

***Interactive comment on “Detailed heterogeneous chemistry in an urban plume box model: reversible co-adsorption of O<sub>3</sub>, NO<sub>2</sub>, and H<sub>2</sub>O on soot coated with benzo[a]pyrene” by M. Springmann et al.***

**Anonymous Referee #1**

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General Comments:

This article explicitly models the adsorption, desorption, and surface reactions of ozone and NO<sub>2</sub> on soot particles and analyzes their potential to effect gas-phase ozone concentrations in the atmosphere. The paper is the first to use the dynamic uptake coefficient approach to simulate heterogeneous processes in a photochemical box-model. The authors demonstrate that this approach has the ability to simulate certain types of heterogeneous reactions that are not well characterized by typical parameterizations of reactive uptake coefficients. The work is unique and the techniques used are, for

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the most part, well supported by theory and experimental findings. The article will be of interest to ACP readers. The paper could benefit from some more discussion of how the idealized assumptions are likely to effect results, especially the assumption of a Langmuir isotherm for water adsorption and the assumption that no reactions between NO<sub>2</sub> and water will occur on the particle surface. The paper would also benefit from performing another model simulation exploring the possibility of using two constant uptake coefficients for each species (one for the first hour and the second for the remaining time in the model simulation). With these additions, as well as minor changes suggested below, this article will be a valuable addition to Atmospheric Chemistry and Physics.

Specific Comments:

Page 10057, line 13: here you should also cite the Osthoff et al (2008) article from Nature Geoscience

Page 10057, line 23: What about reactions with other common oxidants (OH, NO<sub>3</sub>, etc.)? Are these reactions likely to be important compared to the O<sub>3</sub> and NO<sub>2</sub> reactions?

Page 10057, line 28: This aging of soot particles may be important for several reasons. Later in the article you discuss its potential to lead to CCN. I also wonder if this may be an SOA formation mechanism that has not been well quantified. Recently there has been a great deal of attention on potential reasons that models under-predict SOA in the atmosphere. Do you think this oxidation of soot surfaces could contribute non-negligibly to total atmospheric SOA? Please add a discussion of the expected importance (or lack of importance) of this process to SOA formation in your conclusion.

Page 10058, line 22: I see what you are saying here, but it is a bit misleading to say that this technique takes exposure time into account while previous treatments of gamma do not. Exposure time is really just a surrogate for surface coverage; you could simply say that gamma depends on surface coverage. Current model treatments of gamma

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that you cite also vary gamma with exposure time, since their uptakes depend on bulk aerosol composition which changes with time (and which changes as a result of the heterogeneous chemistry). I think the distinction that you really want to make here is that 1) your gamma varies with gas-phase concentrations (since it takes into account desorption as well as adsorption) and 2) your gamma depends not only on the bulk composition but also on the surface composition.

Page 10064: The choice of the Langmuir isotherm for ozone and NO<sub>2</sub> adsorption in dry conditions seems reasonable. However, I am not convinced that this isotherm is appropriate for the adsorption of water, since water has a higher affinity for other water molecules than for the BaP coating. Therefore, it seems likely that the adsorption of water would increase as more of the particle surface was covered in water molecules and that more than a single layer of water molecules would coat the particle. In addition, although it seems reasonable to assume competitive co-adsorption for water and ozone, I am not sure that competitive co-adsorption is a good assumption for water and NO<sub>2</sub>, since NO<sub>2</sub> could adsorb to an aqueous surface. I understand that it would be complex to model such processes. Not only would it require a different treatment of the H<sub>2</sub>O and NO<sub>2</sub> adsorption, but it would also require the addition of surface reactions between nitrogen species and water and possibly a change in surface area concentration (m<sup>2</sup>/g) if the hydrated molecule became more spherical in shape. However, it would be useful for you to discuss your current set-up as an idealized system and identify the possible effects on your results if 1) water and NO<sub>2</sub> did not adhere to a Langmuir isotherm and 2) NO<sub>2</sub> reactions with water molecules were included in the chemistry.

Page 10068: What time step is used in this modeling?

Page 10070, line 23-25: Even though ozone adsorption appears to decrease with RH, NO<sub>2</sub> adsorption could increase because the NO<sub>2</sub> will be able to adsorb onto aqueous as well as soot surfaces (and may have more affinity for the water coating than the BaP coating). Is there any way to quantify this effect in your model?

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Page 10077, line 3: What boundary conditions are being set for ozone? I thought this was a box model with no advection/dispersion? Do you mean to say that initial conditions of ozone were set to 30 ppb?

Page 10077, line 17-18: The change in the soot particle's hydrophobicity would have the opposite effect of what you are seeing (it would increase theta(H<sub>2</sub>O), decrease theta(ozone), and thus increase the half-life of BaP. However, your modeled half-life is already too long).

Section 4.4: I think this section doesn't add very much since your previous results already show that the initial reactive uptake coefficients decrease rapidly within the first hour (the results you present here seem like they are obvious based on what was presented earlier in the paper). A more useful analysis would be if you did a second "constant uptake" simulation where you use two uptake values, one for the first hour and a second for the remainder of the model simulation (i.e. for ozone use gamma = 1 x 10<sup>-3</sup> for the first hour and then use gamma = 1 x 10<sup>-7</sup> for the rest of the model run or until new soot surfaces are "emitted"). Then compare these to your initial results to see if this simplified scheme could be used to fairly accurately simulate the more complicated process you have explicitly modeled. Coming up with a simple way to model this chemistry based on your initial detailed runs would be useful to modelers who want to incorporate this chemistry into full photo-chemical models but who need to worry about computational time and complexity. Also, can you comment on the change in computation time between the constant uptake coefficient run and the dynamic uptake coefficient approach? Did your explicit treatment of this process increase your computation time by 50%? 100%? 200%?

Page 10084, line 1-5: Are there other reactions that occur on particle surfaces that you expect to be important to gas-phase atmospheric chemistry? If so, it would be useful to mention them here.

Technical Corrections:

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Page 10057, line 5: typo – change “are” to “is”

Page 10058, line 26: awkward – change to something like: “the uptake coefficient can not a priori be treated as a constant value”. Also, as you just mentioned, most models do not assume a constant  $\gamma$  . . . maybe it would be more accurate to say that the uptake coefficient can not be parameterized only based on bulk composition, temperature, and RH.

Page 10074, line 7: The statement that  $\gamma$  decreases by more than five orders of magnitude is not quite accurate . . .  $\gamma$  becomes negative.

Page 10076, line 14: typo – remove “with” from the statement “the BaP half-life is with 30 min”. Add “,” after “min”.

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