Response to reviewer comments:

We thank the reviewer and editor for re-assessing our manuscript and giving us another opportunity to respond to the reviewer's concerns. We have considered these comments seriously and as requested, added an additional quantitative explanation to further explain, clarify, and support our arguments. Below the reviewer's comments are highlighted in blue, our responses are in standard black text, and *additions to the manuscript are in italic black text*.

Comment #1:
I appreciate the authors' detailed responses to the initial set of comments. The manuscript presents valuable observations of a complex smoke event. However, upon reviewing the authors' responses, several critical concerns regarding the physical interpretation and methodological rigor remain unresolved. The core issue lies in the treatment of aerosol absorption and mixing state. The manuscript consistently downplays the role of absorption and relies on a homogeneous sphere model, while the reported data (3-5% BC mass, AAE ~ 2) strongly suggest a more complex, absorbing aerosol system. This leads to logical circularity in the modeling and a potentially incorrect mechanistic explanation for the observed spectral signatures. Major revisions are required to address these fundamental points before the manuscript can be considered for publication.
Major Comments:
• The authors justify their use of a homogeneous sphere Mie model by stating that the high Single Scattering Albedo (SSA ~0.95) means extinction is "primarily driven by scattering" and thus "insensitive" to absorption. This reasoning is flawed and overlooks key aspects of the data and established aerosol science. A 3-5% BC mass fraction in an aged biomass burning plume is not negligible. This is especially so, since these values are reported a thousand or more kilometers downwind from where the fires occurred, and therefore the initially emitted particles would be even more absorbing, since they had not yet aged. For internally mixed aerosols, this amount of BC, when coated by organics/sulfates, can experience significant absorption enhancement (the "lensing effect"). This very process is a leading explanation for the non-monotonic SSA spectra was addressed by Tiwari et al. (2023) and Liu et al. (2024a) through variable constrained sizes of core and shell and wide range of probabilistic DRF solutions. Smoke plume specific studies have also highlighted ambient smoke plumes exhibiting absorption enhancement of BC aerosol, with coating playing a crucial role (Lee et al., 2022). The authors must quantitatively address why this established mechanism is not applicable here.

Response #1:
We thank the reviewer for the comment and appreciate these fundamental concerns about our treatment of aerosol absorption and mixing state, and acknowledge our confusing presentation of these aspects in our earlier responses and versions. We would like to stress that we are not trying to neglect or argue that absorption effects due to BrC and particle mixing are not present and important in this plume, simply that in this case, they are not responsible for observed curvature in the spectral extinction and AOD profiles. This conclusion is actually independent of any model choice one might make to calculate aerosol absorption in this smoke plume. To more clearly demonstrate this point, we have added an additional quantitative analysis of the spectral optical properties as requested. In particular, we have added a new Figure 5 to the revised manuscript showing the direct measurements of the spectral optical properties of the smoke plume particles made from JFJ. We

think that these direct, in situ measurements are the best way to illustrate this point because they contain no underlying assumptions about the underlying aerosol properties. They simply represent the complex, absorbing aerosol system as it was measured on JFJ, including all possible absorption effects due to BC mixing state and BrC presence. As expected, the curvature in the spectral extinction profile is consistent with that observed in the AOD profiles. It is also clear that this feature is driven by the same curved shape observed in the spectral scattering profile. The purpose of the Mie calculations that follow this figure are simply to explore the factors that produces this unique, curved scattering profile – i.e., the particle size effect. These Mie calculations do not form the basis for the conclusion that the curved extinction profile is due to scattering, not absorption.

To explain and discuss these points we have added the following to the updated manuscript in Section 3.1.3:

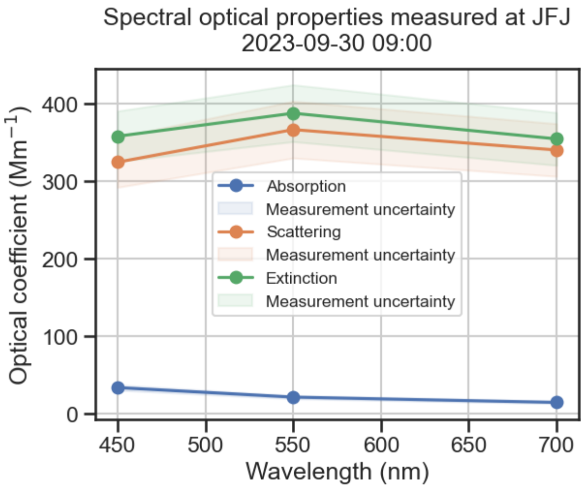

Figure 5: Spectral absorption, scattering and extinction coefficient measured during the peak of the smoke plumes passage over Jungfraujoch at 09:00 UTC on 30 September, 2023. Errors of ±10% in the independently measured scattering and absorption coefficients are propagated to produce the uncertainty estimates for extinction.

"To further investigate the observed spectral dependence of AOD in for this wildfire plume, we plot the spectral dependencies of absorption, scattering and extinction that were measured in situ during the peak of the smoke plume's passage over JFJ. The absorption coefficients have been shifted to the three wavelengths where the scattering coefficients were measured (450, 550, and 700 nm) using the measured AAE values, and the extinction coefficients at these same wavelengths calculated as the sums of scattering plus absorption coefficients. Measurement errors of 10% are considered for the independently measured scattering and absorption coefficients, and these are propagated to produce the uncertainty estimates for the extinction coefficients. As expected, the in-situ extinction profile is curved with positive gradient below 550 nm wavelength, consistent with the columnar AOD profiles measured for this plume. Figure 5 shows that this curvature is driven by the same curved feature present in the measured scattering profile. In contrast, the measured absorption profile has a negative gradient across the entire spectral range (as also demonstrated by the AAE values substantially greater than unity plotted in Fig. 3). Given the absolute values of the measured scattering and absorption coefficients (which are also reflected by the high SSA values reported in Fig. 3), one can calculate that AAE would need to increase to a value of ~4, or total absorbing

aerosol concentrations by a factor of ~4, for the absorption profile to have large enough magnitude to affect the shape of the extinction profile (i.e., to remove its curvature). Such increases are well beyond the scattering and absorption coefficient measurement uncertainties. Therefore, the curved spectral AOD and extinction profiles measured in this plume are due to the similarly curved spectral scattering profiles."

Regarding the nonmonotonic spectral SSA profiles, there we agree with the reviewer's point that absorption effects play an important role. In particular, it is clear that the higher relative absorption values at lower wavelengths (as indicated by the high AAE values) combined with the lower relative scattering values (the particle size effect) to produce the sharp decreases in SSA at low wavelengths. This result is already highlighted in the abstract, for example in Line 26-27 ("*The SSA concave spectral curvature denotes the mix of black carbon and non-absorbing particulate matter and influence of particle size…*"). Exploring and disentangling these effects in further detail is hampered by the limitations of AERONET-derived SSA values, which are inverted products that represent effective values over atmospheric columns. Rather, we have modified our statements at several points throughout the main text to emphasize the importance of absorption to the spectral SSA profiles as presented below:

The modified statements in the Section 3.2.2 as "*It is is to be noted that the AERONET-inverted SSA values represent effective values averaged over atmospheric columns, and care should therefore be taken when comparing these to the direct, in situ measurements, as well as when thinking about the fundamental factors that affect these AERONET products*." and "*The uniqueness of the case in the present manuscript is that similar nonmonotonic spectral SSA curvature occurred under conditions of large submicron particles with narrow size distribution (as presented in Fig. 4 and Fig. 7) and containing BrC and/or tarballs, as indicated by the high AAE values reported in Fig. 3*."

Finally, we have thoroughly investigated the papers suggested (here and below) by the reviewer. These papers use multi-wavelength AOD and SSA products to infer various aerosol properties like BC mixing state. However, since our manuscript deals with the uniquely curved AOD spectra that we observe in our study, we have added the following discussion to Section 3.2.3 in the updated manuscript as examples to better communicate and highlight the importance of BC mixing state and associated absorption processes:

"*The evolution of such coated BC particles occurs also in other settings (e.g., urban outflows), and has important implications that can be considered in calculations of the direct effects of aerosols on climate (Tiwari et al., 2023; Liu et al., 2024c; Lee et al., 2022), as well as when considering the relationships between BC emissions (and associated policy actions), BC properties and remotely-sensed optical properties (Liu et al., 2024a; Liu et al., 2024b)*."

We want to thank the reviewer for this in-depth comment and hope that our above explanations satisfactorily address the reviewer's concerns.

Comment #2:

• The reported high AAE(~ 2) indicates strong, wavelength-dependent absorption, typically associated with Brown Carbon (BrC) and/or coated BC. It is contradictory to report this signature while simultaneously arguing that absorption can be neglected in interpreting the overall spectral curvature. The presence of these absorbers must be integrated into the physical explanation or limitations.

Response #2: We thank the reviewer for this comment and we apologize for this confusion. We hope that we have now clarified in our response above that we are not neglecting the presence of these absorbers in our analysis. Indeed, at all points in the manuscript, we consider absorption profiles with AAE values as high as 2. As our new analysis hopefully shows more clearly, it is simply that these AAE values are still not high enough to influence (i.e., dampen) the observed curvature in spectral extinction/AOD.

Comment #3:

• I would like to confirm is the manuscript attributing the concave AOD curvature and non-monotonic SSA almost entirely to the large size of the accumulation-mode particles. While particle size is undoubtedly a key factor, again, the authors have not sufficiently ruled out the complementary role of aerosol mixing state and composition. The response to earlier query defers a quantitative analysis of growth pathways (coagulation, SOA formation, or coating induced changes in behaviours of per particle spectral properties) to future work. However, these very processes are critical for creating the large, coated particles that could explain the combined observations of large size, high SSA, and non-monotonic SSA. The manuscript would be significantly strengthened by a discussion that quantitatively links possible growth and aging, as studies have attempted to highlight this using multi-platform data integration with constrained core shell Mie modeling over urban cores which frequently have both ambient and transported BC (Z. Liu et al., 2024; Liu et al., (2024b)), to the observed microphysical and optical properties, rather than relying on qualitative terms like "low dilution" alone.

Response #3: We thank the reviewer for this comment. To confirm and reiterate, our findings indicate that the concave AOD curvature is a particle size effect, while the non-monotonic SSA profiles demonstrate the interplay of both particle size and absorption effects. For example, this is stated in the abstract in Line 26-27: "*The SSA concave spectral curvature denotes the mix of black carbon and non-absorbing particulate matter and influence of particle size, while the AOD concave spectral curvature is attributed to particle size*". Further explorations of the SSA phenomena are complicated by the fact that our observations are mostly limited to inverted products that represent effective values averaged over atmospheric columns. Instead, we have tried to expand our discussion of the processes mentioned by the reviewer, including citation of the studies mentioned in Lines 584-587:

"*The evolution of such coated BC particles occurs also in other settings (e.g., urban outflows), and has important implications that can be considered in calculations of the direct effects of aerosols on climate (Tiwari et al., 2023; Liu et al., 2024c; Lee et al., 2022), as well as when considering the relationships between BC emissions (and associated policy actions), BC properties and remotely-sensed optical properties (Liu et al., 2024a; Liu et al., 2024b).*"

References:
Lee, J. E., Gorkowski, K., Meyer, A. G., Benedict, K. B., Aiken, A. C., & Dubey, M. K.: Wildfire smoke demonstrates significant and predictable black carbon light absorption enhancements. Geophysical Research Letters, 49(14). https://doi.org/10.1029/2022gl099334, 2022.
Liu, J., Cohen, J.B., He, Q., Tiwari, P., Qin, K.: Accounting for NOx emissions from biomass burning and urbanization doubles existing inventories over South, Southeast and East Asia. Commun Earth Environ 5, 255, https://doi.org/10.1038/s43247-024-01424-5, 2024a.
Liu, J., Cohen, J. B., Tiwari, P., Liu, Z., Yim, S. H.-L., Gupta, P., Qin, K.: New top-down estimation of daily mass and number column density of black carbon driven by OMI and AERONET observations, Remote Sensing of Environment, 315, 114436, https://doi.org/10.1016/j.rse.2024.114436, 2024b.
Liu, Z., Cohen, J.B., Wang, S., Wang, X., Tiwari, P., Qin, K: Remotely sensed BC columns over rapidly changing Western China show significant decreases in mass and inconsistent changes in number, size, and mixing properties due to policy actions. npj Clim Atmos Sci 7, 124, https://doi.org/10.1038/s41612-024-00663-9, 2024c.
Tiwari, P., Cohen, J.B., Wang, X., Qin, K.: Radiative forcing bias calculation based on COSMO (Core-Shell Mie model Optimization) and AERONET data. npj Clim Atmos Sci 6, 193, https://doi.org/10.1038/s41612-023-00520-1, 2023.

We thank the reviewer for the valuable comments that has further improved the quality of this manuscript.