruments (Fig. 1b). A physical picture of the system is shown in Fig. S1.



130 **Figure 1. Structure diagram of the particle isokinetic sample tube (1-Aerosol outlet; 2-Screws for fixing; 3-Main pipe; 4-Gradual expansion channel; 5-Connecting pipe; 6-O-ring; 7-Isokinetic sampling tube; and 8-Connecting pipe) (a). Sketch map of integrated system (IPC=Industrial Personal Computer) (b).**

2.4 Design of the data analytics platform

To integrate online data, a data analytics platform (Fig. S2) was designed and used to export data from the integrated instruments with a uniform time resolution of 1 hour, and it was also able to display the variation trends of PM_{2.5} and its chemical components in real time and back up these data in an SQL server database. More details of the platform can be seen in SI.

3 Application of the online integrated system

3.1 Sampling site

140 The sampling site was in the Peking University Shenzhen Graduate School (22°35' 45" N, 113°58'23" E) which is in the western urban area of Shenzhen. Shenzhen is an international metropolis in China, surrounded by the south China sea to the southeast and industrial cities such as Dongguan and Huizhou to the west and north. It is located in the subtropical marine

climate zone, with more rainfall in summer influenced by monsoons and heavy pollution in autumn and winter due to the influence of inland air mass. The sampling site was surrounded by a large reservoir and recuperation base, with a high vegetation coverage ratio. There is no obvious pollution source except a city road about 100m away. The measurement campaign took place from 25 September to 30 November 2019, when the pollution usually started to worsen in Shenzhen. The meteorological conditions during the campaign were shown in Fig. S3. The average ambient temperature and relative humidity were $26.7\pm 3.8^{\circ}\text{C}$ and $71.9\pm 19.0\%$, respectively. The wind speed ranged from 0.1 to 6.9 m s^{-1} , with an average value of $0.6\pm 0.5\text{ m s}^{-1}$. The sampling site was mainly influenced by wind from the northeast and northwest.

3.2 Sampling instruments

During the sampling period, in addition to the online integrated system, another AE-31 and MARGA system were set for independent measurements at the same site. In addition, the offline $\text{PM}_{2.5}$ were simultaneously conducted every two days and each sample was collected for 24 hours. The sampling instruments and analytical methods of $\text{PM}_{2.5}$ chemical composition refer to previous studies by Huang et al. (2018). The performance of the online integrated system was thoroughly evaluated by comparison with the measurements above.

3.3 Source apportionment modeling

3.3.1 Multilinear engine (ME-2) model

ME-2 is a factorization tool for multivariate factors, which was developed by Paatero in 1999(Paatero, 1999). The basic principle of ME-2 can be expressed that the sample data matrix X are grouped into two constant matrix G and F, as follow: and make sure that all elements of G and F are non-negative.

$$X = G \times F + E \quad (1)$$

G and F are factor contribution and factor profile, respectively, which are non-negative. E is residual error matrix that the difference between measured value and the model value (Paatero and Tapper, 1994).

The objective of the ME-2 model is to minimize the equation Q, as follow:

$$Q = \sum_{i=1}^m \sum_{j=1}^n (e_{ij}/u_{ij})^2 \quad (2)$$

where e_{ij} is the element of the matrix E and u_{ij} is the error/uncertainty of the measured concentration x_{ij} . Source Finder (SoFi) software was developed by the Paul Schell Institute (PSI) in Switzerland, which can provide some constrained factors to realize the source constraint of ME-2(Canonaco et al., 2013). The species uncertainties (u_{ij}) are estimated as follows:

$$u_{ij} = k_j \times x_{ij} \quad (3)$$

where the x_{ij} is the concentration of the species and k_j is the j^{th} species' error fraction (Huang et al., 2018), which is usually thought to be between 5% and 30% (Zou, 2018). Through testing, the k_j in this study was set as 20%, and some species were expanded or decreased according to the results of model operation. When the species concentration is greater than or equal to the detection limit (DL), the uncertainty can be estimated according to the Eq. (3). Conversely, the concentration was treated

by 1/2 DL and its uncertainty was set as 5/6 DL. Missing data were treated by the species' average value (geometric), and their uncertainties were assumed to be 4 times of the average value.

3.3.2 Constraint setup in ME-2 modeling

175 SoFi was performed to initiate and control ME-2 model, and it was run for the online datasets observed by integrated system in this study. Species that satisfied one of the following conditions were excluded: (1) more than 40% data were smaller than the DL of species, (2) less relevant to other species ($r^2 \leq 0.4$), and (3) low concentration and can not to be used as a tracer for pollution sources. Therefore, 13 species, accounting for 98.6% total mass concentrations of the measured species (except m/z 44), were input into the models: OM, BC, Cl⁻, NO₃⁻, SO₄²⁻, NH₄⁺, K, Ca, Fe, Zn, V, m/z44.

180 Compared with some other interrelated studies, fragments of organic matter with m/z44 were input into the model to track the SOA. m/z44 is mainly composed of fragments of carboxylic acid ions CO₂⁺, which is produced from the cracking of carboxylic acid in organic aerosols and can represent the strength of oxidation of organic aerosol (Hu, 2012). Therefore, m/z44 was used to characterize the SOA with strong oxidization.

Based on the experience of our previous studies on source resolution in Shenzhen (Huang et al., 2018; Shen et al., 2019) and 185 the introduction of SOA tracers, four factors were constrained as listed in Table 1: SOA, secondary sulfate, secondary nitrate, and fugitive dust. For the secondary sulfate and nitrate sources, the primary source components, OM, and m/z44 in the factors were set to 0 while NH₄⁺ and SO₄²⁻/NO₃⁻ were not limited. For the SOA, OM and m/z44 were not limited. Based on a study of fugitive dust source profiles (Peng et al., 2016a), the earth crust elements (e.g., Si, Ca, and Fe) and OM were not limited in the fugitive dust.

190 **Table 1. Detailed constraints of the four factors using in ME-2.**

Factors	OM	BC	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻	NH ₄ ⁺	K	Si	Ca	Fe	Zn	V	m/z44
Secondary sulfate	0	0	0	-	0	-	0	0	0	0	0	0	0
Secondary nitrate	0	0	0	0	-	-	0	0	0	0	0	0	0
SOA	-	0	0	0	0	0	0	0	0	0	0	0	-
Fugitive dust	-	0	0	0	0	0	0	-	-	-	0	0	0

3.3.3 Potential source contribution function (PSCF) analysis

The PSCF was based on the analysis results of a backward trajectory, and it was used to analyze the potential regions of the possible sources of PM_{2.5}. Unlike the backward trajectory, which could only obtain the pathways of the air masses, PSCF can also analyze the regional transmission contribution of pollutants from different sources in the region of a given day. In TrajStat 195 software, the movement of an air mass is described by segment endpoints of latitude and longitude coordinates (Wang et al., 2009). Before performing the PSCF analysis, the coverage area of the trajectory was 15-40°N and 90-140°E and the grid

resolution was set to $0.4^{\circ} \times 0.4^{\circ}$ grid cells. The PSCF values for grid cells were calculated by the ratio of the number of contamination trajectory full in the grid cells and the number of all trajectories passing through the area. The PSCF can be defined as follows:

$$200 \quad PSCF_{ij} = \frac{m_{ij}}{n_{ij}} \quad (4)$$

where: i and j are latitude and longitude, respectively; $PSCF_{ij}$ is the PSCF value for the ij^{th} grid cell; m_{ij} represents the number of endpoints corresponding to specific source contribution above the threshold criterion, which is set to the 75th percentile of each source contribution; and n_{ij} represents the total number of endpoints falling in the grid cell ij .

To avoid the uncertainty caused by the limited number of endpoints in a single grid, a weight function W_{ij} is also considered here as shown in Eq. (5) and Eq. (6). For example, when the total number of trajectory endpoints in each grid (n_{ij}) is higher than 20 (the average endpoint) but less than 40 (4 times of average endpoint), the weighted PSCF value (WPSCF) of that grid is reduced by multiplying its original value by 0.7. The WPSCF results were used in the following discussion and called PSCF in this work.

$$WPSCF = PSCF_{ij} \times W_{ij} \quad (5)$$

$$210 \quad W_{ij} = \begin{cases} 1.00 & n_{ij} > 40 \\ 0.70 & 20 < n_{ij} \leq 40 \\ 0.42 & 10 < n_{ij} \leq 20 \\ 0.05 & n_{ij} \leq 10 \end{cases} \quad (6)$$

4 Results and discussion

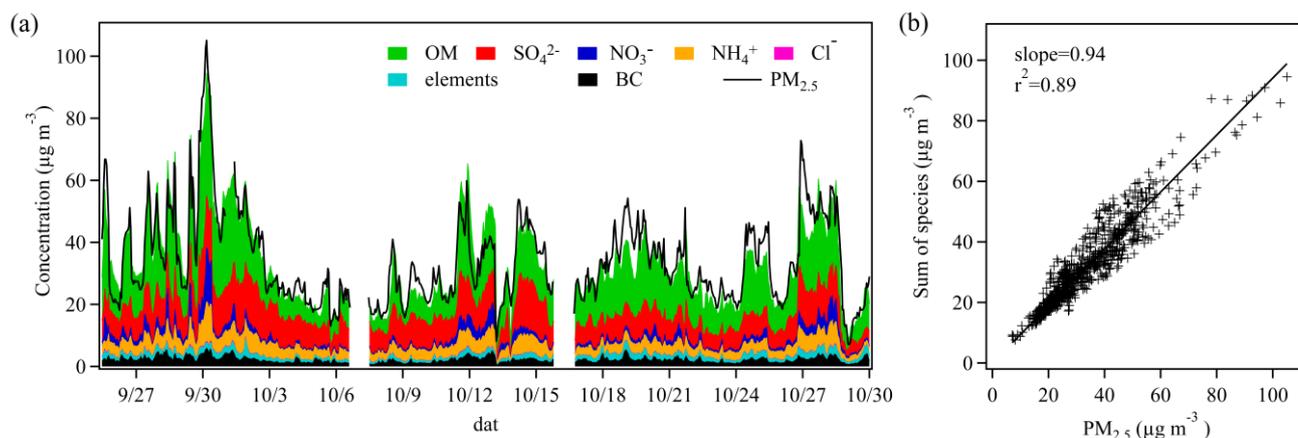
4.1 Overview of chemical species and PM_{2.5} concentrations

The time series of hourly PM_{2.5} concentration and chemical species and the average concentration results are shown as Fig. 2a and Table S1, respectively. Based on hourly data, PM_{2.5} concentrations ranged from 5 to 107 $\mu\text{g m}^{-3}$, with an average value 215 $33 \pm 14 \mu\text{g m}^{-3}$, which was lower than the NAAQS (National Ambient Air Quality Standards, China, 2012) and the Grade II national standards for air quality (with an annual mean of $35 \mu\text{g m}^{-3}$). OM ($14.1 \pm 7.4 \mu\text{g m}^{-3}$), SO_4^{2-} ($8.6 \pm 3.3 \mu\text{g m}^{-3}$), NO_3^- ($1.8 \pm 1.9 \mu\text{g m}^{-3}$), NH_4^+ ($3.8 \pm 1.7 \mu\text{g m}^{-3}$), and BC ($2.1 \pm 1.0 \mu\text{g m}^{-3}$) were the major species, with average percentages of 41%, 25%, 5.3%, 11%, and 6.4% in PM_{2.5}, respectively. The major elements included Si (1.3%), K (1.3%), Fe (0.91%), Ca (0.35%), Zn (0.31%), and the trace elements accounted for 0.84% in PM_{2.5} (Fig. 3).

220 4.2 Evaluation of PM_{2.5} mass closure

To access the accuracies and mass closure of the receptor data from the integrated system, we reconstructed the PM_{2.5} mass concentration according to the summation of chemical components. However, the correlation between the reconstructed and measured PM_{2.5} mass concentration was shown as Fig. 2b. Reliable data were measured by the online integrated system and supported by the good correlation (correlation coefficient squared $r^2=0.89$) and the slope (0.94), which was close to 1, and the

225 results indicated that the integrated system can measure 94% of the particulate matter components and achieve mass closure.
The average error margin of mass closure during the observation period is about 6%, which might be due to the measurement
error of the integrated instruments, particle composition, temperature and relative humidity (Su et al., 2018; Zhang et al., 2017).
A significant mass discrepancy between reconstructed and measured $PM_{2.5}$ appeared in some periods (Fig. 2a). For example,
the underestimation on October 3 and the overestimation on October 20 occurred when the temperature was the highest and
the lowest during the observation period, respectively. Therefore, it was speculated that temperature might affect the
composition of $PM_{2.5}$, causing the mass closure to deviate. The online integrated system can measure more chemical
components than other online instruments, for example, online continuous monitoring and analysis systems (AIM-URG9000d,
USA) for water-soluble components of fine particulate, which can measure water-soluble ion contents and accounted for about
40% of $PM_{2.5}$ mass concentrations (Yuan et al., 2018). A semicontinuous OC/EC analyzer with 1 h time resolution could obtain
the concentrations EC and OC, which accounted for approximately 30% of the $PM_{2.5}$ (Liu et al., 2017). Wang et al. (2018)
measured the chemical compositions using MARGA, a semicontinuous OC/EC analyzer, and Xact-625 and reported the sum
mass concentration of measured species accounted for ~78% of $PM_{2.5}$.



240 **Figure 2.** The trend in hourly $PM_{2.5}$ and chemical species during the sampling campaign (a). The correlation between $PM_{2.5}$
reconstructed and measured (b). Note that the term of “Sum of species” means the total mass concentration of chemical species from
online integrated system, and “ $PM_{2.5}$ ” indicates mass concentration of SHARP-5030i $PM_{2.5}$.

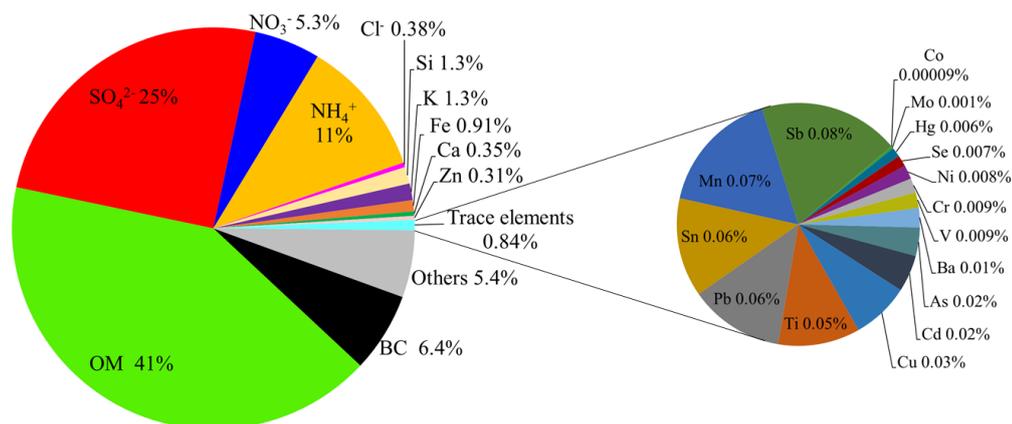


Figure 3. Chemical compositions of average PM_{2.5} during the sampling campaign.

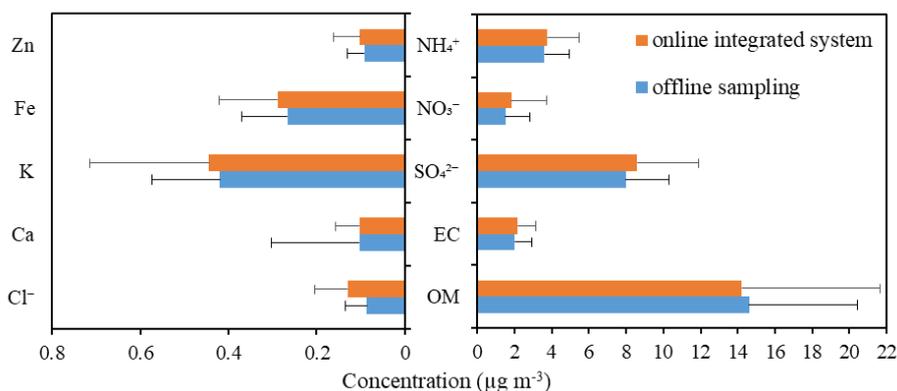
4.3 Comparison with colocated measurements

245 The average of PM_{2.5} concentrations from offline sampling was 32 $\mu\text{g m}^{-3}$, which was consistent with the integrated system, and the chemical components in PM_{2.5} also obtained similar results (Fig. 4), in which OM measured by online integrated and offline system were 14.6 $\mu\text{g m}^{-3}$ and 14.2 $\mu\text{g m}^{-3}$, while SO₄²⁻, NO₃⁻, NH₄⁺ were 7.9%, 19.7%, and 5.0% higher in online integrated system, respectively, which is possibly due to the volatilization and loss of sample during the process of offline sampling, storage, and analysis. The BC measured by the online integrated system was 8.4% higher than the EC in the offline system, and the differences of important elements were relatively small. In general, the online and offline measurement were close to each other, which indicated that the online integrated system was accurate to some extent.

250 Comparing the data with the results of other method analysis usually be used to further examine the reliability of online instruments. The BC showed high correlation with measurements of another AE-31 ($r^2=0.99$). On average, the mass concentrations of BC measured by integrated system reports 95% of those measured by the independent instruments (Fig. S4), suggesting the sampling model of online integrated system could avoid sampling loss effectively and was reliable. This slight underestimation of BC mass might be primarily due to the distance between sampling ports or the systematic errors between instruments.

255 Figure S4 shows the intercomparisons of the measurements by the ACSM with MARGA, including SO₄²⁻, NO₃⁻, NH₄⁺, and Cl⁻. Overall, the three ions measured by the ACSM correlated well with MARGA ($r^2=0.94-0.96$). The sulfate average concentrations between ACSM and MARGA were consistent (slope=0.97). The ammonium concentrations measured by ACSM accounted for 88% of that determined by MARGA, which might relate to the aerodynamic lens transmission efficiency of ACSM. When the particle size was less than 300 nm, the transmission efficiency was lower (Middlebrook et al., 2012). For nitrate, the ACSM measurements approximately 64% of what was reported by the MARGA. ACSM measured a lower Cl⁻ concentration (slope=0.39) and a relatively poor correlation with MARGA's Cl⁻ ($r^2=0.42$). Another study also found a large difference between ACSM and MARGA when measuring chloride and nitrate (Zhang et al., 2017). Besides, the evaluation of

PM_{2.5}-AMS also found a large difference in the measurements of Cl⁻ (Hu et al., 2017), which might be caused by the measuring principle of the instrument. K obtained good correlation between the Xact-625 and MARGA ($r^2=0.75$, Fig. S4), and the average ratio of Xact-625 to MARGA was 1.18, which might be caused by the slight difference between the K element and K⁺ in PM_{2.5} as well as the differences of measurement principles. This result suggested the reliability of the Xact-625 in measuring elements.



270

Figure 4. Concentrations of major chemical compositions of PM_{2.5} measured by online Integrated system and offline sampling. Note that the EC in the online integrated system was referred to as BC.

4.4 Source apportionment analysis

4.4.1 Source apportionment results

275 In this study, the SoFi tool was used to run the ME-2 model based on the predetermined constraints (Table 1) and to realize the source apportionment, 7-10 factors solution were tried, and the result of nine factors showed the best source profiles ($Q_{\text{true}}/Q_{\text{exp}}$ ratio was 1.2), with the scaled residuals distributed between -3 and +3 approximately symmetrically (Fig. S5). when the factor number was less than 9, the $Q_{\text{true}}/Q_{\text{exp}}$ was too high, while the factor number was more than 9, a meaningless high OM source would appear. The total mass concentration of the components (m/z44 was not included here because it was the
280 part of OM) input to the ME-2 model was significantly consistent with the total mass concentration of the model reconstruction ($r^2=0.99$, slope=0.98).

Profiles of each factor were shown Fig. 5a. From top to bottom, factor 1 had large percentage explained variation (EV) values of SO₄²⁻ and NH₄⁺, and was identified as secondary sulfate (Huang et al., 2018). Factor 2 was related to secondary nitrate, due to significant EV values of NO₃⁻ and NH₄⁺ (Huang et al., 2018). Factor 3 was identified as SOA, which has a significant EV
285 value of m/z44 and OM, m/z44 had high concentration in this factor, thus suggesting it is a good tracer of SOA. Previous study tried to identify SOA using receptor model and indicated SOA mixed with secondary sulphate and/or secondary nitrates due to the lack of tracer (Huang et al. 2018), in this study, the effective tracer of SOA was introduced into the model resulting in the SOA was identified separately. **Factor 4 was associated with coal burning due to the high EV value of Cl⁻, which is formed by the rapid combination of HCl and ammonia in the atmosphere, and the potential source of HCl is coal burning in China**
290 **(Yudovich and Ketris, 2006; Wang et al., 2015) and the concentration distribution of Cl⁻ in the Pearl River Delta was consistent**

with the distribution of coal-fired power plants in the source list (Huang et al., 2018), This factor also had some mass contributions from SO_4^{2-} , NO_3^- , and EC, further confirming that it was from coal burning (Zheng et al., 2013). Factor 5 was explained as fugitive dust due to its high EV values of Si and Ca, which came from the earth crust and building dust, respectively (Feng et al., 2003). The integrated system does not involve the measurement of oxygen (O) and Al. Instead, the contents of O and Al in factor 5 were estimated indirectly based on the abundance of the three (Al, O, Si) in the crust. (Taylor and McLennan, 1995). Factor 6 has a high loading of K and a certain of OM and BC. K has been used as a clear tracer for biomass burning (Yamasoe et al., 2000; Sillapapiromsuk et al., 2013). Biomass burning is a significant source of $\text{PM}_{2.5}$ and organic matter in China. The Zn contained in this factor might be related to garbage-burning (Yuan et al., 2006). Besides, biomass burning has a high contribution from north and south-west (Fig. 8), which is consistent with the distribution of fire points in Guangdong (Fig.S6). The activities of biomass burning often occurs during the daytime, which consisted with the diurnal pattern of biomass burning that high day concentration and low night-time (Fig. 7). Factor 7 was identified as vehicle emissions due to the high concentrations of OM and BC related to oil combustion. This factor also showed certain loading of Fe might come from tires and the brake wear of vehicle (He et al., 2011; Yuan et al., 2006). Factor 8 displayed large EV values of Zn, and Fe and Ca also had high enrichment factors. The Zn might have been due to industrial sources, such as plastic incineration, coating and metallurgy (Zabalza et al., 2006; Cruz Minguillón et al., 2007); the Ca might come from the soot produced by the inferior coal and diesel combustion in the industry (Lewis and Macias, 1980); and the Fe might be related to ceramic production (Querol et al., 2007) and thus was considered to be related to industrial processes. Factor 9 was ship emissions due to a large EV values of V. V is mainly produced by burning of heavy oil, which is the fuel of ships in the port of Shenzhen (Huang et al., 2014). The factor of sea salt cannot be identified in this study, because the measurement of its tracer (Na) is limited for X-ray fluorescence method and ACSM. However, the contribution of sea salt is little for Shenzhen (about 1% to 3%), and is not the main source of pollution. High time resolution of source contributions could be output when source apportionment was performed using online datasets. Fig. 5b shows the time series of each source as well as their corresponding tracers during source resolution in Shenzhen. The sources had a very good correlation with the tracer species ($r^2=0.79-0.99$), suggesting that the model could identify representative pollution factors. Compared with primary sources, secondary sources fluctuate more dramatically with time. Among all the sources, the trend of secondary sulfate was closer to $\text{PM}_{2.5}$, reflecting that it was the one of the main contributors to $\text{PM}_{2.5}$.

Figure 6a showed the average contributions of the $\text{PM}_{2.5}$ sources during the sampling period. It can be seen that the SOA, secondary sulfate, vehicle emissions, and biomass burning were the main sources in Shenzhen, contributed 23%, 22%, 18%, and 11% of $\text{PM}_{2.5}$ mass concentration, respectively. The total contribution above four sources was more than 70%. The contributions of the other source were smaller (2%-8%), from large to small were coal burning (8%), secondary nitrate (5.3%), fugitive dust (3.8%), and ship emissions (3.7%). The unidentified sources accounted for 3.4%, which was caused by a combination of residuals from ME-2 model and measurement deviations of integrated system.

As shown in Fig. 6b, the contribution change of $\text{PM}_{2.5}$ factors with the change of total $\text{PM}_{2.5}$ concentration was analyzed. Secondary sulfate and biomass burning decreased when pollution was heavy while the secondary nitrate and SOA increased.

325 Therefore, secondary conversion of carbon-containing and NO_x components were the causes of heavy PM_{2.5} pollution during the observation period.

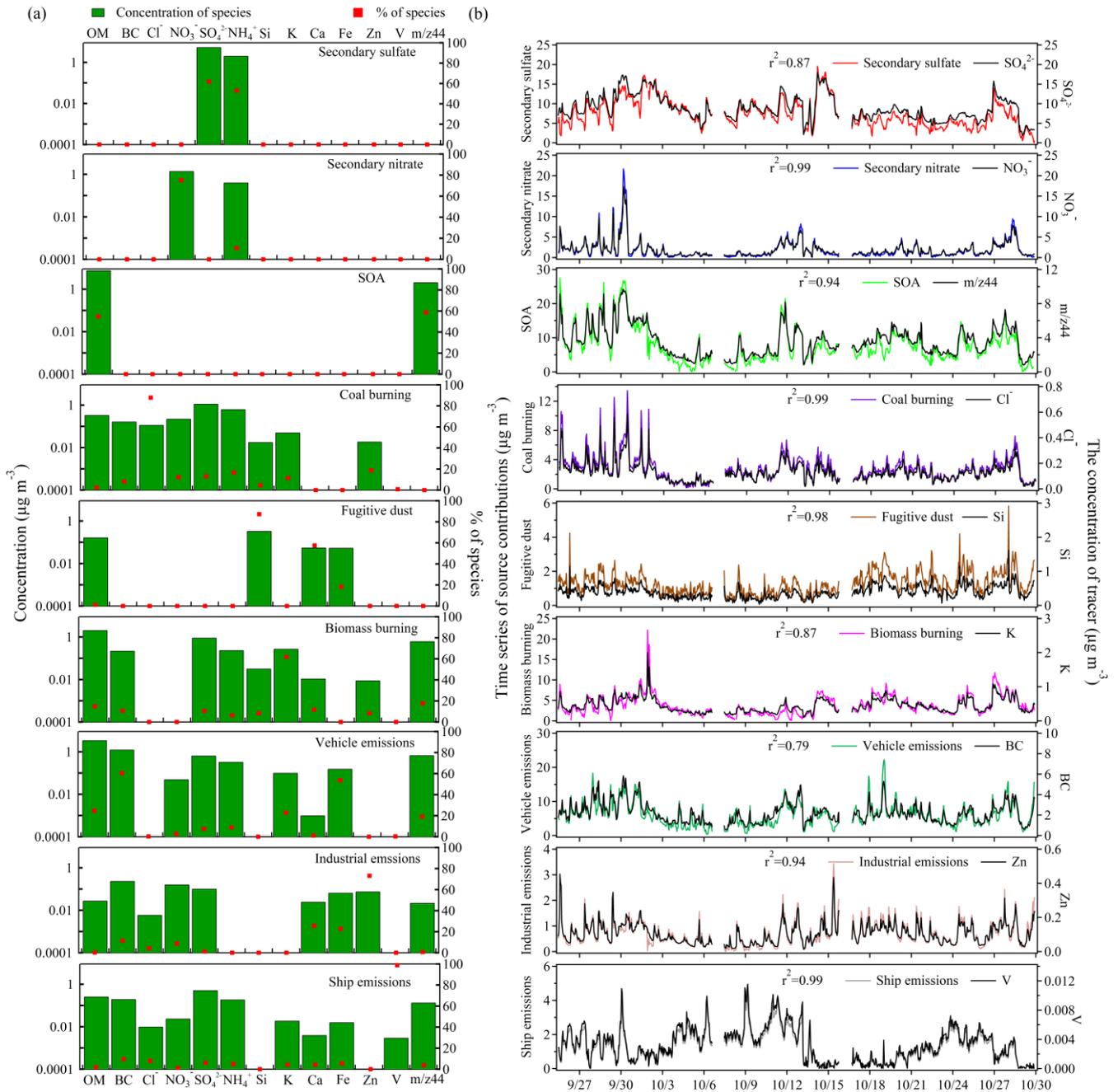


Figure 5. Factor profiles and EV in the ME-2 model results(a). Time series of PM_{2.5} sources and tracers (b).

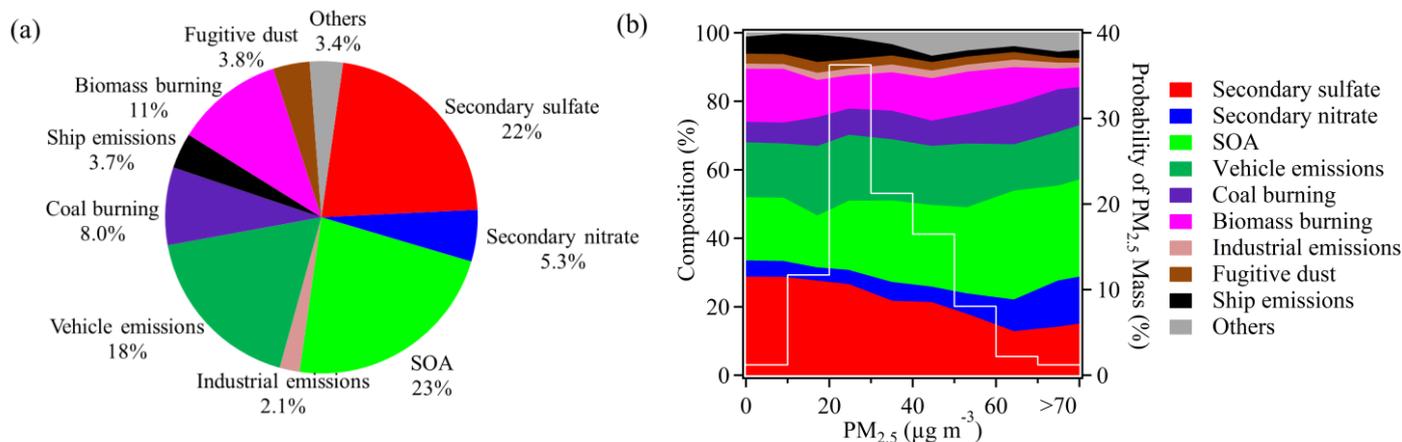


Figure 6. Average contributions of each source to PM_{2.5}(a). Variation in the proportion of sources in PM_{2.5} during the observation period. The white curve represents the occurrence probability of the PM_{2.5} concentration (b).

335 4.4.2 Diurnal variations

Diurnal variations of source were obtained based on the high time-resolution data, which could help to evaluate the validity of the source apportionment and investigate the causes of PM_{2.5} pollution further. The average diurnal trends of major sources are shown in Fig. 7. Secondary sulfate diurnal variations presented relative high afternoon concentrations and low night-time concentrations; moreover, a broad peak from 12:00 to 20:00 might be related to light intensity, suggesting that sulfate was largely formed by photochemical processes (Liu et al., 2008). In contrast, secondary nitrate had a peak during 9:00-10:00 that was slightly later than the morning rush hour for motor vehicles because the NO_x in vehicle exhaust was an important source of secondary nitrate. The pattern (high night-time concentration and low afternoon concentration) might be caused by the diurnal variation of boundary layer. Decreasing in solar activity at night resulted in the height of boundary layer decreased and the inversion layer occurred. (Xu et al., 2014), which was not conducive to the diffusion of pollutants. Moreover, the pattern might due to the evaporation of ammonium nitrate produced by the secondary reaction at high temperature in the afternoon. The variation of SOA was related to the photochemical reaction of VOCs. When the sun rises during the day, the boundary layer was gradually elevated, which led to lower concentrations of residual SOA in the atmosphere, and it reached its lowest point between 8:00 and 9:00. After that, SOA rose and peaked at 14:00 due to the enhancement of light. It was consistent with the theoretical changes in SOA (Liu et al., 2018). For primary sources, vehicles, ships and industrial emissions showed the characteristics of "two peaks and one valley", which were basically consistent with the law of human activities. This finding suggested that human activities have a significant impact on environmental pollution. Biomass burning and fugitive dust showed a trend of high day concentration and low night-time, which might be because of the local emissions (such as biomass boiler, construction activities) during daytime that are mixed with the pollutants transported from other regions as the rise of

boundary layer at morning (Sun et al., 2019). Analyzed with the time series of pollution sources (Fig. 5b), the results showed, the peaks around 22:00 and 1:00 of biomass burning was mainly due to the abnormally high source contribution, on the night of October 1, which is China's National Day, and there were displays of fireworks from September 25 to October 1 at 3 playgrounds 10 km away from sampling site. Previous study has shown that the concentration of species (e.g. K, Ca, Cl⁻, NO₃⁻) in the PM_{2.5} would have greatly increase due to the fireworks (Tsai et al., 2012). The spike at 1:00 of fugitive dust and biomass burning mainly caused by several abnormally high values at 1:00, suggesting it might be due to the influence of local short-term activities. The daily variation of coal burning and Cl⁻ was consistent (Fig. S7), and there is a peak around 9:00 in the morning. It might because the temperature starts to rise in the morning and the vertical air convection activity is strengthened, bringing the pollutants transmitted by overhead sources to the near ground. The spike around 22:00 was mainly because of firework shows during September 25 to October 1. The peak around 14:00 mainly came from local sources on September 25. Diurnal variations of each source were more consistent with the actual situation, which indicated that the results of source apportionment were reasonable.

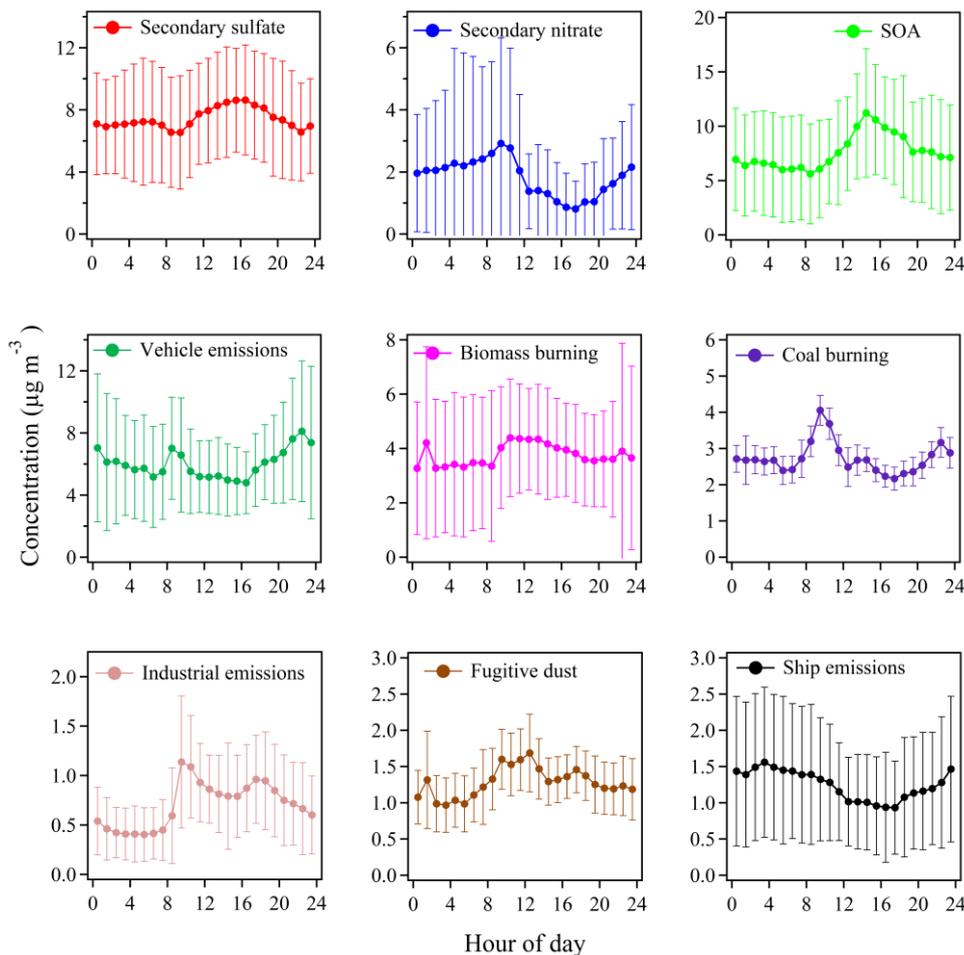


Figure 7. Diurnal variations of the nine sources resolved by ME-2.

4.4.3 Potential source areas

The potential source areas for different sources were identified by the PSCF model as shown in Fig. 8. During the observational campaign, Shenzhen City mainly influenced by the continental and coastal air masses coming from the northeast of the domain and to a lesser extent by the air masses originating from southwest of the city. The continental air masses transported from the northern of Guangdong Province, Jiangxi Province, and Yangtze River Delta region, where there are highly urbanized and industrialized areas. The coastal air masses stemming from the East Sea and Taiwan Strait. The secondary sulfate showed two potentially important source areas located in the northern and southwestern of the sampling site. The southwestern potential source areas indicated that regional influences were important to the secondary sulfate. Compared with secondary sulfate, the high potential source region of secondary nitrate was closer to the sampling site and mainly located in the southwestern and northern areas. These findings implied that secondary nitrate was from local secondary aerosol rather than regional transport. The PSCF plot of SOA displayed a clear high-potential source region in northern Guangdong Province, including the cities of Dongguan, Huizhou, and Shaoguan. The PSCF plot of vehicle emissions showed potential source areas around the sampling site. Fugitive dust and biomass burning have similar potential source region originated from the northeast area of the site, suggesting the two sources may be influenced by the regional transport. This result was consistent with the high fugitive dust and biomass burning contributions to PM_{2.5} at daytime, which are partly related to regional transport (Fig. 7). Sun et al. (2019) conducted vertical observations of air pollutants (SO₂, O₃, NO_x, PM₁₀, PM_{2.5}) and revealed the obvious regional transport in Shenzhen. In addition, biomass emission also showed high-potential source regions in the northern area Guangdong Province. The PSCF plot of biomass burning indicates local emissions as well as regional influences. Coal burning high-potential source areas were similar but smaller compared to those of industrial emissions, which were mainly located in the northern area of Shenzhen. The potential areas of ship emissions were consistent with the coastal regions, where there are many shipping ports, especially the Shenzhen ports, which are the third largest in the world and have active shipping lanes with traffic volumes up to 500,000 transits in 2015 (Mou et al., 2019). In summary, the PSCF analysis indicated that the northern domain was the high potential source region for secondary aerosol, coal burning, and industrial emissions. Vehicle emissions and secondary nitrate were mostly influenced by local emissions. For fugitive dust, biomass burning, ship emissions, and secondary sulfates, the potential source areas on a regional scale were important in this study.

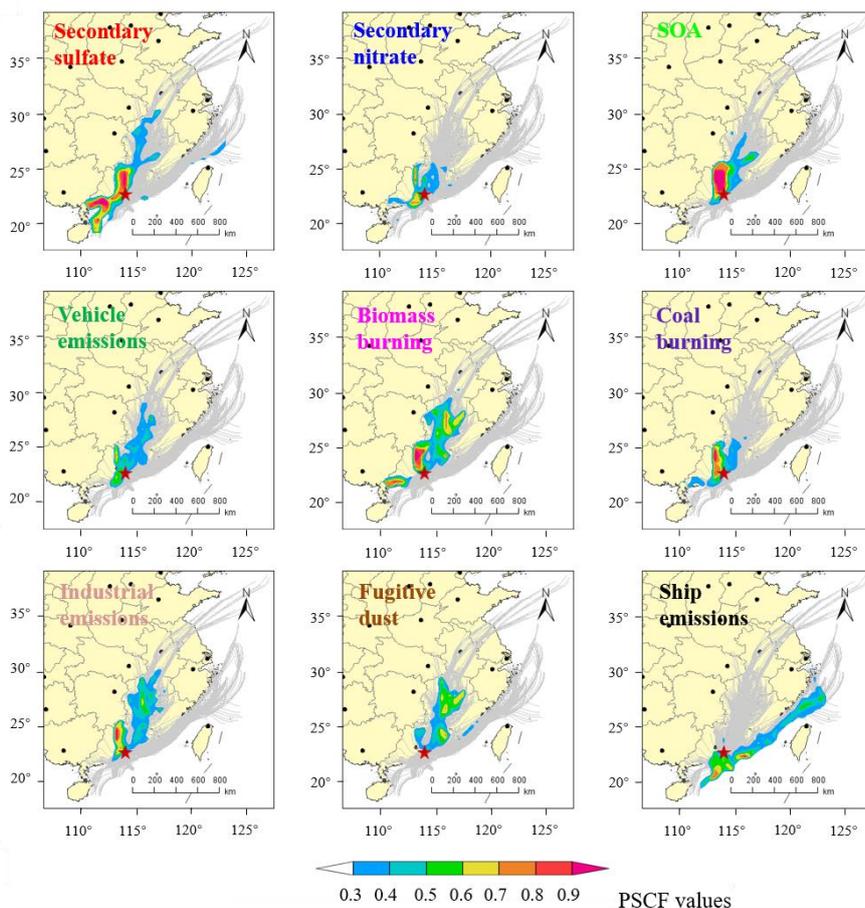


Figure 8. Spatial distributions of PSCF values for the nine sources resolved by ME-2.

395 5 Conclusions

In this work, a new online integrated system for the measurement of chemical species in $PM_{2.5}$ was developed by combining ACSM, Xact-625, AE-31, and SHARP-5030i. A sampling tube was designed to reduce aerosol transmission loss. Approximately 94% of $PM_{2.5}$ components can be detected, and the data (except Cl⁻) were well correlated with those measured by other independent online instruments (MARGA, AE-31), with r^2 values ranging from 0.74 to 0.99. The concentrations of chemical components were similar to those of offline sampling. To more accurately reveal the $PM_{2.5}$ pollution characteristics, the new online integrated system was applied at the university area of Shenzhen in the autumn of 2019. The average $PM_{2.5}$ concentration was $33 \mu g m^{-3}$ during the sampling period, of which SO_4^{2-} , OM, NH_4^+ , BC, NO_3^- , important elements, and Cl⁻ contributed 25%, 41%, 11%, 6.4%, 5.3%, 5.0%, and 0.38%, respectively. The chemical composition measured was close to the mass closure.

400

405 An improved source apportionment method was established by employing the ME-2 model on the mass spectra information
(m/z44) and chemical species measured from the online integrated system to solve the SOA contributions. SOA was found to
be the dominant source (23%), followed by secondary sulfate (22%), vehicle emissions (18%), biomass burning (11%), coal
burning (8.0%), secondary nitrate (5.3%), fugitive dust (3.8%), ship emissions (3.7%), and industrial emissions (2.1%). The
online integrated systems applied for source apportionment could obtain more accurate results through the analysis of time
410 series trend and diurnal variation. The emission source had high correlations with the tracer species ($r^2=0.79-0.99$). Secondary
sulfate and SOA showed high concentrations during the daytime, which was associated with photochemical processes. The
concentration of secondary nitrate was high at nighttime and low in the afternoon, and the variation of primary sources was
basically consistent with the law of human activities, indicating that the results of source apportionment were reasonable. The
results of the PCSF model indicated that the northern area of the sampling site was the potential source region during the
415 sampling campaign and regional transmission (e.g., biomass burning, fugitive dust, etc.) and played an important role in PM_{2.5}
pollution in this work. The development and successful application of the online integrated system and source apportionment
method suggested that they can be used for precise regulation of PM_{2.5}. **The high time resolution source analysis of the new
integrated system is helpful to study the variation of the primary and secondary sources of PM_{2.5} in the process of heavy
pollution (such as fireworks), and to identify the key sources and its mechanism, then to assess the impact of different sources.**
420 **The system can run stably for a long time, and provides a key scientific basis for particulate matter control of China.**

Data availability. Datasets are available by contacting the corresponding author, Xiao-Feng Huang (huangxf@pku.edu.cn).

Author contributions. XFH, CPS, and XP analyzed the data and wrote the paper. XFH, LWZ, and LYH designed the study.
425 CPS, MXT, YC and YW performed the chemical analysis. BZ performed the PSCF modelling. All authors reviewed and
commented on the paper.

Competing interests. The authors declare that they have no conflict of interest.

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