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Understanding summertime peroxyacetyl nitrate (PAN) formation and its relation to aerosol pollution: Insights from high-resolution measurements and modeling

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Abstract: Peroxyacetyl nitrate (PAN), a key indicator of photochemical pollution, is generated through a process similar to ozone (O_3), involving the photochemical reactions of specific volatile organic compounds (VOCs) in the presence of nitrogen oxides. Notably, PAN has been observed at unexpectedly high concentrations (maximum: 3.04 ppb) during summertime that the daily maximum values of PAN were better correlated to black carbon (BC) (R^2=0.85) than ozone (O_3) (R^2=0.75), suggesting that summertime haze and photochemical pollution were deeply connected. We addressed the puzzle of summertime PAN formation and its association with aerosol pollution under high ozone conditions by analyzing continuous high temporal resolution data utilizing box modeling in conjunction with the master chemical mechanism (MCM). With an IOA value of 0.75, the MCM model proves to be an ideal tool for investigating PAN photochemical formation. The model performed better during the clean period (R^2: 0.6782, slope K: 0.9097) than during the haze period (R^2: 0.4708, slope K: 0.7477). Through the machine learning method of XGBoost, we found that the top three factors leading to simulation bias were NH_3, NO_3, and $PM_{2.5}$. Moreover, the net production rate of PAN becomes negative with PAN constrained, suggesting the existence of an unknown compensatory mechanism. Both RIR and EKMA analyses indicate that PAN formation in this region is VOC-controlled. Controlling emissions of VOCs, particularly alkenes, C_5H_8, and aromatics, would mitigate PAN pollution. RIR results also show that during the clean period, PAN is more sensitive to changes in various pollutants than during the haze period, underscoring the importance of deep emission reductions. PAN promotes OH and HO_2 while inhibiting the formation of O_3, RO_2, NO, and NO_2. This study deepens our comprehension of PAN photochemistry while also offering scientific insights for guiding future PAN pollution control strategies.

Introduction

Peroxyacetyl nitrate (PAN, $CH_3C(O)ONO_2$) is a significant secondary gaseous pollutant commonly present in photochemical smog and poses risk to human health and plant growth, being 1-2 magnitudes more phytotoxic than ozone (O_3) (Yukihiro et al., 2012; Taylor, 1969). Additionally, PAN's low aqueous solubility, minimal reactivity with hydroxyl radicals (OH), and slow photolysis contribute to its capacity for long-range transport of nitrogen oxides (NOx) (Xu et al., 2018; Zhai et al., 2024; Marley et al., 2007b). Therefore, its formation in polluted areas holds significant importance beyond local concerns. Similar to surface O_3, PAN is produced during the oxidation of volatile organic compounds (VOCs) in the presence of NOx (R1-R3). PAN is formed when NO_2 reacts with peroxyacetyl (PA) radicals ($CH_3C(O)OO\bullet$) (R2), but the presence of NO consumes PA radicals, inhibiting PAN production (R3), which creates a comparable dependence of PAN and O_3 on NO and NO_2 levels (Xu et al., 2021). Unlike O_3, however, PAN is influenced by only a limited number of oxygenated VOCs (OVOCs) that generate PA radicals. These OVOCs, which are second-generation precursors of PAN, include acetaldehyde (CH_3CHO), acetone ($CH_3C(O)CH_3$), methylglyoxal (MGLY, $CH_3C(O)CHO$), methyl vinyl ketone (MVK, $CH_2CHC(O)CH_3$), methyl ethyl ketone (MEK, $CH_3C(O)CH_2CH_3$), methacrolein (MACR, $CH_2C(CH_3)CHO$), and biacetyl ($CH_3C(O)C(O)CH_3$). These compounds are typically formed from the oxidation of alkenes, aromatics, and isoprene, which are the first-generation precursors of PAN (Xue et al., 2014; Zhang et al., 2015). Identifying the dominant precursors is crucial for managing PAN pollution effectively. In the troposphere, thermal decomposition (R4) is the primary process responsible for PAN loss (Xu et al., 2021).

$$VOC_s + hv/OH/O_3\ /NO_3 \overset{O_3}{\rightarrow} CH_3C(O)OO\cdot + products \qquad \text{R1}$$

$$CH_3C(O)OO\cdot + NO_2 \overset{k_2}{\rightarrow} PAN \qquad \text{R2}$$

$$CH_3C(O)OO\cdot + NO \overset{k_3}{\rightarrow} CH_3\cdot + NO_2 + CO_2 \qquad \text{R3}$$

$$PAN \overset{k_4}{\rightarrow} CH_3C(O)OO\cdot + NO_2 \qquad \text{R4}$$

In recent years, wintertime photochemical air pollution has increasingly garnered attention. At this time, the concentration of O_3 is low due to the strong titration of NO, while the concentration of aerosol is high, and it is found that aerosol promotes PAN generation. Surprisingly high concentrations of OH radical, particularly under hazy conditions, have been observed and are largely attributed to HONO photolysis. Winter photochemical and haze pollution often exacerbate each other, with photochemical trace gases supplying both oxidants and precursors for aerosol formation, and aerosols acting as mediums for heterogeneous reactions that produce key oxidants such as HONO, H_2O_2, and OH radicals (Xu et al., 2021). The OH produced by HONO photolysis can partially replace the UV action to promote PAN formation in winter in southeast coastal area of China when particulate matter is high ($\geq 35 \mu g \cdot m^{-3}$) (Hu et al., 2020). Zhang et al. (2020) found the potential HONO sources significantly improved the PAN simulations in wintertime heavy haze events with high concentrations of PAN. High concentrations of PAN are a consequence of the increased levels of precursors and HONO observed during haze episodes (Liu et al., 2018). In conclusion, most previous studies have studied the effect of aerosol on PAN generation in winter. Further research on PAN should determine whether particulates significantly contribute to its formation during warmer seasons with elevated ozone concentrations (Xu et al., 2021). In Eastern China, photochemical air pollution often involves high concentrations of both O_3 and PAN, a persistent issue during the warm season (April-September) for many years (Lu et al., 2020). The characteristics and formation pathways of PAN during summer have been increasingly studied in regions such as the North China Plain (NCP), the Yangtze River Delta, the Pearl River Delta, and southwestern China. These studies have generally shown consistent diurnal patterns and strong correlations between PAN and O_3, identifying acetaldehyde—primarily derived from the degradation of aromatics and alkenes—as the key direct precursor of PAN in the summer. However, there has been limited research on the formation of peroxyacetyl nitrate (PAN) and its relationship with aerosol pollution during the summertime.

Ximen is one of the fastest urbanizing regions in the southeast China and is also one of the cities with the best air quality in China, where the air quality could represent the future of other Chinese urban regions. Xiamen is also often affected by typhoons and subtropical weather forms in summer. The West Pacific Subtropical High (WPSH) creates weather conditions that promote the formation and accumulation of photochemical pollutants and particulate matter (Wu et al., 2019). This setting provides an ideal "laboratory" for investigating the complexities of summertime PAN formation and its relationship with aerosol pollution under high ozone concentrations. In this study, continuous measurements of trace gases, substances related to aerosols, photolysis rate constants and meteorological parameters were performed at a suburban site in Xiamen from July 10th to July 31st, 2018. Firstly, we provide an overview of pollutant concentrations, meteorological parameters, and weather conditions during the observation period. Secondly, we simulate PAN concentration with the aid of box modeling combined with master chemical mechanism (MCM). Using a machine learning-XGBoost looks for the key factors that affect the model's simulation result and clarified the mechanisms linking haze pollution to photochemical air pollution, as indicated by PAN and O_3. Thirdly, the study identified the main precursors and oxidants responsible for summertime PAN production in Xiamen and evaluated the influence of PAN on local atmospheric oxidation capacity. This study further emphasized the interplay between haze and photochemical air pollution and highlighted significant implications for future research.

2 Methodology

2.1 Field observations

Trace gases (including PAN, O_3, HONO, HNO_3, HCl, NH_3, VOCs, NO*x*, CO, and SO_2), substances related to aerosols (including BC, PM_1, $PM_{2.5}$, PM_{10}, SO_4^{2-}, NO_3^-, NH_4^+, Cl^-, Na^+, K^+, Ca^{2+}, Mg^{2+}), photolysis rate constants (including JO^1D, JNO_2, JHONO, JHCHO_M, JHCHO_R, JNO_3_M, JNO_3_R, JH_2O_2), and meteorological parameters (including temperature, relative humidity, atmospheric pressure, wind speed, and wind direction) were continuously measured at an suburban site in Xiamen from July 10th to July 31st, 2018. All instruments were placed inside an air-conditioned container situated on the rooftop of a 20-story building at the Institute of Urban Environment, Chinese Academy of Sciences (IUE: 118.06°E, 24.61°N) (Fig. S1(a)). When southerly winds prevailed, Xiamen Island, characterized by dense population and traffic congestion, was located upwind of the IUE (Fig. S1(b)). The IUE supersite is surrounded by Xinglin Bay, several universities and institutes, and major roadways with heavy traffic, such as Jimei Road (< 200 m), Shenhai Expressway (870 m), and Xiasha Expressway (2300 m) (Fig. S1(c)).

PAN measurements were conducted using a PANs-1000 analyzer (Focused Photonics Inc., Hangzhou, China), which features an automated system consists of a gas chromatograph, an electron capture detector, and a calibration unit. The analyzer provided PAN readings every 5 minutes, with a detection limit of 50 ppt. The uncertainty and precision of the PAN measurements were ±10% and 3%, respectively. The PAN standard gas was produced through the reaction of acetone and NO under UV light. Calibration procedures included monthly multi-point calibrations and weekly single-point calibrations. Detailed information about the PAN detection system and calibration can be found in previous studies (Hu et al., 2020; Liu et al., 2022). HONO measurements were conducted using a customized Incoherent BroadBand Cavity Enhanced Absorption Spectroscopy (IBBCEAS) system developed by the Anhui Institute of Optics and Fine Mechanics (AIOFM), Chinese Academy of Sciences. The HONO detection limit was 100 ppt, with a time resolution of 1 minute. The measurement principle and calibration method of IBBCEAS can be found in the previous literature (Hu et al., 2022; Duan et al., 2018; Hu et al., 2024). The concentrations of inorganic components in $PM_{2.5}$ aerosols (including SO_4^{2-}, NO_3^-, NH_4^+, Cl^-, Na^+, K^+, Ca^{2+}, Mg^{2+}), as well as the concentrations of gases such as NH_3, HCl, and HNO_3 were analyzed using a Monitor for AeRosols and Gases in ambient Air (MARGA, Model ADI 2080, Applikon Analytical B.V., the Netherlands) (Hu et al., 2022). The criteria air pollutants O_3, NO*x*, CO, and SO_2 were measured using different methods: ultraviolet (UV) absorption for O_3 (TEI model 49i), chemiluminescence with a molybdenum converter for NO*x* (TEI model 42i), non-dispersive infrared for CO (TEI model 48i), and pulsed UV fluorescence for SO_2 (TEI model 43i). A tapered element oscillating microbalance (TEOM1405, Thermo Scientific Corp., MA, USA) was used to continuously measure the mass concentrations of PM_1, $PM_{2.5}$, and PM_{10} online. A photolysis spectrometer (PFS-100, Focused Photonics Inc., Hangzhou, China) was employed to measure the photolysis rate constants. An ultrasonic atmospherium (150WX, Airmar, USA) was used to measure meteorological parameters.

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2.2 Box modeling

This study employed a box model framework utilizing the Master Chemical Mechanism (MCMv3.3.1, https://mcm.york.ac.uk/MCM/home.htt) to investigate sensitivity and mechanisms of PAN formation. The model constraints were derived from observations of trace gases and meteorological parameters, which were averaged to 1-hour intervals. The reliability of model simulation results is often assessed using the index of agreement (IOA), which ranges from 0 to 1, with a higher IOA signifying greater alignment between observed and simulated values. Note that the model simulation values at this time are not constrained by PAN. For specific formulas, please refer to the supplementary information (Eq. S1). Other formulas, including PAN production rates (P(PAN)), net production of PAN (Net (PAN)), and the relative incremental reactivity (RIR), are provided in the supplementary information (Eq. S2- Eq. S4).

The MCM simulates the nonlinear interaction between PAN and its precursors by altering the VOCs-to-NOx ratio across multiple scenarios, while keeping all other parameters fixed. In this study, a 20% step size was applied, reducing VOCs and NOx from 200% down to 0% to construct a scenario matrix. A total of 121 scenarios were generated to model the PAN production rate. The scenario representing the average VOCs and NOx mixing ratio during the sampling period was designated as the base case, with the remaining 120 scenarios created by systematically adjusting the VOC-to-NOx ratio. The output from these 121 simulations was used to construct isopleth diagrams depicting the relationship between VOCs, NOx, and PAN.

2.3 Machine Learning Model

To identify the key factors influencing the performance of the model simulation, the Machine Learning (ML) model was applied to establish the prediction model of bias between simulation of OBM and observation. XGBoost is a supervised boosting algorithm that reduces the risk of over-fitting, captures the nonlinear relationships among predictor variables, and solves numerous data science problems in a rapid and accurate way (Li et al., 2024). It has demonstrated high performance in O_3 studies in over China. As compared to other bagging tree models like random forest, XGBoost can handle more complex data while consuming fewer computing resources. To further improve the interpretability of the ML model, the feature importance of independent input variables in the XGBoost model is quantified using the Shaply Additive explanation (SHAP) approach. The SHAP calculates a value that represents the contribution of each feature to the model′s outcome, which has been successfully applied in atmospheric environmental studies. When the model was being adjusted, 90% of the data was used as the training set, and 10% of the data was used as the test set. The hyperparameters were tuned using grid search and cross-validation method. Specifically, for a single hyperparameter, grid search was used to obtain its more appropriate value range, and for the combinations of hyperparameters, the whole training set was split into ten folds and then run a grid search over pre-adjusted combinations of hyperparameters by training nine folds and predicting on the one fold in cross-validation procedure. For key hyperparameters of XGBoost model, the number of trees was 100, learning rate was 0.1, max depth was 6. The model was trained and tested on hourly data during the whole observation and the established model was examined by coefficient of determination (R^2) value, the root-mean-squared error (RMSE) and mean absolute error (MAE). The formulas of RMSE and MAE are provided in the supplementary information (Eq. S5 & Eq. S6). The performance of both models is illustrated in Fig. S3. The R^2, MAE, and RMSE for the training set are 0.9037, 0.08, and 0.12, respectively, while the corresponding values for the test set are 0.7664, 0.10, and 0.14, respectively. These statistical metrics indicate that the XGBoost model is promising for further analysis.

3. Results and discussion

3.1 Overview of observation

The measured data of PAN, related trace gases and meteorological parameters at IUE over 10-31 July 2018 are documented in Fig. 1. Combine with the synoptic situation (Fig. S4), the 8th typhoon of 2018, Typhoon Maria, made landfall on the morning of the 11th in Huangqi Peninsula, Lianjiang County, Fujian. Due to the influence of the typhoon's outer spiral rain bands, there was moderate to heavy rain on the 11th. Correspondingly, there was a noticeable decrease in ultraviolet radiation and the temperatures. Starting from the 12th, a Western Pacific subtropical high (WPSH) strengthened and extended westward, exerting control over Xiamen city. In the lower atmosphere, it was influenced by the eastward flow, resulting in predominantly cloudy weather. From the 16th to the 18th, the area was affected by the outer periphery of Typhoon Shan Shen, which formed on the 17th in the northeastern part of the South China Sea and moved westward, making landfall along the coast of Wancheng Town, Wanning City, Hainan Province in the early hours of the 18th. During this period, the city experienced strong winds with gusts reaching 5 to 6 on the Beaufort scale in the urban areas. At the same time, the concentration of various pollutants reached their lowest levels, and the daily variation patterns were less pronounced. From the 20th to the 21st, Xiamen City experienced the influence of the peripheral descending airflow associated with Typhoon Ampil (which formed in the northwest Pacific Ocean around 8:00 P.M. on the 18th and moved northwest, making landfall along the coast of Chongming Island, Shanghai, around noon on the 22nd). During this period, there were fewer clouds and higher temperatures. From the 22nd to the 24th, the city was successively affected by the outer periphery of Typhoon Ampil and a tropical low-pressure system, resulting in occasional showers or thunderstorms. From the 25th to the 31st, a WPSH once again strengthened and controlled Xiamen City. As a result, Xiamen city experienced stable meteorological conditions, with light winds (ws = 1.04 m/s), persistently high temperatures (daily maximum average of 37.82°C), and high relative humidity (daily maximum average of 81.65%). These factors created an environment that favored the buildup of particulate matter and enhanced the photochemical formation of O_3 and PAN (Wu et al., 2019). The daily maximum average of $PM_{2.5}$, O_3 and PAN were 49.26 $\mu g.m^{-3}$, 93.62 ppb, and 1.37 ppb, respectively.

The phenomenon of simultaneous high levels of photochemical and particulate matter appears. Throughout the 22-days campaign, 12 days (including July 11th, 13th, 21st to 23rd, and 25th to 31st) were observed with 1 h concentrations of $PM_{2.5}$ exceeding 35 $\mu g \cdot m^{-3}$; 13 days (including July 11th, 13th, 15th, 20th to 23rd, and 26th to 31st) were observed with 5-min concentrations of PAN exceeding 1 ppb. The maximum concentration was recorded at 3.04 ppb (5-min data) at 11:09 local time of 13 July 2018. This concentration of PAN is comparable to the levels recorded at downwind of Guangzhou, southern China (3.9 ppb) (Wang et al., 2010), 2.51 ppb in Nashville, U.S (Roberts et al., 2002). However, this value was significantly lower than heavily polluted areas in northern China in the summer, such as Beijing (9.34 ppb, (Xue et al., 2014)), Lanzhou (9.12 ppb, (Zhang et al., 2009)), and Jinan (13.47 ppb, (Liu et al., 2018)). This is likely because the higher summer temperatures in the southeastern coastal region are conducive to the thermal decomposition of PAN, and the precursor concentration of PAN is significantly lower than in the northern region. Throughout the observation period, the variations in O_3 and PAN were almost identical, but the maximum concentration of O_3 occurred at 3:00 p.m. on July 29th (114.12 ppb). The correlation between the daily maximum values of PAN and BC is the strongest (R=0.85), followed by O_3 (R=0.75), suggesting that summertime haze and photochemical pollution were deeply connected.

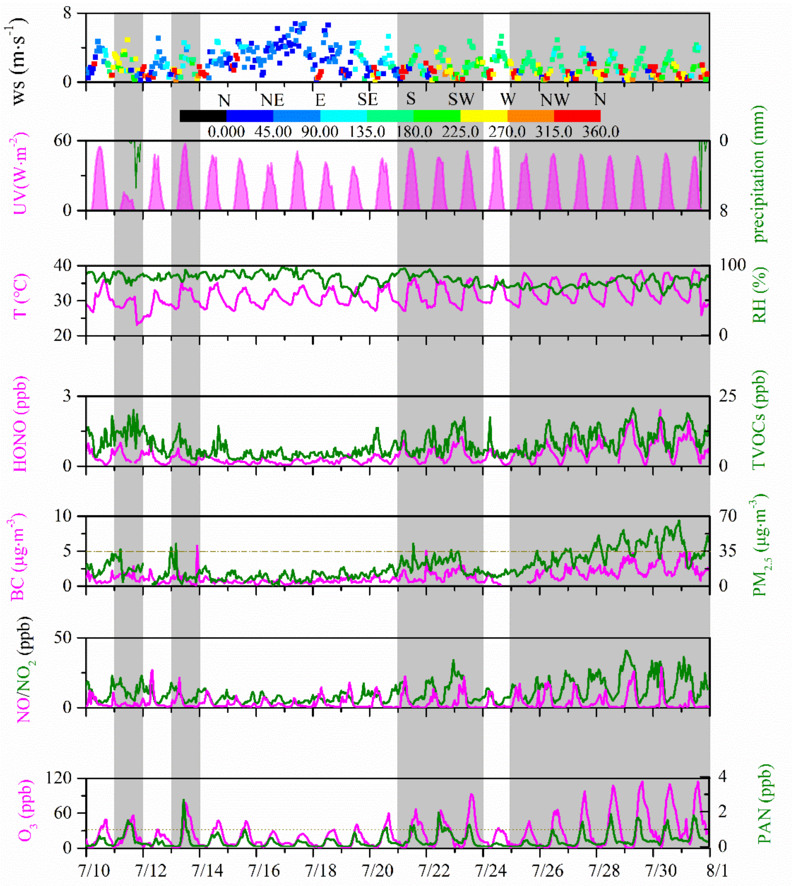

Figure 1. Time series of trace gases and meteorological parameters observed at IUE during 10-31 July 2018. The gray shading represents days when the $PM_{2.5}$ hourly daily maximum value exceeded 35 µg·m^{-3}.

We categorize it as "haze" and "clean" based on whether the $PM_{2.5}$ hourly daily maximum value is greater than 35 µg·m^{-3}.

Specifically, "haze" includes July 11th, 13th, 21st to 23rd, and 25th to 31st, while other days are categorized as 'clean'. To provide a quantitative perspective, the statistics for PAN and associated species were calculated and compiled in Table 1. $PM_{2.5}$ concentrations during the haze period were significantly higher than during the clean period, being 2.49 times that of the clean period. There was no significant difference of UV levels between clean and haze periods, while temperatures in the haze phase were notably higher than those in the clean phase. Therefore, without considering precursors, PAN concentrations should be lower during the haze phase due to higher thermal decomposition. In fact, PAN concentrations during the haze period were 2.35 times higher than those during the clean period. During the haze period, ozone concentrations were also significantly higher than during the clean period, being 2.04 times that of the clean period. These observations indicate that the atmospheric oxidation capacity is relatively strong during the haze period. Similar to PAN, HONO also exhibits higher concentrations during the haze phase (approximately 2.33 times that of clean conditions), which is consistent with current research findings that particles promote the generation of HONO (Ye et al., 2017). NO also experienced an increase from clean (3.28 ppb) to hazy (4.30 ppb) conditions, albeit less prominently than NO_2 (from 7.21 to 14.55 ppb). This observation further underscores that, during hazy periods, the atmosphere demonstrates heightened oxidizing potential, facilitating the conversion of NO to NO_2. While the increased NO levels on hazy days reduced PA radicals and hindered PAN formation, this effect was offset by the concurrently higher concentrations of PAN precursors (NO_2 and VOCs) during those days. The TVOCs have increased to some extent, but in hazy conditions, they are only 1.34 times that of clean conditions. This is also because the strong oxidizing conditions during haze periods convert VOCs into secondary pollutants, such as O_3 and PAN. The TVOC levels at this site are comparable to that at a rural site in a coastal city-Qingdao (7.6 ppb), significantly lower than inland sites (such as Wuhan (30.2, (Liu et al., 2021a)) and Chengdu (28.0 ppb, (Yang et al., 2020))) or economically more developed coastal cities (such as Shanghai (25.3 ppb, (Zhu et al., 2020)) and Hong Kong (26.9, (Wang et al., 2018))), and significantly higher than regional background locations like Mt. Wuyi (4.7 ppb, (Hong et al., 2019)), Mt. Waliguan (2.6 ppb, (Xue et al., 2013)), and Mt. Nanling (4.7 ppb, (Wang et al., 2023)). The isoprene level during haze period was significantly higher than that during clean period probably due to haze period with higher temperature (Wang et al., 2023). The wind speed was very low during both the clean and haze periods, especially during the haze period with only 1.12 m·s^{-1}. The relative humidity was high during both periods, and there was no significant difference between the clean and haze periods.

Table 1. Descriptive statistics of major trace gases (ppb), particulate matter (μg·m^{-3}) and meteorological parameters during 10-31 July 2018.

Species	Clean (mean ± SD)	Haze (mean ± SD)
PAN	0.20 ± 0.23	0.47 ± 0.46***
O_3	16.07 ± 12.73	32.79 ± 29.73***
HONO	0.27 ± 0.18	0.63 ± 0.43***
NO	3.28 ± 4.03	4.30 ± 8.39***

NO_2	7.21 ± 3.87	14.55 ± 8.89***
TVOCs	6.13 ± 1.73	8.19 ± 2.55***
C_5H_8	0.13 ± 0.04	0.17 ± 0.05***
PM_1	10.13 ± 3.91	24.36 ± 10.77***
$PM_{2.5}$	11.21 ± 5.33	27.93 ± 13.16***
PM_{10}	24.26 ± 9.45	47.28 ± 20.63***
UV ($W \cdot m^{-2}$)	14.29 ± 17.38	13.18 ± 17.40
T (°C)	30.68 ± 2.39	31.92 ± 3.36***
RH (%)	81.94 ± 8.60	77.18 ± 8.22
WS ($m \cdot s^{-1}$)	1.64 ± 0.69	1.12 ± 0.61*

Note: *, **, and *** indicate that they passed the significance test at 0.05, 0.01 and 0.001 levels, respectively.

The average diurnal patterns of PAN and related variables have been averaged separately for clean and hazy conditions. The daily variation of PAN exhibits a clear unimodal pattern, with concentrations starting to rise after sunrise and decreasing after 12:00 caused by thermal decomposition of PAN at high temperatures. The peak occurring at noon indicates that PAN primarily originates locally, as a delay of about 1-2 hours would be expected if it were influenced by transportation (Liu et al., 2024). The daytime increment was much larger for hazy condition (1.17 ppb) than for clean condition (0.52 ppb), indicating stronger photochemical production of PAN for hazy condition. The daily variation pattern of ozone is similar to PAN, except that ozone reaches its peak relatively later compared to PAN, with the peak occurring at 16:00 during the clean phase and 14:00 during the haze phase. Although PAN and O_3 are both products of photochemical reactions involving NO*x* and VOCs, their production efficiencies differ. PAN is specifically formed from VOCs that are precursors to the acetyl radical (CH_3CO), whereas O_3 can be produced from the oxidation of any VOCs. Analyzing the correlation between PAN and O_3 can offer insights into their respective photochemical production efficiencies. As shown in Fig. S5, the positive correlation between the daily maximum values of PAN and O_3 for clean condition (R^2=0.6701) was better than that for hazy condition (R^2=0.1504). The slopes of the linear regression were 0.021 ppb/ppb for clean conditions and 0.009 for hazy conditions. This indicates that, on average, approximately 2.1 ppb of PAN could be produced for each 100 ppb of O_3 formed under clean conditions, and about 0.9 ppb of PAN for each 100 ppb of O_3 under hazy conditions in the air masses reaching IUE. The slope of linear regression for clean condition is comparable to those determined in Hongkong (0.028, (Xu et al., 2015)), Mexico (0.02, (Marley et al., 2007a)), and Nashville (0.025, (Roberts et al., 2002)). The lower efficiency of PAN production relative to O_3 indicates that PAN precursors represent only a small portion of the total VOCs, especially during hazy conditions. Additionally, the high temperatures in the southeast coastal region likely contribute to the lower production efficiency of PAN. This result is consistent with the result that RIR during the cleaning period is higher than that during the haze period. As shown in Fig. S6, in the clean period, the correlation between PAN and O_3 is the strongest (R^2=0.7042), indicating that O_3 and PAN are both photochemical end products during clean periods. In contrast, during hazy periods, the correlation between PAN and $O_3 \times JO^1D$ is the strongest (R^2=0.6597), suggesting that O_3 plays a more significant role in promoting PAN formation through photolysis to generate OH during hazy periods.

Unlike the daily variation patterns of PAN and O_3, HONO exhibits a swift concentration decrease after sunrise in both clean and hazy conditions, undergoing photolytic conversion into OH radicals. Subsequently, in clean conditions, HONO starts to increase in concentration after sunset. In hazy conditions, however, the increase begins from 16:00 LT and not after sunrise. This suggests a robust daytime net production or transport of HONO, where the rates surpass those of HONO photolysis and other sinks in the afternoon in hazy conditions. The NO levels reach their peak at 7:00 during the morning rush hour, reflecting advection of fresh urban plumes to the study site. The daily variation of NO_2 exhibits a 'U' shape, reaching its minimum value at 13:00, mainly owing to effects of emission, boundary layer height and photochemical reactions. In the clean period, the daily variation of $PM_{2.5}$ is similar to that of NO_2, both showing a 'U' shape, reaching their lowest values at noon. However, during the haze phase, the daily variation pattern of $PM_{2.5}$ appears somewhat different. There is a noticeable trough in the early morning, remains stable during the day, and starts to rise after sunset.

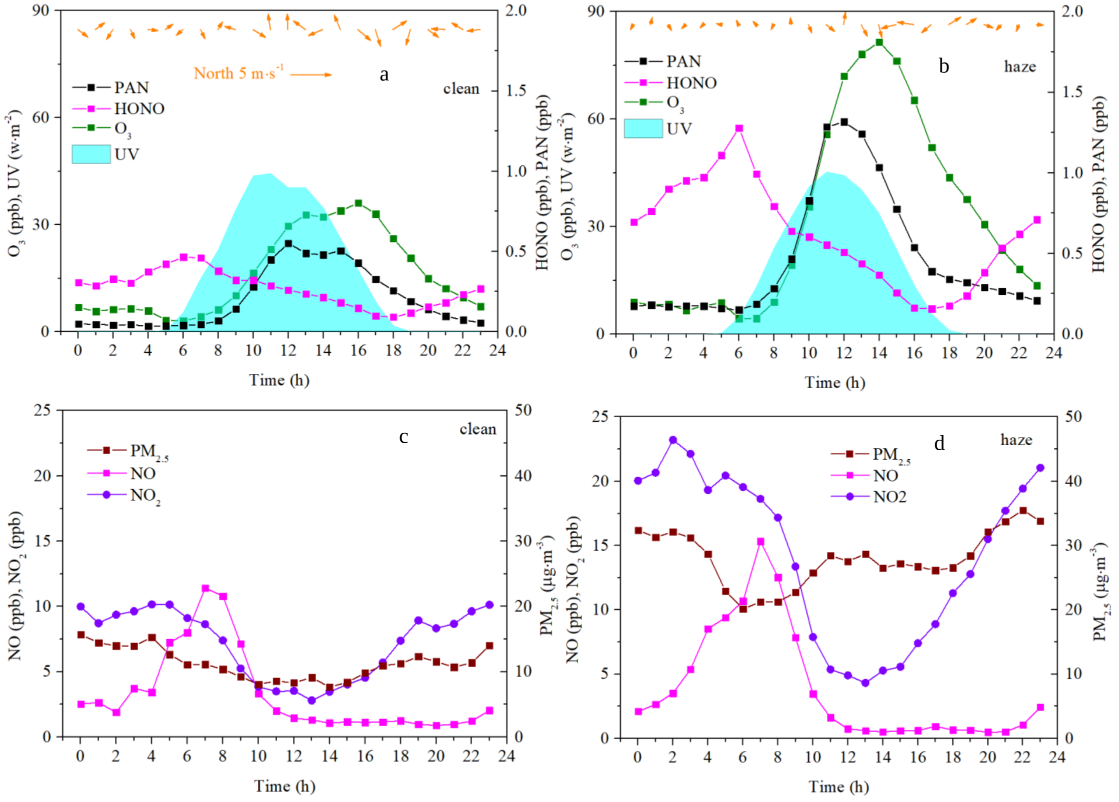

Figure 2. The diurnal variations of PAN, HONO, O_3, and UV during clean (a) and hazy (b) periods, as well as the diurnal variations of $PM_{2.5}$, NO, and NO_2 during clean (c) and hazy (d) periods.

3.2 PAN formation: key factors and mechanisms

To investigate the key factors and mechanisms of PAN formation, PAN was simulated by constraining the MCM-based box model with meteorological conditions and observed concentrations of precursor gases. The model successfully replicated the variations in PAN, achieving an IOA of 0.75. (Fig. 3(a)), which was within the accepted range (0.66-0.87) in previous studies (Zeng et al., 2019). The model captured its formation rate well in general, with observed rates varying from 0.04 to 0.52 ppb·h^{-1} (average: 0.20 ppb·h^{-1}) and modeled rates ranging from 0.09 to 0.46 ppb·h^{-1} (average: 0.19 ppb·h^{-1}) (see Fig. 3(b)). The similar result was found in the North China Plain (NCP) region in the wintertime (Xu et al., 2021). When calculating the IOA separately for clean and hazy periods, it was found that the IOA significantly increased to 0.89 and 0.81 (Fig. 3(c)), respectively. This phenomenon indicates a substantial difference in the PAN production and destruction mechanisms between clean and hazy periods. Furthermore, the simulated values are closer to the observed values during clean period, reflected in a higher R^2 value (R^2=0.6782) and a K value closer to 1 (K=0.9097) (Fig. 3(c)). In contrast, the R^2 value and the K value during hazy period are only 0.4708 and 0.7477, respectively (Fig. 3(c)). This phenomenon suggests that reactions without considered in MCM may enhance PAN generation during hazy periods.

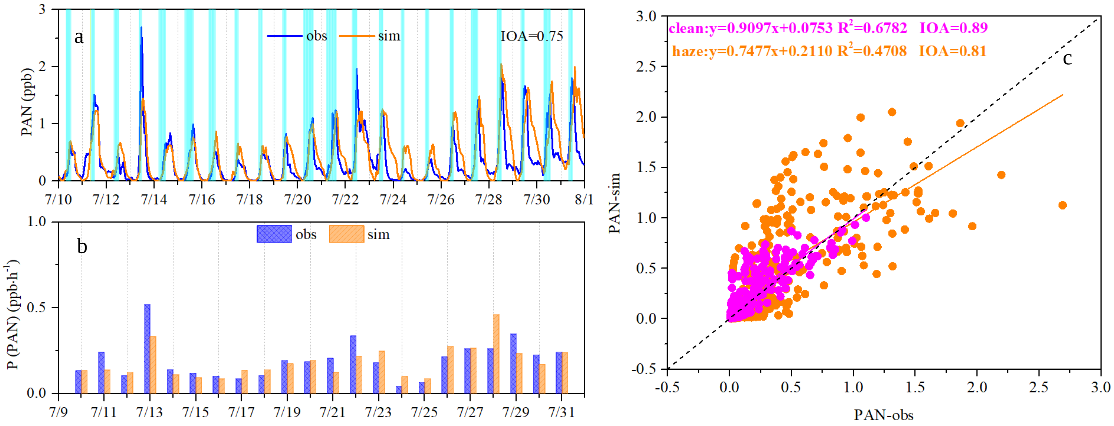

Figure 3. Comparisons of modeled PAN and observed PAN (a) variation (daytime photochemical PAN production periods indicated by cyan shading), (b) production rates, (c) correlation between PAN observations and simulated values

To identify the key factors influencing the performance of the model simulation, we used the difference between the model simulation values and the observed values (bias) as the target. The remaining variables, which were not input into the OBM model, such as NH_3, HNO_3, HCl (alkaline and acidic gaseous pollutants), $PM_{2.5}$ concentrations and their components, as well as physical process parameters like wind speed and wind direction, were used as features. As shown in Fig. 4 (a), through XGBoost-SHAP machine learning, we found that NH_3 is the most significant parameter affecting bias, contributing 19.68 %. A scatter plot analysis of the SHAP values of NH_3 versus NH_3 concentrations revealed that as NH_3 concentrations increase (Fig. 4 (b)), the OBM model tends to overestimate more significantly. To date, there are very few studies that directly address the impact of NH_3 on PAN formation. Xu et al. (2021) suggested that NH_3 could promote the formation of HONO, which in turn affects

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PAN formation. However, since we included HONO as an input to constrain the model, the indirect influence of NH_3 on PAN formation through HONO can be excluded. NH_3 in the atmosphere can preferentially react with sulfuric acid (H_2SO_4) to form ammonium sulfate ($(NH_4)_2SO_4$) secondary inorganic aerosols (Behera et al., 2013), leading to the heterogeneous reaction removal of PAN by secondary inorganic aerosols. This result is validated by the negative correlation between the SHAP values of NH_4^+ and SO_4^{2-} and their respective concentrations. NO_3^- is the second most significant parameter influencing the bias between the two, contributing 11.33 % (Fig. 4 (a)). NO_3^- has a negative correlation with the bias (Fig. 4 (c)), indicating that higher NO_3^- levels lead to more significant underestimation by the model, suggesting that NO_3^- promotes PAN formation in the actual atmosphere (Hanst, 1971). $PM_{2.5}$ is the third most significant parameter (Fig. 4 (a)), contributing 9.4 %. $PM_{2.5}$ has a positive correlation with the bias (Fig. 4 (d)), indicating that higher $PM_{2.5}$ levels lead to more significant overestimation by the model, suggesting that PAN can undergo heterogeneous removal on the surface of $PM_{2.5}$ in the actual atmosphere (Sun et al., 2022).

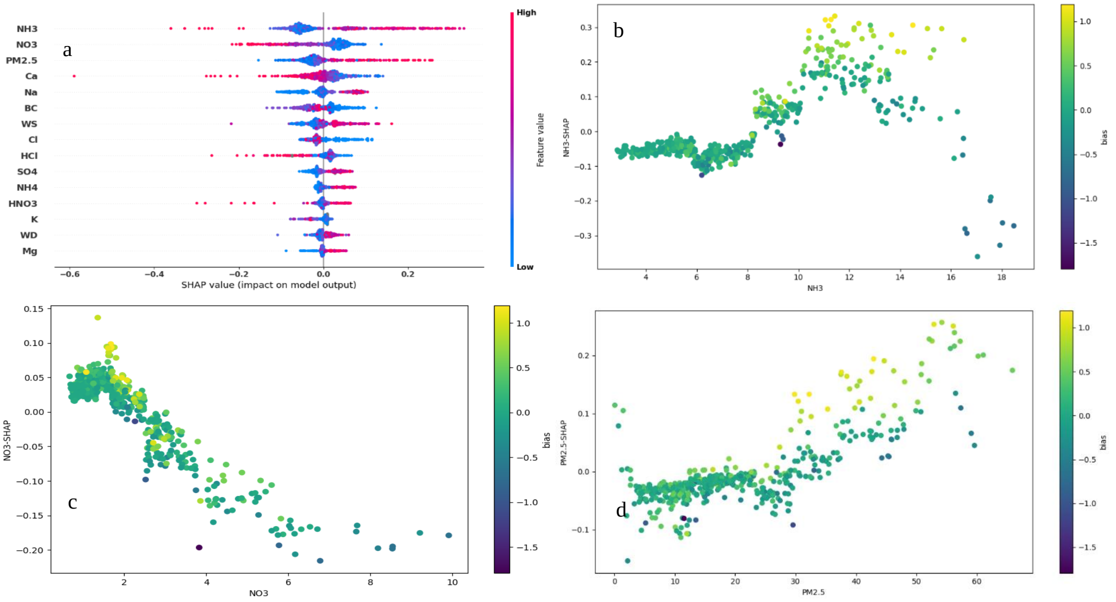

Figure 4. Feature importance was obtained by XGBoost-SHAP method (a). The scatter plots between concentration of top three important features and their SHAP values (b-d), and colored with the difference between the model simulation values and the observed values (bias).

Figure 5 (a) and (b) show the average production and destruction rates of PAN during clean and haze periods without PAN constrained. During the haze period, both the production and destruction rates of PAN are significantly higher than during the clean period. The higher production rate of PAN during the haze period is due to the higher concentration of PAN precursors, while the higher destruction rate is because both the temperature and PAN concentration are higher. Regarding the net production rate, it is also higher during the haze period than during the clean period, which corresponds to the previously observed diurnal variation. From 6:00 to 12:00 during the haze period, the net production rate of PAN is positive, with an average value of 0.19 ppb·h^{-1}. During the clean period, from 6:00 to 12:00, the net production rate of PAN is 0.12 ppb·h^{-1}. The diurnal variation of PAN shows that from 6:00 to 12:00, the average net production rates during the haze and clean periods are 0.20 ppb·h^{-1} and 0.09 ppb·h^{-1}, respectively. The model-simulated net production rate is close to the observed net production rate, further indicating that the model can simulate PAN well, and also confirming that PAN in summer mainly comes from local production. The net production rate of PAN during the haze period is similar to the summer results in urban areas of the Pearl River Delta (PRD), which is 0.17 ppb·h^{-1}, while the net production rate of PAN during the clean period is similar to the summer results in rural areas of the PRD, which is 0.12 ppb·h^{-1} (Liu et al., 2024).

Figure 5 (c) and (d) show the average production and destruction rates of PAN during clean and haze periods with PAN constrained. The net production rate of PAN is approximately zero at night during both clean and haze periods, while there is a significant difference in the net production rate during the day. During the clean period, the daytime net production rate of PAN is greater than zero, with an average value of 0.19 ppb·h^{-1}. In contrast, during the haze period, the net production rate of PAN is negative from 6 a.m. to 1 p.m., with an average value of -0.47 ppb·h^{-1}, and positive from 2 p.m. to 5 p.m., with an average value of 0.47 ppb·h^{-1}. Previous research has shown that an increase in temperature, an increase in PAN concentration, or a decrease in PAN precursors (including VOCs and NO_2) can cause the net production rate of PAN to change from positive to negative (Liu et al., 2024). We conducted a correlation analysis of the net production rate of PAN with temperature, PAN concentration, VOCs, and NO_2 and found that the net production rate of PAN had the best correlation with PAN concentration (R^2=0.1316), showing a significant negative correlation (k=-0.5283) (Fig. S7). Additionally, we also observed that when the net production rate of PAN is negative, the PAN concentration is often very high (Fig. S7). As shown in Fig. 5, we conducted sensitivity experiments by reducing the PAN concentration by 80 %, i.e., 0.2 times the observed value, and found that the net production rate of PAN was positive throughout the observation period. Conversely, when the PAN concentration was increased by 140%, i.e., 2.4 times the observed value, the net production rate of PAN was found to be almost negative throughout the observation period. Besides, we also conducted sensitivity experiments on temperature and found that when simulating winter temperatures, i.e., 0.4 times the observed value, with a temperature range of 9.25-15.29°C, the net production rate of PAN was positive throughout the observation period. Similarly, when simulating spring and autumn temperatures, i.e., 0.6 times the observed value, with a temperature range of 13.87-23.39°C, the net production rate of PAN was also positive throughout the observation period. In conclusion, the net production rate of PAN becomes negative with PAN constrained, further suggesting the existence of an unknown compensatory mechanism.

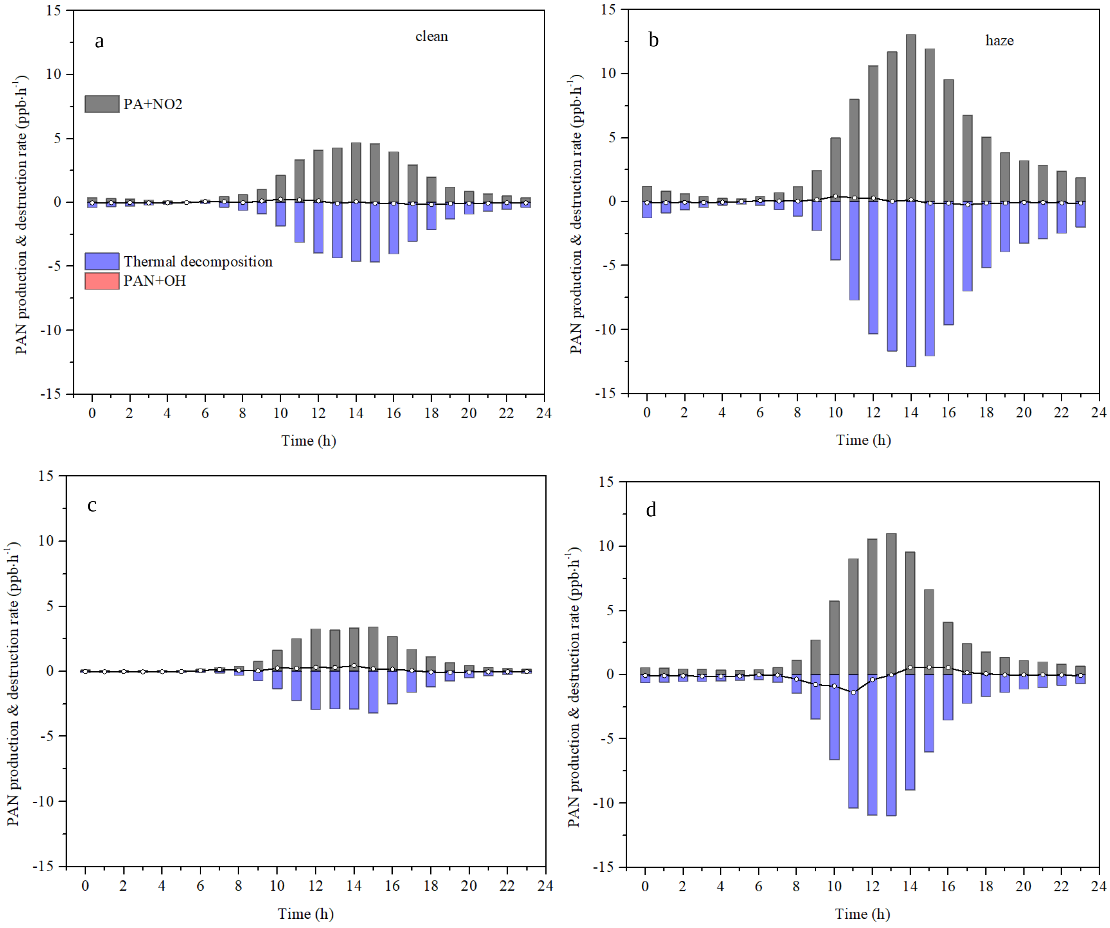

Figure 5. Average diurnal variation of the simulated production, destruction and net rates of PAN during clean (a) and haze (b) without PAN constrained. And average diurnal variation of the simulated production, destruction and net rates of PAN during clean (c) and haze (d) with PAN constrained.

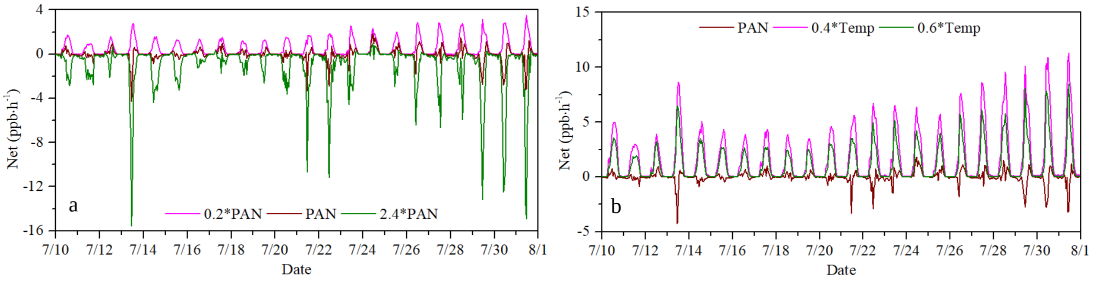

Figure 6. Net PAN production rates at different PAN concentrations (a) and different temperatures (b)

PAN is formed when the PA radical reacts with NO_2. Given the swift equilibrium between R2 and R4 at high temperatures, budget

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analysis of PA's production and consumption pathways is frequently used to detail the mechanisms behind PAN formation (Sun et al., 2020). Figure 7 illustrates the diurnal patterns of the primary production and loss pathways for the PA radical across different periods. As shown in Fig. 7, during haze days, the rates of PA production and destruction were twice as high as those on clean days. This indicates that radical cycling and photochemical formation were more efficient during haze days, driven by higher temperatures and a greater abundance of precursors (Zeng et al., 2019). The PA radical production rate from PAN thermal decomposition reached its peak at 15:00 (3.22 ppb·h^{-1}) and 13:00 (10.99 ppb·h^{-1}) for clean and haze days, perfectly coinciding with the peak temperature time. In addition, the conversion of PAN into PA radical through thermal decomposition had high correlations with temperature during both haze (R^2=0.82) and clean days (R^2=0.77). The conversion of PAN into PA radical through thermal decomposition during haze days was significantly higher than that during clean days, which was not only enhanced by higher temperature but also maintained by higher PAN concentration during haze days. The thermal decomposition of PAN to PA radical during the day (5:00-18:00 local time) accounted for 68.22 % and 45.59 % during haze and clean days, respectively. The pathways that did not account for the transformation between PA and PAN reached their peak around noon (11:00 local time), coinciding with the highest solar radiation and the most intense photochemical reactions, which has been observed in spring and autumn at the same site (Liu et al., 2022).

Production rates of PA from other pathways related to precursors showed single-peak patterns of these four pathways around noon, which suggested that the PA radical generated from these pathways was primarily increased by intense solar radiation at noontime (Sun et al., 2020). The average day PA radical production rates from CH_3CHO via reactions with OH and NO_3 were 1.10 and 0.93 ppb·h^{-1}, accounting for 48.85% and 49.35 % (exclude PAN thermal decomposition sources) during haze and clean days, respectively. These percentages were comparable to previous studies in Guangzhou (46 %) (Yuan et al., 2018) and Beijing (34.11-50.19 %) (Xue et al., 2014), suburban site of Chongqing (47.72 %) (Sun et al., 2020). The second production pathway involved MGLY undergoing photolysis and oxidation through reactions with OH and NO_3 (haze: 0.50 ppb·h^{-1} and clean: 0.42 ppb·h^{-1}), contributing to 22.27 % and 22.12 % for haze and clean days, respectively. Subsequently, radical cycling processes—including the decomposition of RO radicals and the reactions of acyl peroxy radicals with NO—were also significant contributors to PA production, accounting for 18.98% on haze days and 19.54% on clean days. PA from the other OVOCs (excluding CH_3CHO, MGLY) via photolysis and oxidation reactions involving OH, NO_3, and O_3, accounted for 9.90 % and 8.99% during haze (0.22 ppb·h^{-1}) and clean days (0.17 ppb·h^{-1}). There were no notable differences in the proportions of individual pathways contributing to PA between haze and clean days, indicating comparable pollutant compositions in the atmospheric around IUE (Zeng et al., 2019).

The primary contributor to the PAN destruction rate was the reaction between PA and NO_2, accounting for 67.72 % and 51.09 % during haze (4.74 ppb·h^{-1}) and clean days (1.76 ppb·h^{-1}), respectively, followed by PA+NO, contributing to 32.28 % and 48.91 % during haze (2.26 ppb·h^{-1}) and clean days (1.69 ppb·h^{-1}), respectively.

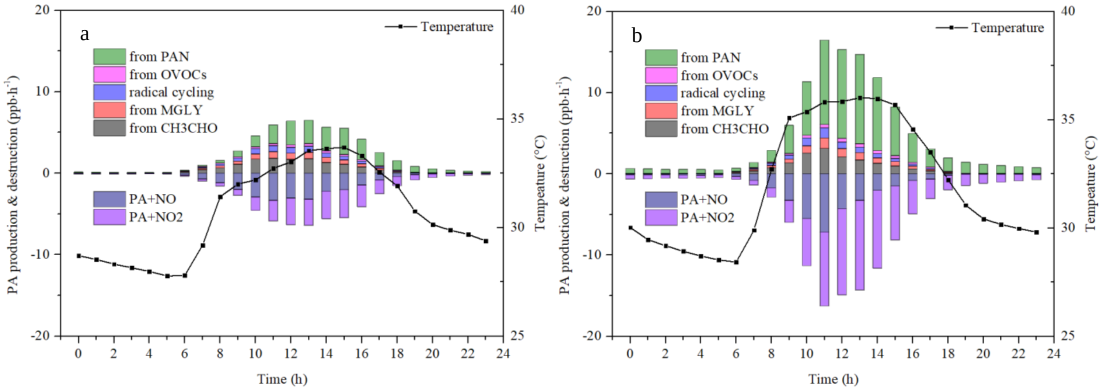

Figure 7. PA radical production and destruction pathways on (a) clean days and (b) haze days.

3.3 Sensitivity of PAN formation and its impact on the local atmosphere

To determine the principal precursors influencing PAN formation, sensitivity modeling analyses were carried out to investigate how PAN relates to its precursors. The RIR reflects how sensitive PAN formation is to changes in its precursor levels. As shown in Fig.8 (a), decreases in NO led to strong negative RIR ranging from -0.67 to -0.27 (-0.52 ± 0.13) throughout the observation period. However, RIR is positive for other species, with NO_2 (0.50 ± 0.11) and VOCs (0.50 ± 0.15) having the highest RIR, followed by HONO (0.12 ± 0.04) and O_3 (0.10 ± 0.03). Around 50 types of VOCs were classified as alkanes, OVOCs, halogenated hydrocarbons (Halo), alkenes, aromatics (Arom), and isoprene (C_5H_8 representing biogenic hydrocarbons). Among these VOCs, the RIR of alkenes (0.22 ± 0.07) is the highest, followed by C_5H_8 (0.13 ± 0.04) and Arom (0.13 ± 0.04), while OVOCs (0.06 ± 0.01) and Halo (0.05 ± 0.01) have very low RIRs (Fig. 8 (b)). These phenomena indicated that increased NO level would inhibit the production of PAN while increased NO_2, VOCs (especially alkenes, C_5H_8, and Arom), HONO, and O_3 would promote the production of PAN. Because the values of NO and NO_2 RIR are approximately equal but with opposite signs, the RIR for NOx is almost zero, indicating that the PAN generation at this site is not sensitive to NO*x*. Zeng et al. (2019) also observed that NO_2 had a positive effect on PAN formation, while NO had a negative effect, in a suburban area of Hong Kong. This finding aligns with the fact that NO_2 directly contributes to PAN production, whereas NO reduces PA radicals, thereby inhibiting PAN formation. Based on the scenario analysis (Empirical Kinetic Modeling Approach (EKMA)), all data points for the 22 days fell above the ridge line (Fig. 8(c)). A reduction in VOCs at these points resulted in lower PAN concentrations, indicating that PAN formation at IUE was influenced by VOCs and thus VOC-sensitive. Our previous research also found that in this coastal city, PAN generation is limited by VOCs during the spring and autumn seasons. The difference is that previous studies indicated that reducing NO_2, like reducing NO, also leads to an increase in PAN concentration in spring and autumn (Liu et al., 2022). This is because the NO*x* concentration in spring and autumn is significantly higher than in summer, which is consistent with that both NO_2 and NO inhibit the formation of PAN in regions with high NO*x* concentrations (Liu et al., 2024).

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We divided the RIRs for different species into haze and clean periods and found that the RIRs during clean periods were consistently higher than those during haze periods (Fig. 8(d)), which indicated that altering the concentrations of these species during clean periods had a greater impact on PAN formation. The rapid thermal decomposition of PAN at high temperatures is likely the primary reason. During the haze period, the main source of PA radical was PAN decomposition, which accounted for 68.22%, and the other sources were smaller than that during the clean period (the source of the PA radical would be demonstrated in the following paragraph). Therefore, the sensitivity of PAN production to precursors and HONO & O_3 producing OH became lower during the haze period (Liu et al., 2021b; Liu et al., 2022).

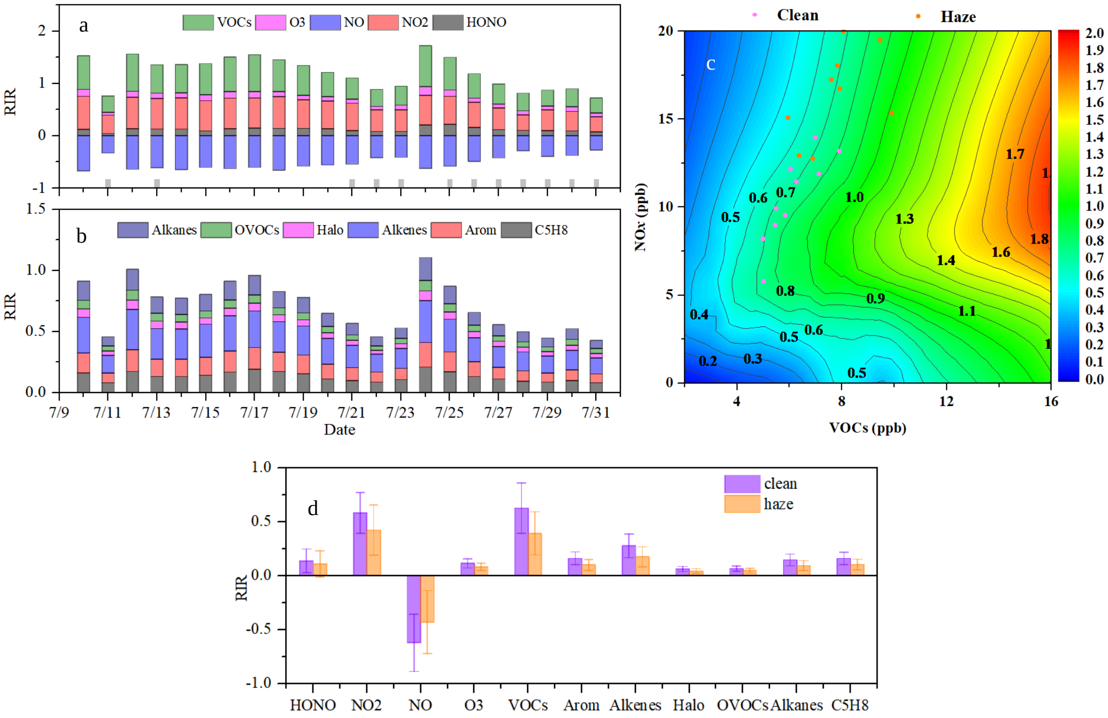

Figure 8. These four figures illustrate the RIR of PAN formation to major precursors (a), the impact of different VOCs species (b), the isopleth diagrams of PAN formation (c), and a comparison of RIRs between clean and polluted periods (d).

As shown in Fig. 9, ΔHO_2 and ΔOH are positive for most periods, indicating that the PAN mechanism promotes the generation of HO_2 and OH. Over the entire period, ΔHO_2 is 8.43×10^{-5} ppb, with no significant difference between clean and hazy periods, being 8.18×10^{-5} ppb and 8.64×10^{-5} ppb respectively. OH behaves similarly, with ΔOH being 4.55×10^{-7} ppb over the entire period, and also showing no significant difference between clean and hazy periods, being 4.93×10^{-7} ppb and 4.23×10^{-7} ppb respectively. The increase in simulated OH and HO_2 concentrations suggests that PAN photochemistry is enhancing radical formation and AOC at this site (Liu et al., 2024). Unlike HO_2 and OH, ΔRO_2, ΔNO_2, and ΔNO are negative for most periods, because PAN formation uses up PA and NO_2, the reduction in PA leads to a decrease in the amount of RO_2. Over the entire period, ΔRO_2 is -6.4×10^{-4} ppb, with no significant difference between clean and hazy periods, being -6.1×10^{-4} ppb and -6.5×10^{-4} ppb respectively. The average values of ΔNO_2 and ΔNO during the entire observation period are -0.17 and -0.01 ppb respectively, with significant differences between hazy and clean periods. Specifically, ΔNO_2 is -0.22 during hazy periods and only -0.11 during clean periods, indicating that the PAN mechanism consumes more NO_2 during hazy periods. Similarly, ΔNO is -0.05 during hazy periods, showing an inhibitory effect, while it is 0.03 during clean periods, showing a promoting effect.

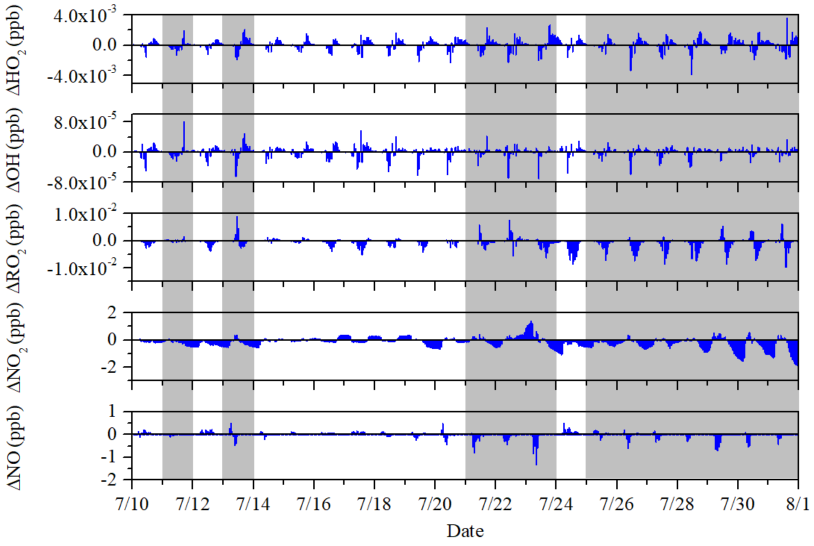

Figure 9. The difference of HO_2, OH, RO_2, NO_2, and NO between base scenario with PAN mechanism and scenario without PAN mechanism

As shown in Fig.10 (a), the PAN mechanism inhibited 85.80% of net ozone production during the entire observation period, with inhibition rates of 83.75% and 87.50% during clean and haze periods, respectively. This result is consistent with previous spring observations at the same site, where the inhibition rate was 83% (Liu et al., 2022). The PAN mechanism mainly inhibits the net ozone generation by increasing the RO_2+NO_2 reaction (Fig.10(a)), with negligible impact from other reactions (Fig. S11). As shown in Fig.10(b), the diurnal variation trend indicates that the PAN mechanism's inhibitory effect on ozone is significantly greater during haze periods than during clean periods. Additionally, regardless of whether it is during haze periods or clean periods, the PAN mechanism's inhibitory effect on ozone is significantly greater during the day than at night. These phenomena all indicate that the higher the PAN concentration, the more pronounced the inhibitory effect of the PAN mechanism on ozone (Fig.10(c)). Under low precursor conditions, competition among these precursors may limit their secondary formation, thus resulting in inhibition (Liu et al., 2024).

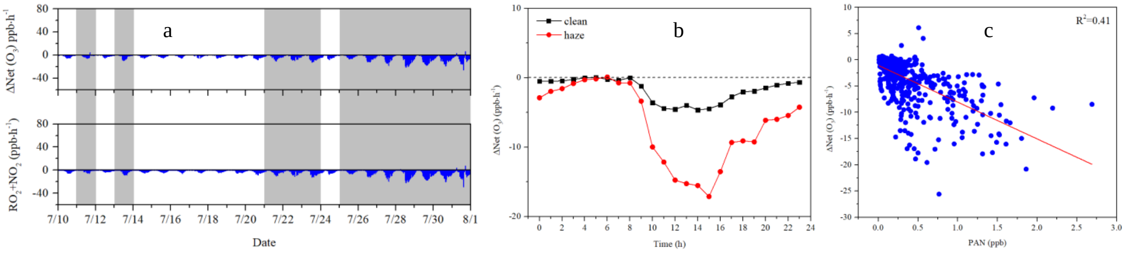

Figure 10. (a) Time series plot of ΔNet (O_3) and the reaction of RO_2+NO_2, (b) Diurnal variation of ΔNet (O_3) during clean and hazy conditions, (c) Correlation between ΔNet (O_3) and PAN.

Conclusion

This study thoroughly investigated the summertime PAN formation mechanism and established its connection to haze pollution. In addition to NO and TVOCs, the concentration of all pollutants during the haze period is above twice that during the cleaning period, indicating that the oxidation of NO and TVOCs during the haze period is stronger, which is conducive to the oxidation of NO and TVOCs into secondary pollutants, such as O_3 and PAN. The slopes of linear regression between the daily maximum values of PAN and O_3 were 0.021 ppb/ppb and 0.009 for clean and hazy condition, respectively, implies that PAN precursors accounted for only a small fraction of the total VOCs, especially for hazy condition. High temperature should be another factor contributing to the lower production efficiency of PAN in the southeast coastal region. During the whole observation period, the IOA=0.75, indicating that the MCM model is well-suited for exploring the photochemical formation of PAN. During the clean period, simulation results were better than during the haze period (R^2: 0.6782 vs. 0.4708, slope K: 0.9097 vs. 0.7477), indicating that PAN during the haze period may originate from reactions without considered in MCM. Additionally, the net production rate of PAN becomes negative with PAN constrained. This further indicates that, despite the high temperatures, there is still a significant concentration of PAN, suggesting the existence of an unknown compensatory mechanism. Through XGBoost-SHAP machine learning, this unknown compensatory mechanism may involve NO_3^- promoting PAN formation. Both RIR and EKMA indicate that PAN formation in this region is VOC-controlled. Controlling emissions of VOCs, particularly alkenes, C_5H_8, and aromatics, would be beneficial for mitigating PAN pollution. The RIR results also show that during the clean period, PAN is more sensitive to changes in various pollutants than during the haze period, highlighting the significant importance of deep emission reductions. PAN presented the promotion effects on OH and HO_2, while inhibited O_3 formation, RO_2, NO and NO_2. This study improves our thorough understanding of PAN photochemistry and offers valuable scientific guidance for the future management of PAN pollution.

Data availability

The observation data at this site are available from the authors upon request.

Authorship Contribution Statement

Baoye Hu: Methodology, Formal analysis, Investigation, Data curation, Writing – original draft. **Naihua Chen**: Software, Formal analysis. **Rui Li:** Software, Formal analysis. **Mingqiang Huang**: Software. **Jinsheng Chen**: Funding acquisition, Supervision, Writing - Review & Editing. **Youwei Hong**: Formal analysis. **Lingling Xu**: Investigation. Xiaolong Fan: Investigation. **Mengren Li**: Investigation. **Lei Tong**: Investigation. **Qiuping Zheng**: Investigation. **Yuxiang Yang:** Writing - Review & Editing

Competing interests

The authors declare that they have no conflict of interest.

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Supplementary information

Attached please find supplementary information associated with this article.

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