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Comment

Interactive comment on “Kinetic double-layer model of aerosol surface chemistry and gas-particle interactions (K2-SURF): degradation of polycyclic aromatic hydrocarbons exposed to O₃, NO₂, H₂O, OH and NO₃” by M. Shiraiwa et al.

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Response to Referee #1

We thank anonymous Referee #1 for the review of our manuscript. The constructive suggestions for improvement are very welcome and will be implemented upon revision. Detailed responses to the individual comments are given below.

Referee Comment 1:

The paper under review presents a detailed model treatment of the degradation of
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PAHs on the surface of aerosol particles. It focuses on PAH exposed to O₃, NO₂, H₂O, OH and NO₃ and combines parallel and sequential surface reactions between different gas phase species and species on the particle surface. The paper fits nicely within the scope of ACP. It provides an up-to-date compilation of recent experimental studies on PAH degradation for different substrates and illustrates how the Poeschl-Rudich-Amman framework can be applied to a specific reaction system. The paper could be improved by adjusting the environmental conditions, so that they reflect more typical ambient conditions. This applies in particular to the chosen RH and the NO₂ mixing ratio. I recommend this paper for publication after the comments below are addressed.

Response:

Thanks for the positive evaluation of our manuscript. We will adjust the RH level and clarify the assumptions concerning NO₂ as detailed below.

Referee Comment 2:

p. 18030, l 15: Steady state assumption for O₃, H₂O and NO₂: It is not clear why the steady state assumption is applied to these three species but not for PAH and NO₃. Please include a justification for making this assumption. Furthermore it is not clear if the steady state assumption is applied for the model calculations presented in section 4 (Fig. 6 and 8 look like steady state is not assumed). Please clarify this point.

Response:

Steady-state assumptions for O₃, H₂O and NO₂ were applied only to derive Langmuir adsorption constants (Figs. 3 and 5), which was not done for NO₃ and PAHs. For the model calculations illustrated in Figs. 6 and 8 no steady-state assumptions were applied but the differential equations were solved numerically. We will clarify this point in the revised manuscript.

Referee Comment 3:

p. 18037, line 1: Wet conditions of 25% RH: While 25% RH means that there is some water vapor present, this is still pretty dry for atmospheric conditions. I certainly would not consider this as “typical ambient conditions at night time”, as it is stated in section 4.3.3. The paper would benefit from adjusting the environmental conditions to be more representative of ambient atmospheric conditions. I suggest to change the cases with 25% RH to, say, 60% RH.

Response:

We will increase RH to 60%. Note that at higher RH water is likely to exhibit multi-layer adsorption rather than Langmuir-type adsorption behavior (Thomas et al., 1999; Mikhailov et al., 2009).

Referee Comment 4:

Section 4.1, and Fig. 6: It would be helpful to add one sentence why the PAH degradation is different on the soot surface compared to the organic surface.

Response:

The differences of PAH degradation on soot and on the solid organic surface are mainly caused by the different desorption lifetimes of ozone as derived and discussed in Sect. 3 (~ 10 s vs. ~ 0.1 s). We speculate that the longer apparent desorption lifetime on soot may reflect stronger electron donor-acceptor interactions between the graphene layers (aromatic rings) and the adsorbed ozone molecules or oxygen atoms.

Referee Comment 5:

Section 4.3.1 and section 4.3.2: The NO₂ mixing ratio of 500 ppb is very large for atmospheric conditions. It would be interesting to see the results for much lower but atmospherically relevant NO₂ mixing ratios, e.g. 50 ppb.

Response:

It is true that 500 ppb NO₂ is too large for atmospheric conditions, but we used it to

compare with experimental results of PAH-O3-H2O-NO2 system shown in Table 4. We use more realistic concentration level of NO2 (100 ppb) to calculate chemical half-life of PAH in Fig. 9.

Referee Comment 6:

Section 3.1.2, description of Fig. 4: What was [H2O]gs for these calculations?

Response:

[H2O]gs was assumed to be 0, since most of the data were under dry condition (0% RH). We will specify this information in the revised manuscript.

Referee Comment 7:

In Fig. 8 only γ O3 is shown. It would be interesting to include γ NO2 as well.

Response:

As suggested, we could also calculate γ NO2 as well. Initially up to 10-2 seconds, γ NO2 was 0.064 which is equal to α s,0,NO2. As it is shown by [NO2]s which reached steady-state condition very quickly, γ NO2 decreased away to 0 quickly. We will add this information in the text but we would not include γ NO2 in Figure, as it makes figure more complicated.

Referee Comment 8:

Minor comments: p. 18027, l. 1 and 2: Units for Dg should be in SI units.

Response:

Torr will be converted to Pa using 1 Torr = 133 Pa. $D_{g,OH} = 163 \text{ Torr cm}^2 \text{ s}^{-1} = 217 \text{ hPa cm}^2 \text{ s}^{-1}$, $D_{g,NO3} = 80 \text{ Torr cm}^2 \text{ s}^{-1} = 107 \text{ hPa cm}^2 \text{ s}^{-1}$.

Referee Comment 9:

p. 18027, l. 4: Sentence should read: "The diffusion effect . . ." p. 18033, l. 4: Omit

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“as”. p. 18034, l. 25: Should read “on the order of 10⁻⁸”. p. 18037, l. 27: Should read “shorter”.

Response:

Sentences will be revised.

Referee Comment 10:

Fig. 1: I suggest adding [NO₃]s to this schematic figure.

Response:

[NO₃]s will be added in Figure 1.

References:

Mikhailov, E., Vlasenko, S., Martin, S. T., Koop, T. and Pöschl, U.: Amorphous and crystalline aerosol particles interacting with water vapor – Part 1: Microstructure, phase transitions, hygroscopic growth and kinetic limitations, *Atmos. Chem. Phys. Discuss.*, 9, 7333-7412, 2009.

Thomas, E., Rudich, Y., Trakhtenberg, S. and Ussyshkin, R.: Water adsorption by hydrophobic organic surfaces: Experimental evidence and implications to the atmospheric properties of organic aerosols, *Journal of Geophysical Research-Atmospheres*, 104, 16053-16059, 1999.

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