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 #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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