Response to editor and reviewers' comments

We thank the editor and reviewers for the comments and suggestions on the manuscript, which have improved the paper substantially. Our responses (in blue) and the corresponding edits in the manuscript (in red) are shown below. All the page and line numbers mentioned below are referred to the **revised manuscript with track changes**.

Reviewer #1:

The manuscript investigates the atmospheric degradation of three anhydrosaccharides (levoglucosan, mannosan, and galactosan) using hourly TAG-GC/MS measurements conducted in three regions in China (Zibo, Changzhou, Hong Kong). Daytime decay rates are quantified using a relative rate constant method with K^+ from biomass burning (K^+_{BB}) as a reference tracer, and the influence of environmental factors is examined using generalized additive models (GAM). This study provides observational evidence for the atmospheric instability of commonly used biomass-burning tracers, complementing previous laboratory and modeling work. The dataset is strong, and the multi-city comparison offers useful insights.

Overall, this work falls within the scope of ACP and could be suitable for publication after the authors address several issues related to methodological assumptions, uncertainty treatment, and interpretation to strengthen the scientific robustness of the conclusions.

A central concern is the use of K^+_{BB} as an inert, co-emitted tracer for decay-rate calculations. Potassium has significant contributions from dust and sea salt, which may potentially introduce substantial uncertainty. In addition, the relative rate method assumes stable emissions during the 8-hour daytime window, but this assumption may not be valid and is not supported by field observations. In addition, field decay rates are derived from linear regressions of $\ln(C_i/C_k)$ vs. time, yet no statistical acceptance criteria, uncertainty estimates, or confidence intervals are provided. The manuscript repeatedly acknowledges atmospheric mixing but the analysis does not attempt to separate dilution-driven concentration changes from true chemical degradation. The absence of boundary layer height information further complicates interpretation. These issues need to be explicitly addressed to enhance confidence in the derived decay rates.

The GAM analysis is a major component of the paper, but the modeling framework is insufficiently described, Key information on smoother specifications, k values, multicollinearity diagnostics, and handling of missing data is not sufficiently described. In addition, pooling data from all three cities into a single GAM may be statistically inappropriate given the large regional differences.

Response: We sincerely thank the reviewer for the valuable and constructive comments, which have provided important guidance for improving our study.

(i) We acknowledge that dust and sea salt are potential sources of potassium. In the original manuscript, contributions from sea salt and dust were excluded when calculating potassium ions derived from biomass burning (K^+_{BB}), and we employed the ratio of anhydro-saccharides to K^+_{BB} to investigate the diurnal decay pattern of anhydro-saccharides. This ratio provides a key advantage for effectively mitigating the confounding effects of boundary layer dynamics (e.g., diurnal variations in mixing height and vertical diffusion processes). Since both anhydro-saccharides and K^+_{BB} originate from biomass burning, they experience similar boundary layer-driven dilution processes (Li et al., 2021; Mochida et al., 2010; Wang et al., 2025).

(ii) We assume that emissions of anhydro-saccharides and K^+_{BB} were either equivalent or negligible during the daytime window (08:00–16:00 LST). This assumption allowed the observed decrease in the anhydro-saccharides/K^+_{BB} ratio to be primarily attributed to degradation processes. We acknowledge that data from certain days do not conform to the linear decay pattern. During the observation period, each day was characterized by distinct biomass burning (BB) emission intensities (or the absence of BB emissions), accompanied by varying meteorological conditions and oxidant levels. Days with poor fitting performance only indicate that the combination of atmospheric conditions on those days violated the core assumptions underlying Equation (8). The method employed in this study is only applicable to specific scenarios that satisfy the fundamental assumptions. To mitigate the bias arising from days with unsuccessful fitting, we exclusively retained days characterized by positive decay rates and a coefficient of determination ($R^2>0.5$) for the estimation of decay rates and subsequent GAM analysis in the original manuscript. This approach was necessary because the inclusion of such poorly fitted data points would artificially depress the average rate constant k, thereby potentially resulting in an underestimation of the authentic degradation rate. Consequently, valid data were obtained for 31 out of 67 days (46%) in Zibo, 21 out of 45 days (47%) in Changzhou, and 69 out of 106 days (65%) in Hong Kong. The mean decay rates for the three anhydro-saccharides across the three cities, derived from linear regression fitting, are presented in the supporting information of the original manuscript. We apologize for not providing a detailed explanation regarding the certain days which do not conform to the linear decay pattern in the original manuscript. In response to your detailed comments, we have carefully revised, supplemented, and improved the manuscript accordingly.

(iii) We incorporated the calculated effective decay rates into the GAM model. The primary objective of this modeling approach is to elucidate the universal relationship between the decay rates of anhydro-saccharides and environmental factors. This enables our research conclusions to be extended to regions with diverse meteorological conditions and provides scientific insights into the atmospheric decay processes of anhydro-saccharides. We acknowledge that the description of the GAM modeling process in the original manuscript was indeed insufficient. In accordance with your valuable comments, we have added more detailed information on the modeling procedures.

Detailed comments:

Lines 15-33 (Abstract): please report the number of valid decay days per city to better contextualize the analysis.

Response: Suggestion taken, we have incorporated the information into the abstract.

Page 1, Line 24-25: A total of 31, 21, and 69 valid decay days were identified for Zibo, Changzhou, and Hong Kong, respectively.

Lines 165-170: the manuscript acknowledges that K^+ has contributions from sea salt and dust, which challenges the assumption of K^+ being solely biomass-derived. Please provide quantitative justification for the use of K^+_{BB}, especially for dust-influenced Zibo and marine-influenced Hong Kong.

Response: For quantitative validation, the relative contributions of non-biomass burning sources to total K^+ at each sampling site were quantified from measured ionic concentrations. Sea-salt contributions were corrected for using Na^+ with seawater reference ratios of $(K^+/Na^+)_{sw} = 0.037$ and $(Ca^{2+}/Na^+)_{sw} = 0.038$, while crustal dust contributions were corrected for via Ca^{2+} using literature-reported maximum and minimum $(K^+_{Nss}/Ca^{2+}_{Nss})$ ratios.

For Zibo, the average contribution of dust to the total K^+ concentration is 3.0%, while that of sea salt is 3.6%. This data reflects the characteristics of sporadic dust events at this site. Following the correction for the interference from dust and sea salt, the average proportion of potassium derived from biomass burning sources (K^+_{BB}) relative to total K^+ is approximately 93.4%. The reliability of the correction method is supported by the correlation analysis between K^+_{BB} and anhydro-saccharides. Specifically, the Pearson correlation coefficient between K^+_{BB} and levoglucosan is 0.65, while it is 0.52 for both mannosan and galactosan, with all correlations being significant at $p < 0.05$ (see Fig. S3). These results demonstrate that, despite the influence of dust, K^+_{BB} serves as a reliable indicator of biomass burning emissions at the Zibo station.

For Changzhou, the contribution of non-biomass burning sources to total K^+ is also relatively low, with dust accounting for an average of 6.3% and sea salt for 2.3%. Compared to the Zibo station, the correlation between K^+_{BB} and anhydro-saccharides at the Changzhou station is more pronounced: the correlation coefficient with levoglucosan is 0.76, with mannosan it is 0.58, and with galactosan it is 0.54, all of which are significant at $p < 0.05$. This further confirms the robustness of the method used. Notably, potassium from biomass burning sources (K^+_{BB}) constitutes approximately 91.4% of total K^+ at the Changzhou station, indicating that biomass burning remains the primary source of K^+ in $PM_{2.5}$ during the sampling period.

For Hong Kong, due to the limited availability of water-soluble K^+ data, we utilized total elemental K (as measured by the Xact 625i) as a proxy for K^+_{BB}, given that elemental K is predominantly influenced by biomass burning at this suburban site, which has low dust inputs. The calculated K_{BB} accounted for 82% of the total K, indicating that biomass burning is the major source of K in $PM_{2.5}$ during the campaign period. However, considering Hong Kong's coastal location, we acknowledge the potential for overestimation. Nevertheless, the strong correlation between total K and levoglucosan ($R_p = 0.63$; $p < 0.05$) supports its utility as a biomass burning tracer, consistent with previous studies in similar environments (e.g., Wang et al., 2025). Assuming a 20% underestimation of sea salt contributions in our K_{BB} calculations (based on the typical proportion of marine aerosols), the adjusted decay rates of anhydro-saccharides changed by less than 10%. For instance, the decay rate of levoglucosan increased slightly from $0.070 \pm 0.008\ h^{-1}$ to $0.074 \pm 0.01\ h^{-1}$. Such a minor variation did not affect the main conclusions of the present study. Relevant descriptions have been added in lines 179-181 and 377–380 of the revised manuscript.

Page 6, Line 184-186: To estimate the potassium ions derived from biomass burning (K^+_{BB}), this study subtracted the contributions of sea salt and dust by Equations (2)~(7).

Page 14, Line 377-380: In Zibo and Changzhou, the K^+_{BB} concentrations were calculated using Equations (2)~(7), and the results showed that K^+_{BB} accounted for 93.4% and 91.4% of the total K^+, respectively, thus biomass burning as the major source of K^+ in $PM_{2.5}$ during the sampling campaign.

Lines 201-219: The description of the GAM lacks essential details: spline type, basis dimension (k), link function, variable scaling, and treatment of missing values. Without this information, the analysis is not reproducible.

Response: We sincerely appreciate the reviewer's valuable comments regarding the insufficient reporting of essential methodological details for the GAM model. To ensure the reproducibility of our analyses, we have supplemented the critical technical details of the GAM implementation. All the aforementioned details have been added to the revised manuscript (Lines 233–257) to enhance the transparency and reproducibility of our GAM analyses. Furthermore, the dataset input into the GAM exclusively included days with valid decay rate records, which inherently ensured complete data for all variables (i.e., no missing values). In addition, we have included a dedicated explanation of this point in Lines 545–549.

Page 8, Line 233-257: In this study, the generalized additive model (GAM) was implemented using the LinearGAM class from the Python library pygam, with cubic regression splines as the default basis function. The model utilized a linear link function (the default setting for LinearGAM), aligning with the assumption of a linear relationship between the response variable and the smooth terms of the predictor variables. All variables were retained in their original units and ranges, and no scaling was applied before model fitting. To optimize the spline-related parameters, we conducted a two-dimensional grid search over the basis dimension (defined as the number of splines k) and the penalty parameter (λ). The enumerated range for k was set at 8, 10, and 12, while λ was exhaustively tested across a predetermined logarithmic range (from 10^{-3} to 10^{3}, encompassing 10 logarithmic points). This process generated 30 parameter combinations, which were evaluated by minimizing the generalized cross-validation (GCV) loss function. The results indicated that when k = 10, the model achieved optimal performance, with the corresponding optimal penalty parameter λ = 46.42. Moreover, with k = 10, all smooth curves of the variables exhibited no anomalous oscillations or overfitting artifacts, clearly reflecting the true nonlinear trends of the variables. This parameter combination achieved the best balance between fitting accuracy and structural complexity, leading to the final selection of k = 10 for the basis dimension of all predictor variables, thereby determining the optimal effective degrees of freedom (Edf) for each smooth term of the predictors. This optimization step effectively balanced the accuracy of the model fit with its structural complexity, enhancing the model's generalization performance on unseen data. Furthermore, to optimize the set of predictor variables, a multicollinearity check was performed using the variance inflation factor (VIF) before model fitting, with a conservative threshold of 4 used to identify significant multicollinearity; variables with VIF > 4 were carefully evaluated and excluded from the final model. The retained predictor variables demonstrated acceptable levels of collinearity, ensuring the stability of model parameter estimates and improving the reliability and interpretability of subsequent analytical results.

Page 17, Line 545-549: In this study, we incorporated the calculated effective decay days into the GAM model. The daytime degradation rate calculated for the three cities was used as the response variable in the GAM model, and the various influencing factors (O_x, ALWC, SSR, RH and T) were used as the corresponding explanatory variables.

Lines 250-284: When interpreting Lev/Man or Man/Gal ratios, consider discussing potential influences of regional differences in burning practices or fuel types.

Response: We have added time series of anhydro-saccharides and K^+_{BB} at the three cities, with relevant discussions added in lines 386-407 of the revised manuscript.

Page 14, 15, Line 386-407: The detailed time series of anhydro-saccharides and K^+_{BB} for the three cities is presented in Fig. S4. Overall, the concentrations of anhydro-saccharides and K^+_{BB} in these three locations exhibit a synchronous increase and decrease trend, verifying the similarity in their sources. From Fig. S4 (a) and (b), it is evident that the concentrations of anhydro-saccharides and K^+_{BB} in Zibo and Changzhou exhibit frequent spikes within a short time frame, aligning with the characteristics of concentrated emissions associated with open burning of straw during the autumn and winter seasons in these regions. Such combustion under high temperatures and strong oxygen supply conditions generates a higher proportion of levoglucosan (Chen et al., 2017; Cheng et al., 2013; Fabbri et al., 2009). Additionally, Zibo, as a typical heavy industrial city, experiences biomass combustion emissions that are influenced by the incomplete combustion processes of industrial burning and residential heating with coal at low temperatures, leading to higher concentrations of galactosan compared to mannosan (Haque et al., 2022; Yan et al., 2018). These factors collectively enhance the chemical characteristic differences between Zibo and other sites. In contrast, Fig. S4(c) shows that the time series from Hong Kong displays stable fluctuations in the concentrations of anhydro-saccharides and K^+_{BB}, without frequent sudden peaks. This aligns with the biomass burning pattern in this region, primarily relying on residential cooking and small-scale commercial activities (such as wood and kitchen waste)(Lee et al., 2013; Leung et al., 2024). On the contrary, the biomass burning sources in Hong Kong are characterized by low emission intensity and a sustained, dispersed release process. The regional characteristics of these three cities provide important background and data support for subsequent analyses of the daytime decay rates of anhydro-saccharides, aiding in the deeper understanding of their sources and variations under different environmental conditions, thereby laying the foundation for developing relevant pollution control strategies and optimization plans.

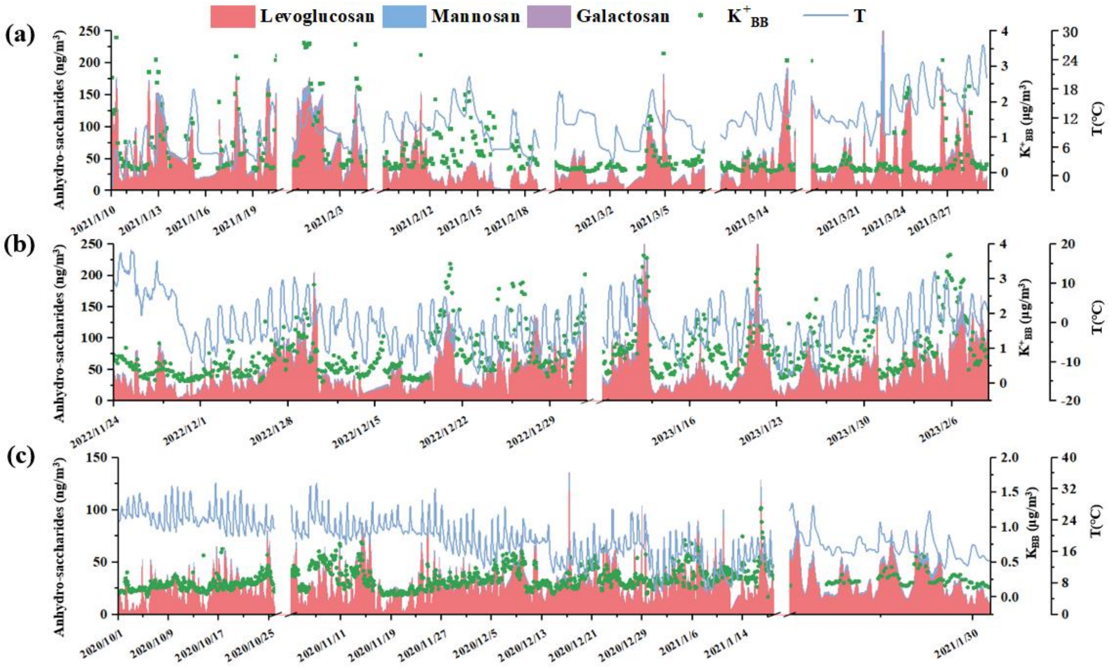

Fig. S4 Time series of concentrations of levoglucosan, mannosan, galactosan and K^+_{BB}, as well as temperature in (a) Zibo, (b) Changzhou and (c) Hong Kong

Lines 258-264: The manuscript notes r = 0.63 correlation between total K and levoglucosan, but this alone does not establish total K as a reliable biomass-burning tracer. Please include comparison of total K variability with expected sea-salt potassium contributions and an assessment of potential bias in derived decay rate k if K^+_{BB} is misrepresented.

Response: Regarding the Hong Kong sampling campaign, this issue has been elaborated in our previously published work (Wang et al., 2025), and we provide a concise summary here. At the Hong Kong sampling site, a strong correlation was observed between total K and K^+ ($R_p = 0.84$), which strongly indicates that the majority of ambient K exists in water-soluble form. Additionally, the detection rate of total K was considerably higher than that of K^+ during the sampling period (97% vs. 46%).

Therefore, we selected total potassium for the calculation, and after excluding the effects of sea salt and dust, the final calculation yielded potassium produced by biomass combustion (K_{BB}). The calculated K_{BB} accounted for 82% of total K, confirming that biomass burning (BB) was the dominant source of K in $PM_{2.5}$ during the observation period. The sample deviation of total potassium was 0.19 μg m^{-3}, which was substantially higher than the sea salt-derived potassium ion (K^+) concentration (0.007 ± 0.006 μg m^{-3}). This observation indicates that the fluctuations in total potassium were predominantly attributed to biomass combustion. Nevertheless, given the coastal location of Hong Kong, we acknowledge that the sea salt contribution may have been underestimated in the present study. To address this potential uncertainty, a sensitivity analysis was conducted: assuming a 20% underestimation of sea salt contributions in our K_{BB} calculations, the adjusted decay rates of anhydro-saccharides changed by less than 10%. For example, the decay rate of levoglucosan increased slightly from 0.070 ± 0.008 h^{-1} to 0.074 ± 0.01 h^{-1}. Such a minor variation was insufficient to alter our key conclusions. Furthermore, K_{BB} exhibited a good correlation with levoglucosan (R_p = 0.63), which further reinforces that they share the same primary source. Thus, it is reasonable to use K_{BB} as a tracer for BB at the Hong Kong site. However, we acknowledge that day-to-day variations in the sources of K cannot be ruled out, which could result in some systematic biases in the estimated K_{BB} and in the derived k's by extension. We have explicitly highlighted this limitation in Lines 299–308 of the revised manuscript.

Page 10, Line 299-308: It is important to note that, due to insufficient observational data for K^+ in Hong Kong, we selected total potassium for the calculation, and after excluding the effects of sea salt and dust, the final calculation yielded potassium produced by biomass combustion (K_{BB}). The calculated K_{BB} accounted for 82% of total K, confirming that biomass burning (BB) was the dominant source of K in $PM_{2.5}$ during the observation period. Furthermore, K_{BB} exhibited a good correlation with levoglucosan (R_p = 0.63), which further reinforces that they share the same primary source. Thus, it is reasonable to use K_{BB} as a tracer for BB at the Hong Kong site. However, daily heterogeneity in the sources of potassium cannot be ruled out, which may introduce systematic biases in the estimation of K_{BB} and the inference of k's.

Lines 315-318: It is noted that concentrations depend on diffusion, meteorology, and deposition, yet decay-rate interpretation does not account for boundary layer effects.

Response: We acknowledge that the absolute concentrations of aerosol species are jointly governed by multiple factors, including primary emissions, chemical degradation, atmospheric diffusion, and deposition processes. However, relative concentrations serve as a more robust indicator for quantifying the particulate-phase loss of organic species compared to absolute concentrations. Therefore, in the original manuscript, in addition to performing diurnal variation analyses on the three anhydro-saccharides (levoglucosan, mannosan, and galactosan), we further conducted diurnal variation analyses of the ratio of each anhydro-saccharide to biomass-burning potassium($\mathrm{C_i}/\mathrm{C_{K^+_{BB}}}$), as shown in Fig. 1. Our results reveal that $\mathrm{C_i}/\mathrm{C_{K^+_{BB}}}$ exhibits a consistent decreasing trend during the daytime (08:00–16:00), which provides direct observational evidence for the subsequent calculation of the daytime decay rates of anhydro-saccharides. Notably, the utilization of this ratio can effectively eliminate the confounding effects of boundary layer dynamics (e.g., diurnal variations in mixing height and vertical dispersion), since both anhydro-saccharides and K^+_{BB} are derived from biomass burning and thus subject to the same boundary layer-driven dilution processes. We have supplemented detailed explanations of this methodological rationale in the revised manuscript (see Lines 350–365 for specific revisions).

Page 12, 13, Line 350-365: However, relative concentration is a more effective indicator for detecting the loss of organic species particles. In addition, previous studies have indicated that the ratio of levoglucosan to potassium ions (K^+) from BB sources (levoglucosan/K^+_{BB}) is an effective indicator of the aging degree of BB aerosols (Cheng et al., 2013; Li et al., 2021; Mochida et al., 2010). Therefore, to investigate the diurnal decay pattern of anhydro-saccharides, we selected C_i/K^+_{BB} to examine the decay of anhydro-saccharides. As shown in Fig. 2, the diurnal variations of anhydro-saccharides and K^+_{BB} in the three cities also exhibit a decreasing trend from 08:00 to 16:00, providing a key basis for the subsequent calculation of the decay rate of anhydro-saccharides. Furthermore, the utilization of this ratio can effectively eliminate the confounding effects of boundary layer dynamics (e.g., diurnal variations in mixing height and vertical diffusion), since both anhydro-saccharides and K^+_{BB} are derived from biomass burning and thus subject to the same boundary layer-driven dilution processes.

Lines 360-364: It is stated that some days show negative decay rates due to fresh BB emissions, which contradicts the assumption that emissions remain constant during 8:00-16:00. Please clarify how such deviations influence the decay rate estimates?

Response: We thank the reviewer for raising this important point regarding the assumptions in our relative rate constant method (Equation 8) and the implications of deviations from those assumptions. As stated in Section 2.3, the method assumes equivalent or negligible emissions of anhydro-saccharides and K^+_{BB} within the daytime window (8:00–16:00 LST), so the observed decline in the anhydro-saccharide/K^+_{BB} ratio can be ascribed chiefly to degradation rather than to differential source strength. However, the observational data for certain days do not conform to the linear decay pattern. This phenomenon is primarily attributed to factors such as interference from fresh emissions and changes in air mass origins, which cannot be directly ascertained based solely on ground-based observations. The presence of invalid data during the fitting process does not contradict the research hypothesis, it merely reflects the complexity of real ambient conditions. During the observation period, each day was characterized by distinct biomass burning (BB) emission intensities (or the absence of BB emissions), accompanied by varying meteorological conditions and oxidant levels. Days with poor fitting performance only indicate that the combination of atmospheric conditions on those days violated the core assumptions underlying Equation (8). The method employed in this study is only applicable to specific scenarios that satisfy the fundamental assumptions, and the two-hourly measurement data enabled us to sample the target compounds under a wide range of diurnal ambient conditions. We have added these explanations in lines 437–458 of the revised manuscript.

To mitigate the bias arising from days with unsuccessful fitting, this study exclusively retained days characterized by positive decay rates and a coefficient of determination ($R^2>0.5$) for the estimation of decay rates and subsequent generalized additive model (GAM) analysis. The inclusion of such poorly fitted data points would artificially depress the average rate constant k, thereby potentially resulting in an underestimation of the authentic degradation rate. This resulted in analyzing 31 out of 67 days for Zibo (46%), 21 out of 45 days for Changzhou (47%), and 69 out of 106 days for Hong Kong (65%). The proportion of days in Hong Kong that could be linearly fitted is significantly higher than that in Zibo and Changzhou. This outcome may be closely related to the differences in climatic conditions and burning practices across regions. The relevant analysis has been supplemented in Lines 459–480 of the revised manuscript. By focusing on valid days, our reported decay rates (e.g., $0.13 \pm 0.05\ h^{-1}$ for levoglucosan in Changzhou) represent conservative estimates under conditions where degradation dominates over emissions.

We assessed potential residual bias through a sensitivity test: For borderline days (near-zero k), including them reduced average k by less than 10% across sites (e.g., Changzhou levoglucosan k from 0.13 to 0.12 h^{-1}), with no change to key conclusions like inter-city differences. This suggests deviations have minimal impact on our results, as the method's selectivity prioritizes reliable decay signals. However, we acknowledge that variable emissions could introduce uncertainty in real atmospheres, and future studies might incorporate dynamic emission modeling (e.g., via back-trajectory analysis) to refine estimates.

Page 17, 18 Line 437-458: In such a short time frame (approximately 8 hours), the combustion conditions of burning plants and biomass sources are expected to remain relatively constant, making the influence of source emissions on the changes in normalized sugar concentration negligible. The obtained k values can be regarded as the average daytime decay rate for the day of observation. However, the observational data for certain days do not conform to the linear decay pattern. This phenomenon is primarily attributed to factors such as interference from fresh emissions and changes in air mass origins, which cannot be directly ascertained based solely on ground-based observations. The presence of invalid data during the fitting process does not contradict the research hypothesis; it merely reflects the complexity of real ambient conditions. During the observation period, each day was characterized by distinct biomass burning (BB) emission intensities (or the absence of BB emissions), accompanied by varying meteorological conditions and oxidant levels. Days with poor fitting performance only indicate that the combination of atmospheric conditions on those days violated the core assumptions underlying Equation (8). The method employed in this study is only applicable to specific scenarios that satisfy the fundamental assumptions, and the two-hourly measurement data enabled us to sample the target compounds under a wide range of diurnal ambient conditions. The fitting results for the three cities are as follows: Zibo sampled for a total of 67 days, with 31 days fitting the linear decay pattern (46%); Changzhou sampled 45 days, with 21 days fitting the linear decay pattern (47%); and Hong Kong sampled 106 days, with 69 days fitting the linear decay pattern (65%). The proportion of days in Hong Kong that could be linearly fitted is significantly higher than that in Zibo and Changzhou. This outcome may be closely related to the differences in climatic conditions and burning practices across regions.

Page 18 Line 459-480: The analysis in Fig. S4 indicates that both Zibo and Changzhou experience frequent outdoor straw burning activities in autumn and winter, where continuous fresh emissions release substantial amounts of anhydro-saccharides and other biomass combustion tracers into the atmosphere. The emission rates of these tracers within an 8-hour window far exceed the natural diffusion and chemical degradation rates of pollutants, disrupting the stable concentration changes required for linear decay, ultimately resulting in fitting failures. Furthermore, we compared the concentrations of atmospheric oxidants on successful and unsuccessful fitting days. The results show that the mean concentrations of atmospheric oxidants on successful fitting days are higher across all three cities compared to unsuccessful fitting days. Specifically, the atmospheric oxidant concentration on successful fitting days in Zibo was 41.2 ±8.5 ppb (range: 24.2~61.8 ppb), while it was 37.6 ± 7.8 ppb (range: 17.9~65.7 ppb) on unsuccessful fitting days. In Changzhou, the concentration for successful days was 46.1±13.0 ppb (range: 21.6~81.8 ppb), compared to 44.3 ± 10.6 ppb (range: 14.6~60.8 ppb) on unsuccessful days. In Hong Kong, successful fitting days showed an atmospheric oxidant concentration of 31.9 ± 6.3 ppb (range: 19.7~53.4 ppb), while the concentration on unsuccessful days was 27.8 ± 6.8 ppb (range: 14.9~42.0 ppb). These results suggest that the relative deficiency of atmospheric oxidants may also be a significant factor preventing the concentration of anhydro-saccharides from exhibiting a clear linear decay pattern. To mitigate the bias arising from days with unsuccessful fitting, this study exclusively retained days characterized by positive decay rates and a coefficient of determination ($R^2>0.5$) for the estimation of decay rates and subsequent generalized additive model (GAM) analysis. The inclusion of such poorly fitted data points would artificially depress the average rate constant k, thereby potentially resulting in an underestimation of the authentic degradation rate.

Lines 365-367: it is reported that only a subset of days exhibit “good linear fitting,” please define explicit acceptance criteria (e.g., R^2 cutoff).

Response: We sincerely thank the reviewer for the valuable comments. Only the days with positive decay rates that satisfied the statistical criteria of $R^2 > 0.5$ and $p < 0.05$ were included in the decay rate estimation and subsequent generalized additive model (GAM) analyses. We have added clarifications in the manuscript on Lines 475–478.We have added clarifications in the manuscript on Lines 475–480.

Page 18, Line 475-480: To mitigate the bias arising from days with unsuccessful fitting, this study exclusively retained days characterized by positive decay rates and a coefficient of determination ($R^2>0.5$) for the estimation of decay rates and subsequent generalized additive model (GAM) analysis. The inclusion of such poorly fitted data points would artificially depress the average rate constant k, thereby potentially resulting in an underestimation of the authentic degradation rate.

Lines 381-389: The conclusion that differences in BDE cannot fully explain decay rate differences, but the explanation is brief. Consider expanding the discussion to include potential roles of aerosol phase state, aqueous-phase versus heterogeneous oxidation pathways, and differences in aerosol composition (e.g., inorganic ions influencing aerosol liquid water content and viscosity).

Response: We thank the reviewer for the valuable comments. In Lines 392-408 of the original manuscript, our discussion focused on why decay rate differences exist among the three anhydro-saccharides at the same sampling site (rather than across three cities). This clarification was not explicitly stated in the original version, and we have added the explanation in the revised manuscript (see Lines 484–504). When the three anhydro-saccharides are exposed to identical environmental conditions, their structural differences lead to variations in the reactivity potential of hydroxyl radicals (·OH) with each sugar molecule. We acknowledge that bond dissociation enthalpy (BDE) do not fully account for the decay rate differences among the three anhydro-saccharides, as the BDE-based trend was only validated in Hong Kong and Changzhou. The decay rates of anhydro-saccharides are likely governed by additional driving factors. To address this, we conducted a separate analysis of the generalized additive model (GAM) results for Zibo (original manuscript Lines 521–531), where we quantified the contributions of five environmental factors (O_x, ALWC, SSR, RH, and T) to the calculated decay rates. Our results show that the contribution of O_x to the decay rate of levoglucosan is higher than that to the other two anhydro-saccharides, while the contribution of ALWC to the decay rates of mannosan and galactosan is greater than that to levoglucosan. Thus, the degradation rates of anhydro-saccharides are not only related to their BDE. Even within the same urban macro-atmospheric environment, the differences in the aerosol particle microenvironments of the three anhydro-saccharides can still regulate the oxidation processes. For instance, variations in aerosol phase state (e.g., viscosity influenced by RH and T) may affect oxidant diffusion, leading to differential rates, as higher RH in Hong Kong could reduce viscosity and enhance heterogeneous oxidation for mannosan and galactosan (Slade and Knopf, 2014). Additionally, aqueous-phase oxidation (promoted by high ALWC) may dominate in Changzhou, while heterogeneous pathways prevail in lower-ALWC sites like Hong Kong, explaining pathway-specific sensitivities beyond BDE (Lai et al., 2014; Slade and Knopf, 2014). Differences in aerosol composition, such as inorganic ions (e.g., SO_4^{2-}, NO_3^-, NH_4^+), further influence ALWC and viscosity; for example, higher sulfate in Zibo may acidify aerosols, potentially slowing certain pathways (Riva et al., 2016a; Riva et al., 2016b). The combined effects of multiple driving factors, along with the differing sensitivities of the anhydro-saccharides to these factors, lead to inconsistent intensities of oxidation pathways such as liquid-phase oxidation and heterogeneous oxidation, ultimately resulting in the variations in their degradation rates. We have added the relevant discussions on pages 652-668 of the revised version.

Page 16, 17, Line 484-504: The three anhydro-saccharides exhibit differences in their molecular structures, particularly concerning the C-H bonds situated at various positions on the sugar rings. This results in variations in the reaction potential of hydroxyl radicals (·OH) with each sugar molecule. In the same city, all three sugars undergo oxidation by ·OH radicals. We conducted a correlation analysis of the decay rates of these anhydro-saccharides across different cities. As illustrated in Fig. S5, there is a strong correlation among the decay rates of anhydro-saccharides in the three cities. This suggests that despite the differences in molecular structures, the oxidation mechanisms involving ·OH are similar, accounting for the high correlation between their decay rates. The differences in decay rates for the three anhydro-saccharides in the same city may also relate to bond dissociation enthalpy (BDE). According to John et al. (2020a and 2020b), the BDE of levoglucosan, mannosan, and galactosan can be estimated using the accurate bond dissociation enthalpy tool (ALFABET) available online (https://bde.ml.nrel.gov/, last accessed: October 21, 2025). The findings indicate that the C-H bonds that are most susceptible to breakage in levoglucosan, mannosan, and galactosan are predominantly located at positions 2 and 3, with corresponding BDE of 85.3–86.9 kcal mol^{-1}, 84.6–85.1 kcal mol^{-1}, and 82.9–84.6 kcal mol^{-1}, respectively. This implies that the decay rates of the three anhydro-saccharides should follow the order: galactosan > mannosan > levoglucosan (St John et al., 2020a; St John et al., 2020b). However, this trend was only observed in Hong Kong and Changzhou. Hence, besides BDE, there should be other influencing factors affecting the decay rates. Section 3.4 provides a detailed exploration of the environmental factors that influence the decay rates of anhydro-saccharides, with a particular focus on Zibo.

Page 22, Line 652-668: These findings demonstrate that the degradation rates of anhydro-saccharides are not only correlated with their structural BDE but also regulated by other driving factors with distinct contribution patterns. Even within the same urban macro-atmospheric environment, microenvironmental differences in the aerosol particles hosting the three anhydro-saccharides can modulate their oxidation processes. For instance, variations in aerosol phase state (e.g., viscosity influenced by RH and T) may affect oxidant diffusion, leading to differential rates, as higher RH in Hong Kong could reduce viscosity and enhance heterogeneous oxidation for mannosan and galactosan (Slade and Knopf, 2014). Additionally, aqueous-phase oxidation (promoted by high ALWC) may dominate in Changzhou, while heterogeneous pathways prevail in lower-ALWC sites like Hong Kong, explaining pathway-specific sensitivities beyond BDE (Lai et al., 2014; Slade and Knopf, 2014). Differences in aerosol composition, such as inorganic ions (e.g., SO_4^{2-}, NO_3^-, NH_4^+), further influence ALWC and viscosity; for example, higher sulfate in Zibo may acidify aerosols, potentially slowing certain pathways (Riva et al., 2016a; Riva et al., 2016b). Collectively, the combined effects of multiple driving factors and the differential sensitivities of the three anhydro-saccharides to these factors lead to inconsistent intensities of oxidation pathways (e.g., aqueous-phase oxidation and heterogeneous oxidation), thereby producing the divergent degradation rates observed.

Lines 426-468: The model pools all three cities, but their meteorology differs dramatically (lines 391-399). Consider using city-specific GAMs or including city as a factor.

Response: We thank the reviewer for the constructive comments. In this study, the effective decay rates of the three anhydro-saccharide species across three cities with distinct meteorological conditions were set as the dependent variable. The independent variables included aerosol liquid water content (ALWC), relative humidity (RH), temperature (T), atmospheric oxidants (O_x), and solar surface radiation (SSR). The unified generalized additive model (GAM) was constructed to explore the generalizable relationships between the decay rates of anhydro-saccharides and environmental factors. We also attempted to incorporate the city factor as a categorical predictor into the GAM framework; however, this inclusion yielded no meaningful improvements in model fitting performance. Specifically, the adjusted R^2 of the GAM increased by only 0.001 (e.g. 0.70 to 0.701) after adding the city factor, while the generalized cross-validation (GCV) score, a key metric for evaluating GAM fitting quality, remained unchanged. Furthermore, the city factor exerted a statistically non-significant effect on the response variable in the augmented model ($p = 0.25 > 0.05$). Based on these results, the original unified GAM framework was retained for the final analysis. The core objective of this modeling approach is to elucidate the universal relationships between the decay rates of anhydro-saccharides and environmental factors, which enables the research conclusions to be applicable across regions with varying meteorological contexts and thereby providing insights into the atmospheric decay processes of anhydro-saccharides.

Lines 430-431: The GAM response variable is decay rate k, which itself may embed meteorological dilution effects. Please clarify whether the environmental variables are intended to explain chemical degradation alone or a combination of chemical and physical processes.

Response: In this study, the ratio of anhydro-saccharides to potassium ions generated from biomass burning ($C_i/C_{K^+_{BB}}$) was utilized to analyze and calculate the degradation rate of anhydro-saccharides. Notably, sea salt and dust interferences were excluded when calculating K^+_{BB}. This ratio effectively mitigates perturbations from boundary layer dynamical processes (e.g., diurnal variations in mixing layer height and atmospheric vertical diffusion), which represent meteorological dilution effects. The underlying principle is that both anhydro-saccharides and K^+_{BB} originate from biomass combustion and are subject to the same physical dilution effects driven by boundary layer processes during atmospheric transport. Consequently, their ratio can cancel out these physical effects on the concentration of individual species. Thus, the environmental variables in the GAM model are intended to explain chemical degradation alone. We have added a clarification in revised Section 3.4 (Discussion) to explicitly address this point and avoid any potential ambiguity.

Page 22, Line 550-559: Notably, this study used the natural logarithmic function of the ratio of anhydro-saccharides to K^+_{BB} for linear fitting to analyze and calculate the degradation rate of anhydro-saccharides. This ratio effectively mitigates the interference of boundary layer dynamical processes, such as diurnal variations in mixing layer height and atmospheric vertical diffusion, which are meteorological dilution effects. The underlying principle is that both anhydro-saccharides and K^+_{BB} originate from biomass combustion and are subject to the same physical dilution effects driven by boundary layer processes during atmospheric transport. Consequently, their ratio can cancel out these physical effects on the concentration of individual species. Thus, the degradation rates included in the GAM model have removed the contributions from meteorological physical dilution effects, reflecting solely the intrinsic chemical degradation process of anhydro-saccharides.

Lines 432-433: An adjusted $R^2 = 0.70$ is reported but there is no discussion about multicollinearity. Ox, SSR, and T are correlated (Fig. 5), and such multicollinearity may distort smooth functions. Please provide concavity diagnostics.

Response: The corresponding results of multicollinearity diagnosis have been added in Lines 572–579 of revised manuscript.

Page 19, Line 572-579: "To avoid the potential impact of multicollinearity among variables on the stability of model fitting and the accuracy of parameter estimates, this study performed a multicollinearity assessment on the explanatory variables using the variance inflation factor (VIF) prior to conducting the GAM analysis. A high VIF value points to strong multicollinearity between a given explanatory variable and the remaining explanatory variables; specifically, a VIF value exceeding 4 denotes the existence of significant multicollinearity in regression analysis (Shrestha, 2020; Xiao et al., 2018). The results of the multicollinearity test are presented in Table S6, where the VIF for all explanatory variables is less than 4, indicating that they successfully passed the multicollinearity assessment."

Table S6 Variance inflation factors (VIF) of the influencing factors for the decay rate of anhydro-saccharides in GAM analysis

Smooth variables	ALWC	T	O_x	RH	SSR
k_lev	1.3	1.5	1.4	1.5	1.6
k_man	1.3	1.5	1.4	1.5	1.6
k_gal	1.3	1.5	1.4	1.5	1.6

Lines 487-488: Diurnal patterns attributed to chemical decay could reflect dilution when BLH increases during the day. Including BLH data (e.g., from ERA5 reanalysis) would strengthen the interpretations.

Response: In calculating the decay rates of anhydro-saccharides in this study, we adopted the natural logarithmic function of the ratio of anhydro-saccharides to K^+_{BB} for linear fitting; meanwhile, the influence of sea salt and dust has been eliminated in the calculation of K^+_{BB}. Theoretically, both K^+_{BB} and anhydro-saccharides are mainly derived from biomass combustion, and they are both affected by the dilution process driven by the same boundary layer. Therefore, this ratio can eliminate the confounding effect of boundary layer dynamics. We have added a clarification in revised Section 3.4 to explicitly address this point and avoid potential ambiguity.

Page 22, Line 550-559: "Notably, this study used the natural logarithmic function of the ratio of anhydro-saccharides to K^+_{BB} for linear fitting to analyze and calculate the degradation rate of anhydro-saccharides. This ratio effectively mitigates the interference of boundary layer dynamical processes, such as diurnal variations in mixing layer height and atmospheric vertical diffusion, which are meteorological dilution effects. The underlying principle is that both anhydro-saccharides and K^{+}_{BB} originate from biomass combustion and are subject to the same physical dilution effects driven by boundary layer processes during atmospheric transport. Consequently, their ratio can cancel out these physical effects on the concentration of individual species. Thus, the degradation rates included in the GAM model have removed the contributions from meteorological physical dilution effects, reflecting solely the intrinsic chemical degradation process of anhydro-saccharides."

Fig. 6: confidence bands need clear labeling.

Response: We have uniformly specified the labeling of the confidence bands in the caption of Fig. 6.

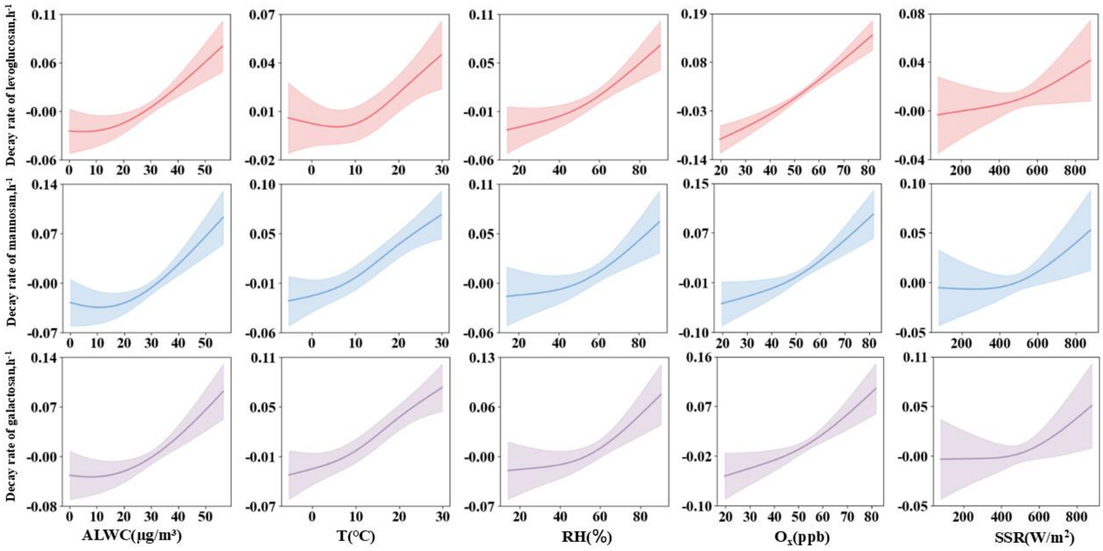

Fig. 1 Influences of various factors on the daytime degradation rates of different saccharides analyzed using the GAM model: (a) levoglucosan, (b) mannosan, and (c) galactosan, as a function of ALWC, T, RH, Ox, and SSR. (The solid lines in each subplot represent the partial dependence trends of the saccharide degradation rates with respect to the corresponding factors. The shaded areas indicate the 95% confidence bands, reflecting the uncertainty of the model predictions at a 95% confidence level)

Reviewer #2:

This paper presents results from near real-time measurements of anhydro-sugars made at 3 sites in China during autumn and winter. The data is used to examine the decay rate of the anhydro-sugars at each site. A generalized additive model was employed to examine the parameters influencing the decay rate.

Overall, this is a good paper. As anhydro-sugars are often used as biomass burning markers, understanding their decay in the atmosphere is important. But I do feel the authors don't provide enough details on the differences between the sites, how that could play a role in the ratios observed/fuels burned/burn practices, and what separates a day with a linear decay rate to one without. Also, often what is being plotted is not accurately described in the figure caption. I have tried to note and make suggestions about these along with number of other items. These are all outlined below in the specific comments which need to be addressed before this paper can be considered for publication.

Response: We appreciate the valuable feedback. In response to the comments, we have made detailed additions and corresponding revisions to the manuscript. Inappropriate expressions in the original manuscript have been revised, and time series data of anhydro-saccharides, biomass burning-derived potassium ions (K^+_{BB}), and temperature at the three sampling sites have been supplemented to investigate the regional differences among the three cities. We observed that the concentrations of anhydro-saccharides and K^+_{BB} exhibited synchronous increasing and decreasing trends in the three cities, namely Zibo, Changzhou and Hong Kong. Notably, the concentrations of anhydro-saccharides and K^+_{BB} in Zibo and Changzhou showed frequent peaks within a short period, which is highly consistent with the emission characteristics of intensive open burning of crop straw in these regions during autumn and winter. Furthermore, as a typical heavy industrial city, the biomass burning emissions in Zibo are additionally influenced by incomplete combustion processes such as industrial combustion and residential low-temperature heating in winter. This leads to a higher concentration of galactose than mannose (Haque et al., 2022; Yan et al., 2018). In contrast, the concentrations of anhydro-saccharides and K^+_{BB} in Hong Kong fluctuated steadily without frequent peaks, which aligns with the local biomass burning pattern dominated by residential cooking and small-scale commercial activities (e.g., the utilization of wood and kitchen waste) (Lee et al., 2013; Leung et al., 2024). The regional characteristics of these three cities provide vital background and data support for subsequent analyses on the daytime decay rates of anhydro-saccharides, contributing to a more in-depth understanding of their sources and variations under diverse environmental conditions, and thus laying a foundation for the formulation of corresponding pollution control strategies and optimization plans.

Moreover, we sincerely apologize for the omission of details regarding the certain days do not conform to the linear decay pattern in the original manuscript. The revised manuscript has been supplemented with explanations for days characterized by failed fitting. We have also added comparisons of the number of days with valid decay rates across the three cities, along with an analysis of potential factors underlying these differences. To mitigate the bias arising from days with unsuccessful fitting, this study exclusively retained days characterized by positive decay rates and a coefficient of determination ($R^2>0.5$) for the estimation of decay rates and subsequent generalized additive model (GAM) analysis in the original manuscript. This approach was necessary because the inclusion of such poorly fitted data points would artificially depress the average rate constant k, thereby potentially resulting in an underestimation of the authentic degradation rate. Consequently, valid data were obtained for 31 out of 67 days (46%) in Zibo, 21 out of 45 days (47%) in Changzhou, and 69 out of 106 days (65%) in Hong Kong. The mean decay rates for the three anhydro-saccharides across the three cities, derived from linear regression fitting, are presented in the supporting information of the original manuscript. We acknowledge that the original manuscript indeed lacked sufficient descriptions of the generalized additive model (GAM) process and other relevant methodological details. To address this issue, we have supplemented the manuscript with detailed information about the GAM modeling process and specifically discussed the results of the multicollinearity test. In accordance with your valuable suggestions, the revised manuscript has revised the manuscript thoroughly and comprehensively. Meanwhile, we have provided accurate and standardized descriptions for all figures and tables in the original manuscript, ensuring that the information presented in these visual materials clearly supports the conclusions of the study.

Specific Comments:

Line 64: I am not sure what the phrase universal of this phenomenon means. Should it be universal impact of this phenomenon?

Response: The inappropriate expression in this part of our manuscript has been revised in accordance with the suggestions.

Page 3, Line 65-66: “but the universal impact of this phenomenon, and their driving factors that influence this degradation process have not been thoroughly investigated

(Wang et al., 2025)”

Line 85: Suggest changing during cold season to during various cold seasons

Response: We have revised the manuscript in accordance with your suggestions.

Page 3, Line 85-87: “The bihourly resolution data of $PM_{2.5}$-bound levoglucosan, mannosan and galactosan were collected at Zibo, Changzhou and Hong Kong during various cold seasons using the TAG-GC/MS system.”

Lines 94-95: Suggest changing during autumn and winter season across three typical cities in the three regions to during multiple autumn and winter season deployments in three different typical cities in three regions

Response: Revised.

Page 4, Line 95-97: “Field observations using TAG-GC/MS were conducted during multiple autumn and winter season deployments in three different typical cities in three regions (Zibo, Shandong province, NCP; Changzhou, Jiangsu province, YRD; and Hong Kong, PRD region) over eastern China (Fig. S1).”

Line 103: Suggest removing the comma after February

Response: Revised.

Page 4, Line 104-105: “The observation period was from November 2022 to February 2023.”

Line 117: Suggest adding a the before Changzhou

Response: Revised.

Page 5, Line 117-118: “At the Changzhou site”

Line 119: Suggest adding an a before WXT520, and a before BAM1020, a the before beta-ray, and an and before NO_x

Response: Revised.

Page 5, Line 119-121: “by a WXT520 (VAISALA, FL); $PM_{2.5}$ by a BAM1020 (Met One, US) via the beta-ray method; O_3, and NO_x by a MODEL 49i, and MODEL450i (Thermo Fisher Scientific, US) respectively”

Line 120: Suggest adding an a before MODEL 49i, an and before MODEL 450i, and an a before RT-4

Response: Revised.

Page 5, Line 120-121: "O_3, and NO_x by a MODEL 49i, and MODEL450i (Thermo Fisher Scientific, US) respectively"

Line 121: Suggest adding an an before ADI2080

Response: Revised.

Page 5, Line 121-123: "OC/EC by a RT-4 (Sunset Laboratory, US), water-soluble ions (Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}) and NH_3 by an ADI2080 (Metrohm, CHN)."

Line 122: Suggest removing the The before Solar

Response: Revised.

Page 5, Line 123-124: "Solar surface radiation data (SSR) were obtained from the ERA5-Reanalysis (https://cds.climate.copernicus.eu/datasets)."

Line 126: Suggest adding an a before MODEL and an and before NO_x

Response: Revised.

Page 5, Line 127-128: "$PM_{2.5}$ by a MODEL 5014i (Thermo Fisher Scientific, US); O_3, and NO_x by a MODEL 49i, and MODEL 42i (Thermo Fisher Scientific, US) respectively"

Line 127: Suggest adding an a before MODEL 49i, an and before MODEL 42i, a respectively before OC/EC, and an a before MODEL ECOC-610

Response: Revised.

Page 5, Line 128-129: "O_3, and NO_x by a MODEL 49i, and MODEL 42i (Thermo Fisher Scientific, US) respectively; OC/EC by a MODEL ECOC-610 (Hangzhou Pengpu Technology Co., Ltd., China)"

Line 129: Suggest adding an a before MODEL S611

Response: Revised.

Page 5, Line 129-131: "water-soluble ions (Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}) and NH_3 by a MODEL S611 (Fortelice International Co., Ltd., Taiwan, China)."

Line 130: Suggest adding a the before Hong Kong

Response: Revised.

Page 5, Line 132: “At the Hong Kong site”

Line 131: Suggest adding an a before Model 5030i

Response: Revised.

Page 5, Line 132-133: “$PM_{2.5}$ was measured by a MODEL 5030i (Thermo Fisher Scientific, US)”

Line 132: Suggest adding an an before ADI2080

Response: Revised.

Page 5, Line 136- 137: “water-soluble ions (Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}), NH_3 and OC/EC by an ADI2080 (Metrohm, CHN) and RT-4 (Sunset Laboratory, US), respectively”

Line 134: Suggest adding an and before NO_x

Response: Revised.

Page 5, Line 139-140: “atmospheric pressure (P), rainfall (RF), and solar surface radiation (SSR) by the 10 m automatic weather station tower.”

Lines 134-135: The authors note in Hong Kong that the meteorological parameters, O_3, and NO_x were measured by AWS tower. Is that the name of the instrument or the location? It seems like that might be a location and the name of the instruments are missing.

Response: We appreciate the reviewer’s valuable comments. AWS is short for the automatic weather station, which is located on the Hong Kong University of Science and Technology campus. At this site, O_3 and NO_x were determined using a MODEL 49i analyzer and a MODEL 42i analyzer (Thermo Fisher Scientific, USA), respectively. We have supplemented the above instrument information in Lines 135-142 of the revised manuscript.

Page 5, Line 135-142: O_3, and NO_x by a MODEL 49i, and MODEL 42i (Thermo Fisher Scientific, US); meteorological parameters wind speed (WS), wind direction (WD), relative humidity (RH), temperature (T), atmospheric pressure (P), rainfall (RF), and solar surface radiation (SSR) by the 10 m automatic weather station tower. Standard calibrated sensors on the automatic weather station (AWS) tower were used for measurements: a temperature/humidity sensor (HMP155) for air temperature and relative humidity, an ultrasonic anemometer (CSAT3A) for wind speed and direction, a barometric pressure sensor (CS106) for atmospheric pressure, a pyranometer (LI200R) for shortwave solar radiation, and a tipping-bucket rain gauge (TE525MM) for precipitation at the tower base.

Line 135: Suggest adding an an before Xact

Response: Revised.

Page 5, Line 142-143: "The elemental species (K, Ca) by an Xact 625i (Cooper Environmental Services) via an X-ray method."

Line 136: Suggest adding an an before X-ray

Response: Revised.

Page 5, Line 142-143: "The elemental species (K, Ca) by an Xact 625i (Cooper Environmental Services) via an X-ray method."

Line 139: Suggest adding an A before Detailed and a the before TAG

Response: Revised.

Page 5, Line 146-147: "A detailed description and the schematic diagram of the TAG can be found in our previous studies"

Line 141: Suggest changing observation to observations and adding an a before deuterium-labeled

Response: Revised.

Page 5, Line 148-149: "During the observations, a deuterium-labeled internal standard solution was injected into each sample to monitor instrument condition and analyze the contamination levels of key species."

Line 155: The authors note here the species used in there ISOROPPIA runs to calculate pH and ALWC. But I don't recall measurements of NH_3 being mentioned in the site description and field observation section. Aren't measurements of HNO_3 also needed in the calculation?

Response: We appreciate the reviewer's valuable comments. The forward mode of the ISORROPIA-II model was adopted to calculate the aerosol liquid water content (ALWC). The input parameters required for this model primarily include water-soluble inorganic ions (SO_4^{2-}, NO_3^-, NH_4^+, K^+, Ca^{2+}, Na^+, Mg^{2+}, and Cl^-), NH_3, temperature (T), and relative humidity (RH). We have added this information in the site description and field observation section. NH_3 was measured by a MODEL S611 (Fortelice International Co., Ltd., Taiwan, China). Regarding HNO_3 measurements, due to the absence of corresponding analytical instruments at all three sampling sites, the observational data of this species are currently unavailable. Thus, data of HNO_3 were not incorporated into the calculation of aerosol liquid water content (ALWC) in the present study.

Page 5, Line 121-123: "OC/EC by a RT-4 (Sunset Laboratory, US), water-soluble ions (Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}) and NH_3 by an ADI2080 (Metrohm, CHN)."

Page 5, Line 129-132: "OC/EC by a MODEL ECOC-610 (Hangzhou Pengpu Technology Co., Ltd., China), water-soluble ions (Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}) and NH_3 by a MODEL S611 (Fortelice International Co., Ltd., Taiwan, China) and solar surface radiation (SSR) by CMP11 (Kipp & Zonen, Zuid-Holland, Netherlands)."

Page 5, Line 133-134: "water-soluble ions (Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}), NH_3 and OC/EC by an ADI2080 (Metrohm, CHN) and RT-4 (Sunset Laboratory, US), respectively;"

Line 179: The V after Kumar can be removed and a period should be added after et al as part of the citation

Response: Revised.

Page 7, Line 193-195: "The study of Kumar et al. (2018) suggests that the maximum and minimum differences in the mass ratio of (K^+_{Nss}/Ca^{2+}_{Nss}) are considered to represent emissions from biomass burning (Kumar et al., 2018; Pio et al., 2008; Pio et al., 2007)."

Line 188: The citation should be written as Wang et al. (2025)

Response: Revised.

Page 7, Line 201-202: "According to Wang et al. (2025)"

Lines 262-263: The phrase while the total potassium (total K) data is relatively complete can be removed from the sentence as it has already been previously stated

Response: Revised.

Page 10, Line 299-302: "It is important to note that, due to insufficient observational data for K^+ in Hong Kong, we selected total potassium for the calculation, and after excluding the effects of sea salt and dust, the final calculation yielded potassium produced by biomass combustion (K_{BB}).”

Line 314: Suggest removing the was after LST

Response: Revised.

Page 10, Line 359-360: “In Hong Kong, the galactosan concentration decreased from 1.08 ± 0.09 ng m^{-3} at 8:00 LST to 0.67 ± 0.06 ng m^{-3} by 16:00 LST.”

Lines 320-322: The authors mention that the ratio of levoglucosan to potassium can be an indicator of the aging degree of biomass burning. But levoglucosan and potassium don’t have to be correlated. If there is or isn’t a relationship it is often based on the type of fuel being burned and the type of burning. All the measurements were made in autumn and winter, but the sites have very different characteristics. So, couldn’t there be some regional influences on this? I think the authors allude to this in the previous section and Figure S3. While the data from all sites clumps together in Figure S3, it is also on a log scale, so it covers a large range of ratios. Although the sites are described in section 2.1, the authors don’t go into the regional differences other than mention of the impacts they see from the monsoon. It would be helpful to provide these additional details. Maybe it would also be helpful to the reader to present time series of levoglucosan, potassium, and temperature along with the diurnal profile as the diurnal pattern could be driven by “special” days.

Response: We agree with the reviewer that the emission ratio of levoglucosan to potassium can vary significantly depending on the fuel type and combustion conditions. However, for this study, we utilized a tracer ratio space (Fig. S2) of Lev/Man and Lev/K^+ to identify the primary sources across the three regions. Our analysis indicates that the BB emissions during the autumn and winter sampling periods were consistently dominated by crop residue burning in all three cities. This commonality in source profile explains the significant positive correlations observed between levoglucosan and the K^+_{BB} at all sites (Pearson’s R = 0.6–0.76). Furthermore, by using K^+_{BB}, calculated after subtracting contributions from sea salt and dust, we ensured that the reference tracer specifically represents the BB plume, thereby minimizing confounding regional factors from non-BB sources.

We appreciate the suggestion to provide more detail on the regional differences beyond the monsoon influence. While the source types were similar, the distinct environmental conditions at each site significantly influenced the degradation rates. Zibo is a heavy industrial city on the North China Plain characterized by high emission intensities and cold, dry winters, and the unique galactosan enrichment observed here suggests influences from industrial combustion or region-specific incomplete burning conditions (Haque et al., 2022; Yan et al., 2018). Changzhou, located in the Yangtze River Delta region, exhibited the highest average ALWC. This may promote faster levoglucosan decay via liquid-phase reactions that reduce particle viscosity and enhance OH uptake. The Hong Kong observation site, a suburban location, is subject to stringent local emission constraints but is strongly influenced by a maritime climate, with the highest humidity and temperature among the studied sites.

Owing to climatic discrepancies across the study regions, the contributions of driving factors to anhydro-saccharide degradation varied distinctly among the investigated cities. For instance, the high aerosol liquid water content (ALWC) in Changzhou accelerated the aqueous-phase oxidation of anhydro-saccharides; in contrast, the elevated ambient temperature in Hong Kong significantly enhanced the degradation rates of mannosan and galactosan, which exhibit higher temperature sensitivity.

In the statistical analysis of anhydro-saccharides decay rates and generalized additive model (GAM) analyses across the three cities, days with negative decay rates were excluded in the original manuscript, corresponding to periods with anomalous data induced by direct emissions or air mass transport processes. For example, only 31 out of 67 sampling days in Zibo met the predefined screening criteria for subsequent analyses. This data filtering procedure ensured that the diurnal variation characteristics presented ultimately reflected atmospheric degradation processes rather than stochastic fluctuations in emissions. A detailed discussion of the time series and regional discrepancies in anhydro-saccharides, biomass burning-derived potassium (K^+_{BB}), and temperature across the three study cities has been added in Lines 386-407 of the revised manuscript.

Page 14, 15, Line 386-407: The detailed time series of anhydro-saccharides and K^+_{BB} for the three cities is presented in Fig. S4. Overall, the concentrations of anhydro-saccharides and K^+_{BB} in these three locations exhibit a synchronous increase and decrease trend, verifying the similarity in their sources. From Fig. S4 (a) and (b), it is evident that the concentrations of anhydro-saccharides and K^+_{BB} in Zibo and Changzhou exhibit frequent spikes within a short time frame, aligning with the characteristics of concentrated emissions associated with open burning of straw during the autumn and winter seasons in these regions. Such combustion under high temperatures and strong oxygen supply conditions generates a higher proportion of levoglucosan (Chen et al., 2017; Cheng et al., 2013; Fabbri et al., 2009). Additionally, Zibo, as a typical heavy industrial city, experiences biomass combustion emissions that are influenced by the incomplete combustion processes of industrial burning and residential heating with coal at low temperatures, leading to higher concentrations of galactosan compared to mannosan (Haque et al., 2022; Yan et al., 2018). These factors collectively enhance the chemical characteristic differences between Zibo and other sites. In contrast, Fig. S4(c) shows that the time series from Hong Kong displays stable fluctuations in the concentrations of anhydro-saccharides and K^+_{BB}, without frequent sudden peaks. This aligns with the biomass burning pattern in this region, primarily relying on residential cooking and small-scale commercial activities (such as wood and kitchen waste)(Lee et al., 2013; Leung et al., 2024). On the contrary, the biomass burning sources in Hong Kong are characterized by low emission intensity and a sustained, dispersed release process. The regional characteristics of these three cities provide important background and data support for subsequent analyses of the daytime decay rates of anhydro-saccharides, aiding in the deeper understanding of their sources and variations under different environmental conditions, thereby laying the foundation for developing relevant pollution control strategies and optimization plans.

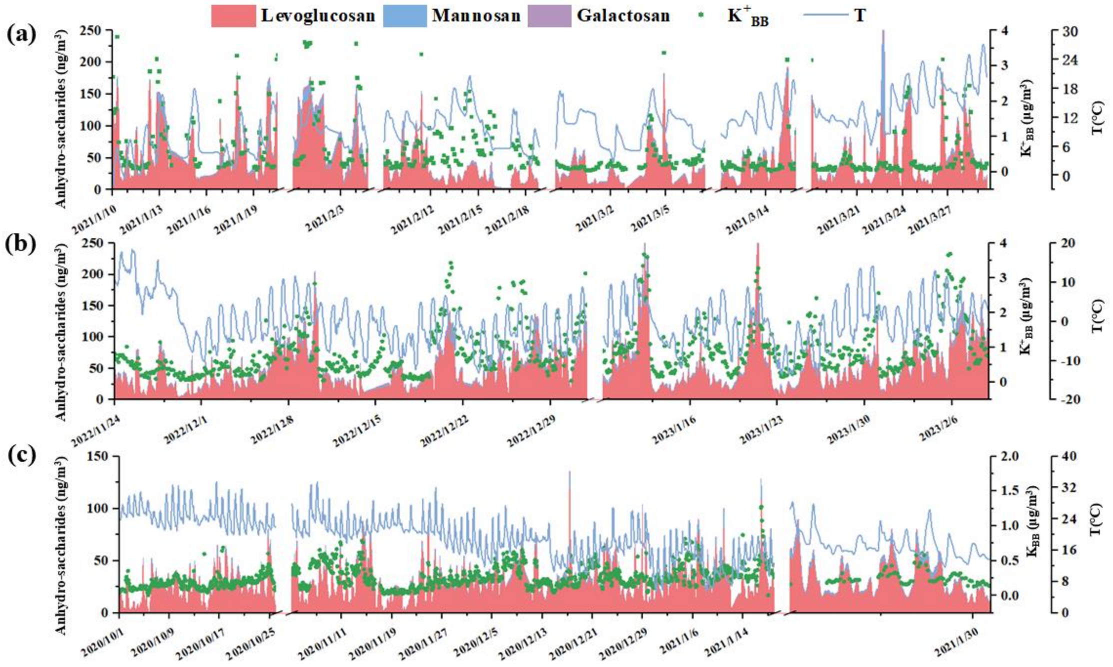

Fig. S4 Time series of concentrations of levoglucosan, mannosan, galactosan and K^+_{BB}, as well as temperature in (a) Zibo, (b) Changzhou and (c) Hong Kong

Lines 324-326: Suggest removing this sentence as it has already been previously stated

Response: Removed.

Line 327: Detailed information on what can be found in the previously published paper?

Response: Details regarding the rationale for employing total potassium to calculate the K_{BB} and the validation of the rationality of using K_{BB} as a tracer for biomass burning at the Hong Kong site are available in our previously published work (Wang et al., 2025).

Page 11, Line 299-308: It is important to note that, due to insufficient observational data for K^+ in Hong Kong, we selected total potassium for the calculation, and after excluding the effects of sea salt and dust, the final calculation yielded potassium produced by biomass combustion (K_{BB}). The calculated K_{BB} accounted for 82% of total K, confirming that biomass burning (BB) was the dominant source of K in $PM_{2.5}$ during the observation period. Furthermore, K_{BB} exhibited a good correlation with levoglucosan ($R_p = 0.63$), which further reinforces that they share the same primary source. Thus, it is reasonable to use K_{BB} as a tracer for BB at the Hong Kong site. However, daily heterogeneity in the sources of potassium cannot be ruled out, which may introduce systematic biases in the estimation of K_{BB} and the inference of k's.

Lines 328-329: I am not sure what the authors mean here by calculated formula and the range of (2)-(7) being noted.

Response: We agree that our original description was inappropriate, and we have revised the relevant sentence in Lines 377–380 of the revised manuscript accordingly.

Page 13, Line 377-380: In Zibo and Changzhou, the values of K^+_{BB} were calculated using Equations (2)~(7) , and the results showed that K^+_{BB} accounted for 93.4% and 91.4% of the total K^+, respectively, thus biomass burning as the major source of K^+ in $PM_{2.5}$ during the sampling campaign.

Line 331: Suggest changing galactosan and K^+ to galactosan with K^+

Response: Revised.

Page 13, Line 381-383: "In Zibo, the Pearson correlation coefficients between levoglucosan, mannosan, and galactosan with K^+_{BB} were 0.65, 0.52, and 0.52, respectively."

Line 333 - Suggest changing galactosan and K^+ to galactosan with K^+.

Response: Revised.

Page 13, Line 383-384: "In Changzhou, the Pearson correlation coefficients between levoglucosan, mannosan, and galactosan with K^+_{BB} were 0.76, 0.58, and 0.54, respectively”

Line 334: I am not sure what the authors mean here by calculation formulas

Response: The potassium ions derived from biomass burning (K^+_{BB}) were calculated by subtracting the contributions of sea salt and dust from total K^+ using Equations (2) ~ (7).

Figure 2

-In caption suggest adding the phrase (left column) after galactosan and (right column) after ratios

Response: Thanks, and revised accordingly.

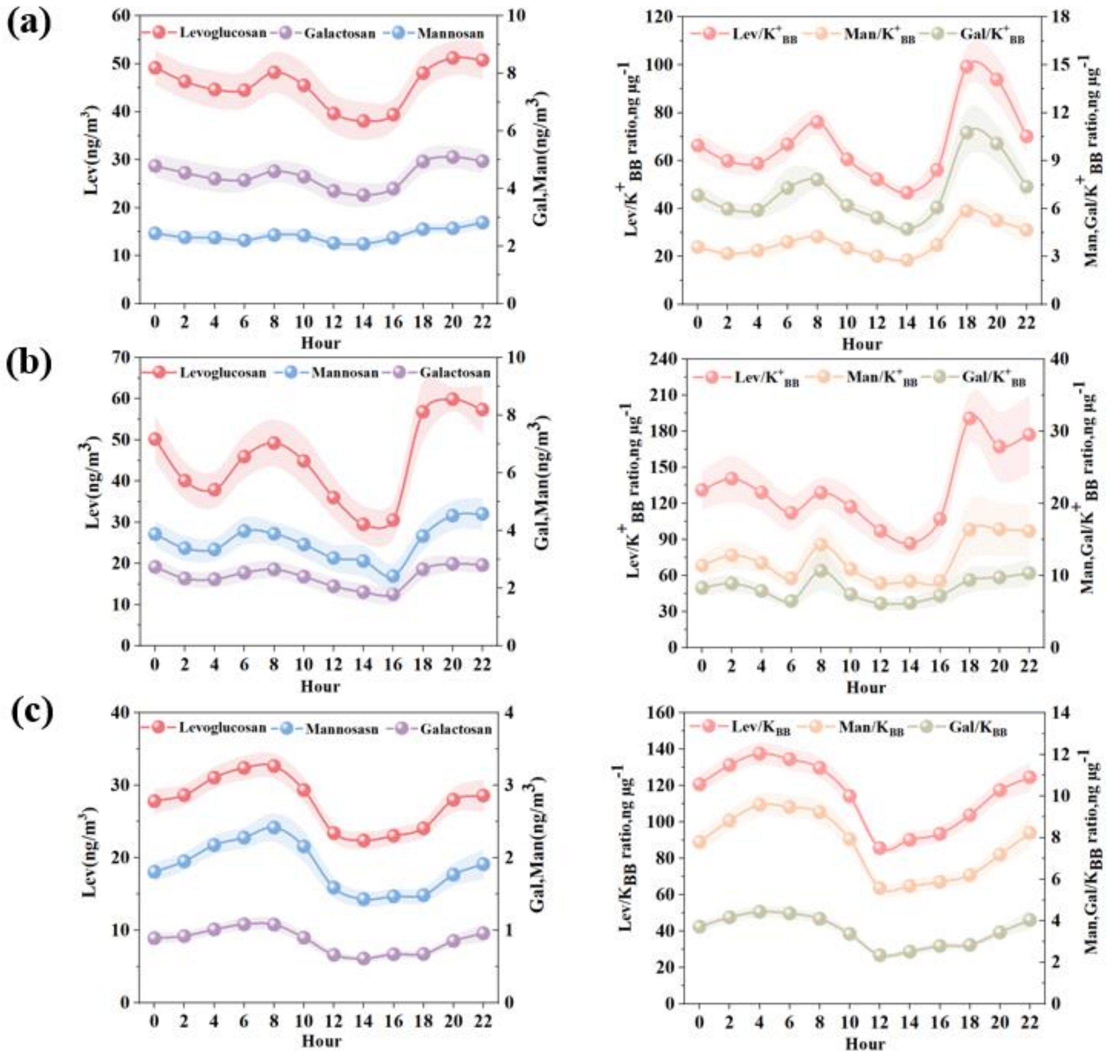

Fig. 2 Diurnal variations of levoglucosan, mannosan, and galactosan (left column); Lev/K^+_{BB}, Man/ K^+_{BB}, and Gal/ K^+_{BB} ratios (right column) at (a) Zibo, (b) Changzhou and (c) Hong Kong.

-It is surprising in plot a in the left column that galactosan is higher than mannosan. Is this correct? Do the authors know why this is for Zibo?

Response: We appreciate the reviewer's valuable comments. Regarding the observation that galactosan concentrations are higher than those of mannosan in Zibo City, we have discussed this in the original manuscript and added some new information, which is now located in lines 318-330 of the revised manuscript.

Page 14, Line 318-330: However, the average Man/Gal value in Zibo was 0.56 ± 0.19 (range: 0.23~2.24), significantly lower than those in Changzhou and Hong Kong, with a relatively higher concentration of galactosan, which may be related to differences in the type of combustion source or combustion conditions (Haque et al., 2022; Kuo et al., 2011; Yan et al., 2018). For example, the combustion of coal and certain industrial fuels may lead to higher galactosan content due to differences in the organic composition of these fuels compared to biomass fuels (Yan et al., 2018). Furthermore, incomplete combustion or low-temperature combustion may increase galactosan concentration (Haque et al., 2022), which could be a characteristic feature of combustion in Zibo. As a heavy industrial city, Zibo has more industrial combustion sources and incomplete combustion phenomena, leading to the relative enrichment of galactosan and exhibiting distinct chemical characteristics compared to common biomass combustion. In addition, residential coal combustion for heating was also an important emission source in suburban areas of North China in winter, which possibly corresponds to the low-temperature combustion scenario in Zibo.

Line 339: Suggest adding a the before three

Response: Revised.

Page 14, Line 412-413: "Using equation (8), we calculated the daytime decay rates of anhydro-saccharides in the three cities."

Lines 362-364: The authors note that not all days showed good linear fitting and this could be due to the direct emissions and transmission of biomass burning. Are there any other characteristics that could be different across the sites and various study periods? More warmer days observed? Burning practices the same at each location? Fuel type at each location? It would be helpful to provide more context for the reader.

Response: We appreciate the reviewer's valuable comments. More details have been supplemented and discussed regarding the regional differences and abnormal causes of linear fitting results. These contents have been added to Lines 437-480 of the revised manuscript.

Page 17, 18 Line 437-480: In such a short time frame (approximately 8 hours), the combustion conditions of burning plants and biomass sources are expected to remain relatively constant, making the influence of source emissions on the changes in normalized sugar concentration negligible. The obtained k values can be regarded as the average daytime decay rate for the day of observation. However, the observational data for certain days do not conform to the linear decay pattern. This phenomenon is primarily attributed to factors such as interference from fresh emissions and changes in air mass origins, which cannot be directly ascertained based solely on ground-based observations. The presence of invalid data during the fitting process does not contradict the research hypothesis; it merely reflects the complexity of real ambient conditions. During the observation period, each day was characterized by distinct biomass burning (BB) emission intensities (or the absence of BB emissions), accompanied by varying meteorological conditions and oxidant levels. Days with poor fitting performance only indicate that the combination of atmospheric conditions on those days violated the core assumptions underlying Equation (8). The method employed in this study is only applicable to specific scenarios that satisfy the fundamental assumptions, and the two-hourly measurement data enabled us to sample the target compounds under a wide range of diurnal ambient conditions. The fitting results for the three cities are as follows: Zibo sampled for a total of 67 days, with 31 days fitting the linear decay pattern (46%); Changzhou sampled 45 days, with 21 days fitting the linear decay pattern (47%); and Hong Kong sampled 106 days, with 69 days fitting the linear decay pattern (65%). The proportion of days in Hong Kong that could be linearly fitted is significantly higher than that in Zibo and Changzhou. This outcome may be closely related to the differences in climatic conditions and burning practices across regions.

The analysis in Fig. S4 indicates that both Zibo and Changzhou experience frequent outdoor straw burning activities in autumn and winter, where continuous fresh emissions release substantial amounts of anhydro-saccharides and other biomass combustion tracers into the atmosphere. The emission rates of these tracers within an 8-hour window far exceed the natural diffusion and chemical degradation rates of pollutants, disrupting the stable concentration changes required for linear decay, ultimately resulting in fitting failures. Furthermore, we compared the concentrations of atmospheric oxidants (O_x) on successful and unsuccessful fitting days. The results show that the mean concentrations of atmospheric oxidants on successful fitting days are higher across all three cities compared to unsuccessful fitting days. Specifically, the atmospheric oxidant concentration on successful fitting days in Zibo was 41.2 ± 8.5 ppb (range: 24.2~61.8 ppb), while it was 37.6 ± 7.8 ppb (range: 17.9~65.7 ppb) on unsuccessful fitting days. In Changzhou, the concentration for successful days was 46.1 ± 13.0 ppb (range: 21.6~81.8 ppb), compared to 44.3 ± 10.6 ppb (range: 14.6~60.8 ppb) on unsuccessful days. In Hong Kong, successful fitting days showed an atmospheric oxidant concentration of 31.9 ± 6.3 ppb (range: 19.7~53.4 ppb), while the concentration on unsuccessful days was 27.8 ± 6.8 ppb (range: 14.9~42.0 ppb). These results suggest that the relative deficiency of atmospheric oxidants may also be a significant factor preventing the concentration of anhydro-saccharides from exhibiting a clear linear decay pattern. To mitigate the bias arising from days with unsuccessful fitting, this study exclusively retained days characterized by positive decay rates and a coefficient of determination ($R^2>0.5$) for the estimation of decay rates and subsequent generalized additive model (GAM) analysis. The inclusion of such poorly fitted data points would artificially depress the average rate constant k, thereby potentially resulting in an underestimation of the authentic degradation rate.

Lines 365-367: The authors note how many days at each site could be fit with a linear decay pattern. But they don’t really mention anything else about the days without this pattern. What is different about the days that don’t have a linear decay?

Response: On these days, pollutant concentrations exhibited an increasing trend during the daytime rather than the expected linear decay, or the coefficient of determination (R^2) of the linear fit was less than 0.5. During the observation period, each day was characterized by distinct biomass burning (BB) emission intensities (or the absence of BB emissions), accompanied by varying meteorological conditions and oxidant levels. Days with poor fitting performance only indicate that the combination of atmospheric conditions on those days violated the core assumptions underlying Equation (8). The method employed in this study is only applicable to specific scenarios that satisfy the fundamental assumptions, and the two-hourly measurement data enabled us to sample the target compounds under a wide range of diurnal ambient conditions. To mitigate the bias arising from days with unsuccessful fitting, this study exclusively retained days characterized by positive decay rates and a coefficient of determination ($R^2>0.5$) for the estimation of decay rates and subsequent generalized additive model (GAM) analysis. The inclusion of such poorly fitted data points would artificially depress the average rate constant k, thereby potentially resulting in an underestimation of the authentic degradation rate.

Line 389: Suggest adding to the end of the sentence the phrase which we explore in the next section.

Response: We have revised the manuscript in accordance with your suggestions. The analysis of differences in linear fitting results has been elaborated in our response to your previous comment.

Page 18, Line 500-504: However, this trend was only observed in Hong Kong and Changzhou. Hence, besides bond dissociation enthalpy (BDE), there should be other influencing factors affecting the decay rates. Section 3.4 provides a detailed exploration of the environmental factors that influence the decay rates of anhydro-saccharides, with a particular focus on Zibo.

Line 391: Suggest change sampling points to sampling sites

Response: Revised.

Page 18, Line 506: "The three sampling sites represent cities with distinct meteorological conditions."

Line 429: I believe the reference is missing

Response: Thanks. We have added the corresponding references in Line 488-491 of the revised manuscript.

Page 19, Line 541-544: "When the relationship between the response variable and explanatory variables is unclear, the generalized additive model (GAM) can be used to fit the explanatory and response variables by plotting smooth functions, further assessing their linear or nonlinear relationship (Shrestha, 2020; Stone, 1985; Xiao et al., 2018)."

Figure 5

-In caption suggest adding a the before three

Response: Revised.

-In caption the parameters O_3 through T are denoted by letters, but they are actually all shown together on plot b

Response: We have made the corresponding corrections accordingly.

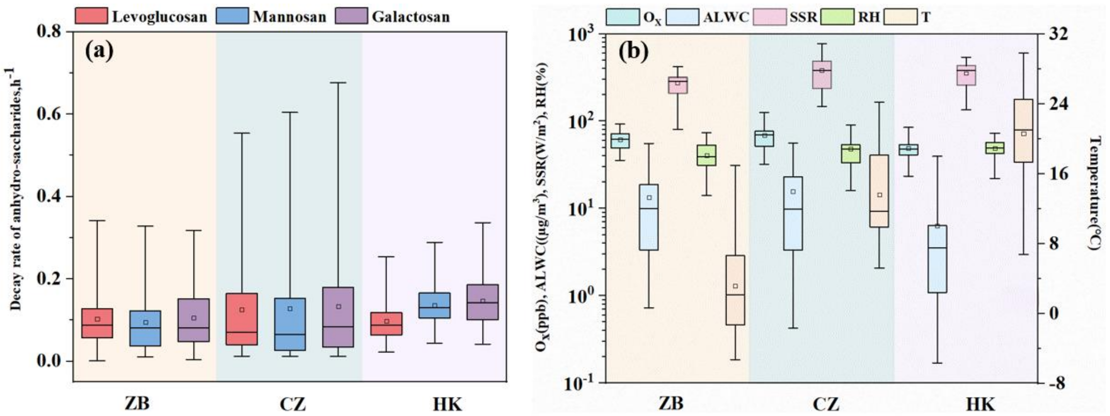

Fig. 3 Comparison of environmental factors and decay rates across the three cities: (a) decay rates of levoglucosan, mannosan and galactosan, (b) O$_x$, ALWC, SSR, RH and T.

Line 459: Suggest changing Fig. 6(a) show to Fig. 6(a) shows

Response: Revised.

Page 21, Line 609-611: "Fig. 6(a) shows that both are positively correlated with the daytime decay rate of levoglucosan, especially RH>60%, which nearly increases linearly."

Line 476: mannosan and galactosan are misspelled

Response: Thanks. We have revised accordingly.

Page 21, Line 626-628: "Hong Kong has the highest average temperature among the three cities, which may explain why the daytime degradation rates of mannosan and galactosan are higher in Hong Kong than in the other two cities."

Figure 6

-In caption the labels noted do not match what are in the plots, suggest changing text from degradation rate of to (a) levoglucosan, (b) mannosan, and (c) galactosan analyzed as a function of ALWC, T, RH, O3, and SSR using the GAM model.

Response: We appreciate the reviewer's valuable comments. We have revised the manuscript in accordance with your suggestions.

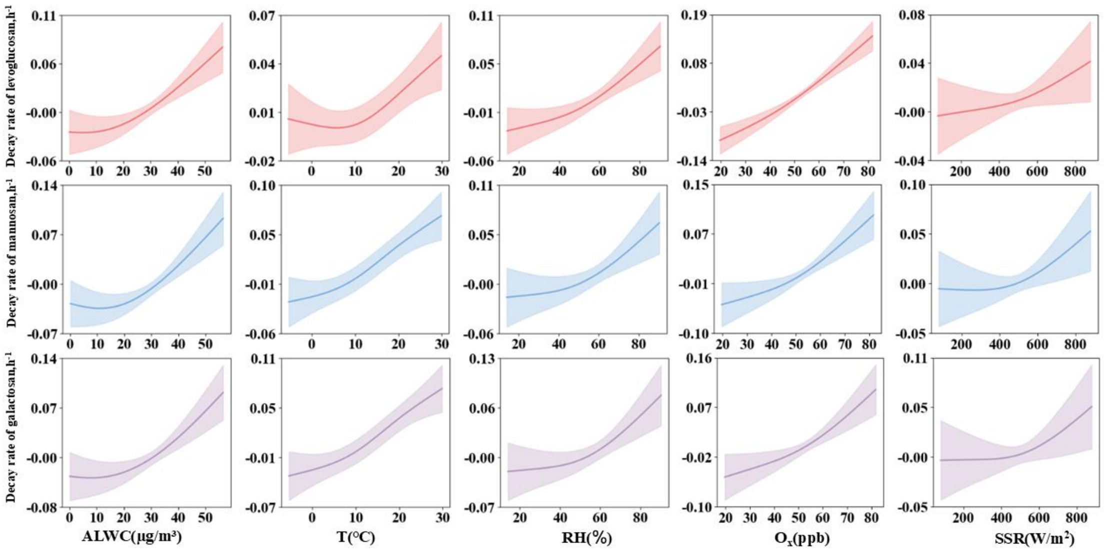

Fig. 4 Influences of various factors on the daytime degradation rates of different saccharides analyzed using the GAM model: (a) levoglucosan, (b) mannosan, and (c) galactosan, as a function of ALWC, T, RH, Ox, and SSR. (The solid lines in each subplot represent the partial dependence trends of the saccharide degradation rates with respect to the corresponding factors. The shaded areas indicate the 95% confidence bands, reflecting the uncertainty of the model predictions at a 95% confidence level)

Lines 481-488 and Figure 7: In this section the authors note and show that ALWC, RH, and O_x show a positive correlation with levoglucosan degradation rate from the factors tested. But aren't T, SSR, and O_x naturally linked to begin with? Ozone formation is related to temperature and sunlight. In addition, RH and ALWC are not the exact same thing, but are quite similar. I guess I am not totally following how there can't already be a relationship among these factors whether or not levoglucosan decays?

Response: We appreciate the reviewer's valuable comments. To address the potential associations among variables, we conducted a multicollinearity check on all variables involved in the modeling prior to performing the generalized additive model (GAM) analysis. Specifically, we employed the Variance Inflation Factor (VIF) method to examine factors such as temperature (T), solar surface radiation (SSR), oxidants (O_x), relative humidity (RH), and aerosol liquid water content (ALWC). the results showed that all variables had low VIF values, suggesting the absence of significant linear multicollinearity interference among them. The relevant testing methods and results have been included in the revised manuscript on lines 506–514. It is important to note that the primary objective of this study is not to elucidate the intrinsic associations between meteorological and pollution factors but rather to focus on quantifying the independent effects of each factor on the degradation rate of levoglucosan.

Page 19, Line 572-579: To avoid the potential impact of multicollinearity among variables on the stability of model fitting and the accuracy of parameter estimates, this study performed a multicollinearity assessment on the explanatory variables using the variance inflation factor (VIF) prior to conducting the GAM analysis. A high VIF value points to strong multicollinearity between a given explanatory variable and the remaining explanatory variables; specifically, a VIF value exceeding 4 denotes the existence of significant multicollinearity in regression analysis. (Shrestha, 2020; Xiao et al., 2018). The results of the multicollinearity test are presented in Table S6, where the VIF for all explanatory variables is less than 4, indicating that they successfully passed the multicollinearity assessment.

Line 488: Should promoting be prominent?

Response: Thanks, revised.

Page 22, Line 641-643: In contrast, when the levels of these three factors are relatively low, the degradation rate generally remains in a lower range, further confirming that these factors play a prominent role in the degradation process of levoglucosan.

Line 524: Suggest changing substance to species

Response: Revised.

Page 21, Line 691-693: “We selected K^+_{BB} as a reference species and calculated the daytime degradation rates of the three anhydro-saccharides in the three cities using the relative rate constant method.”

Lines 597- 598: I believe the format of this reference is not the same as the others as it lists the authors first initial then last name

Response: Revised.

Page 29, Line 795-797: Hoffman, D., Tilgner,A., Iinuma, Y. and Herrmann, H.: Atmospheric stability of levoglucosan A detailed laboratory and modeling study, Environ. Sci. Technol., 44, 694-699, http://dx.doi.org/10.1021/es902476f, 2010.

Supplemental Information

Line 51: Suggest changing use the stock to used the stock and changing standard to standards. A period is also missing from the end of the sentence.

Response: Revised.

Page 3, Line 51-52: “We used the stock solution for dilution to make the standards, which is all purchased from Anple.”

Line 53: There should be commas before and after respectively. The chemical abbreviations used are not defined. Suggest adding a the before final working.

Response: Revised.

Page 3, Line 57-59: “The working standard solution was freshly prepared by diluting stock solutions several times using 10 mL flasks, respectively with acetonitrile (ACN) and dichloromethane (DCM) solvent, producing final working solution concentrations are shown showed in Table S2.”

Line 54: Suggest changing are showed to that are shown.

Response: Revised.

Page, Line 57-59: “The working standard solution was freshly prepared by diluting stock solutions several times using 10 mL flasks, respectively with acetonitrile (ACN) and dichloromethane (DCM) solvent, producing final working solution concentrations that are showed in Table S2.”

Line 56: Suggest changing with range to ranging.

Response: Revised.

Page, Line 62-64: “Different volumes ranging from 5 to 25 μL of working standard solution and a fixed volume (5μL) of ISs were injected into the collection and thermal desorption cell (CTD) to build calibration curves using the same analysis procedure as that for the samples.”

Lines 56-57: Suggest removing the phrase (ranging from 5 to 25 uL)

Response: Revised.

Page, Line 62-64: “Different volumes ranging from 5 to 25 μL of working standard solution and a fixed volume (5μL) of ISs were injected into the collection and thermal desorption cell (CTD) to build calibration curves using the same analysis procedure as that for the samples.”

Table S2

-In the caption should the word identified be added after compounds?

Response: Yes, revised.

Page 6, Line 104-105: "Table S2 A list of corresponding internal standard (IS) and other details for external standards (ESs) and compounds identified in samples"

-For the solvent and quantification IS are they the same for all 3 anhydro-sugars?

Response: For the quantitative analysis of the three anhydro-saccharides (levoglucosan, mannosan, and galactosan), this study consistently employed deuterated levoglucosan (Levoglucosan-d_7) as the internal standard. Given that these three target analytes share the same molecular formula and possess highly similar molecular structures, Levoglucosan-d_7 can effectively correct for recovery rates during extraction, separation, and detection processes for all three compounds. Furthermore, this internal standard shows no background interference in actual atmospheric samples, ensuring the accuracy and reliability of the quantitative results. We have added the corresponding descriptions in Lines 150-156 of the main text in the revised manuscript.

Page 6, Line 150-156 (manuscript): This study consistently utilizes deuterated levoglucosan (Levoglucosan-d7) as an internal standard to quantify three anhydro-saccharides. Given that these three target analytes share the same molecular formula and exhibit highly similar molecular structures, Levoglucosan-d_7 can effectively correct for recovery rates during extraction, separation, and detection processes for all three compounds. Furthermore, this internal standard shows no background interference in actual atmospheric samples, ensuring the accuracy and reliability of the quantitative results.

Tables S4

-In caption suggest adding the phrase average +/- standard deviation of before hourly concentrations

Response: Revised.

Page 6, Line 112-114: "Table S4 Statistical summary of meteorological conditions, average ± standard deviation of hourly concentrations of conventional atmospheric pollutants and TAG-determined anhydro-saccharides during the field campaign"

Table S6

-In the caption the authors call these the smoothing function parameters, but I don't believe they have been called that elsewhere in the text. Maybe it would be helpful to note what equation they refer to?

Response: We appreciate the reviewer's valuable comments. We have added the corresponding model equations and parameter interpretations for the GAM analysis in

Lines 502–512 of the revised manuscript.

Page 20, Line 549, Line 560-568 (manuscript): The corresponding GAM is expressed as Equations (10)~(12).

$$g(\mathrm{Lev}) = \mathrm{s(ALWC)} + \mathrm{s(T)} + \mathrm{s(O_x)} + \mathrm{s(RH)} + \mathrm{s(SSR)} + \beta \quad (10)$$

$$g(Man) = \mathrm{s(ALWC)} + \mathrm{s(T)} + \mathrm{s(O_x)} + \mathrm{s(RH)} + \mathrm{s(SSR)} + \beta \quad (11)$$

$$g(Gal) = \mathrm{s(ALWC)} + \mathrm{s(T)} + \mathrm{s(O_x)} + \mathrm{s(RH)} + \mathrm{s(SSR)} + \beta \quad (12)$$

In the equations, β represents the model intercept, while s(i) denotes the smooth function corresponding to each influencing factor. Table S7 presents the relevant parameters of the GAM smooth functions, including effective degrees of freedom (Edf), reference degrees of freedom (Ref.df), F-statistic (F), and p-value (p). These parameters are used to reflect the strength and significance of the nonlinear associations between each influencing factor and the degradation rate of anhydro-saccharides.

Table S7 Results of GAM analysis

Smooth variables	Edf	Ref.df	F	*p*
ALWC	1.0	9.0	5.2	0.02
T	2.5	9.0	8.7	0.001
O_x	1.8	9.0	6.5	0.01
RH	3.2	9.0	3.1	0.08
SSR	4.0	9.0	2.3	0.12
Deviance explained (%) = 65.8% R^2=0.66				

-Should it be SSR or SSRD? I believe throughout the text it was SSR.

Response: Thanks, it should be SSR.

Figure S3

-In caption the way it is written does not match what is actually plotted. Suggest changing correlation between K^+_{BB} and decay rates of levoglucosan, mannosan, and galactosan to correlation of levoglucosan, mannosan, and galactosan as a function of K^+_{BB}.

Response: Revised.

Page 10, Line 140-141: Fig. S3 Scatter plots showing the correlation of levoglucosan, mannosan, and galactosan as a function of K^+_{BB} in (a) Zibo and (b) Changzhou

Figure S4

-I believe the y-axes labels are not correct. It looks like the decay rate of levoglucosan is missing and the decay rate of galactosan is used twice.

Response: We appreciate the reviewer's valuable comments. This figure comprises nine subplots that collectively illustrate the pairwise correlations of the decay rates of three types of anhydro-saccharides across the three studied cities: Zibo, Changzhou, and Hong Kong. Specifically, Fig. S5 (a) pertains to Zibo City, with the subsequent three subplots depicting the correlations among the following pairs: decay rate of mannosan vs. decay rate of levoglucosan, decay rate of galactosan vs. decay rate of levoglucosan, and decay rate of galactosan vs. decay rate of mannosan. Fig. S5 (b) and (c) correspond to Changzhou and Hong Kong, respectively, with the variable relationships in these subplots being entirely consistent with those in (a). Since a consistent set of axis scales is required for correlation analyses of similar metrics across different cities, the repetition of y-axis labels is a reasonable arrangement. Additionally, the decay rate data for levoglucosan have been comprehensively presented in the first two subplots for each city, and there are no omissions in the data.

Figure S5

-In caption the way part of it is written does not match what is actually plotted. Suggest changing predicted values vs. residuals to residuals vs. predicted values and predicted values vs. observed values to observed values vs. predicted values. Also suggest changing for GAM to for the GAM model

Response: Revised.

Page 11, Line 166-168: Fig. S6 Results of residual tests for GAM on the diurnal decay rate of levoglucosan: (a) residual Q-Q plot; (b) scatter plot of residuals vs. predicted values; (c) histogram of residuals; (d) scatter plot of observed values vs. predicted values

Reviewer #3:

This work investigated the decay rates and their driving factors of anhydro-saccharides (levoglucosan, mannosan, and galactosan) at daytime at three different major city clusters in eastern China, with field measurements by TAG-GC/MS, rate calculation using the relative rate constant method, and factor contributions from the generalized additive model. The results are interesting and robust, highlighting the strong daytime decay and the dominant roles of aerosol liquid water, oxidants, temperature, and humidity. There are some minor comments which require to be addressed.

Response: We appreciate the kind comments and constructive feedback. We will carefully addressed all the points you have raised to further enhance the manuscript's quality and rigor.

Line 47, nitro phenolic compounds, in particular nitro catechols, are also tracers for biomass burning, and thus can be included here.

Response: Thanks, we have made the modifications accordingly.

Page 2, Line 47-50: BB releases various organic compounds, such as anhydro-saccharides, polycyclic aromatic hydrocarbons, nitro phenolic and n-alkanes, with levoglucosan generally being the most abundant anhydro-saccharides (Chen et al., 2017; Fang et al., 2024; Yan et al., 2019; Zhang et al., 2022).

Line 94, the same or three different TAG-GC/MS instruments were employed in three sampling sites?

Response: In the experiments conducted in Zibo and Changzhou, we used the same TAG-GC/MS instruments, whereas a separate TAG-GC/MS instrument was employed for the Hong Kong study. Notably, the two instruments were identical in terms of configuration, analytical principle, and operational workflow.

Line 141, deuterium-labeled internal standards of the three targeted compounds?

Response: Regarding the internal standards for the three types of anhydro-saccharides, we provided an explanation in the supporting information of the original manuscript. To clarify further for the readers, we have added supplemental information in lines 148-151 of the revised manuscript.

Page 6, Line 148-151: During the observations, a deuterium-labeled internal standard solution was injected into each sample to monitor instrument condition and analyze the contamination levels of key species. The detailed description is provided in Text S1. This study consistently utilizes deuterated levoglucosan (Levoglucosan-d_7) as an internal standard to quantify three anhydro-saccharides.

Line 217, what explanatory variables were selected finally?

Response: In the section introducing GAM, our intention was to present this method clearly. We have described the response and explanatory variables for the GAM analysis in this study in lines 544-548 of the revised manuscript.

Page 20, Line 544-548: In this study, we incorporated the calculated effective decay days into the GAM model. The daytime degradation rate of anhydro-saccharides calculated for the three cities was used as the response variable in the GAM model, and the various influencing factors (O_x, ALWC, SSR, RH and T) were used as the corresponding explanatory variables.

Line 282-284, in addition to industrial coal combustion, residential coal combustion for heating was also important emission source in suburban areas in North China in winter, which possibly corresponds to the low-temperature combustion at Zibo.

Response: We have made corrections accordingly.

Page 11, Line 328-330: In addition, residential coal combustion for heating was also an important emission source in suburban areas of North China in winter, which is corresponding to the low-temperature combustion scenario in Zibo.

Line 322-324, the contributions of environmental factors to daytime decay of anhydro-saccharides also happened at nightime in theory. Why only significant declines of the ratio of levoglucosan/K^+_{BB} were observed at daytime?

Response: We appreciate the reviewer's valuable comments. Theoretically, anhydro-saccharides may indeed undergo degradation at night via reactions with ozone or nitrate radicals ($NO_3\cdot$). However, the significant decrease in the ratio observed in this study was primarily concentrated during the daytime (8:00-16:00, LST), which can be attributed to the following two key reasons:

Differences in oxidant intensity: previous laboratory studies have demonstrated that the reaction of anhydro-saccharides with ·OH is their dominant degradation pathway (Hennigan et al., 2010). The generation of ·OH is highly dependent on solar surface radiation (SSR) during the daytime. Thus, the elevated oxidant concentrations and sufficient solar radiation in the daytime collectively accelerate the oxidative degradation of anhydro-saccharides.

Emission-driven dynamic equilibrium: As shown in Fig. 2, the absolute concentrations of anhydro-saccharides exhibited an increasing trend during nighttime, which reflects intense biomass burning emissions and unfavorable planetary boundary layer (PBL) meteorological conditions at night. A large number of fresh plumes emitted from these processes tend to mask the relatively slow chemical loss of anhydro-saccharides during nighttime periods, resulting in a statistically significant decrease in the anhydro-saccharide / K^+_{BB} ratio being observed exclusively in the daytime.

Line 399-401, what are the potential mechanisms for the complex relationship between decay rate and temperature?

Response: An increase in temperature generally accelerates molecular thermal motion, increases the collision frequency between reactive radicals (e.g., ·OH, SO_4^-) and anhydro-saccharides molecules, and thereby facilitates the occurrence of oxidative degradation reactions (Bai et al., 2013; Lai et al., 2014). Temperature variations are typically positively correlated with solar surface radiation intensity. During the daytime, temperature increases is usually accompanied by high solar surface radiation intensity; their synergistic effects can significantly promote atmospheric photochemical reactions and the generation of reactive radicals, thus accelerating the degradation of anhydro-saccharides (Bai et al., 2013; Wennberg, 2006). We have added the corresponding discussion in Lines 598-605 of the revised manuscript.

Page 24, Line 598-605: An increase in temperature generally accelerates molecular thermal motion, increases the collision frequency between reactive radicals (e.g., ·OH radical and SO_4^- radical) with anhydro-saccharides molecules, and thereby facilitates the occurrence of oxidative degradation reactions (Bai et al., 2013; Lai et al., 2014). Temperature variations are typically positively correlated with solar surface radiation intensity. During the daytime, temperature increases is usually accompanied by high solar surface radiation intensity; their synergistic effects can significantly promote atmospheric photochemical reactions and the generation of reactive radicals, thus accelerating the degradation of anhydro-saccharides (Bai et al., 2013; Wennberg, 2006).

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