Interactive comment on “Kinetic multi-layer model of aerosol surface and bulk chemistry (KM-SUB): the influence of interfacial transport and bulk diffusion on the oxidation of oleic acid by ozone” by M. Shiraiwa et al.

Anonymous Referee #1

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This manuscript describes the application of a novel multi-layer model to interpret the oxidation kinetics of oleic acid aerosol. This model represents an extension of a previously published framework for treating gas-particle interactions, referred to as the PRA framework. In particular, the oxidation kinetics of oleic acid (OA) are compared with experimental measurements, considering three plausible limiting scenarios. The observed lifetime of OA is shown to be consistent with either rapid bulk phase chemistry limited by interfacial transport, or slow bulk phase chemistry. The observed lifetime is inconsistent with slow bulk diffusion, as would be expected if OA were embedded in a
semi-solid matrix. The manuscript is largely clearly written, although the authors should consider the following comments before the manuscript is accepted for publication.

1. A simple model for treating the surface coverage dependence of the surface accommodation coefficient is considered. It is not clear that assuming a simple coverage dependence is a reasonable approximation. How might the surface accommodation coefficient change with chemical composition if the surface varies with oxidation and aging of OA? Indeed, a same comment extends to the treatment of the diffusion constant of ozone (and OA) in the particle - given the variety of low and high molecular weight products that could form, how valid is it to consider that the diffusion constants are independent of time?

2. It appears that there is no consideration that the products may be volatile as well as involatile. Figure 1 indicates that it is only ozone that is allowed to partition between the gas and condensed phases. As this is unlikely to be true for the experimental measurements, how is this likely to impact on the kinetics modelling? Presumably some contraction of the number of layers must be allowed to occur over time as product is lost from the particle. There is no discussion of how this might be incorporated.

3. Given that the model is being applied to a specific system, it would be very helpful to the reader if the equations were formulated first in the general framework, but then also shown explicitly for the components of the OA system.

4. The discussion in the first paragraph at the top of page 290 strictly applies to set the starting surface and bulk concentration of OA. Indeed, it is stated that this is for pure Yj. It is not clear how the changing composition of the particle is accounted for in this treatment of the rate constants for the fluxes between the surface and bulk layers.

5. On a point of clarity, the difference between Xp and Xq on page 292 is not clear.

6. The parameters for the model treatments considered are presented in Table 1. It is not clear how these values are arrived at and how feasible they are. Some justifi-
cation for the choice of these numbers must be given. Given enough parameters in a model, it is always possible to vary the values in such a way that an observation can be reproduced. But the physical significance must be considered and justified.

7. For the third model treatment, given that bulk diffusion limits the oxidation kinetics, is it not critical that volatilization of products be included, allowing new surface layers to be oxidised repeatedly, rather than by forcing reaction to occur by diffusion only?