

Interactive comment on “Detailed heterogeneous oxidation of soot surfaces in a particle-resolved aerosol model” by J. C. Kaiser et al.

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Response to reviewer #2:

1. *“This modeling effort is very nicely done and reveals interesting details about the oxidation mechanisms of PAHs on soot particles. I think the most novel scientific finding (as opposed to new model application) is the importance of NO₃ – although I believe the potential importance of NO₃ was already discussed in general by Reisen and Arey, EST 2005 39(1), 64 – 73. I did not see a reference to this work, or generally, constraints from field observations on the overall applicability of this modeling effort. I think the paper would improve by at least discussing briefly the model results in the context of observations of PAHs. I realize the model is not set up to compare*

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directly with any observations, but instead to analyze in general the lifetimes and likely products. But, there would still be some utility in noting that nitro-PAHs are detected, e.g. with evidence of NO₃ radical chemistry (though also via OH chemistry – implying gas-phase PAH oxidation channels for more volatile species as expected) etc.”

The reviewer points out the potential importance of NO₃ for the nitration of PAHs which implies an emphasis on the products of the reactions between PAHs and atmospheric oxidants. Since our study does not attempt to resolve individual products but rather focuses on the degradation mechanisms of particle-bound PAHs, we may not have given this subject enough attention. Hence, we follow the referee's advice and include the reference to Reisen and Arey (2005).

We make the following adjustments:

P. 5129, I. 24: We change “For example, certain substances on particle surfaces become mutagenic upon reaction with NO_x (Finlayson-Pitts and Pitts, 2000).” to “For example, certain substances found on particle surfaces become mutagenic upon nitration, i.e. reaction with NO_x (Finlayson-Pitts and Pitts, 2000; Reisen and Arey, 2005).”.

P. 5152, I. 13: We add the sentence “The potential importance of such a reaction for nitro-PAH formation was also indicated by field observations in a study by Reisen and Arey (2005).”.

P. 5152, I. 22: We change “...but then again, according to Finlayson-Pitts and Pitts (2000), nitration may lead to increased mutagenicity.” to “...but then again, nitration may lead to increased mutagenicity (Finlayson-Pitts and Pitts, 2000; Reisen and Arey, 2005).”.

2. *“In the abstract, the lifetimes of PAHs on soot particles is reported as derived from the model for ozone, NO₂, OH, and NO₃. However, it is not very clear that*

these lifetimes are only for PAHs absorbed at the surface of the soot particle. Without carefully reading the manuscript, one could easily misinterpret these values to assume that PAHs have a very short atmospheric lifetime (which is obviously not true given their transport days downwind of source regions). This issue should also be discussed again in the conclusions section as well. It implies that condensation of other gases (as noted in the text) is important for blocking the oxidation process, or that PAHs exist buried within particles in a manner inaccessible to atmospheric oxidants.”

In order to clarify that we are modeling particles coated only with a monolayer of PAHs, we make the following changes to the document:

P. 5128, I. 2: We change “We simulate the heterogeneous oxidation of condensed phase polycyclic aromatic hydrocarbons (PAHs) on soot particles in an urban atmosphere using the particle-resolved aerosol model PartMC-MOSAIC.” to “Using the particle-resolved aerosol model PartMC-MOSAIC, we simulate the heterogeneous oxidation of a monolayer of polycyclic aromatic hydrocarbons (PAHs) on soot particles in an urban atmosphere.”

P. 5128, I. 12: We change “Such short PAH half-lives may lead to efficient conversion...” to “Such short half-lives of surface-bound PAHs may lead to efficient conversion...”

P. 5140, I. 5: We add the sentence: “Furthermore, we do not include the concurrent condensation of inorganic or secondary organic aerosol mass on the particles, i.e. in our simulations the PAHs and their oxidized derivatives stay on the surface and are not located within the particle bulk.”

P. 5152, I. 11: We change “...the PAH layer was oxidized...” to “...the PAH monolayer was oxidized...”

P. 5152, I. 18: We add the sentence “When comparing the above results to field measurements, it has to be kept in mind that PAHs are not only found in the surface layer but also in the particle bulk which significantly increases their atmospheric lifetime since those PAHs may not be readily accessible for oxidation.”

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3. *“It seems there is a general assumption that the oxidation products are less volatile and thus remain on the surface. For understanding oxidation of the initial surface bound PAHs only, this assumption isn’t so important, but it would matter in a complete treatment of oxidation of PAHs throughout the particle bulk during the course of a particle’s atmospheric lifetime. Volatilization of some products would then potentially allow oxidation of PAH’s below the surface more feasible. I may have missed a discussion of such a possibility in the paper.”*

Indeed, we assume oxidation products to remain on the particle surface as stated in I. 8 on p. 5140 of the manuscript. As described above, our study only considers a monolayer of PAHs on the surface of soot particles.

If volatilization of the surface-bound PAHs due to reaction with OH and NO₃ occurred, this would, as remarked by the referee, allow a more efficient oxidation pathway of organic material located below the topmost layer, including PAHs, and affect respective atmospheric lifetimes. The description of such a scenario is beyond the scope of this study. However, in order to make clear that we are aware of the issue we add the following paragraph to our paper:

P. 5153, I. 22: “All the above results are based on the assumptions of only a single PAH monolayer on the surface of an unreactive substrate and that the oxidation products remain on the particle surface. To account for PAHs and oxidative processes in multiple layers as well as in the particle bulk, a multilayer model (e.g., Shiraiwa et al., 2010) has to be applied. If a particle consists of multiple layers of PAHs and the volatilization of organic material occurs as observed for other organic substrates (Molina et al., 2004, Knopf et al., 2006, Kroll et al., 2011), this can significantly affect PAH degradation processes since PAHs from lower layers could be exposed to atmospheric oxidants upon such reactions.”

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