

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 anhydro-saccharides (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 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 apologize for not providing a detailed explanation regarding the certain days 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 $0.070 \pm 0.008 \text{ h}^{-1}$ to $0.074 \pm 0.01 \text{ h}^{-1}$. 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 $\lambda = 46.42$. 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.

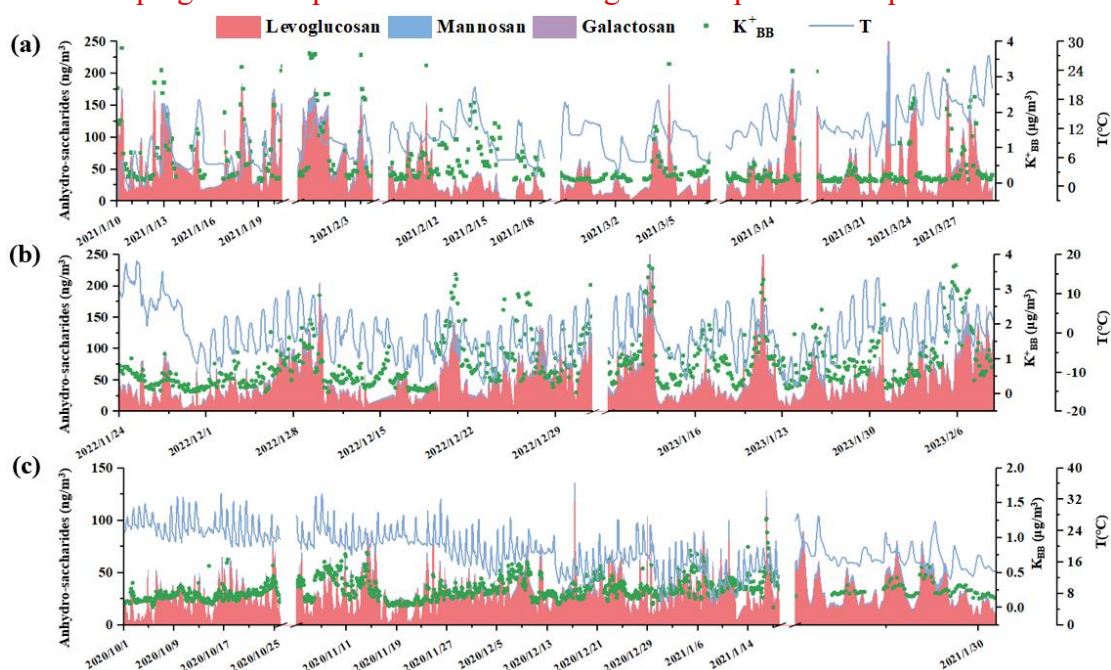


Fig. S4 Time series of concentrations of levoglucosan, mannosan, galactosan and K^{+}_{BB} , as well as temperature in (a) Zibo, (b) Changzhou and (c) Hong Kong

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 $0.19 \mu\text{g m}^{-3}$, which was substantially higher than the sea salt-derived potassium ion (K^+) concentration ($0.007 \pm 0.006 \mu\text{g m}^{-3}$). 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 $0.070 \pm 0.008 \text{ h}^{-1}$ to $0.074 \pm 0.01 \text{ h}^{-1}$. 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 ($C_i/C_{K_{BB}^+}$), as shown in Fig. 1. Our results reveal that $C_i/C_{K_{BB}^+}$ 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., $0.13 \pm 0.05 \text{ h}^{-1}$ 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 ($\cdot\text{OH}$) 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 ($\cdot\text{OH}$) with each sugar molecule. In the same city, all three sugars undergo oxidation by $\cdot\text{OH}$ 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 $\cdot\text{OH}$ 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.

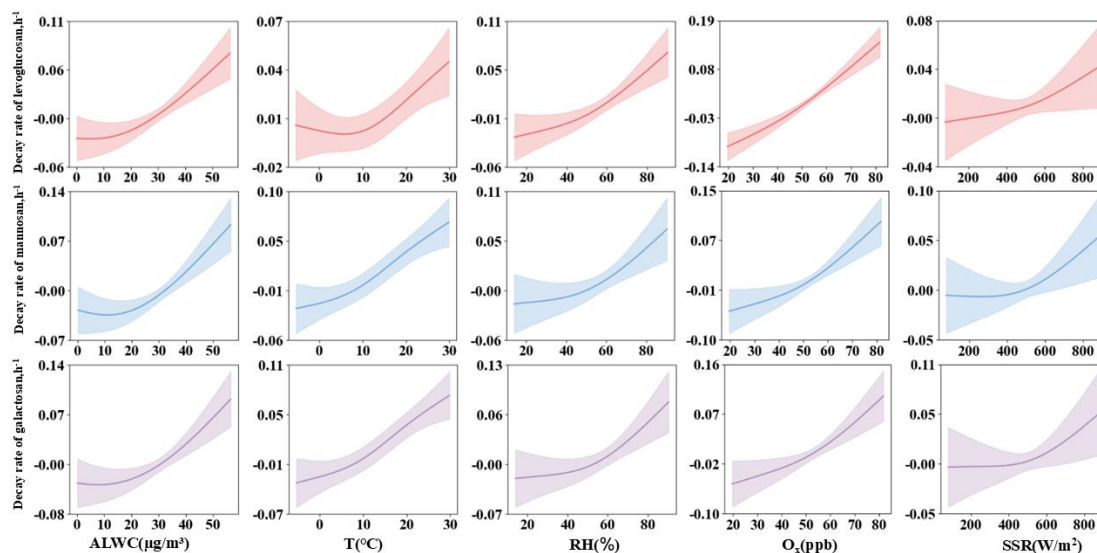


Fig. 1 Influences of various factors on the daytime degradation rates of different saccharides analyzed using the GAM model: (a) levoglucosan, (b) mannosan, and (c) galactosan, as a function of ALWC, T, RH, O_x , and SSR. (The solid lines in each subplot represent the partial dependence trends of the 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)

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