

We thank the reviewer for these additional comments. We have revised the manuscript to clarify the interpretation of the toluene–benzene photochemical clock, the meaning of the back-extrapolated ERs in Fig. 5, and the strength of the O3–PM2.5 conclusions in Sect. 6. Our point-by-point responses are provided below. Reviewer comments are shown in green, and our responses are shown in black.

Reviewer’s comments:

Section 5: Smoke EnR and ERs:

This section remains rather confusing and not clear what we should conclude.

The clock itself for all observations goes back to -2 days, which the authors explain only as “some negative values”.. Clearly some assumptions in the clock calculation must be wrong. Its not clear how the authors are getting the initial ERs (line 341). Are these at time 0 or negative 2? Its also not clear what we should draw from the very different values in GeosChem. The authors don’t address this. I am guessing its due to too low emissions of VOCs, but would like to get the authors interpretation if they are going to include this. Note that in Figure 5, I am not clear what are the values on the figures.

Response: The assumptions and associated sensitivity tests were described in Supplement Sect. S1. Specifically, the toluene–benzene photochemical clock assumes: (1) a representative and approximately invariant initial Δ toluene/ Δ benzene ratio for the contributing fire emissions; (2) co-emission of toluene and benzene followed predominantly by first-order loss through reaction with OH; (3) sufficiently accurate compound-specific background subtraction; and (4) no substantial differential mixing or post-emission input from non-fire sources that changes the toluene-to-benzene enhancement ratio. Conversion of the derived OH exposure to an age in days additionally assumes a constant mean daytime OH concentration.

Mathematically, a negative clock value occurs when the observed background-corrected enhancement ratio exceeds the assumed initial toluene-to-benzene ratio of 0.7 ppbv/ppbv. Values extending to approximately -2 days therefore do not represent physical negative plume ages; rather, they show that the absolute clock age is not valid for those observations because one or more assumptions are imperfect. In Supplement Sect. S1, sensitivity tests using alternative initial toluene/benzene emission ratios shifted the inferred OH exposure and back-extrapolated time-zero ERs by ~10–40%, confirming that absolute ages and intercept-derived ERs are assumption-sensitive. However, the qualitative VOC evolution and the model–observation comparison remain useful when the same $\ln(\text{EnR})$ -age framework is applied consistently to observations and GEOS-Chem.

We have also clarified the meaning of the “initial ERs” in Sect. 5. These values are not evaluated at -2 days and are not direct near-source measurements. They therefore correspond to the back-extrapolated EnR at the clock-defined $t = 0$, where $t = 0$ is established by the assumed initial toluene-to-benzene ratio of 0.7. We now refer to them as “back-extrapolated time-zero ERs” and

emphasize that they are assumption-dependent, source-like estimates, subject to large uncertainties, rather than independently measured source emission ratios.

In the revision, we softened the discussion of the derived ERs because the back-extrapolated time-zero ERs are indeed sensitive to the assumed clock origin. However, the slope of the $\ln(\text{EnR})$ -age relationship, used to infer effective OH loss rates, is less directly affected by this time-zero assumption than the intercept-derived ERs. More importantly, applying the same framework to observations and GEOS-Chem provides a useful constraint on model chemical processing. For example, as described in Sect. 8, underestimated BB emissions are a major contributor to the low modeled VOC/CO EnRs. Tripling BB emissions improves CO and many VOCs and reduces the inferred OH-exposure bias, although it may overestimate PM_{2.5}. This indicates that emission magnitude is important, but species-specific emission factors and chemical processing also matter.

Section 6.

The small number of points limits the conclusions. One other thing that is important is that generally Missoula is a very low O₃ city, which makes it different urban areas where this relationship has been looked at (see fig below). Presumably the small size and relatively modest NO_x concentrations keep O₃ from going to high levels in Missoula. The discrepancy with models does point out an important point; Models seem to make O₃ during transport, whereas most urban O₃ enhancements due to smoke are probably due to local production of smoke VOCs with NO_x. In my opinion, if the authors want to keep this section, they should discuss it in the context of what is normal O₃ in Missoula.

Response: The figure referenced in the comment was not available in the review materials. Nevertheless, we understand the reviewer's central point to be that the observed O₃-PM_{2.5} relationship should be interpreted in the context of Missoula's local O₃ and NO_x environment.

We agree that the limited number of daily observations, particularly at the highest PM_{2.5} concentrations, constrains our ability to identify a precise transition point. We have therefore clarified that the LOWESS curve represents a descriptive non-monotonic tendency rather than a statistically defined threshold. We retain this section because similar behavior was observed at Eugene and Cheeka Peak during the same September 2020 episode and has also been reported in previous multi-year, multi-site studies across the western United States.

We have also clarified the event-specific local context using the September 2020 urban background already presented in Fig. 4. MDA8 O₃ was only approximately 3 ppb (7%) higher during smoke-impacted periods, while NO_x showed no discernible enhancement. This modest O₃ response and the absence of a corresponding NO_x enhancement are consistent with limited local O₃ production during this event. Reduced shortwave radiation and a shallower boundary layer under heavier smoke may also have contributed to lower surface O₃. We present these as plausible interpretations rather than firm mechanistic conclusions.

The reviewer also suggests that the models may produce O₃ during regional transport, whereas urban smoke-related O₃ enhancements may depend on local mixing of smoke VOCs with NO_x. We agree that this is a plausible interpretation. However, because our simulations do not diagnose where modeled O₃ production occurs, we have not attributed the model–observation discrepancy to this mechanism in the manuscript, and instead framed this interpretation cautiously.