Response to Reviewers

Comment on acp-2021-948

RC1 Anonymous Referee #1

Comments on "Seasonal characteristics of atmospheric peroxyacetyl nitrate (PAN) in a coastal city 2 of Southeast China: Explanatory factors and photochemical effects" by Liu et al

The manuscript reports influencing factors to PAN pollution in China. The manuscript reports important results. It is suitable for the Journal Atmospheric Chemistry and Physics. I suggest authors incorporate the below suggestions before its publication.

Response: Thank you very much for your exploratory and constructive advice. Here, we have carefully revised the manuscript.

Major comments:

- In the abstract section, the authors state that the current paper reports the formation mechanism of PAN and its effect on ozone were identified. I suggest the authors explain it in brief.

Response: Thank you for your suggestions. PAN can be produced only through the reaction of PA+NO_2 (Liu et al., 2021; Xue et al., 2014). Hence, the production and sink of PA can represent that of the PAN mechanism indirectly. In the abstract section, we have explained the PA formation mechanism (hence PAN formation mechanism). The effect of PAN on ozone represented that PAN could promote or inhibit O_3 formation under high or low ROx levels, respectively. For better understanding, we revised the relevant expression, as follows:

"Model simulations revealed that acetaldehyde oxidation (46±4%) contributed to the dominant formation pathway of PA (hence PAN), followed by methylglyoxal oxidation (28±3%) and radical cycling (19±3%)".

"The analysis of PAN formation mechanism and its positive or negative effect on ozone provided scientific insights into photochemical pollution mechanism under various pollution scenarios in coastal areas".

- In section 2.2, some details of the box model should be added here, although it is explained in the previous study, e.g., details of computation of net production rate of O_3.

Response: Thank you for your suggestions. More details about the box model have been added, as follows:

"The observed data with a time resolution of 1 h of pollutants (i.e., O_3, CO, NO, NO_2, HONO, SO_2, and VOCs), meteorological parameters (i.e., T, P, and RH), and photolysis rate constants ($J(O^1D)$, $J(NO_2)$, $J(H_2O_2)$, J(HONO), J(HCHO), and $J(NO_3)$), which were mentioned in Section 2.1, were input into the OBM-MCM model as constraints".

"The production pathways of O_3 include HO_2+NO and RO_2+NO reactions, and the destruction pathways of O_3 involve reactions of O_3 photolysis, O_3+OH, O_3+HO_2, O_3+VOCs, NO_2+OH, and NO_3+VOCs. The net O_3 production rate ($P(O_3)$) is calculated by the difference of O_3 production rate and destruction rate".

- The study used a non-parametric regression model. How good is it? Have you compared it with traditional chemistry models? Have you compared results with them?

Response: Thank you for your suggestions. We have added the validation of the GAM model in the supplementary material of Text 1, as follows.

Text 1 Model Validation.

Figure T1 and T2 show the residual test results of the Generalized Additive Model (GAM) in spring and autumn, respectively. From the residual Q-Q plots (Fig. T1 (a) and Fig. T2 (a)), the points were mostly on a straight line, indicating that the residuals conformed to a normal distribution. Meanwhile, the residual histogram of the model in Fig. T1 (c) and Fig. T2 (c) showed that the residuals were mainly concentrated around 0, which demonstrated the good fitting degree of the model. From the scatter plot of residuals and linear prediction values (Fig. T1 (b) and Fig. T2 (b)), the residuals were randomly distributed. From the scatter plot of the observed values and the fitted values (Fig. T1 (d) and Fig. T2 (d)), the response variables and the fitted values were well matched, and basically showed a "y = x" distribution. Therefore, the fitting effect of this model was good.

The function of the Generalized Additive Models (GAM) is to analyze the correlation between the explanatory variables and the response variables. The GAM has been widely used in air pollution research and can effectively deal with the complex nonlinear relationship between air pollutants and influencing factors. Although GAM offers a flexible approach to calculating trends, the model is just a regression statistical model/method, which could not establish a connection with traditional chemistry models. Hence, comparing results with them might be very difficult and less significance.

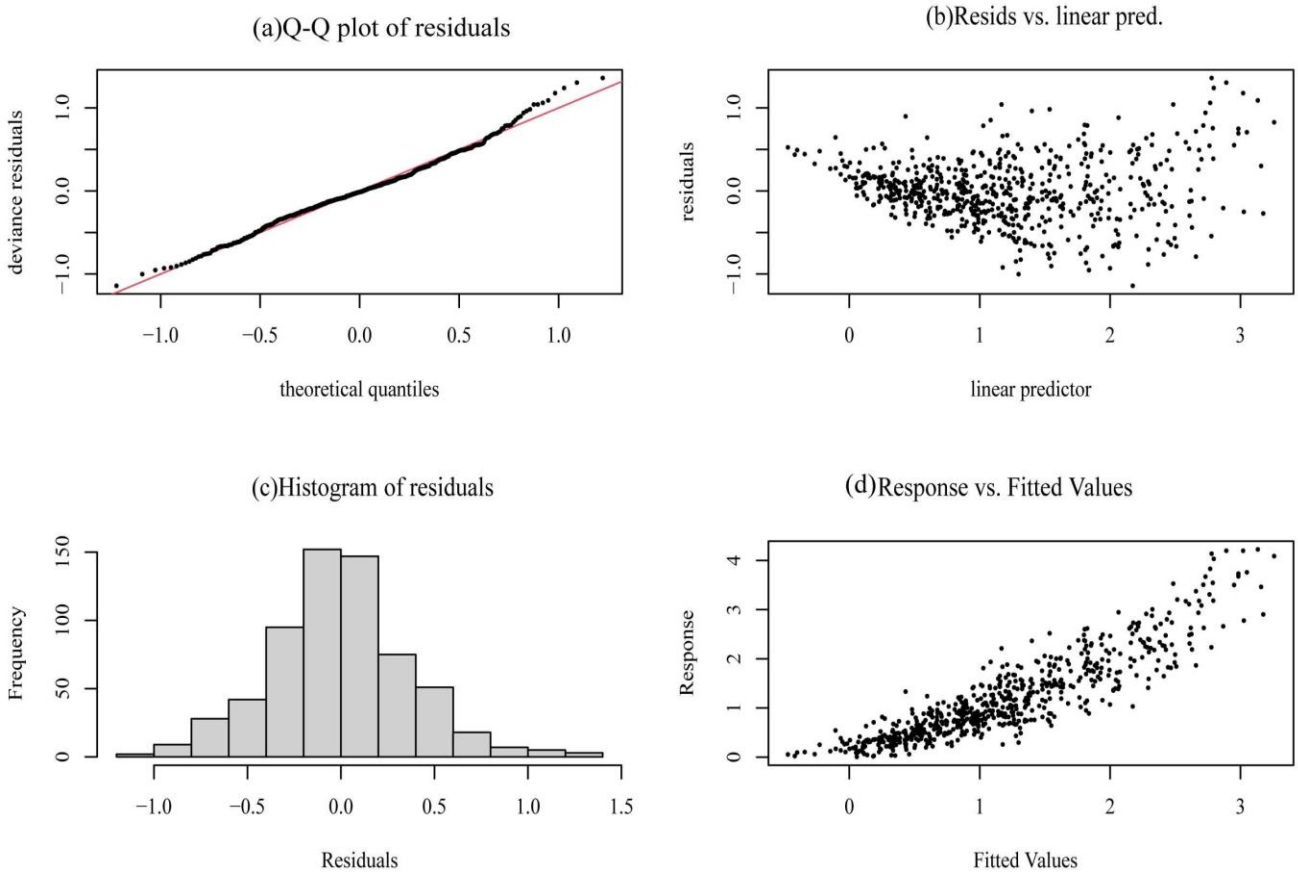

Fig. T1 Residual test results of the Generalized Additive Model (GAM) in spring.

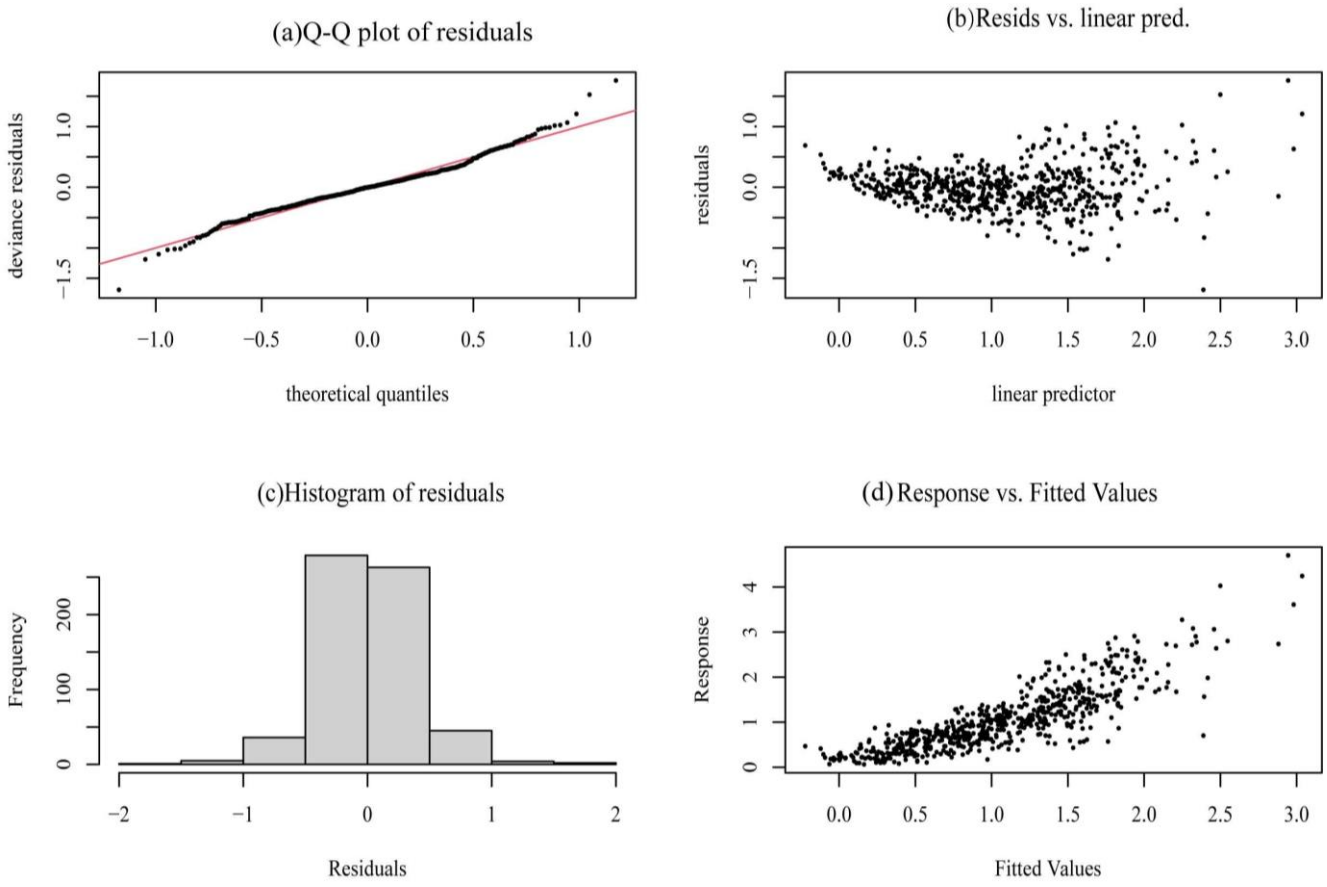

Fig. T2 Residual test results of the Generalized Additive Model (GAM) in autumn.

- Section 3.2, L226-229, statements are not clear. The statement "PAN pollution was mainly from local production" should be explained.

Response: Thank you for your suggestions, and we're sorry for the unclear expressions. We have revised the relevant contents in our manuscript.

"High PAN values in spring easily happened in the wind direction of the southeast with low wind speed (<3 $m \cdot s^{-1}$), showing the influence of urban plumes from the downtown of Xiamen island. High PAN values in autumn also appeared in the wind direction of the southeast, as well as the northeast with a relatively high wind speed (from Quanzhou city, an industrial city adjacent to Xiamen). Anymore, PAN lifetimes in our observation site were relatively short due to the high ambient temperature, and the PAN lifetimes in autumn (2.02 hours) were significantly lower than that in spring (6.39 hours), which was not conducive to regional transport (Hu et al., 2020; Liu et al., 2018). Accordingly, O_3 showed obvious characteristics of long-range transport, and PAN pollution was mainly from local production/accumulation in spring and autumn, but short-range transport from adjacent cities might contribute to the high PAN concentrations in autumn to a certain extent".

- L230-235, it is not clear how local mixing is computed.

Response: Thank you for your suggestions. The mixing ratio in our study represents the volume concentration, which could be acquired directly from monitoring instruments. The mixing ratio of a gas component refers to

the occupied volume ratio of this gas component in dry air under the same temperature and pressure conditions. Mixing ratio values strictly speaking may not need a unit, but commonly ppb, nmol/mol or similar would be used. In our study, the units of the monitored pollutants (such as O_3, PAN, and VOCs) were ppbv. Hence, we named their volume concentration as mixing ratio. For better understanding, we have changed the expression in this part. The detailed modifications are as follows:

"Based on the above analysis, we found that the photochemical reactions were still intense and even stronger under the low precursor levels. Although the precursor abundances of PAN and O_3 in spring were significantly higher than those in autumn ($P<0.01$), PAN values were comparable to and O_3 values were much higher in autumn than those in spring, respectively".

- Fig. 3 and Fig. S4, nonlinear relations between variables (NO, UV, RH, T Ox) and PAN are well known. What is new in these figures should be explained.

Response: Thank you for your suggestions, we rewrote this part and added some new discussions in these figures. The details are as follows:

"The PAN in both seasons showed a downward trend with the increase of NO. PAN in spring was constant with NO fluctuation between 10 and 23 ppbv, and the confidence interval (CI) of NO concentration was relatively narrow. As we all know, the reaction of PA+NO is one of the most important loss pathways of PA, and the NO_2 production by NO oxidation in the O_3 formation cycle can react with PA radical to produce PAN, suggesting the fact that NO can consume and produce PAN indirectly (Liu et al., 2021). The consumption of NO to PAN was basically equal to the production when the NO levels were relatively high (>10 ppbv), and the consumption of NO to PAN is greater than the production when the NO levels were low in spring. High values of NO mainly happened during rush hour traffic, thus controlling vehicle emissions can effectively alleviate PAN pollution. Ox had a positive correlation with PAN, representing the promotion effects of atmospheric oxidation capacity on PAN formation. The Ox levels <70 ppbv (with narrow CI) played a significant promotion role in PAN formation (Fig. 3(b) and Fig. S4(b)). High Ox >70 ppbv showed little influence on PAN, which could be explained as high Ox with relatively high air temperature leading to intense PAN thermal decomposition. When TVOCs were between 10 and 30 ppbv and $PM_{2.5}$ levels were <17 $\mu g \cdot m^{-3}$, PAN showed an upward trend with narrow CI. According to our previous study (Liu et al., 2022; Hu et al., 2020), the results of sensitivity analysis in Xiamen was VOCs-sensitive; the relatively low $PM_{2.5}$ concentrations in Xiamen showed limited influence on solar radiation through scattering and absorption, but promoted heterogeneous reactions producing radicals to a certain extent. UV and T had significant positive and negative nonlinear correlations with PAN, respectively. When UV changed between 0 and 50 $W \cdot m^{-2}$ and T changed between 15 and 35 $W \cdot m^{-2}$, the CIs barely increased. In addition, when RH was more than 40%, the increase of RH was unfavorable for PAN production in both seasons. Some studies also found that high water vapor content could remove PAN and its precursors (Yan et al., 2018; Ma et al., 2020). Overall, the multiple-factor GAM analysis could better simulate the variations of PAN under real atmospheric conditions and evaluate the contributions of the influence factors to PAN formation".

- L261-263: The solar radiations are stronger in spring than autumn; hence UV, T, and OX will be more effective in PAN formation during spring and vice-a-versa in autumn. Why should you mention it explicitly?

Response: Thank you for your suggestions, we agree that this summary was not accurate enough. In the previous question of Fig. 3 and Fig. S4, we rewrote this section and added some new information. Hence, we have rewritten this summary for a new version to avoid unnecessary misunderstandings.

"Overall, the multiple-factor GAM analysis could better simulate the variations of PAN under real atmospheric conditions and evaluate the contributions of the influence factors to PAN formation".

- L292-302. These statements are huge. It is unclear whether they are supported by the model simulations or observations.

Response: We agree with your suggestions, and we rewrote these statements based on observations. The revisions in the manuscript are as follows.

"Diurnal variations of air pollutants during episodes and non-episodes are shown in Fig. 4, which could be explained by the evolution of the planetary boundary layer, local emissions, and atmospheric photochemistry. PAN reached a maximum value at 12:00-14:00, then decreased with weak solar radiation and reached the lowest in the early morning. Similar diurnal patterns of PAN and O_3 were observed, indicating the dominance of local photochemistry during the observation period (Zeng et al., 2019). CO, NOx and TVOCs showed highest values in the morning and the lowest values in the afternoon".

- L325-328: All possible factors, meteorological conditions, accumulation of pollution, local transport, etc., are mentioned here. What is the most influencing factor?

Response: Thank you for your suggestions, we are sorry for the complicated and indirect expression of this sentence. We have revised the sentence as "These results indicated favorable meteorological condition was the dominant factor to produce PAN through accelerating its production rate and accumulation".

Section 3.4 is lengthy but informative. It should be divided into two sections.

Response: Thank you for your suggestions, we have divided this section into two sections (Section 3.4.1 Inhibition and promotion effect of PAN on O_3 formation; Section 3.4.2 The influencing factors during inhibition and promotion stages).

Minor comments:

- The quality of figure 7 should be improved.

Response: Thank you for your suggestions, and we have improved the quality of figure 7.

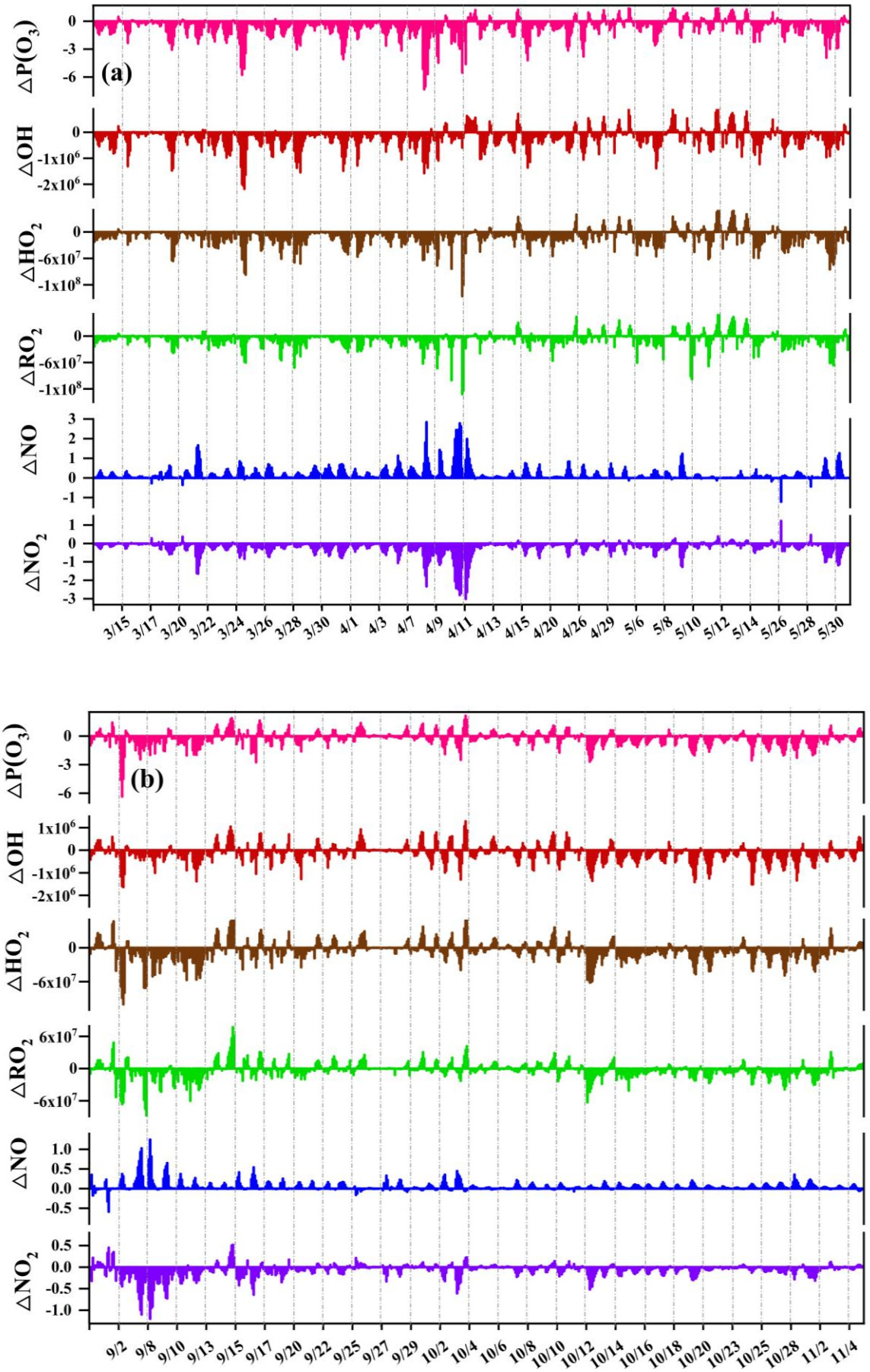

Fig. 7. The differences of O_3 net production △P(O_3), △OH, △HO_2, △RO_2, △NO and △NO_2 between the SC1 and the SC2 during the daytime (06:00-17:00) in (a) spring and (b) autumn (Unit: ppbv·h^{-1} for △P(O_3); ppbv for △NO and △NO_2; molecules·cm^{-3} for △OH, △HO_2 and △RO_2). The SC1 scenario was the base scenario putting all detected data (i.e. VOCs, trace gases, and meteorological parameters) into the model with all reaction pathways of the MCM mechanism, and the SC2 disabled the PAN chemistry, which is the only difference between SC1 and SC2.

- Section 2.1 can be moved to the supplementary material. I have difficulty in reading the x-axis labels in Figure 1.

Response: Thanks for your suggestion. We have changed a high resolution picture. Considering the importance of observation experiment details, we have simplified this part and divided them into two sections (Section 2.1 Observation site; Section 2.2 Measurement techniques). About Figure 1, the specific changes are as follows.

2.1 Observation site

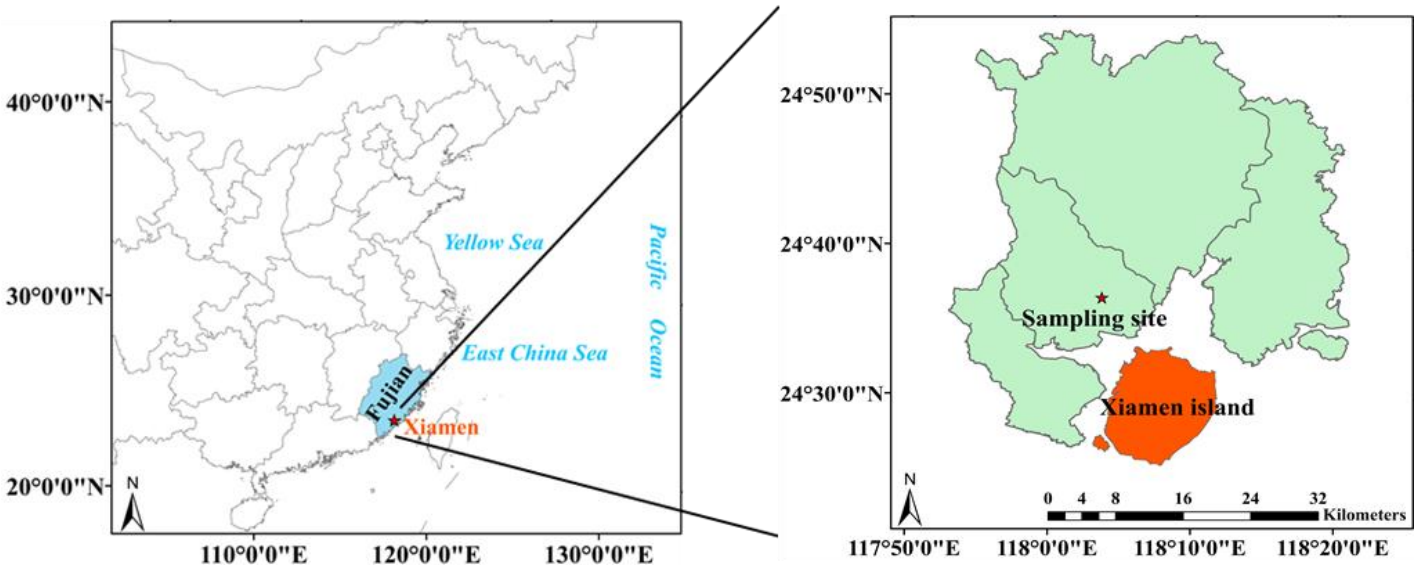

Fig. 1. Location of Xiamen and the observation site.

Observations were carried out at the Atmospheric Environment Observation Supersite (AEOS, 24.61° N, 118.06° E; Fig. 1), located on the rooftop of around a 70 m high building in the Institute of Urban Environment, Chinese Academy of Sciences. The observations site is surrounded by highways, educational institutions, and residential buildings, which was characterized by rapidly urbanizing development area. When the prevailing wind direction was southerly winds, our observation site is downwind of the densely populated downtown (Xiamen island) (Hu et al., 2020; Liu et al., 2022). The field observations were continuously conducted from March 15 to November 4, 2020. The photochemical pollution events mainly appeared during spring and autumn in Xiamen, and we preferred to choose the periods with relatively high O_3 and PAN levels, then the measured data of 53 days in each season was chosen after excluding some special circumstances, such as extreme synoptic situations and instrument calibration.

2.2 Measurement techniques

PAN was monitored using a PAN analyzer (PANs-1000, Focused Photonics Inc., Hangzhou, CN) containing gas chromatography with electron capture detector (GC-ECD). During the observation period, multi-point standard curve calibration was conducted once a month, and single-point calibration was conducted every week, respectively. In the calibration mode of the PAN analyzer, the Mass Flow Controller (MFC) controls the flow rate of NO, acetone, and zero gas separately. The PAN standard gas is generated by the reaction of NO and acetone under ultraviolet light irradiation, and the sample is diluted to the required calibration mixing ratio for injection analysis. PAN was detected every 5 min and the detection limit was 50 pptv. The uncertainty and precision of PAN measurement were ±10% and 3%, respectively.

A gas chromatography-mass spectrometer (GC-FID/MS, TH-300B, Wuhan, CN) was used for monitoring the atmospheric VOCs with a 1-hour time resolution. The instrument conducted sampling with a

30 L/min sampling rate, then samples were pre-concentrated by cooling to -160 °C in a cryogenic trap followed by heating to 100 °C, and subsequently transferred to the secondary trap by high-purity helium (He). The flame ionization detector (FID) detected the low-carbon (C2-C5) hydrocarbons by a PLOT (Al_2O_3/KCl) column (15 m × 0.32 mm × 6.0 μm); the other species were quantified using a DB-624 column (60 m × 0.25 mm × 1.4 μm). The instrument system can quantitatively analyze 106 VOCs in the ambient atmosphere, including 29 alkanes, 11 alkenes, one alkyne, 17 aromatics, 35 halogenated hydrocarbons, and 13 OVOCs. The single-point calibration was performed every day at 23:00 with the standard mixtures of PAMS and TO15, and multi-point calibration was performed one month. The detection limits of the measured VOCs were in the range of 0.02 ppbv to 0.30 ppbv, and the measurement precision was ≤10%.

Criteria air pollutants of O_3, CO, SO_2, and NOx, were monitored by using Thermo Instruments TEI 49i, 48i, 43i, and 42i (Thermo Fisher Scientific, Waltham, MA, USA), respectively. HONO was monitored using an analyzer for Monitoring Aerosols and Gases in Ambient Air (MARGA, ADI 2080, Applikon Analytical B.V., the Netherlands). Particulate matters ($PM_{2.5}$) were monitored by oscillating microbalance with tapered element (TEOM1405, Thermo Scientific Corp., MA, US), and the uncertainty of the $PM_{2.5}$ measurement was ±20%, respectively. The meteorological parameters (i.e. wind speed (WS), wind direction (WD), pressure (P), air temperature (T), and relative humidity (RH)) were measured by a weather station with sonic anemometer (150WX, Airmar, USA). Ultraviolet radiation (UV) was determined by a UV radiometer (KIPP & ZONEN, SUV5 Smart UV Radiometer). Photolysis frequencies including $J(O^1D)$, $J(NO_2)$, J(HONO), $J(NO_3)$, J(HCHO), and $J(H_2O_2)$ were analyzed by a photolysis spectrometer (PFS-100, Focused Photonics Inc., Hangzhou, China), and the uncertainty and detection limit of photolysis rates measurement were ±5% and around 1×10^{-5}, respectively.

Table S1 shows the detailed uncertainty and detection limit of instruments for trace gas observation. A schedule was applied to operate and inspect the AEOS monitoring station regularly and strictly to ensure the validity of the data. The detailed applications of the atmospheric monitoring procedure were shown in our previous studies (Wu et al., 2020; Liu et al., 2020a; Liu et al., 2020b; Hu et al., 2020).

Reference:

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