



1 Seasonal transitions in peroxyacetyl nitrate (PAN) drivers inform 2 coordinated ozone mitigation in urban basin environments

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12 **Abstract.** Peroxyacetyl nitrate (PAN) is a critical secondary pollutant that drives photochemical smog and threatens ecological
13 health. Despite persistent challenges in controlling photochemical pollution in China, the mechanisms governing seasonal
14 PAN formation and its key driving factors under complex basin topography remain poorly constrained. In this work, we
15 integrated a comprehensive one-year observational dataset, an observation-based box model, and interpretable machine
16 learning to elucidate the seasonal formation pathways and meteorological drivers of PAN at an urban site in the Sichuan Basin.
17 The annual mean PAN mixing ratio reached 0.60 ppbv, with a winter peak hourly value of 6.44 ppbv. Model simulations
18 revealed distinct seasonal formation pathways: thermal decomposition–recombination cycling dominating summer formation
19 (75.5%), whereas precursor oxidation served as the primary source in winter (57.1%). Sensitivity analyses indicated a
20 persistent volatile organic compound-limited regime for both PAN and ozone formation year-round, while nitrogen oxides
21 varied seasonally, suppressing PAN formation in winter but promoting it in summer. Feature attribution analysis further
22 demonstrated an obvious seasonal shift from chemistry-dominated driving mechanisms during warm seasons to stronger
23 meteorological influences in winter, where transport-related variables accounted for 61.0% of the cumulative feature
24 importance. During ozone pollution episodes, peroxyacetyl radical production increased by 77.0%, accompanied by a 91.9%
25 enhancement in PAN decomposition, highlighting intensified PAN cycling driven by elevated photochemical capacity. These
26 findings uncover seasonal regime shifts in PAN formation in complex basin environments, supporting seasonally tailored
27 precursor reduction and coordinated PAN and ozone mitigation strategies.

28 1 Introduction

29 As a typical secondary pollutant formed through photochemical reactions between volatile organic compounds (VOCs)
30 and nitrogen oxides (NO_x), peroxyacetyl nitrate (PAN) serves as a robust indicator of regional photochemical pollution, and
31 acts as a key intermediate in ozone (O₃) formation and a temporary reservoir for NO_x (Song et al., 2025; Xue et al., 2023).



Although its near-surface mixing ratios are generally much lower than those of O_3 , PAN exhibits one to two orders of magnitude greater biological toxicity, posing significant risks to ecosystems and human health (Taylor, 1969). Due to its low water solubility and weak reactivity with hydroxyl radicals (OH), PAN facilitates the long-range transport of reactive nitrogen. Upon thermal decomposition in remote regions, it releases nitrogen dioxide (NO_2) and peroxyacetyl (PA) radicals, thereby influencing the regional and global distributions of atmospheric oxidants (Lee et al., 2025; Zhai et al., 2024). Extensive studies have advanced our understanding of PAN formation pathways, source–sink processes, and spatiotemporal patterns (Payne et al., 2022; Xia et al., 2023). However, the coupled effects of chemical and meteorological processes on PAN remain difficult to disentangle, leading to substantial uncertainty in identifying its dominant controls and limiting our understanding of regional photochemical pollution (Song et al., 2023; Xu et al., 2018).

Observation-based box model (OBM) employs detailed chemical mechanisms to simulate photochemical processes and quantify the formation and loss rates of atmospheric species, providing a process-based framework for interpreting PAN-related photochemistry (Hu et al., 2025; Yang et al., 2022). Meanwhile, chemical transport models (CTMs) are widely used for regional-scale simulations but require accurate emission inventories, meteorological inputs, and substantial computational resources (Lu et al., 2024). As efficient tools for capturing nonlinear atmospheric relationships, machine learning (ML) methods have been increasingly applied in environmental research (Miyazaki et al., 2025), demonstrating substantial potential when combined with positive matrix factorization (PMF) and CTMs for forecasting, source apportionment, and interpretation of major pollutants (e.g., $PM_{2.5}$, O_3 , NO_2 , and HONO) (Chen et al., 2024; Prahesti et al., 2026; Zhang et al., 2022; Zhong et al., 2023). Despite these advantages, ML approaches alone lack explicit chemical interpretability. Given the nonlinear nature of PAN formation and its sensitivity to coupled atmospheric processes, integrating OBM with ML provides a framework for improving mechanistic understanding of PAN drivers under complex chemical-meteorological environments.

The Sichuan Basin is one of the most polluted regions in China and experiences severe and complex air pollution (Zhao et al., 2022). As a topographically enclosed basin surrounded by plateaus and mountains, it significantly constricts pollutant dispersion. The combination of year-round high humidity, persistent cloud cover, weak winds, and limited solar radiation, coupled with intensive anthropogenic emissions and interregional transport, favors the accumulation of air pollutants and frequent photochemical pollution events within the basin, posing challenges for effective photochemical pollution mitigation (Lu et al., 2024; Tong et al., 2026). Although satellite remote sensing reveals distinct PAN hotspots over the region, indicating enhanced regional photochemical activity (Lee et al., 2025; Zhang et al., 2026), current research primarily concentrates on conventional pollutants such as fine particulate matter ($PM_{2.5}$) and O_3 . Systematic studies targeting PAN, encompassing its formation pathways, seasonal variability, and the interplay between precursors and meteorological controls remain inadequate, thereby hindering the refined management and precise mitigation of regional photochemical pollution (Yan et al., 2026).

This study systematically investigates the seasonal variations, chemical formation mechanisms, and non-linear meteorological controls on PAN variability in Suining, a representative urban center situated at the geographical center of the Sichuan Basin. Seasonal source–sink processes, radical cycling, and precursor sensitivities governing PAN formation were quantified, and the relative roles of chemical and meteorological drivers in shaping PAN variability were evaluated. The



evolution of PAN source–sink characteristics and dominant drivers under different pollution conditions was also investigated. This study provides new insights into PAN evolution under complex basin environments and supports the development of seasonally differentiated precursor-control strategies for mitigating PAN and O₃ pollution.

2 Methodology

2.1 Measurement campaign and instrumentation

Continuous online field observations were conducted in Suining (30.52°N, 105.57°E) from December 2024 to November 2025, with the monitoring site situated on the rooftop of a 25 m-high building in the urban core. As shown in Fig. S1, the site is surrounded by expressways, residential buildings, and wetland parks along the Fujiang River, rendering it typical of a rapidly urbanized region. Owing to its central location within the Sichuan Basin and typical urban characteristics, Suining is considered representative of atmospheric conditions in the basin interior.

Atmospheric PAN was measured using an online GC-ECD system (PANs-01, Zhichen Technology, China) with a 5 min temporal resolution. Data were averaged to hourly values for subsequent analysis (Sun et al., 2020). Detailed instrument specifications are provided in Sect. S1. Atmospheric VOCs were continuously monitored at an hourly resolution using a gas chromatograph coupled with flame ionization detection and mass spectrometry (GC-FID/MS, 5800GM, Thermo Fisher Scientific, USA), enabling the quantification of 114 VOC species (including alkanes, alkenes, alkynes, aromatics, OVOCs, and halogenated hydrocarbons). Detailed compound list and their respective method detection limits are summarized in Table S1.

Meteorological parameters, including air temperature (AT), relative humidity (RH), wind speed (WS), wind direction (WD), and barometric pressure (BP), were measured using an integrated weather sensor (Lufft WS500-UMB, Germany). Ultraviolet radiation (UV) was collected via an ultraviolet radiometer (BMET IUV-800S, Beijing MET High-tech Co., Ltd., China). Critical gaseous pollutants (O₃, CO, and SO₂) were continuously monitored using Model 49i, 48i, 43i analyzers (Thermo Fisher Scientific, USA), respectively. Nitrogen oxides (NO and NO_x) were measured using Model 42i analyzer (Thermo Fisher Scientific, USA), and NO₂ was derived from the difference between NO_x and NO. PM_{2.5} and PM₁₀ mass concentrations were measured using a Model 5030i monitor (Thermo Fisher Scientific, USA) employing synchronized hybrid β-ray attenuation and light scattering technology for real-time particulate matter mass determination. Boundary layer height (BLH) as well as zonal wind (wind_u), meridional wind (wind_v), and vertical velocity (wind_w) at the 850 hPa level were retrieved from the fifth-generation reanalysis dataset of the European Centre for Medium-Range Weather Forecasts (ERA5) (Hersbach et al., 2020).

2.2 Observation-based box model

An OBM was implemented using the Framework for 0-D Atmospheric Modeling (F0AM v4.3) coupled with the Master Chemical Mechanism (MCM v3.3.1; <https://mcm.york.ac.uk/MCM>, last accessed on 2 March 2026) to simulate PAN



photochemistry. Based on the observation data, the model was constrained by hourly measurements of NO, NO₂, CO, SO₂, and 79 VOC species compatible with the MCM mechanism (Table S2), together with meteorological parameters (AT, RH, and BP). In the absence of HONO measurements, HONO mixing ratios were parameterized as $0.03 \times [\text{NO}_x]$ following previous studies conducted in the Sichuan Basin (Chen et al., 2023; Elshorbany et al., 2012). Photolysis frequencies (*j*-values) were estimated using a previously developed LightGBM model (Li et al., 2025). To represent physical removal processes, a seasonally adjusted first-order loss rate of $1.6 \times 10^{-5} \text{ s}^{-1}$ was applied to account for atmospheric dilution and deposition (Chen et al., 2026; Qiao et al., 2023; Wolfe et al., 2016). To reduce initialization effects, the first-day constraints were replicated once, allowing unconstrained intermediate species and radicals to stabilize. Neither O₃ nor PAN was constrained, enabling independent evaluation of model performance using the Index of Agreement (IOA, Sect. S2).

Relative Incremental Reactivity (RIR) was used to quantify the sensitivities of O₃ and PAN formation to their precursors (Sect. S3) (Liu et al., 2024a). To further characterize the nonlinear precursor–pollutant relationships, the Empirical Kinetic Modeling Approach (EKMA) was employed. Seasonal baseline levels for NO_x and total VOCs (TVOCs) were derived from in-situ observations. Precursor levels were then varied from 10% to 120% of their seasonal baselines at 10% intervals while keeping all other model parameters unchanged, and the corresponding daily maximum mixing ratios of O₃ and PAN were extracted. Seasonal EKMA isopleths were subsequently constructed to characterize the combined effects of NO_x and TVOCs on O₃ and PAN formation and to identify precursor sensitivity regimes for coordinated pollution control.

Reaction rates for PAN and PA radicals (CH₃CO₃·) were extracted from the OBM-MCM simulations. To quantify pathway-specific contributions on an hourly basis, the rates were multiplied by 3600 and converted to hourly production amounts (ppbv) (Table S3). For simplicity, PA radical production was grouped into two categories: precursor-derived formation and PAN thermal decomposition (see Sect. S4 for pathway definitions) (Hu et al., 2025; Wang et al., 2023b). The contribution of each pathway to PAN production was quantified using the branching ratio of the PA + NO₂ reaction relative to the total PA radical loss pathways. Accordingly, Chem_precursor represents PAN formation from precursor-derived PA radicals, whereas PAN_Cycling represents PAN reformation from radicals released during PAN decomposition. Together, these two indicators characterize the gross chemical production of PAN. Their calculations are given by Eqs. (1)-(4).

$$v_{\text{precursor}} = v_{\text{CH}_3\text{CHO}+\text{OH}} + v_{\text{CH}_3\text{CHO}+\text{NO}_3} + v_{\text{MGLYOX}+\text{OH}} + v_{\text{MGLYOX}+\text{NO}_3} + v_{\text{MGLYOX}+\text{hv}} + v_{\text{CH}_3\text{COCH}_3+\text{hv}} + v_{\text{BIACET}+\text{hv}} + v_{\text{MVK}+\text{hv}} + v_{\text{Radical_cycling}}, \quad (1)$$

$$R_{\text{PA}+\text{NO}_2} = \frac{v_{\text{PA}+\text{NO}_2}}{v_{\text{PA}+\text{NO}_2} + v_{\text{PA}+\text{NO}} + v_{\text{PA}+\text{others}}}, \quad (2)$$

$$\text{Chem_precursor} = v_{\text{precursor}} \times 3600 \times R_{\text{PA}+\text{NO}_2}, \quad (3)$$

$$\text{PAN_Cycling} = v_{\text{PAN_decom}} \times 3600 \times R_{\text{PA}+\text{NO}_2}, \quad (4)$$

where $v_{\text{precursor}}$ and $v_{\text{PAN_decom}}$ denote the rates of PA radical production from precursors oxidation and PAN thermal decomposition (both in ppbv s⁻¹), respectively, and $R_{\text{PA}+\text{NO}_2}$ represents the branching ratio (dimensionless) of PA radicals



reacting with NO_2 . Chem_precursor and PAN_Cycling (both in ppbv) were subsequently incorporated into the machine learning framework as indicators of PAN production pathways (Fig. S2).

2.3 Machine learning

To investigate the relative contributions of chemical production and meteorological processes to PAN variability, a source–sink decoupling approach was applied to estimate net PAN production from observed PAN variability for subsequent ML analyses. Given that non-thermal removal pathways are relatively minor, thermal decomposition was identified as the dominant PAN loss process (Sect. S4). Thermal decomposition was quantified and incorporated into the observed mixing ratio changes to account for the PAN-PA- NO_2 recycling cycle. The resulting variable, defined as net PAN production (PAN_{gen}), represents the combined influence of in-situ chemical formation and meteorological processes:

$$\text{PAN}_{\text{gen}} = \text{PAN}_{t+1} - \text{PAN}_t + \text{PAN}_d, \quad (5)$$

where PAN_t and PAN_{t+1} are observed PAN mixing ratios at two consecutive time steps, and PAN_d represents thermal decomposition loss estimated using IUPAC-recommended kinetics (Atkinson et al., 2006). By accounting for the rapid PAN recycling, PAN_{gen} provides an integrated representation of net PAN formation.

The predictor variables were selected to represent the major processes governing PAN formation. Two chemical features (Chem_precursor and PAN_Cycling) were derived from the OBM-MCM simulations, while four meteorological transport features (BLH, wind_u, wind_v, and wind_w) were obtained from ERA5 reanalysis data (Table 1). Together, these variables characterize precursor oxidation, PAN recycling, atmospheric transport, and boundary-layer dynamics.

Table 1. Summary of target variable, input features, and their descriptions in the ML framework.

Variable	Description	Unit
PAN_{gen} (Target variable)	$\text{PAN}_{t+1} - \text{PAN}_t + \text{PAN}_d$	ppbv
Chem_precursor (Chemical factor)	$V_{\text{precursor}} \times 3600 \times R_{\text{PA}+\text{NO}_2}$	ppbv
PAN_Cycling (Chemical factor)	$V_{\text{PAN_decom}} \times 3600 \times R_{\text{PA}+\text{NO}_2}$	ppbv
wind_u (Meteorological transport factor)	850 hPa zonal wind for horizontal transport	m s^{-1}
wind_v (Meteorological transport factor)	850 hPa meridional wind for horizontal transport	m s^{-1}
BLH (Meteorological transport factor)	Boundary layer height for vertical transport	m



wind_w (Meteorological transport factor)	Vertical velocity for vertical transport	Pa s ⁻¹
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Following quality-control procedures and the removal of records with incomplete predictor information, a total of 3,445 hourly samples were retained for ML analyses. To preserve the temporal structure of the observations, data from each month were divided chronologically, with the first 70% used for training and the remaining 30% used for testing. Monthly training and testing subsets were subsequently merged to construct the annual datasets. Random Forest (RF), Extreme Gradient Boosting (XGBoost), and Light Gradient Boosting Machine (LightGBM) were first evaluated using the six chemical and meteorological transport predictors listed in Table 1. Hyperparameters were optimized using random search, and predictive performance was evaluated using the coefficient of determination (R^2) and root mean square error (RMSE). Among the three algorithms, XGBoost achieved the best predictive performance and was therefore selected for subsequent modeling analyses (Fig. S3).

The annual XGBoost model developed using the six predictors achieved a testing R^2 of 0.68 with an RMSE of 0.56 ppbv. Two harmonic terms (Month_sin and Month_cos) were subsequently incorporated to represent temporal periodicity. The inclusion of these variables improved model performance ($R^2 = 0.73$; RMSE = 0.52 ppbv), indicating that the relationships between PAN_{gen} variability and its drivers exhibited annual-cycle dependence and supporting the subsequent development of season-specific XGBoost models for spring, summer, autumn, and winter (Fig. S3). Finally, SHapley Additive exPlanations (SHAP) and one-factor-at-a-time (OAT) sensitivity analyses were applied to the optimized seasonal models to quantify the relative contributions of individual predictors and characterize the nonlinear responses governing PAN formation under different seasonal conditions (Mueller et al., 2025).

3 Results and discussions

3.1 Comprehensive overview of observational data

During the observation campaign, meteorological conditions exhibited pronounced seasonal variability characteristic of the Sichuan Basin (Table S4 and Fig. S4). Summer was dominated by hot and humid conditions, with a mean air temperature (AT) of 30.1 ± 4.2 °C and strong solar radiation, favoring photochemical activity and secondary pollutant formation. In contrast, winter was characterized by low temperatures (8.9 ± 2.2 °C), persistently high relative humidity (RH) ($74.1 \pm 10.9\%$), and stagnant atmospheric conditions. Combined with the enclosed basin topography, these conditions favored pollutant accumulation and secondary pollution episodes. Ultraviolet radiation (UVA and UVB) displayed consistent seasonal trends, with higher intensities in summer and lower levels in winter. Additionally, light winds predominated throughout the campaign, with speeds mostly ranging from 1 to 2 m s⁻¹ and no clearly dominant wind direction. Together, these meteorological characteristics reflect the influence of basin topography, which restricts air-mass exchange and favors the accumulation of moisture and atmospheric pollutants (Kong et al., 2025).

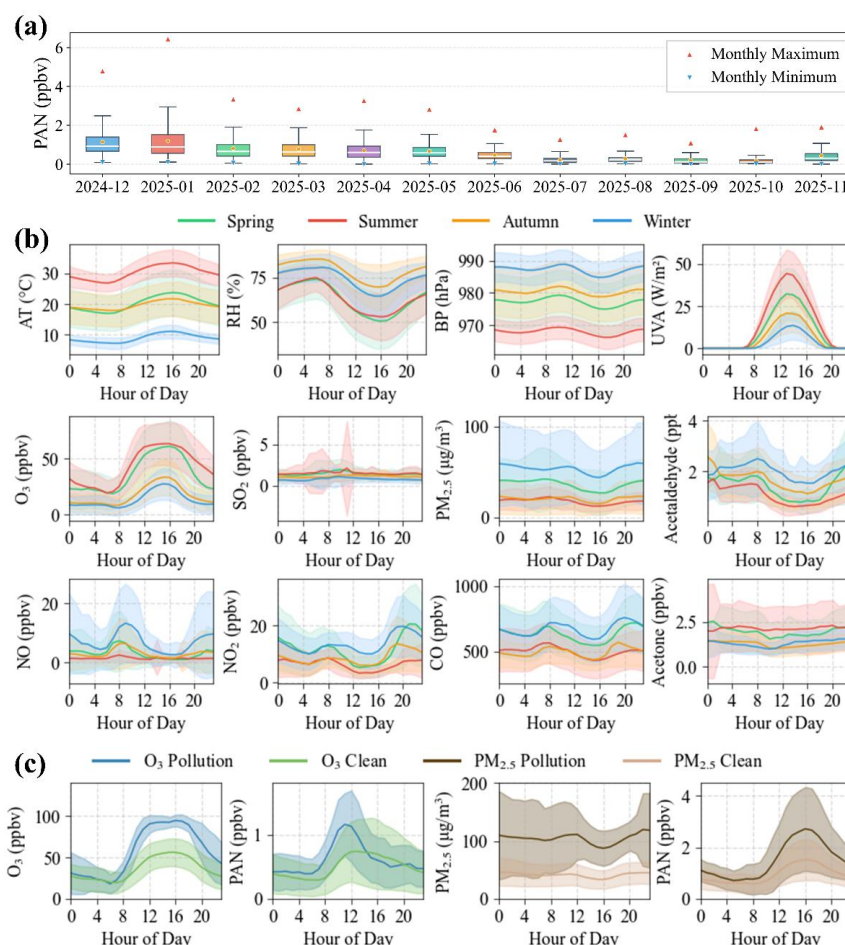


Figure 1. Monthly distributions, seasonal diurnal variations, and pollution-driven patterns of PAN. (a) Monthly boxplots of PAN mixing ratios; orange circles represent monthly means, while red and blue triangles denote monthly maxima and minima, respectively. (b) Seasonal diurnal profiles of core meteorological parameters and major pollutants. (c) Diurnal variations of O₃ and PAN during O₃ episodes (spring and summer) and PM_{2.5} episodes (winter) relative to clean periods. The shaded areas denote one standard deviation (± 1 SD).

Under these basin-specific meteorological conditions, PAN exhibited pronounced seasonal variability (Fig. 1). The annual mean PAN mixing ratio was 0.60 ± 0.60 ppbv, with the highest levels occurring in winter (1.05 ± 0.79 ppbv; maximum: 6.44 ppbv), followed by spring (0.72 ± 0.47 ppbv), while substantially lower values were observed in summer (0.33 ± 0.27 ppbv) and autumn (0.27 ± 0.29 ppbv). The maximum daily 8-h average (MDA8) PAN reached 5.29 ppbv during a winter pollution episode, exceeding the 5 ppbv level previously linked to potential ecological impacts (Hu et al., 2020). Compared with previous observations in Sichuan Basin, summertime PAN levels in Suining were lower than those reported in Chongqing (Sun et al., 2020), whereas wintertime PAN levels exceeded the basin-wide average reported for 2015 (Zhu et al., 2018). Furthermore, comparison with other urban regions (Fig. S5 and Table S5) showed that PAN levels in Suining were substantially lower than those in the North China Plain (NCP), but comparable to those observed in the Yangtze River Delta (YRD) and Pearl River Delta (PRD) regions.



190 Given their shared photochemical origins, the relationship between PAN and O₃ was further examined (Fig. 1c). The
191 average MDA8 O₃ mixing ratio was 44.5 ± 1.2 ppbv, with 30 exceedance days occurring mainly in spring and summer. During
192 O₃ pollution episodes, the mean diurnal peak of PAN reached 1.16 ± 0.49 ppbv, 56.8% higher than under clean conditions
193 (Fig. 1c). In addition, the PAN peak occurred approximately 2 hours earlier on polluted days, possibly reflecting enhanced
194 thermal decomposition and faster daytime photochemical evolution under elevated temperatures. After correcting for thermal
195 decomposition, the correlation between PAN_{gen} and O₃ was substantially enhanced (Table S6 and Fig. S6), indicating a closer
196 linkage between net PAN formation and photochemical activity. During winter PM_{2.5} pollution episodes, PAN levels increased
197 markedly, with the diurnal peak mixing ratios exceeding 2.0 ppbv, nearly three times those observed during clean periods.
198 This enhancement was associated with elevated concentrations of primary pollutants (NO, NO₂, and CO) in winter and stagnant
199 meteorological conditions characteristic of the basin environment, which favored the accumulation of both PAN precursors
200 and particulate matter (Huang et al., 2024).

201 To further elucidate the seasonal variations of PAN, the evolution of its key carbonyl precursors was analyzed (Fig. 1b).
202 Acetone exhibited an annual mean mixing ratio of 1.6 ± 1.0 ppbv and peaked in summer (2.2 ± 1.3 ppbv), while showing
203 relatively weak diurnal variation across all seasons. In contrast, acetaldehyde (1.5 ± 1.0 ppbv) displayed an opposite seasonal
204 pattern, with substantially higher mixing ratios in winter (2.0 ± 1.1 ppbv) than in summer (1.0 ± 0.6 ppbv). Wintertime
205 acetaldehyde also exhibited pronounced diurnal variability, with elevated levels during rush hours and nighttime. This pattern
206 likely reflects enhanced primary emissions and weaker dispersion in winter, together with accelerated photochemical removal
207 by OH radicals in summer (Yang et al., 2026). Overall, the contrasting seasonal behaviors of carbonyl precursors suggest that
208 precursor availability, together with basin meteorology, plays an important role in shaping PAN formation in the Sichuan
209 Basin.

210 **3.2 Box model analysis of the seasonal PAN budget**

211 **3.2.1 PAN budget analysis**

212 The OBM-MCM model was employed to quantify the chemical processes governing PAN formation. Seasonal and
213 overall IOA values for simulated O₃ and PAN are summarized in Table S7. The model reproduced O₃ and PAN with overall
214 IOA values of 0.90 and 0.71, respectively, consistent with previous studies and indicating satisfactory representation of the
215 key atmospheric processes controlling PAN formation (Fu et al., 2024; Hu et al., 2025; Zeng et al., 2019). Given that PAN is
216 formed through the reaction of PA radicals and NO₂, production of the radicals via the Chem_precursor and PAN_Cycling
217 pathways was extracted to quantify their contributions to PAN formation. The corresponding reaction rates and source–sink
218 contributions are summarized in Table S8, and their diurnal variations are shown in Fig. 2. Regarding the Chem_precursor
219 pathway, further analysis revealed that acetaldehyde (CH₃CHO), methylglyoxal (MGLYOX), and radical cycling dominated
220 PA radical production, collectively contributing more than 90% across seasons. In contrast, acetone (CH₃COCH₃), methyl
221 vinyl ketone (MVK), and 2,3-butanedione (BIACET) each contributed less than 1%, indicating minor contributions to PAN



formation under the present conditions. These results are in good agreement with previous studies conducted in Beijing, Guangzhou, and Chongqing, which consistently identify acetaldehyde as the dominant precursor, accounting for 50% to 67% of PA radicals production at urban sites and 34% to 48% at suburban and rural sites. Methylglyoxal and radical cycling constitute the other two major sources, with contributions ranging from 15% to 31% and from 17% to 21%, respectively. By comparison, specific OVOCs such as acetone, MVK, and MACR contribute only marginally to its formation and therefore play a negligible role in PAN production. (Sun et al., 2020; Xue et al., 2014; Yuan et al., 2018).

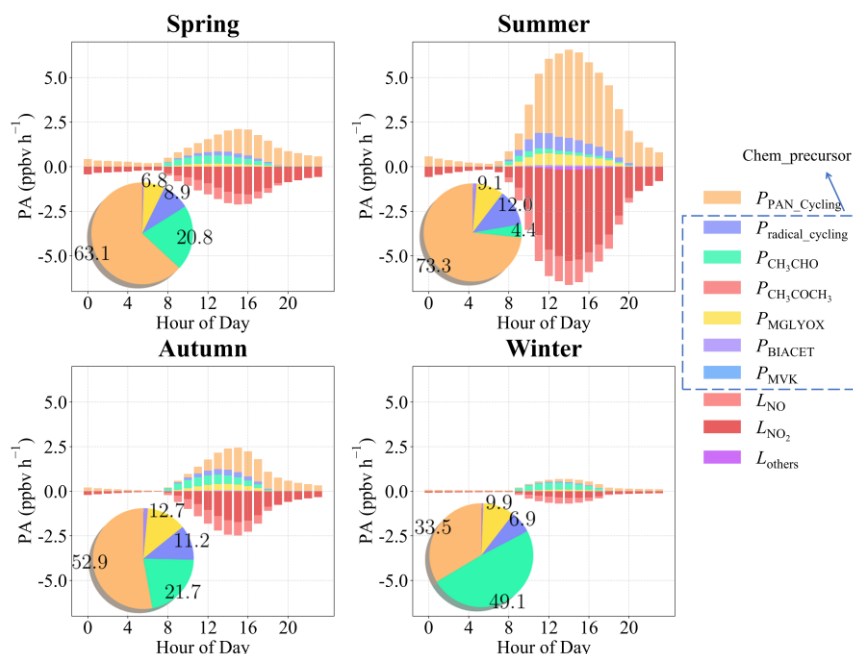


Figure 2. Seasonal diurnal variations and daytime budget of PAN sources and sinks. Stacked bars delineate the 24-h diurnal profiles of chemical formation and loss pathways for PAN across the four seasons. Embedded pie charts illustrate the relative percentage contributions (%) of different precursors to daytime (08:00–20:00) PAN production.

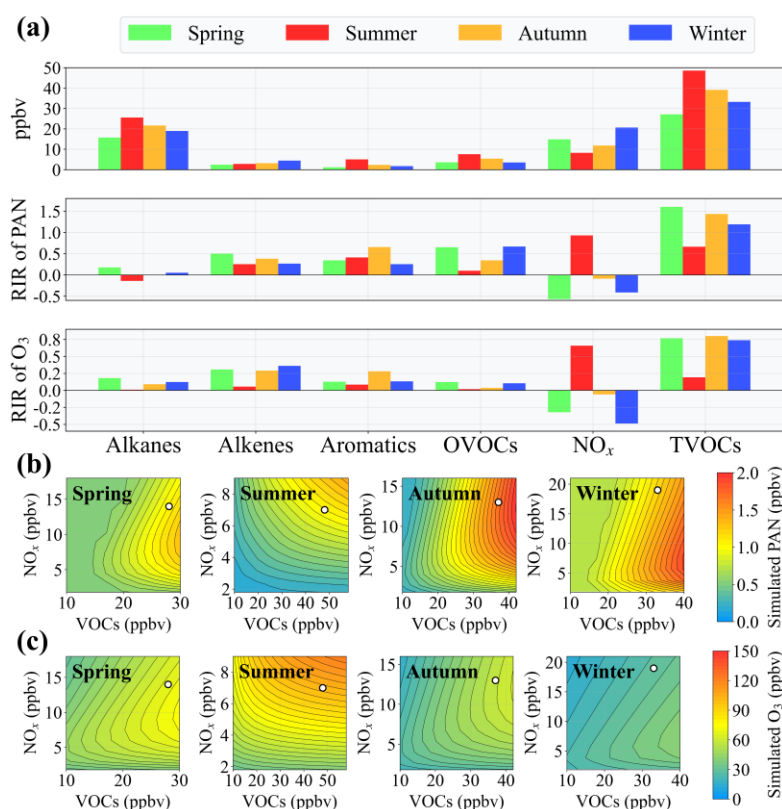
PAN formation pathways exhibited pronounced seasonal shifts, with PAN_Cycling dominating in summer (75.5%), Chem_precursor prevailing in winter (57.1%), and spring and autumn representing transitional regimes. In summer, high temperatures promoted rapid PAN thermal decomposition and recycling. At the diurnal peak (14:00), the PAN decomposition rate reached 4.95 ppbv h⁻¹, and 77.1% of the released PA radicals recombined with NO₂ based on modeled reaction fluxes, making PAN_Cycling the dominant contributor to a total PAN formation rate of 5.11 ppbv h⁻¹. Meanwhile, the contribution of acetaldehyde decreased to only 4.4% owing to rapid photochemical consumption (Yan et al., 2025). In contrast, winter PAN formation was dominated by precursor oxidation, with Chem_precursor contributing 66.5% during daytime (08:00–20:00) and acetaldehyde accounting for 49.1%, nearly 11 times its summertime contribution (Table S9). Spring and autumn exhibited more balanced contributions from the two pathways, with PAN_Cycling accounting for 69.4% and 57.1%, respectively. Distinct peak timings of oxidation (13:00) and thermal decomposition (16:00) further suggest that PAN formation during transitional seasons was jointly regulated by precursor oxidation and thermal cycling (Zhang et al., 2015). Overall, seasonal



243 differences in PAN formation were primarily governed by variations in temperature, radiation intensity, precursor availability,
244 and atmospheric oxidative capacity (Fischer et al., 2014).

245 3.2.2 Precursor sensitivity analysis

246 RIR and EKMA analyses revealed pronounced seasonal differences in precursor sensitivity for PAN and O₃, although
247 their overall control regimes were highly consistent (Fig. 3). TVOCs remained the dominant precursor across all seasons, while
248 NO_x sensitivity varied substantially with season. High summer TVOC mixing ratio combined with relatively low NO_x levels
249 contributed to a VOCs–NO_x co-limited regime, whereas spring, autumn, and winter were predominantly VOC-limited. The
250 EKMA results further illustrated the seasonal shift in precursor sensitivity (Fig. 3). Negative RIR values of NO_x in spring and
251 winter indicate that reductions in NO_x would enhance PAN and O₃ formation under VOC-limited conditions, whereas the
252 positive summer RIR (+0.93 for PAN) suggests that NO_x became an important promoting factor under NO_x-sensitive
253 conditions. The magnitude of NO_x sensitivity generally fell between those reported for Xiamen and Fuzhou, reflecting regional
254 differences in precursor composition and emission characteristics (Hu et al., 2025; Lin et al., 2024).



255
256 **Figure 3. Seasonal sensitivity of PAN and O₃ formation to precursors based on RIR and EKMA models.** (a) Seasonal mean mixing
257 ratios of major precursor groups (top), along with the corresponding seasonal RIR values for PAN (middle) and O₃ (bottom). (b, c) EKMA
258 isopleths showing the responses of (b) PAN and (c) O₃ to varying TVOC and NO_x levels. The white dots represent the seasonal baseline
259 conditions derived from observed precursor concentrations.



The contributions of individual VOC classes varied substantially across seasons and between PAN and O₃ formation pathways. Alkenes, aromatics, and OVOCs were the dominant reactive VOC groups owing to their efficient roles in PA radical formation. Alkenes contributed most strongly in spring, whereas aromatics dominated in summer and autumn. In winter, alkenes played a more dominant role than aromatics, consistent with observations in Zhengzhou and Qingdao (Liu et al., 2021; Qiao et al., 2023), although studies in Xiamen, Chongqing, and Beijing reported a greater contribution from aromatics (Liu et al., 2022; Sun et al., 2020; Xue et al., 2014). As important sources of PA radicals, OVOCs exhibited a strong promotional effect on PAN formation during winter and spring (RIR > 0.6), whereas their influence on O₃ formation was considerably weaker. By contrast, the contribution of alkanes and CO to PAN and O₃ formation remained marginal despite their relatively high abundances because of their low reactivity (Berg et al., 2024). Consistent with RIR and EKMA results, coordinated control of aromatics, alkenes, and OVOCs would provide substantial co-benefits for reducing both PAN and O₃. In addition, seasonal NO_x control should be carefully optimized, as NO_x reductions are most effective during summer, whereas substantial NO_x abatement under wintertime VOC-limited conditions may enhance PAN and O₃ formation.

3.3 Assessment of seasonal PAN drivers via machine learning

3.3.1 Model performance and feature importance analysis

The seasonal distributions of ML inputs and PAN_{gen} are shown in Fig. S7 and summarized in Table S10. The performance of the season-specific XGBoost models is summarized in Table S11, with optimized hyperparameters provided in Table S12. Multicollinearity among the predictors was limited, with the Variance Inflation Factor (VIF) values ranging from 1.15 to 4.25 (Fig. S8), suggesting that severe multicollinearity was unlikely to substantially influence SHAP attribution.

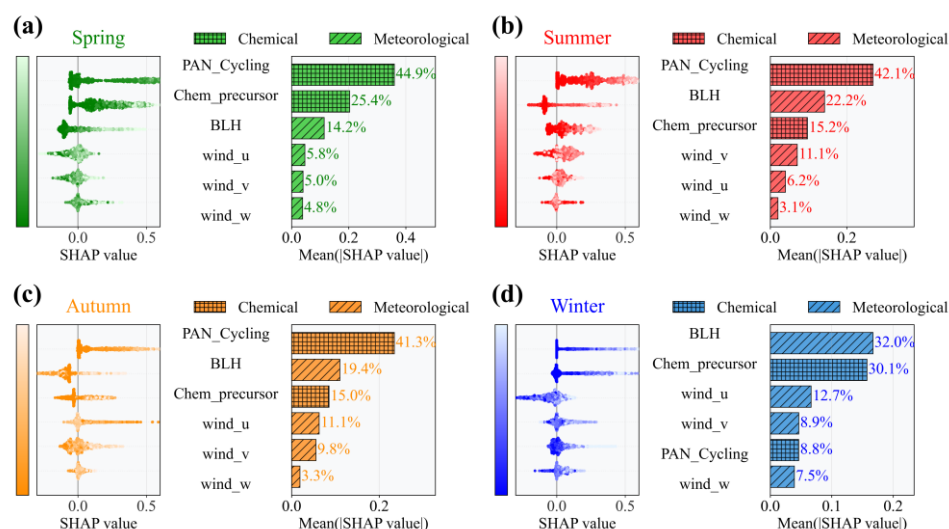


Figure 4. Seasonal variations in the key drivers of PAN_{gen} identified by machine-learning interpretation. (a) Spring, (b) Summer, (c) Autumn, and (d) Winter. For each season, the left panel shows the SHAP beeswarm plot, illustrating the direction and magnitude of feature contributions to PAN_{gen} predictions, whereas the right panel presents the corresponding feature importance plot based on mean absolute SHAP values, with the relative contributions (%) of chemical (grid-filled bars) and meteorological (striped bars) predictors.



SHAP analysis revealed pronounced seasonal differences in PAN drivers (Fig. 4). Both PAN_Cycling and Chem_precursor generally showed positive contributions to predicted PAN_{gen} values, with occasional negative SHAP values likely arising from nonlinear interactions among predictors (Sun et al., 2021). During the warm seasons (spring, summer, and autumn), PAN_Cycling was the dominant driver, accounting for more than 40% of the total SHAP importance, whereas Chem_precursor contributed 25.4% in spring and approximately 15% in summer and autumn. The higher contribution of Chem_precursor in spring was consistent with enhanced precursor oxidation during this season, whereas the increasing dominance of PAN_Cycling in summer coincided with a lower relative contribution of Chem_precursor despite stronger photochemical activity (Guo et al., 2024). Among meteorological variables, BLH was the most influential transport-related factor during warm seasons. In contrast, winter exhibited a distinct regime, with BLH (32.0%) and Chem_precursor (30.1%) becoming the dominant contributors, whereas the contribution of PAN_Cycling decreased to 8.8%, likely reflecting suppressed PAN thermal decomposition and PA radical recycling under low-temperature conditions. Meanwhile, the importance of wind_u, wind_v and wind_w increased to 12.7%, 8.9%, and 7.5%, respectively, indicating a relatively enhanced contribution of meteorological processes in winter. Overall, PAN formation was dominated by chemical cycling in the warm seasons but jointly controlled by boundary-layer meteorology and precursor oxidation in winter.

3.3.2 Seasonal variations in chemical and meteorological influences on PAN

Single-factor sensitivity analysis based on the seasonal ML models (Fig. 5) showed that both PAN_Cycling and Chem_precursor exerted predominantly positive effects on PAN_{gen}, although their influences varied substantially across seasons. The strongest responses occurred in summer, when intense solar radiation and high temperatures enhanced the conversion of carbonyl precursors into PA radicals and PAN. During spring and autumn, PAN_Cycling showed the strongest influence, indicating that PAN thermal decomposition and PA radical cycling largely governed PAN formation. In winter, although the overall chemical sensitivity weakened under low-temperature and low-radiation conditions, the influence of Chem_precursor became relatively more pronounced because PAN thermal cycling was strongly suppressed. These sensitivity patterns are consistent with the OBM and SHAP results and further highlight the seasonally varying roles of chemical pathways in PAN formation.

As indicators of horizontal transport, wind_u and wind_v showed weak and nonlinear influences on PAN_{gen}, primarily reflecting the effects of pollutant transport and dispersion rather than direct chemical regulation (Hu et al., 2026). PAN_{gen} exhibited only modest variations across the observed ranges of wind_u and wind_v. For wind_u, PAN_{gen} generally increased with positive *u* values, particularly during spring and summer, whereas the response remained relatively weak in autumn and winter. In contrast, wind_v displayed a nonlinear response, with relatively higher PAN_{gen} levels occurring under moderate meridional flow and lower values under stronger meridional winds. Overall, horizontal transport exerted a limited influence on PAN variability, consistent with the relatively low importance of wind_u and wind_v in the SHAP analysis (Qiao et al., 2019).

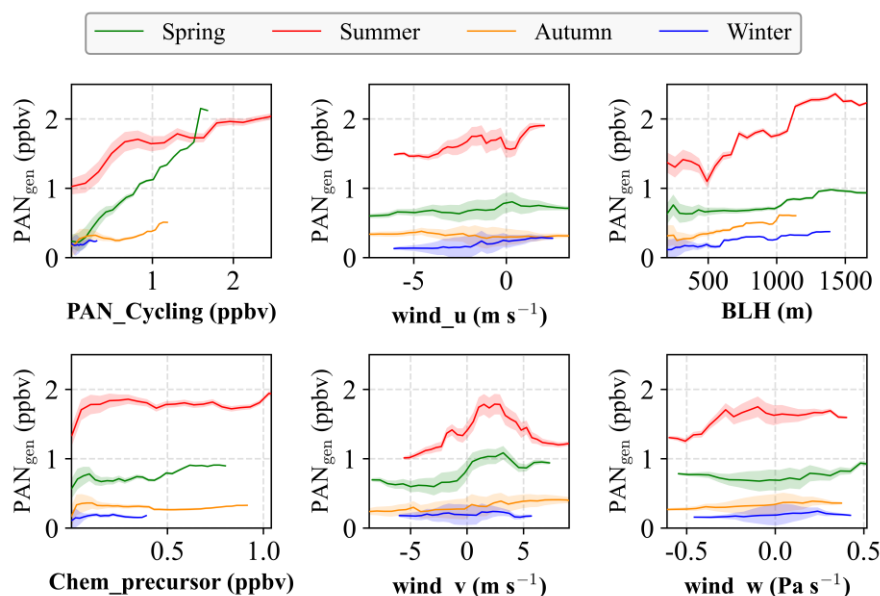


Figure 5. One-factor-at-a-time (OAT) sensitivity responses of key drivers across four seasons. Solid lines represent the predicted responses of PAN_{gen} to individual drivers, while all remaining variables are held constant. Response curves are restricted to the 95% highest-density intervals (HDIs) of each predictor to avoid extrapolation beyond data-supported ranges. Shaded envelopes represent season-specific data densities estimated using kernel density estimation (KDE), with widths proportional to the relative abundance of observations.

Regarding vertical dynamics, BLH and $wind_w$ exhibited distinct influences on PAN_{gen} , with BLH serving as the dominant meteorological transport driver. Unlike the predominantly positive effects of chemical drivers, PAN_{gen} responded nonlinearly to increasing BLH, reflecting the combined influences of vertical diffusion, precursor mixing, photochemical activity, and cross-layer transport. Seasonal responses differed substantially. Summer showed the largest fluctuations during BLH enhancement, indicating high sensitivity to vertical mixing intensity, whereas spring and autumn exhibited more gradual positive responses. Winter displayed the strongest sensitivity to BLH despite having the lowest PAN_{gen} levels. Under the combined effects of basin topography, persistent thermal inversions, and low temperatures, stagnant winter conditions favored PAN accumulation by suppressing vertical dispersion and extending PAN lifetime (Feng et al., 2023). Increased BLH may enhance vertical mixing and precursor exchange, weaken local NO titration effects, and facilitate interactions between the boundary layer and the overlying atmosphere, thereby amplifying its positive influence during winter (Shu et al., 2025; Yang et al., 2021). In contrast, $wind_w$ exerted only a weak influence on PAN_{gen} . PAN_{gen} varied only slightly across the observed range of $wind_w$, and the magnitude of this response was much smaller than that associated with BLH. This suggests that large-scale vertical motion played a secondary role in regulating PAN variability compared with boundary-layer mixing (Zhao et al., 2020).

The SHAP feature importance analysis revealed pronounced seasonal differences in the factors associated with PAN variability. During the warm seasons (spring, summer, and autumn), chemical-related variables accounted for 70.3%, 57.3%, and 56.3% of the total feature importance, respectively, indicating that PAN variability was primarily associated with



photochemical reactions and precursor oxidation. In contrast, meteorological transport variables became more influential in winter, accounting for 61.0% of the total feature importance compared with 38.9% for chemical variables. This shift suggests a transition from predominantly chemically driven PAN variability in the warm seasons to stronger meteorological influence under winter conditions. Previous studies have reported similar seasonal patterns, where local photochemistry plays a more important role during warm periods, whereas transport and meteorological processes become increasingly influential under winter conditions (Liu et al., 2024b; Sun et al., 2021; Wang et al., 2023a; Xu et al., 2024). However, the present results suggest that under the complex terrain of the Sichuan Basin, stagnant meteorological conditions and boundary-layer processes likely exert particularly strong influences on wintertime PAN variability. These findings highlight the important role of basin meteorology in shaping the seasonal balance between chemical production and atmospheric transport.

3.4 Enhanced PAN recycling and dominant drivers during O₃-polluted periods

Comparisons between clean and O₃ episode periods revealed substantial shifts in PA radicals source pathways, influencing radical cycling, ambient oxidation capacity, and O₃ formation potential. Under clean conditions, PA radical formation was dominated by PAN thermal decomposition (65.3%). During O₃ pollution episodes, total PA radical production increased by 77.0% compared with clean conditions, with PAN decomposition exhibiting the largest enhancement (91.9%) and contributing 69.6% of total PA radical production. In contrast, acetaldehyde and methylglyoxal oxidation rates increased more moderately, resulting in relative contributions of 10.1% and 8.9%, respectively. These results indicate that PA radical formation during pollution episodes became increasingly reliant on PAN thermal recycling, highlighting the important role of PAN as a reservoir within the photochemical system. Seasonally, the contribution of PAN decomposition increased most markedly in spring (from 58.1% to 67.4%), while summer exhibited the highest absolute production rates and a dominant PAN decomposition proportion of 72.2%, reflecting intensified photochemical activity under high-temperature conditions.

Sink pathways of PA radicals were dominated by reactions with NO and NO₂, which together accounted for over 98% of total consumption. During O₃ pollution episodes, PA-NO₂ consumption increased from 1.60 to 2.80 ppbv h⁻¹, while its contribution remained dominant (72.3%–73.4%); PA-NO increased from 0.59 to 0.97 ppbv h⁻¹ with a relatively stable contribution (~25%). Seasonal analysis showed that the increase in PA-NO₂ contribution was most pronounced in spring (from 64.9% to 70.0%), whereas summer exhibited the highest absolute reaction rates, with PA-NO₂ exceeding PA-NO by approximately 3.6-fold. Concurrent increases in NO and NO₂ levels increased during polluted episodes (NO: 1.9 to 2.5 ppbv; NO₂: 9.3 to 14.0 ppbv), reduced the NO/NO₂ ratio from 0.20 to 0.18, favoring the PA-NO₂ pathway and promoting PAN formation.

Marked differences in PA radical source–sink patterns between clean and O₃-polluted conditions highlight the role of PAN in regulating atmospheric radical cycling and photochemical processes. During O₃ pollution episodes, PA radical production became increasingly dependent on PAN thermal recycling, while a larger fraction of PA radicals reacted with NO₂ and was converted back to PAN. This enhanced cycling reinforces the role of PAN as a temporary reservoir for reactive nitrogen and peroxyacetyl radicals, thereby influencing the partitioning of reactive species within the photochemical system.



Consequently, PAN may influence the availability of radicals and NO_x for ozone production, thereby modulating regional photochemical pollution and atmospheric oxidation capacity (Liu et al., 2022).

To further investigate the factors associated with PAN variability under different pollution regimes, SHAP values were compared between representative clean and O_3 -polluted periods in spring and summer (Fig. 6). During spring, PAN_Cycling remained the most influential variable, accounting for 42.4% and 49.4% of the total SHAP importance under clean and polluted conditions, respectively. In contrast, the relative importance of Chem_precursor and meteorological transport variables decreased slightly. These changes suggest that PAN variability during pollution episodes became more strongly associated with chemical cycling processes, whereas the relative influence of meteorological factors weakened. Overall, compared with clean conditions, O_3 -polluted periods were characterized by enhanced PAN_Cycling importance and reduced influence of meteorological transport variables, reflecting a redistribution of factors associated with PAN variability under elevated photochemical conditions.

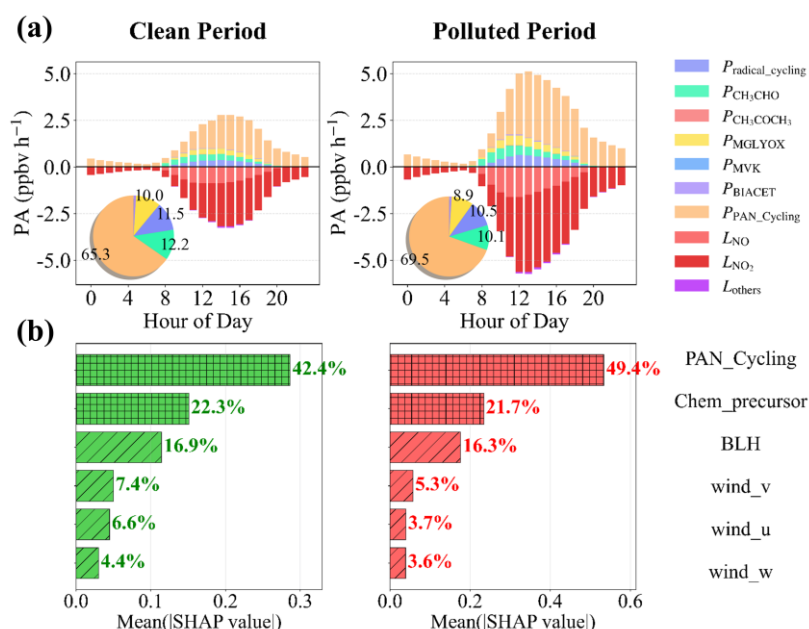


Figure 6. PA radical source-sink pathways and key drivers of PAN_{gen} during clean and O_3 -polluted periods. (a) Mean diurnal profiles of PA radical production and loss pathways, with pie charts showing daytime (08:00–20:00) source contributions (%). (b) SHAP-based feature attribution for PAN_{gen} derived from XGBoost model in spring and summer.

4 Conclusions

Elucidating how chemical mechanisms and meteorological processes jointly regulate PAN is essential for understanding regional photochemical pollution and developing seasonally tailored strategies for coordinated PAN- O_3 mitigation. In this study, we combined one-year field observations, an observation-based box model coupled with the Master Chemical Mechanism, and an interpretable machine learning framework to investigate the seasonal drivers of PAN at a representative urban site in the Sichuan Basin.



391 The observations revealed a pronounced seasonal pattern characterized by wintertime maxima and summertime minima,
392 with winter PAN mixing ratios occasionally exceeding 5 ppbv. Our integrated analyses identified distinct seasonal formation
393 regimes: rapid thermal decomposition–recombination cycling dominated in the warm seasons, whereas primary precursor
394 oxidation was the primary pathway governing wintertime PAN accumulation. RIR and EKMA results demonstrated that local
395 PAN formation remained predominantly VOC-limited year-round, with alkenes, aromatics, and OVOCs identified as the key
396 reactive precursor classes. Meanwhile, NO_x sensitivity exhibited marked seasonal variability, underscoring the necessity of
397 dynamically optimizing emission-control ratios according to prevailing photochemical regimes to achieve concurrent PAN-
398 O₃ reductions.

399 The interpretable machine learning analysis revealed a clear seasonal transition in the governing drivers of PAN
400 variability. Chemical processes governed PAN behavior during the warm seasons, while meteorological factors became
401 increasingly dominant in winter, especially under stagnant conditions. Furthermore, enhanced PAN thermal recycling during
402 O₃ pollution episodes significantly amplified PA radical production and strengthened PAN-O₃ coupling, emphasizing the
403 active role of PAN in sustaining atmospheric radical pools and regional oxidative capacity.

404 Several limitations of this work should be noted. Because the measurements were conducted at a single urban receptor
405 site, the observations may not capture the full spatial heterogeneity across the complex basin terrain. Additionally, the 0-D
406 OBM-MCM framework cannot explicitly account for three-dimensional regional transport. Future research should integrate
407 multi-site observational networks with 3-D chemical transport models to further constrain cross-regional transport and evaluate
408 targeted basin-wide emission control strategies.

409 Overall, this study suggests that coupling chemical box models with interpretable machine learning can serve as a useful
410 diagnostic approach for exploring the multi-scale drivers of atmospheric secondary pollutants. Our findings provide helpful
411 mechanistic insights that may assist in formulating seasonally differentiated, meteorology-informed control strategies for
412 photochemical smog in complex basin.



413 **Code availability**

414 The observation-based model was implemented using the F0AM code (<https://github.com/AirChem/F0AM>), and the machine
415 learning model was developed using the open-source XGBoost package (<https://github.com/dmlc/xgboost>),

416 **Data availability**

417 The observation data used in this study are not publicly available due to institutional restrictions on access to monitoring data.
418 However, the data supporting the findings of this study are available from the corresponding author upon reasonable request
419 and with permission from the data provider.

420 **Supplement**

421 The supplementary information is provided as separate file with this article.

422 **Author contributions**

423 ZD: Writing – original draft, Investigation, Data curation, Methodology, Software, Visualization. HJ: Resources, Writing –
424 review & editing. HW: Resources, Writing – review & editing. WQ: Resources, Writing – review & editing. YC: Resources,
425 Writing – review & editing. LZ: Conceptualization, Funding acquisition, Project administration, Validation, Supervision,
426 Writing – review & editing. DC: Methodology, Writing – review & editing. SL: Writing – review & editing. FY: Writing –
427 review & editing. WW: Funding acquisition, Writing – review & editing. MG: Writing – review & editing.

428 **Competing interests**

429 The contact author has declared that none of the authors has any competing interests.

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