Point-by-point Response to review comments (ACP-2022-100)

We thank both reviewers for their constructive comments. Our point-by-point response to the comments is given in the following. The response text is marked in blue. References cited in this response document are placed at the end.

Anonymous Referee #1

General comments

The essential information for major sources as well as evaluation and planning of control measures in Hong Kong, China, was proposed based on 10 years of long-term monitoring data of $PM_{2.5}$. Overall, it is an interesting study. The test and analysis procedures are reliable and the amount of data are sufficient. The manuscript can be accepted with the following revisions:

Comments

1) *Chlorine loss of sea salt aerosol was always found in the sampling area, however, particulate chloride were not found in the chemical analysis and long term variation analysis. It was also suggested to analyze the trend variation of Criteria gaseous pollutant data.*

Response: As the reviewer has pointed out that chlorine loss of sea salt aerosol was common and was also observed in our sampling location. The chloride concentrations were at very low levels at our study site over the years (e.g., as low as 0.09 $\mu g/m^3$ in 2011). The chloride data were lumped into "salt", which is the sum of Na^+ and Cl^- and shown in the 10-year time series plots of monthly averages and annual averages of $PM_{2.5}$ chemical composition in Figure 2. Shown in Figure 3, "salt" made up a very minor part (<4% in all years) of $PM_{2.5}$. We now also add the individual temporal variation plots of Na^+ and Cl^- in Figure S3.

Due to the low concentration levels, the Cl^- data were associated with large measurement uncertainties. One more complicating factor was that nylon filter substrates were used during 2008-2010 while quartz filter substrates were used during 2011-2017 for IC analysis of the ionic constituents. It is known that nylon filters had higher efficiency in retaining chloride while quartz filters suffer negative sampling artifacts due to volatilization of chloride following acidification to HCl by co-existing sulfate (e.g., HSO_4^-) (Tsai and Perng, 1998; Tsai et al., 2005). The known systematic bias for Cl^- measurements between the two sampling media used during the ten-year period, together with the low concentration levels, does not adequately long-term variation analysis.

The following text is added to comment on chloride data, in association with the "salt" component:

> Line 243 – 244
>
> "Salt", consisting of Na^+ and Cl^-, was a very minor part of $PM_{2.5}$, accounting for less than <4% in all years."

Regarding the trend variation of criteria gaseous pollutants, we'd like to clarify that they are already illustrated in Figure 4 and summarized in Table 2. Extended discussion about the influence effect of gaseous pollutant variation on the secondary formed products (sulfate and nitrate) was provided in section 3.4. Thus, we did not expand the section other than adding a sentence to convey the use of gaseous pollutants in this study.

> Line 152 – 154
>
> "The temporal variations of gaseous pollutants serve as additional data valuable for exploring the effects of changes in precursor gases on the secondary formed $PM_{2.5}$ constituents (e.g., sulfate and/or nitrate)."

2) *Figure 1: The resolution of Figure 1 needs to be improved.*

Response: Thank you for careful checking on the resolution of figures. A higher resolution version of Figure 1 is created and incorporated in the manuscript.

3) *Lines 100-113: The authors collected blank samples as a background correction? and how were filter samples stored after collection? More information about sampling and storage should be presented in Ms.*

Response: Field blanks were collected at a frequency of 10% of a sampler's routine operating frequency. They were used to monitor contamination throughout the process from sampling to analysis and for background correction, if necessary. The field blank filters were stored and analyzed following the same procedures as those of $PM_{2.5}$ sample filters for quality assurance (QA) purposes.

The following text is added to provide more details about the sampling and storage procedures in our study:

> Line 112 – 118
>
> "After the collections, the 47-mm Teflon filters were stored in Petri dishes and the 47-mm quartz filters were stored in the dishes lined with aluminum foil. The dishes were sealed with parafilm. While the 20x25 cm quartz filters were folded in half and stored in aluminum foil. All the filters were packed in a thermal bag for transportation to the laboratory and refrigerated under 4°C before chemical analysis. Field blanks were collected at a frequency of 10% of a sampler's routine operating frequency. They were used to monitor contamination throughout the process from sampling to analysis and for background correction. The field blank filters were stored and analyzed following the same procedures as those of $PM_{2.5}$ sample filters for quality assurance purposes."

4) *Double "in" were found in line 178. Moreover, please recheck the English by a native Editor*

Response: Thank you for careful reading. Line 178 is revised.

5) *Line 136: Table 1 should be revised to a trilinear table.*

Response: We are unsure what is "trilinear table". We now revise the column arrangement of this table to make it more easily comprehended.

6) *Line 230: "For winter PM_5, the relative importance of OM increased (up from 31% in 2008 to 40% in 2017)… as well as EC (down from 7.8% to 5.3%)." I can't find any value of 31% in 2008 to 40% in 2017 in the wintertime figure (Figure 3).*

Response: We double checked the values used for the figures and they were calculated correctly, which means that the number in text are somehow copied wrongly from the results. All the numerical values in the text are now re-examined and any similar issue was now corrected.

The following text is now revised with correct percentage values:

> Line 238 – 239:
>
> "For winter $PM_{2.5}$, the relative importance of OM increased (up from 35% in 2008 to 39% in 2017) while the relative abundance of nitrate decreased (down from 9.1% to 6.6%), as well as EC (down from 6.1% to 4.4%)."

7) *Line 231: Valid numbers should be uniform.*

Response: The numbers in text are now rounded to 2 significant figures. (Please refer to the revised sentence in response#6)

8) *Line 233: Do authors have any ideas about the decrease percentage of EC in summer was about 4 times higher than that in winter?*

Response: The changes in percentage (i.e. the species contribution to $PM_{2.5}$) depend on the concentration variations of both the species and the $PM_{2.5}$ mass. As shown in the table below, EC levels had little seasonal variations and the reductions over the 10-year period was profound (by 59.5% in winter and by 62.7% in summer). On the other hand, the $PM_{2.5}$ levels decreased to a much more significant extent in winter (by 43.8%) than in summer (by 26.8%). Therefore, the contribution of EC to $PM_{2.5}$ was more notable in summer (by 49.1%) since the reduction in EC level is more significant than that in the PM mass.

EC, μg/m^3	2008	2017	%Change
Winter	3.06	1.24	-59.5%
Summer	3.06	1.14	-62.7%
$PM_{2.5}$, μg/m^3	2008	2017	%Change
Winter	50.2	28.2	-43.8%
Summer	18.3	13.4	-26.8%
EC/$PM_{2.5}$	2008	2017	%Change
Winter	6.1%	4.4%	-27.9%
Summer	16.7%	8.5%	-49.1%

9) *Figure 3: The percentage values in the chart use an art font that is unclear and needs to be modified.*

Response: Thank you for the comment. The art styles are now removed for easier reading to audiences in the figure. Valid rounding in 2 significant figures is also updated in the figure.

10) *Line 392: "The concentration levels of shipping emission tracers (V and Ni)… respectively", Is this result from Table 2?*

Response: Yes, it is the result from Table 2. We now quote the table number in text for better tracking of the results.

The following text is now revised:

Line 412 – 413:

"The concentration levels of shipping emission tracers (V and Ni) were reduced by 34% and 36% by mass concentration and at a rate of -0.60 and -0.29 ng m^{-3} yr^{-1} (Table 2), respectively."

11) *Line 418: "K+ more representative of burning crop residues high in K+ content vs. levoglucosan representative of burning of cellulose, thus all types of vegetative biomass including hill fires." Grammar errors. The sentence components are unclear and there is no cause-and-effect relationship in this sentence.*

Response: Thanks for the comment. Here we would like to show the examples where K^+ and levoglucosan can represent two different categories of biomass burning. The sentence is revised as below for improved clarity.

Line 438 – 440:

"Specifically, K^+ is a better marker for emissions from burning crop residues, which are typically enriched in K^+, while levoglucosan, a thermal pyrolysis product of cellulose, is commonly found in burning of all types of vegetative biomass including hill fires."

12) *Line 444: "The two elements are highly correlated, reflecting their common material sources and spatial origins", are the correlation values in the literature or your results?*

Response: The correlation values was computed based on our results with the correlation matrix of the starting and ending years as shown in Figure 5. The *R*-value of correlation results is added in this sentence as additional information. As characteristic elements of crustal materials, the high correlation of these two elements (Al and Si) are commonly found in ambient PM samples.

The following text is now revised:

Line 467 – 468:

> "The two elements are highly correlated (*R: 0.54 in 2015 and* 0.87-0.97 in the other years), reflecting their common material sources and spatial origins."

13) Line 499: Valid numbers in Table 4 should be uniform.

Response: Table 4 summarizes the coefficients resolved from the multiple linear regression. We'd like to clarify that the numbers are uniform in having the same number of significant figures (i.e., 2). Note that the numbers should not round up to the same decimal place, as the concentrations for different species span a few orders of magnitude.

Anonymous Referee #2

General comments

The manuscript presents a ten-year data set of $PM_{2.5}$ major components and source-specific tracers at an urban site in Hong Kong, South China. The authors investigate the trends of these compounds and evaluate the influence of emission control on their variations. They also discuss the impact of ENSO events on the abnormal change in $PM_{2.5}$ components, especially in 2011. Overall, I think the research is quite interesting and valuable to the community. I recommend the manuscript to be published in the journal after considering the following specifics:

Response: Thank you for the positive comments. Our response to the comments is given in the following. The response text is marked in blue. References cited in this response document are placed at the end.

Major concerns:

1) There should be emission inventory data in Hong Kong and the PRD. If so, the authors are suggested to compare the long-term trends of PM_5 species (tracers) with the variations of local and regional emission inventories. For example, when the authors discuss the long-term variations of SO_2 and EC, they list the major emission control measures implemented in Hong Kong (Figure 7 and 8, respectively). Are the changes in these species consistent with the variations in emission inventories in Hong Kong?

Response: We agree with the reviewer that a comparison of the inventory emission data and ambient concentrations would be informative, as one of the data objectives for ambient monitoring is to verify the effectiveness of control measures, thus the broad accuracy of the emission inventories. However, emission is only one of the many factors affecting the ambient concentration of a pollutant. The link between emission and ambient concentration is further complicated by atmospheric transformation processes for secondary pollutant (e.g., sulfate). It is beyond the scope of this study to provide a full examination and comparison between the trends of the emission inventory data and ambient concentrations, which will need emission-based air quality modeling work. Additionally, emission inventories for speciated PM are generally not available. For example, there is no EC Emission inventory available for Hong Kong.

We note that SO_2 emission Inventories are available for both Hong Kong and the Guangdong province. As an illustration of comparison between emission inventories and ambient measurements, we now expand the discussion of 10-year trend of sulfate by inclusion of the emission inventory data for SO_2. We extracted the long-term emission inventories for Hong Kong and Guangdong from the HKEPD website (https://www.epd.gov.hk/epd/english/environmentinhk/air/data/emission_inve.html) and the MEIC data platform (version 1.3, http://meicmodel.org/?page_id=541&lang=en).

Figure R1 shows the emission inventories of SO_2 for Guangdong and Hong Kong. The top two sources for SO_2 emissions in Hong Kong are power plants and marine vessels while the major SO_2 sources in Guangdong are power plants and industries. The emission and ambient concentration trends, normalized to 2018, are examined in Figure R1(c), showing that the yearly variation of ambient SO_2 concentrations at the study site (TW AQMS) was very similar to the total SO_2 emission trend from Hong Kong and

SO_2 emission from power plants in Guangdong.

There was a notable reduction of emissions from power plants in Hong Kong in 2010 owing to the emission caps stipulated by the first Technical Memorandum issued by the HKEPD. A range of marine control measures since 2014 further reduce the SO_2 emissions from marine vessels. The regulation toward shipping industry on switching the low-sulfur content fuel for vessels entering Hong Kong helped in reducing extra 18% (-2920 tons) SO_2 emissions from navigation sector in 2016 (Figure R2b). In Guangdong, the drop of SO_2 emissions begin in 2012, mainly due to the reduced contribution of power plant and industrial sources (Figure R2a). Overall, the changes in SO_2 concentrations during the 10-year period are consistent with the SO_2 emissions estimated for the GBA.

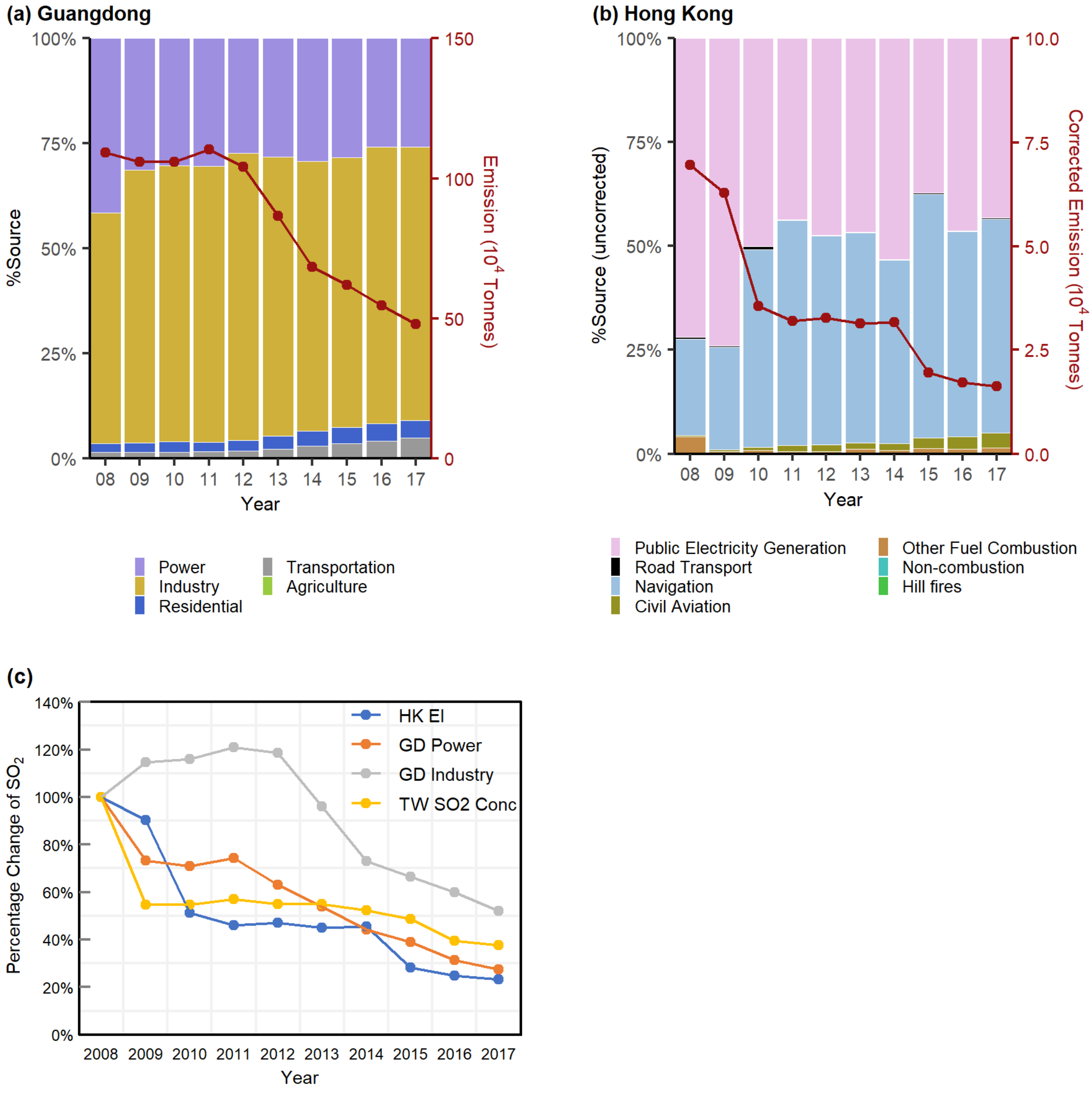
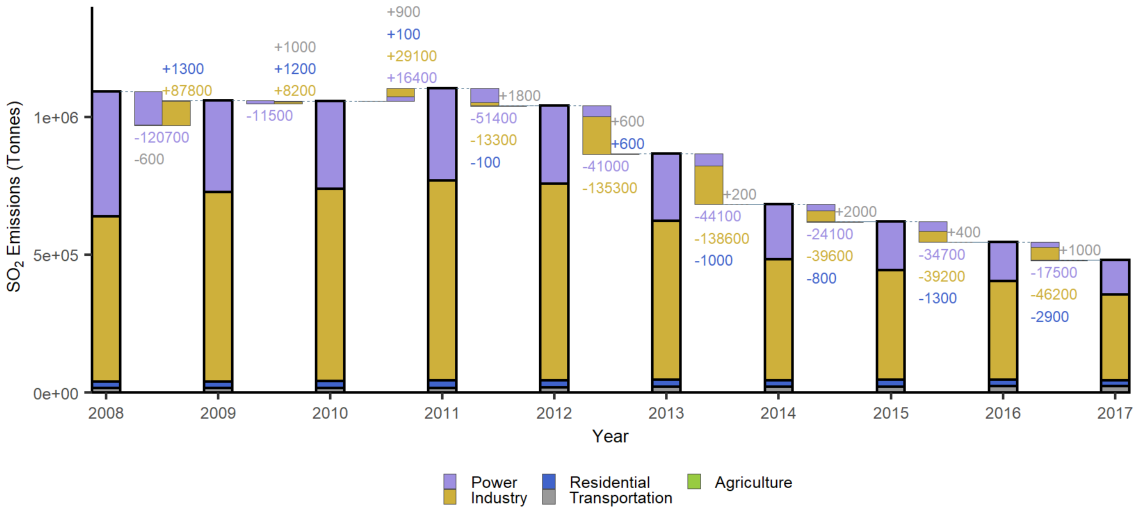


Figure R1 (new Figure S8). The ten-year changes in percentage share of emissions by sources (columns) and the variations in total SO_2 emissions (solid red line) in (a) Guangdong and (b) Hong Kong, with (c) comparing the ten-year trends of ambient SO_2 at TW and major emission sources of SO_2 in Hong Kong and Guangdong for the period of 2008-2017.

(a) Guangdong



(b) Hong Kong

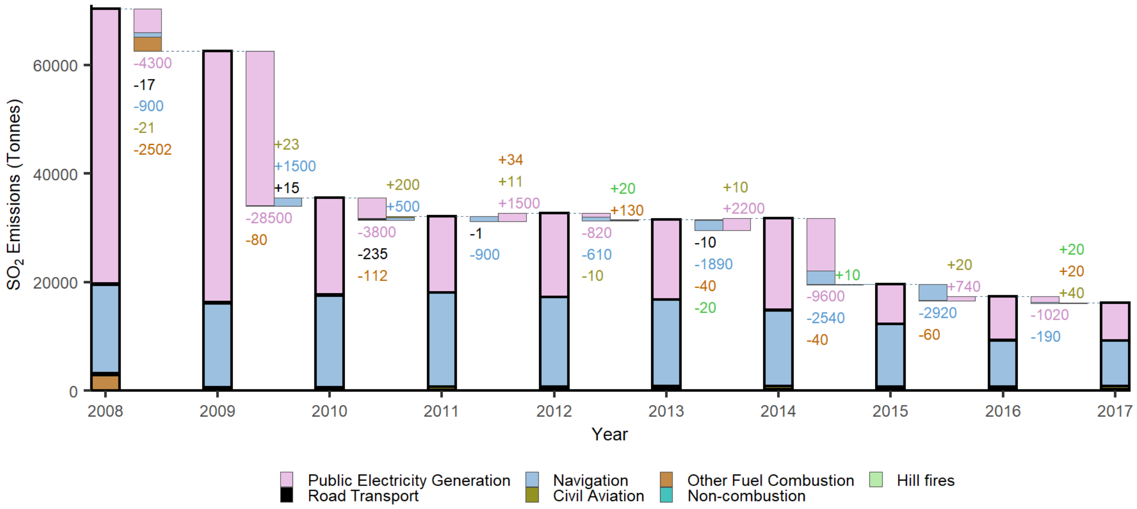


Figure R2 (new Figure S9). The changes in the emissions from individual source sectors in (a) Guangdong and (b) Hong Kong.

The following text is added in main manuscript as supportive information linking the trend in ambient SO_2 ambient concentration with the data based on emission inventories:

> Lines 353-361:
>
> "As a criteria gaseous pollutant, SO_2 has been extensively studied and its emission inventories for Hong Kong and Guangdong province are available (HKEPD, 2021b; Li et al., 2017; Zheng, 2018). The SO_2 emission inventory data for our study decade are shown in Section S3 in Supplementary information. The top two sources for SO_2 emissions in Hong Kong are power plants and marine vessels while the major SO_2 sources in Guangdong are power plants and industries (Figure S8). The emission and ambient concentration trends of SO_2, normalized to 2018, are examined in Figure S8c, showing that the yearly variation of ambient SO_2 concentrations at TW was similar to the total SO_2 emission trend from Hong Kong and SO_2 emission from power plants in Guangdong. Overall, the changes in ambient SO_2 concentrations at TW during the 10-year period are consistent with the SO_2 emissions estimated for the GBA."

A new section (Section S3) is added to the SI file, showing Figures R1 and R2 and briefly describing the SO_2 emission inventories in Hong Kong and Guangdong.

2) *Recent studies have demonstrated that organic compounds, such as levoglucosan and hopanes, are not stable in the atmosphere as previously thought. As Table 2 shows, the levels of ozone continue to increase at the site. This implies that the atmospheric oxidation capacity is increasing. The authors should add some discussion about the influence of the increase in oxidation capacity on the decrease of organic species.*

Response: Our monitoring location (TW AQMS) is in an urban environment. The increasing trend of O_3 (+4.6% yr^{-1} in winter and +2.6% yr^{-1} in summer) at this site is mostly accounted for by the attenuated NO_x titration since NOx has continuously been dropping at a rate of ca. -3% yr^{-1}. We calculated O_x (= $O_3 + NO_2$) at TW site to characterize the atmospheric oxidation capacity (AOC) and found that the AOC over the 10-year period show little discernable change. Nevertheless, we agree with the reviewer that the oxidation capacity of the atmosphere would have impact on the species concentrations. However, the low-resolution nature of our organic tracer data (i.e., daily average), is ill-suited to ascertain the impact of changing atmospheric oxidative capacity on organic degradation rate, and further on concentration levels of the organic markers (e.g., levoglucosan and hopanes).

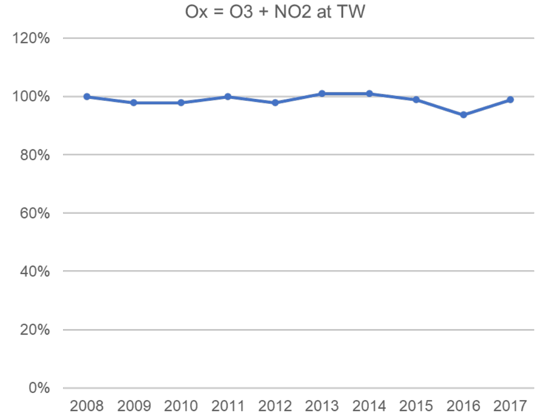


Figure R3. Ten-year variation of O_x (=O_3+NO_2), shown as the normalized percentage against the level in 2008, at monitoring site in the urban environment of Hong Kong

The effect of oxidation capacity changes on degradation remain unclear from the analysis of measurement data. To keep the paper concise and our focus on reporting the temporal variation, we add one sentence to mention the possible influence of oxidation.

> Line 445-447:
>
> "We also acknowledge that the ten-year trend in an organic tracer like levoglucosan could be affected by long-term change in atmospheric oxidation capacity, which would exert its impact through atmospheric degradation kinetics."

3) *In section "3. 4 Secondary inorganic aerosol components", the authors discuss the uneven reduction of SO_2-sulfate and NOx-nitrate. How about the temporal trends of sulfur oxidation rate (SOR) and nitrogen oxidation rate (NOR)? The changes in SOR and NOR might provide additional information about the formation chemistry of sulfate and nitrate.*

Response: Thank you for the suggestions. We calculated the SOR and NOR in winter and summer using Eq. (R1). The 10-year variations of these two ratio quantities are shown in Figure R4.

$$SOR = \frac{nSO_4^{2-}}{nSO_4^{2-} + nSO_2}\,; NOR = \frac{nNO_3^-}{nNO_3^- + nNO_2} \quad where\ n\ refer\ to\ molar\ concentration \quad (R1)$$

The SOR value was higher than 0.1 for our data in all years, indicating the significant oxidation and in line with the large regional transport contribution for sulfate. In the transformation of SO_2 to sulfate, multiple oxidants could be at work (e.g, gaseous OH, H_2O_2(aq), O_3(aq), etc) (Xue et al., 2019). The aqueous oxidation mechanisms are likely not closely coupled with gaseous oxidation capacity. Additionally, the aqueous pathways are dependent on cloud availability. As shown in Figure R5, no clear co-variation temporal patterns can be discerned for ozone and sulfate. This result, although crude, reflects that a straightforward linkage is absent between one of the gaseous oxidants (i.e., O3) and sulfate as an oxidation product of SO_2.

The NOR value was typically low (< 0.05) (Figure R4). Note that $PM_{2.5}$ nitrate is only one part of the oxidation products of NOx. Other forms of nitrate, such as gaseous HNO_3, nitrate on coarse particles, organic nitrates, etc., were not reflected in the NOR calculation, but they could be comparable in abundance to PM2.5 nitrate. Additionally, $PM_{2.5}$ nitrate (mainly in the form of ammonium nitrate) is semi-volatile and its partition in the particle phase is strongly affected by temperature and relative humidity. For example, the stack difference NOR between summer and winter is more likely driven by temperature. As such, we feel using NOR to indicate formation pathway is not well-grounded.

In summary, the complex oxidation chemistry of SO_2 to sulfate, and the multiple significant forms of nitrate plus the semivolatile nature of ammonium nitrate make the SOR and NOR quantities not readily indicative for formation chemistry insights. Thus, we decide not to explore these two ratios in our manuscript.

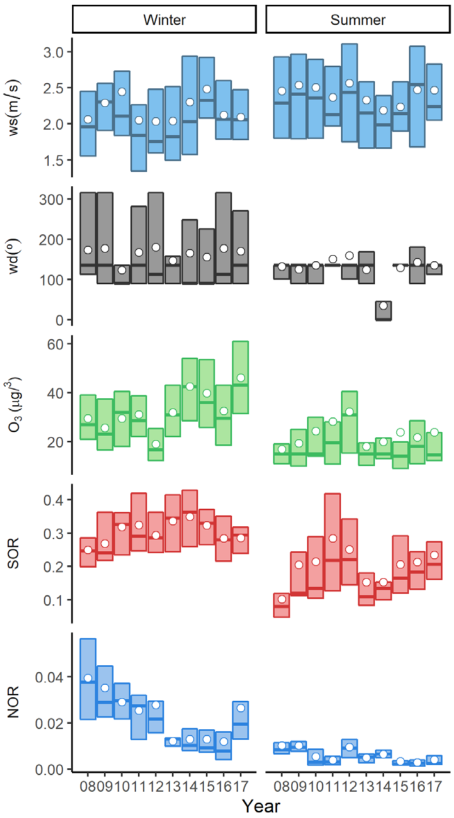


Figure R4. The seasonal variation of meteorological condition (wind speed and wind direction), ozone, SOR and NOR (from top to bottom).

Minor comments:

1) *Page 8 line 233-234. The authors state that the decrease in EC is due to local control of vehicular emissions. However, in addition to vehicular emissions, EC could be emitted from biomass burning and shipping exhaust. In fact, the tracers of the latter two sources (e.g., K^+ and Ni) also continued to decrease (Table 2). The "%Relative change" of EC is close to that of K^+.*

Response: Thank you for the question. Generally speaking, the review is correct that combustion sources, such as vehicular emissions, biomass burning, and ship emissions, all contribute to EC. For our study location, these three sources mentioned by the reviewer have distinct seasonality. Vehicular and shipping emissions are mainly of local origin, thus showing little seasonality. Biomass burning is largely regional/super-regional, displaying clear seasonality of higher in the winter and lower in the summer.

Here, we use season-specific Sen's slope to compare the seasonality and thus verify the origin of emission sources with clustering results of the correlation matrix. The closer the season-specific Sen's slope between winter and summer, the more contribution of local sources to the species. EC shows a comparable Sen's slope of -0.19 µg m^{-3} yr^{-1} in winter and -0.18 µg m^{-3} yr^{-1} in summer, indicating the strong local source contribution in EC. Ni also has similar Sen's slope values in winter and in summer (-0.37 and -0.42 ng m^{-3} yr^{-1}). On the other hand, K^+ has a much higher Sen's slope in winter than in summer (-62 vs. -11 ng m^{-3} yr^{-1}). Although the %relative change of EC is close to that of K^+, their overall temporal and seasonal variation were quite different from each other. In addition, EC had moderate to good correlations (R-values: 0.41-0.74) with species which are emitted/generated locally such as hopanes (tracer for vehicular emissions) and NO_x but was poorly correlated with K^+ (R-value: 0.19). Our source apportionment study for data in 2015 shows that ship emissions make negligible contributions to EC at TW (See Table S4b in Chow et al., 2022). In conclusion, the relevant monitoring data strongly indicates EC at TW was mainly from local vehicular emissions and its reductions over the years were in excellent correspondence to local vehicular emission control measures.

2) *Page 12 Figure 5. SO_2 had a local source in 2008 but a regional source in 2017. What is the explanation?*

Response: Thanks for your comment. We computed the spearman correlation between species in each year to examine and to preliminary classify the sources into local and regional groups by hierarchical clustering. The correlation of SO_2 with species of local origins such as EC, V and Ni became relatively poor in 2017 whilst the correlation with regional species such as Zn and K^+ increased in the same year (Figure R7). We believe it is because the local SO_2 emissions have been greatly reduced since 2010, when the emission caps for power plants in Hong Kong came into effect, so that the regional transport of SO_2 began to play a relatively more important role.

In addition, the annual percentage changes of ambient SO_2 was similar to those from local emission inventory in the beginning years (2008-2010) (ambient: -45%, inventory: -49%), but was lower than local emission inventories in the ending year (2008-2017) (ambient:-62%, inventory:-77%). This further supports that there is a shift of dominant emissions source of SO_2 from local to regional/super-regional over the decade. The below text is added to comment on the shifting of SO_2 dominant sources over the decade.

> Lines 313-315
>
> "It is of interest to note that SO_2 shifted from the local cluster to the regional cluster over the decade, reflecting the changing relative importance of local vs. regional emission sources of SO_2 over the years (see Section S3 for more details)."

3) *Page 19 Table 4. The coefficients in WINTER are not listed in Table 4.*

Response: Table 4 lists the regression coefficients for the variables in the multiple linear regression Eq. (4).

$$X_m = \beta_1\, Year_m + \delta_1 Season_m + \beta_2\, Temp_m + \beta_3 RH + \delta_2 ENSO \qquad (4)$$

In Equation (4), there are three parametric variables (Year, Temperature, and RH) and two categorical (or dummy) variables (Season and ENSO event). The coefficients for the categorical variables are derived by selecting one of the categories as the reference (i.e., winter in our case) and calculating the relative values of each variable with respective to the reference. Hence there is no coefficient for winter in the table. This explanation is now added as part of the table footnote. As Table 4 data is portion of Table S7, we now deleted Table 4 from the main text (the explanation for no coefficient for winter is added as Table S7 footnote). Related to Table 4 data, we also create a new Figure (Figure S15), visually showing the varying magnitude of the effect of Strong La niña event on various gaseous and particle species.

References:

Chow, W. S., Huang, X. H. H., Leung, K. F., Huang, L., Wu, X., and Yu, J. Z., 2022. Molecular and elemental marker-based source apportionment of fine particulate matter at six sites in Hong Kong, China. *Sci. Total Environ.*, 813, 152652.

Tsai, C.J. and Perng, S.N., 1998. Artifacts of ionic species for hi-vol PM10 and PM10 dichotomous samplers. *Atmospheric Environment*, *32*(9), pp.1605-1613.

Tsai, C.J., Huang, C.H. and Lu, H.H., 2005. Adsorption capacity of a nylon filter of filter pack system for HCl and HNO_3 gases. *Separation Science and Technology*, 39(3), pp.629-643.

Xue, J., Yu, X., Yuan, Z., Griffith, S.M., Lau, A.K., Seinfeld, J.H. and Yu, J.Z., 2019. Efficient control of atmospheric sulfate production based on three formation regimes. *Nature Geoscience*, *12*, 977-982.