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

J. C. Kaiser et al.
nriemer@illinois.edu

Received and published: 4 April 2011

1. “The authors report a range of $2 \times 10^{-7} - 2 \times 10^{-6}$ for the uptake coefficient of ozone ($\gamma_{O3}$) on PAH-coated aerosol particles. As shown in Fig. 3, $\gamma_{O3}$ is initially as high as $10^{-5}$ and drops to $10^{-6}$ after degradation of the PAHs. Thus, $2 \times 10^{-7} - 2 \times 10^{-6}$ seems characteristic for the uptake of ozone by oxidized PAHs (Y2,Y3). The authors may address and clarify these aspects.”

The reviewer correctly points out that the initial uptake coefficient of O3 on PAH-coated soot particles decreases by 1-2 orders of magnitude as shown in Fig. 3. However, the results in Fig. 3 show the time series for $\gamma$ for one individual, freshly emitted particle whereas our recommended value cited above is based on the whole population of particles (see Figs. 5 and 6). At a given time the particle population consists of a mixture of particles where the individual particles differ in their levels of oxidation, i.e. freshly emitted (non-oxidized) particles coexist with aged (oxidized) particles as depicted in Figs. 5 and 6. For this reason we cannot attribute the lower reactive uptake coefficient to oxidized PAHs alone, although, as it is evident, those particles play a significant role in lessening the reactive uptake. Furthermore, our recommendation is based on a temporal average over the total simulation time of 24 h.

To make this point clearer we make the following changes:

P. 5148, l. 15: We change “…over the whole population of soot particles:” to “…over the whole population of soot particles which, at a given time, may be photochemically aged to different degrees:”.

P. 5149, l. 26: We change “A reasonable value for $\gamma_{O3}$ in an urban polluted environment…” to “A reasonable value for $\gamma_{O3}$ for particles of different photochemical ages in an urban polluted environment…”.

P. 5149, l. 5: We change “…relatively constant throughout the entire simulated period” to “…relatively constant throughout most of the simulated period”.

P. 5153, l. 3: We change “…averaged over the whole population,” to “…averaged over the whole population of particles aged photochemically to different degrees,”.

2. “In section 4.3, the authors compared their results with Springmann et al. (2009) and Pöschl et al. (2001). Please also compare with Shiraiwa et al. (2009), who demonstrated the PAH half-life on soot can be below ten minutes during nighttime (Fig. 9) due to NO3. They also suggested that OH has a minor contribution and O3 plays a dominant role in PAH degradation on soot.”

Thank you for pointing out the PAH degradation results from Shiraiwa et al. (2009). We make the following changes to the document:
P. 5146, l. 21: We add the following sentence: “A similarly short lifetime at elevated NO$_3$ concentrations has also been observed in a modeling study by Shiraiwa et al. (2009).”.

P. 5148, l. 9: We change “…which neither Pöschl et al. (2001) nor Springmann et al. (2009) considered.” to “…which neither Pöschl et al. (2001) nor Springmann et al. (2009) considered, but which was also observed in a recent study by Shiraiwa et al. (2009) that included oxidation by NO$_3$.”.

3. “Recently, Shiraiwa et al. (2011) showed the formation of long-lived reactive oxygen intermediates upon heterogeneous reaction between ozone and PAH. The desorption lifetime of ozone is actually much shorter (nanoseconds, but not seconds) and ozone decomposes into O atom, which are long-lived and reactive towards PAH. The apparent long desorption lifetime of ozone (10 s) includes the adsorption and decomposition of ozone. This possibility had been mentioned in earlier studies (e.g., Stephens et al., 1986, Rogaski et al., 1997, Pöschl et al., 2001), and it may be worthwhile to mention this aspect and that the kinetics of heterogeneous reactions can be described at different levels of mechanistic detail.”

We agree with the referee. At the time of writing this publication we were not aware of the very recent study by Shiraiwa et al. (2011). We feel to keep the description of the oxidation of particle-bound PAH by O$_3$ as a “simple” Langmuir-Hinshelwood mechanism (Shiraiwa et al., 2011) since it provides, for the purpose of this publication, an adequate description of the heterogeneous oxidation process and is computationally less demanding considering our model setup which consists of coupled gas phase solver and particle resolved model.

We make the following changes to the document:
P. 5131, l. 3: We add the reference Shiraiwa et al. (2011).

P. 5133, l. 28: We add the following sentences: “Note that very recently Shiraiwa et al. (2011) showed that O$_3$ does actually not follow simple Langmuir-Hinshelwood kinetics. Instead, it either desorbs rapidly or dissociates into O atoms and long-lived reactive oxygen intermediates upon adsorption on a PAH surface (Shiraiwa et al., 2011). These intermediates can subsequently react with the PAHs (Shiraiwa et al., 2011). However, for the purpose of our study the Langmuir-Hinshelwood description is detailed enough to adequately represent the O$_3$-PAH interaction.”.

P. 5141, l. 12: We add the following sentences: “The apparent long desorption lifetime of O$_3$ (10 s) employed in this study includes the adsorption and decomposition of O$_3$. Here, we opt to describe the oxidation of particle-bound PAHs by O$_3$ with a simple Langmuir-Hinshelwood mechanism (Shiraiwa et al., 2009). Although, on a mechanistic level, this description is incomplete (Shiraiwa et al., 2011) it does not affect the overall particle surface oxidation and is less demanding in terms of computational power.”.

P. 5153, l. 28: We change “Future research should account for a possible multilayer coating of soot particles with PAHs.” to “Future research should account for a possible multilayer coating of soot particles with PAHs and for multistep Langmuir-Hinshelwood type reactions (Shiraiwa et al., 2009, 2011).”.

References
M. Shiraiwa, R. M. Garland, and U. Pöschl. Kinetic double-layer model of aerosol surface
