Answer to Referee #1:

The authors appreciate the time the reviewer have spent in assisting us to produce a high quality, understandable publication. All the requested corrections and suggestions are addressed and introduced to the revised version of the manuscript. In addition, a few comments which are mentioned both in general and in specific issues are combined to reduce confusion.

Major/ General issues

Comment 1.1

The manuscript as presented falls outside the scope of ACP and appears to be of local interest only.

Reply: The authors are hard to accept this comment. Please see the answer to the anonymous referee for details.

Comment 1.2

The data are presented in the form of bar graphs and tables of averages - which is not the best format. I would have liked to see a figure showing the (full) time series of the data, perhaps as a table in the supplemental, and one or two representative shorter periods.

Reply: This suggestion is accepted. Figures showing the (full and short) time series of the data (see Figure S1 and S2 attached at the end) are given in the revised manuscript.

Comment 1.3

The authors have used MCM box modeling. (a) I wonder why the PA radical concentration calculation in section 3.2 was conducted in the first place as the MCM would have provided a better estimate. (b) How the MCM box model was set up and run was not described. (c) It is unclear if the box model simulations come close to describing the real world, as no comparisons of box model output to actual data (O_3, NO_x, selected NMHCs, etc.) are presented.

pg17105, line 12-14. "We calculate the relative contributions of these 24 NMHCs to PAN formation using MCM". It needs to be described (in detail) how this was done (preferably in section 2, experimental methods). Also, the results, as presented, sound as if there is only 1 possible scenario, whereas in reality mixing ratios of the precursors, temperatures, and actinic flux have varied considerably throughout the year. Perhaps this calculation should be done for selected days for each of the months sampled. Further, a comparison of MCM output with measurements needs to be presented.

Reply: Sorry for making the reviewer confused. In the text, it was stated that “We calculated the relative contributions of these 24 NMHCs to PAN formation using MCM and the results are shown in Table 4”. We admit this statement would seriously mislead the readers.

Actually we did not run any MCM box modeling in this study. MCM was only used as a library to provide the rate constants of the reactions for the production of key PA precursors and PA. This following description is added into the revised manuscript to make this statement clearer.

"We calculated the relative contributions of these 24 NMHCs to PAN formation using the rate constants of involved reactions, which were acquired from the MCM program (MCMv3.1, Master Chemical Mechanism), and the results are shown in Table 4. Note that no MCM simulations are conducted in this study."

Comment 1.4

Section 3.2 presents an estimate of PA radical concentrations. That is almost certainly incorrect (see specific comments below).

pg17102 , line 4 - concentration of PA radicals. This entire section is questionable and should be removed. It seems to me that MCM output would have included estimates of PA radicals also that could have been used instead of the questionable steady state expression (2).

Reply: Thanks for pointing out this issue. We admit there were some related reactions missed in the calculation, but the approach to calculate PA radical concentrations by using the reactions to form key PA precursors (6 oVOCs) is accepted by a number of researchers, such as LaFranchi et al. 2009 and Xu et al. 2015.

Therefore, in the new round of calculation, we have added more reactions related to PA production by referring to more references including Altshuller 1993, Aneja et al. 1999, Fischer et al. 2014, LaFranchi et al. 2009, Zhang et al. 2015.

In addition, as mentioned above, no MCM analysis were conducted in this study. Therefore no PA radical concentrations calculated from MCM model are available.

Comment 1.5

Figure 7 is problematic. Hysplit calculations were performed, but I got the impression that calculations were only carried out for the first of each month, and then the synoptic conditions were assumed to remain constant for the remainder of the month?

Reply: Thanks for pointing out this error. Actually, we did analyzed the backward air-mass trajectories using HYSPLT for every single day and also conducted cluster analysis. However, for some reason, only one day data was included in the the current manuscript. Figure 7 has been updated accordingly in the revised manuscript (see the figure at the end of the document).

Comment 1.6

The authors, correctly, state that a significant fraction of the PAN observed at the measurement location was produced upwind, where VOC mixing ratios were in all likelihood different from those measured. However, this suggests that the MCM box

model simulations should not have been initialized with local measurements for those time periods.

Reply: Yes, we agree that upwind VOC mixing ratios were likely different from the measurement. However, as we stated before, no MCM box model simulation was really conducted.

Comment 1.7

Why were PPN data not reported?

Reply: No PPN measurements were available in this study.

Specific Comments

Comment 1.8

Pg17097, Lines 3-4. Consider also citing the work by Gao et al. (2014).

Reply: The Gao et al. (2014) is cited in the revised manuscript.

Comment 1.9

pg17098, line 9 "air samples were first pre-concentrated". Doesn't the Meteorology Consult instrument use a sample loop? Please confirm that the air samples were indeed pre-concentrated, and if so, describe how.

Reply: The reviewer is right. Air samples in this study do not require pre-concentration process. Instead, air samples first passed a pre-column which acted as a filter to remove fine particles or impurities before injecting into the GC-ECD system. The statement is modified as follows in the revised manuscript:

"Air samples were first filtered by a pre-column to remove fine particles and impurities, then passed through a cooled capillary column to prevent thermal degradation of PAN during contact with the stationary phase, and finally were carried to the ECD with ultrapure nitrogen gas for quantitative analysis."

Comment 1.10

pg17099, line 7-8 "the CCl4 concentration in the air was very stable". I think I know which peak in their chromatogram the authors are referring to, but can you please provide more information for the uninformed reader (e.g., "retention time of x.y min relative PAN, which eluted at z.x min")? Further, "very stable" is a qualitative statement. Please be quantitative how stable is "very stable"?

line 9. "check the stability of PAN signals". Since PAN mixing ratios vary in ambient air and are not expected to be stable between consecutive injections, does this statement refer to the PAN signals during calibrations? If it refers to the calibration, where does the CCl_4

would come from, as it is stated that calibrations were carried out in 99.9999% purity N_2 balance gas? Or did the authors mean "stability of the air volume injected"? Please also add a statement as to how much the instrument response drifted/varied over the course of the year.

Reply: The reviewer is right. The whole sentence of "Since the CCl4 concentration in the air was very stable, its peak signal was used to check the stability of PAN signals." is confusing and misleading. It is removed from the text in the revised manuscript.

In regard to CCl4 peaks, "very stable" means that the peak time and area of CCl4 are relatively stable compared to many other atmospheric chemical compounds due to its distinctive chemical inertness with a half-life time of about 26 years (IPCC, 2005) and almost constant concentration in the atmosphere. CCl4 is widely used as an internal standard matter to evaluate the responses of ECD.

In addition, the PAN calibration was conducted once a month without CCl4 involved. The instrumental drift during the measurement campaign was quite small (less than 5%) due to the monthly calibration. This information is added into the revised manuscript.

Comment 1.11

pg17101, line 16, and Table 1. Here, the average PAN mixing ratio is compared to averages at other (arbitrarily selected) locations and seasons (most of the other data sets are summertime measurements). As there are many more data sets in the literature, a short statement as to how data sets were selected is needed, or the table needs to be more comprehensive.

My preference here would have been to compare max and median values, to also list the corresponding O3 values, and to compare similar seasons (i.e., for a comparison of summertime data, give the max and median values of your summertime values, as including the other seasons skews the data).

Reply: Good suggestion. The table has been improved accordingly and, to reduce the size, only studies published in recent 10 years are selected. Also, the revised table include max and median values whenever they are available.

Comment 1.12

line 15 (R3). Please state the values of the rate constants used in the calculation.

Reply: The rate constant used in the calculation is $k = 2.52\times10^{16}e^{-13573/T}\ s^{-1}$ and has been added into the revised manuscript.

Comment 1.13

Demore et al. 1997 is a very outdated reference, and the expressions for PAN thermal decomposition have been re-measured since. Further, this expression is not valid under conditions when the rate of PAN thermal decomposition is slow (e.g., in winter).

Reply: The comment has been accepted. The reference of Demore et al. (1997) has been

removed and more recent studied (e.g. LaFranchi et al. 2009; Sander et al. 2011) are considered in the new round of analysis.

Comment 1.14

line 20. Eqn (2) is invalid under conditions of high NO concentrations, that also destroy PA radicals. There is also the PA radical reaction with other peroxy radicals to consider。

Reply: We agree with the reviewer's opinion. In regard to the PA radical removal process, more reactions are considered in the new round of analysis mainly according to the reference of LaFranchi et al. (2009).

Comment 1.15

pg17105, lines 24-25 "the observed PAN concentration is about 1.4 times higher than the calculated value". Considerably uncertainty is introduced by performing a single MCM calculation with annually averaged values. Please comment on the potential role of biogenic compounds such alpha or beta-pinene (which were not measured).

Reply: As mentioned above, no MCM calculations were done in this study. Our related statement was confusing and has been modified in the revised manuscript.

Biogenic compounds such as alpha or beta-pinene will certainly play a role in the production of PAN, unfortunately they were not measured in this study. If biogenic compounds are considered, the difference between the measured and the calculated would be further reduced. There is a possibility to estimate the role of biogenic compounds in PAN production by using previous published data in the same area.

Comment 1.16

pg17106, line 3-4, and Table 5. I would have preferred if the correlations had been calculated for (much) shorter timescales, rather than the for values averaged over 3 month periods, in particular since the back trajectories (pg17107, and Figure 7) show that air mass origins differed between the months.

Reply: Thanks for the suggestions. The suggested analysis has been done for one typical day selected for each month and the results are summarized in a new table in the revised manuscript.

Comment 1.17

Table 5. This table is rather descriptive. Are there any significant scientific insights?

Reply: The authors agree with the reviewer. The correlation analysis between daily maximum O3 and PAN are conducted and strong correlations are found. The new results are updated in the revised manuscript. Also these results are compared with previous studies (e.g. Xu et al., 2015) in the revised text to investigate the relationship of the two pollutants under different pollution conditions.

Comment 1.18

Figure 3. I am wondering why solar radiation has units of kWh/m^2. Shouldn't it be W/m2? Also, consider showing the data in the form of box-and-whisker plots (min, 10th percentile, 25th percentile, median and mean, 75th percentile, 90th percentile, and max) for each month.

Reply: Yes, the reviewer is right. The unit of solar radiation should be W/m^2 and this error is corrected in the revised manuscript. Also, the PAN data are presented in the form of box-and-whisker plots.

Comment 1.19

Figure 6. It would be informative here to superimpose the thermal lifetime of PAN to show if it is sufficiently long-lived in the winter months for multi-day transport.

Reply: Thanks for the suggestion. The thermal lifetime of PAN is added into Figure 6 in the revised manuscript.

References

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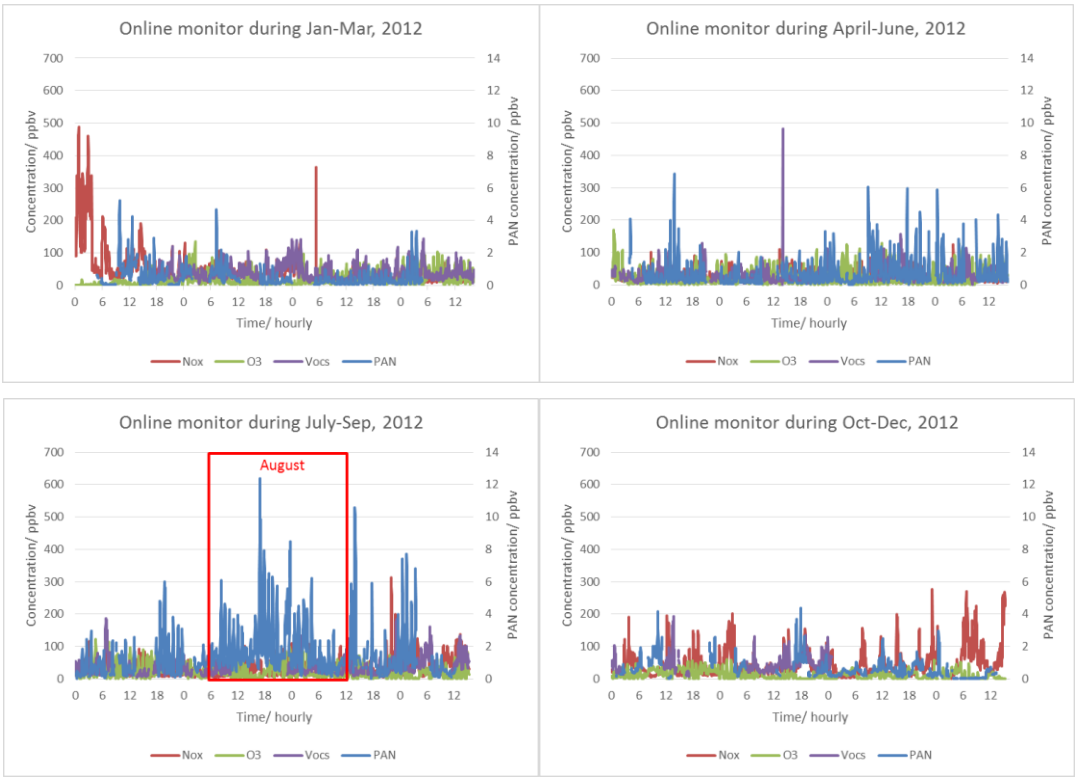


Figure S1. Full time series of PAN, NOx, O3 and VOCs online monitored in 2012.

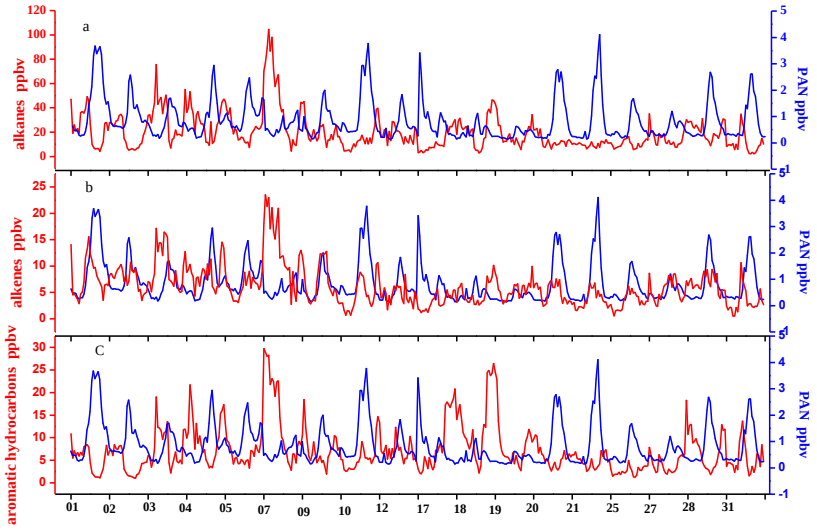
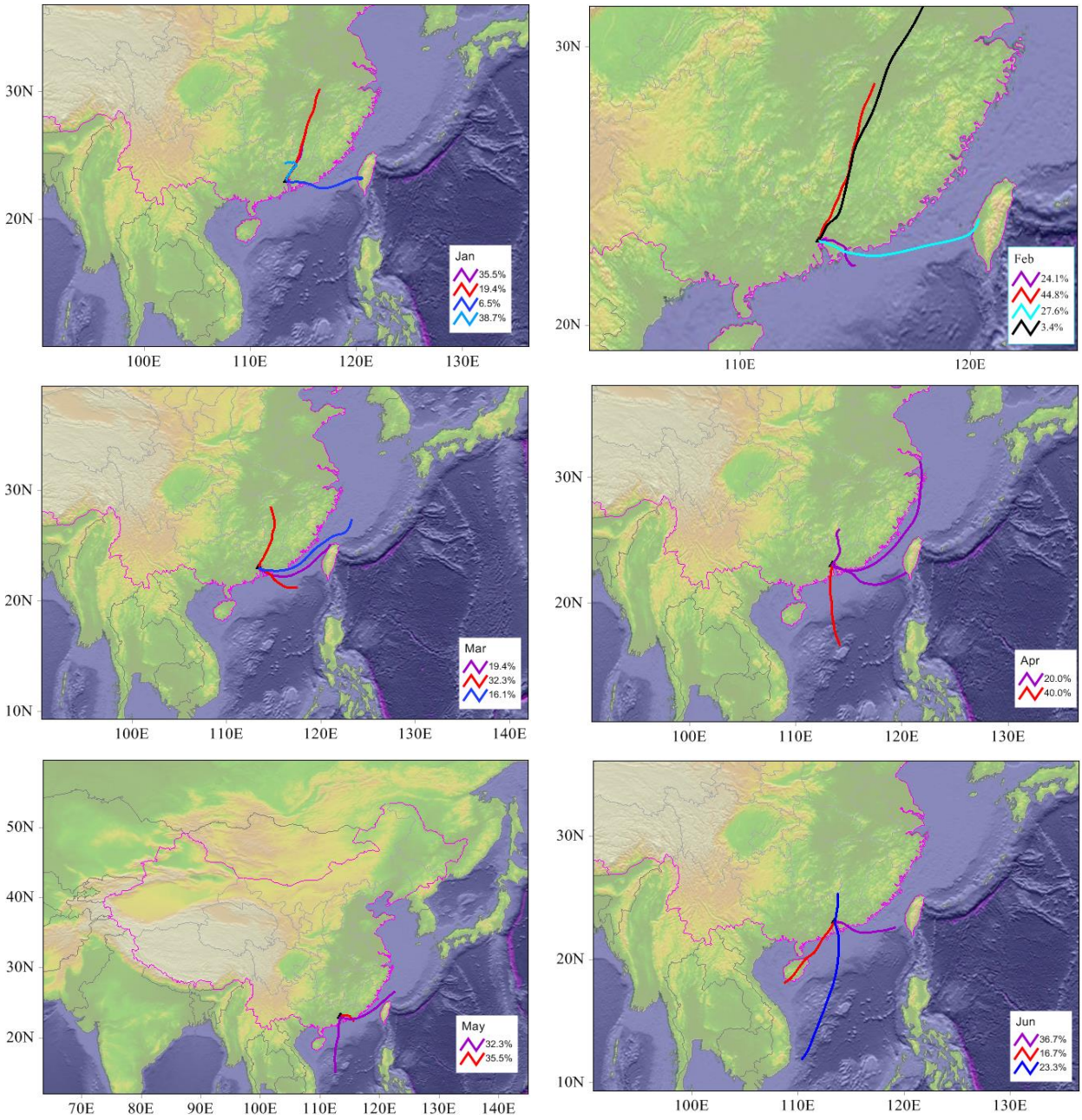


FIgure S2. The case study of PAN, alkanes, alkenes and aromatics in August, 2012.


30N
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Mar
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Apr
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May
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Jun
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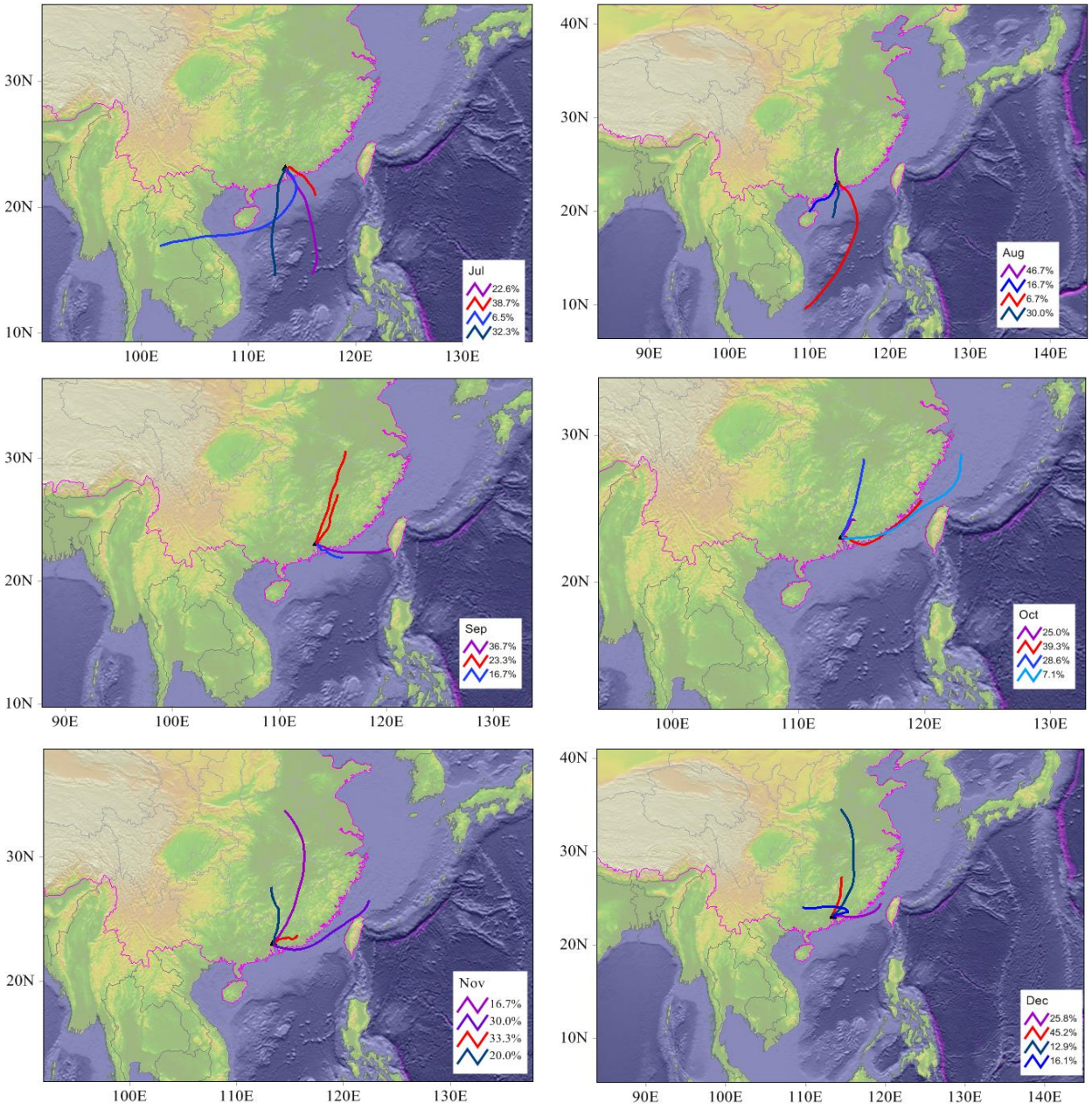

Figure 7 Backward air-mass trajectories cluster simulated by HYSPLIT

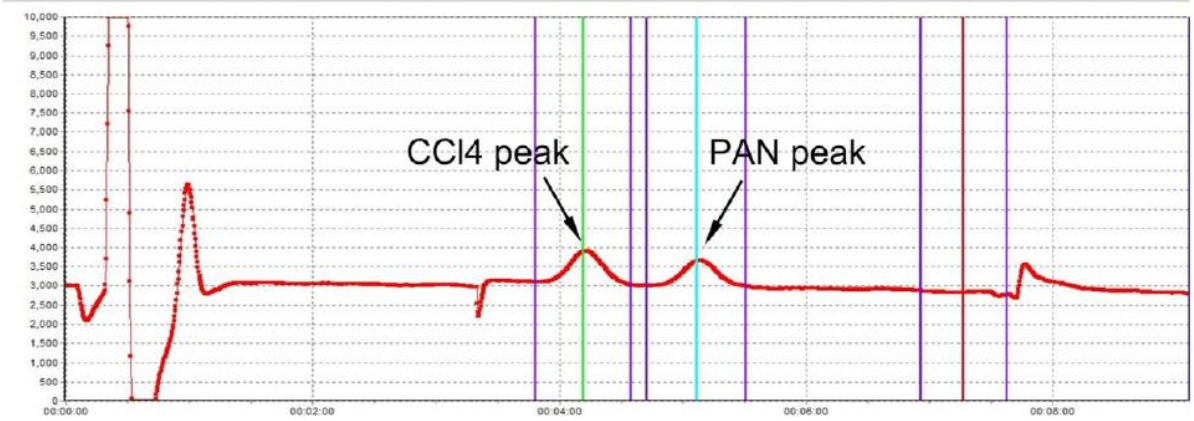

Figure S3. An example of the measured spectrogram with CCl4 and PAN peaks marked out. The CCl4 peaks are relative stable and used to check the stability of PAN signals due to its distinctive atmospheric chemical inertness and almost constant concentration.