**Atmospheric
Chemistry
and Physics
Discussions**

# *Interactive comment on* "Detailed heterogeneous chemistry in an urban plume box model: reversible co-adsorption of $O_3$, $NO_2$, and $H_2O$ on soot coated with benzo[a]pyrene" *by* M. Springmann et al.

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**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 $NO_2$ 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 coefficents for each species (one for the first hour and the second for the remaining time in the model simulation).**

We thank the referee for reviewing our manuscript. The assumptions and limitations of this paper addressed by the referee have been discussed below in further detail. We also performed additional model simulations applying two constant uptake coefficients for $O_3$ and $NO_2$ and including a new reaction channel $NO_2 + H_2O$. These results are discussed below.

**Page 10057, line 13: here you should also cite the (Osthoff et al., 2006) article from Nature Geoscience**

This reference has been included.

**Page 10057, line 23: What about reactions with other common oxidants (OH, $NO_3$, etc.)? Are these reactions likely to be important compared to the $O_3$ and $NO_2$ reactions?**

The reviewer is correct in pointing out that reactions involving OH and $NO_3$ can be important. This paper focuses on reactions following Langmuir adsorption kinetics and subsequent surface reactions (Langmuir-Hinshelwood type reactions). Experimental studies indicate that $O_3$ and $NO_2$ follow this kinds of mechanisms, however, a similar reaction behavior has not been observed for OH and $NO_3$. The integration of hetero-geneous reactions involving OH and $NO_3$ will be subject to a future study.

Our answer is given in the paragraph starting on page 10060, line 20 in combination with the answer to comment to Page 10064. Please see below.

**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 mod-**

**els 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.**

SOA formation describes an organic component of particulate matter that transfers to the aerosol phase from the gas phase as products of gas-phase oxidation of parent organic species (Kanakidou et al., 2005). Applying this definition the heterogeneous reactions described in this study do not represent SOA formation. For this reason we can not state their importance or lack of significance.

**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 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.**

We omitted the reference to "exposure time" and replaced "particle surface coverage" with "particle surface composition" on page 10058, line 22, and on page 10059, line 6: "However, the experimental studies on the adsorption of gas-phase species on soot mentioned above indicate that the heterogeneous kinetics depend also on particle surface composition and gas-phase concentrations, in addition to the environmental conditions described by temperature and relative humidity." and "This treatment, also termed the Pöschl-Rudich-Ammann (PRA) framework (Pöschl et al., 2007; Ammann

and Pöschl, 2007), allows to consider changes in the rate parameters such as the uptake coefficient as a result of changes in the particle surface composition and gas-phase concentrations."

**Page 10064: The choice of the Langmuir isotherm for ozone and $NO_2$ 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 $NO_2$, since $NO_2$ 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 $H_2O$ and $NO_2$ adsorption, but it would also require the addition of surface reactions between nitrogen species and water and possibly a change in surface area concentration ($m^2$/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 $NO_2$ did not adhere to a Langmuir isotherm and 2) $NO_2$ reactions with water molecules were included in the chemistry.**

To address our idealized system we re-wrote the paragraph starting on page 10060, line 20 to

"The scope of this paper is conceptual and relies on some simplifications. For example, the maximum adsorbents' surface coverage is limited to one monolayer, which means that diffusion processes through multiple surface layers are not considered in our model framework. This allows us to treat the uptake of gas-phase species according

to Langmuir adsorption kinetics. To reduce complexity, we neglect changes in particle composition due to coagulation, dilution, and condensation of semi-volatile gas-phase species. We also expect more trace gases than the three considered here to adsorb onto soot particles under atmospheric conditions. However, with limiting the number of adsorbents to three, we are able to specifically assess each adsorbent's influence on the heterogeneous chemistry. Other trace gases, such as OH and $NO_3$, are also involved in important heterogeneous reactions (e.g., Bertram et al., 2001; Molina et al., 2004; Hearn and Smith, 2006; Knopf et al., 2006; Gross and Bertram, 2008; Park et al., 2008; Gross and Bertram, 2009), but do not adhere to Langmuir adsorption kinetics with subsequent surface reactions (Langmuir-Hinshelwood type reactions) and are therefore not the subject of this study. Although we attempt to use realistic values characteristic of an urban plume scenario as input parameters, our purpose is not to make exact atmospheric predictions."

We investigated the effect of $NO_2$ + $H_2O$ reactions in further simulations. On the basis of Cheung et al. (2000), we implemented the dissolution of gaseous $NO_2$ into $H_2O$ with a subsequent reaction producing HONO(g) and $HNO_3$. While the effect from this reaction is a 1 ppb increase in the gas-phase $O_3$ concentration, it also introduces methodological inaccuracies into our model, since dissolution of $NO_2$ into one monolayer of water is assumed to obey Henry's law, usually valid only for bulk solutions. Since we limit our study to Langmuir-Hinshelwood type reactions, such reaction are beyond the scope of this paper. However, as a sensitivity run, we also simulated the reaction between adsorbed $NO_2$ and $H_2O$ based on the parameters given for the reaction of aqueous $NO_2$ and $H_2O$ (Cheung et al., 2000). Since this had no effect on the gas-phase $O_3$ concentration and the produced surface concentration of $HNO_3$ stayed below $1 \times 10^9$ cm$^{-2}$ (five orders of magnitude below the initial BaP concentration), we consider this reaction pathway based on the used parameters as negligible.

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

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We add the following information to page 10068, line 9: "The gas-phase chemistry in RADM2 is solved with a variable chemical time step (Chang et al., 1987) ranging from 0.096 s to 3 s. To resolve the rapid adsorption of water vapor in scenario C, a shorter time step is used for the first day of the simulation period, ranging from 0.003 s to 0.006 s."

**Page 10070, line 23-25: Even though ozone adsorption appears to decrease with RH, $NO_2$ adsorption could increase because the $NO_2$ will be able to adsorb onto aqueous as well as soot surfaces (and may have more affinity for the water coating that the BaP coating). Is there any way to quantify this effect in your model?**

Please see also previous answer to comment regarding $NO_2$ + $H_2O$.

As mentioned above, our model is limited to one monolayer. For this reason, we can not quantify this effect. An extension of this model to multilayers would be beyond the scope of this manuscript. Looking at experimental studies, the uptake of $NO_2$ on aqueous surfaces ranges between $5 \times 10^{-4}$–$1.5 \times 10^{-3}$ (Cheung et al., 2000), whereas the uptake of $NO_2$ by BaP can be up to 0.14 (Gerecke et al., 1998; Ammann and Pöschl, 2007). Sensitivity runs have shown that $NO_2$ adsorption with an uptake coefficient smaller than $1 \times 10^{-3}$ does not have an influence on the gas-phase $O_3$ concentration.

**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?**

We refer to the experimental conditions of the study by Pöschl et al. (2001). We change the original sentence on page 10077, line 2 to the following: "Scenario P represents our modeling results using the experimental conditions of Pöschl et al. (2001) as input parameters. These are a 30 ppbv constant gas-phase $O_3$ concentration, an initial BaP

surface concentration of $1.8 \times 10^{13}$ cm$^{-2}$, a temperature of 296 K, and $O_3$ and $H_2O$ as adsorbing species."

**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 $\Theta_{H_2O}$, decrease $\Theta_{O_3}$, and thus increase the half life of BaP. However, your modeled half life is already too long).**

We change the sentence starting on page 10077, line 15 from "Regarding the latter, physio-chemical processes that are not captured in our model framework are e. g. changes in the soot particle's hydrophilicity which could result in a longer residence time of $H_2O$ on the surface. Diffusion of adsorbents through surface $H_2O$ may lead to surface oxidation and a reduction in the BaP half-life even though most reactive sites are occupied by $H_2O$." to "Regarding the latter, physiochemical processes that are not captured in our model framework are, e. g., the diffusion of adsorbents through surface $H_2O$ which could lead to surface oxidation and a reduction in the BaP half-life even though most reactive sites are occupied by $H_2O$. Also, changes in the soot particle's hydrophilicity could result in changes of the residence time of surface $H_2O$, subsequently affecting particle oxidation."

In response to referee 2, comment 3, we add the following sentence to the above given answer "A variation of the $H_2O$ desorption time, $\tau_{H_2O}$, of about $\pm 10\%$ due to possible changes in particle hydrophilicity changes the BaP lifetime by about $\pm 5$ min."

**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**

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**values, one for the first hour and a second for the remainder of the model simulation (i. e. for ozone use gamma = $1 \times 10^{-3}$ for the first hour and then use gamma = $1 \times 10^{-7}$ 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 you computation time by 50%? 100%? 200%?**

We tried to parameterize our modeling results with a constant uptake value and achieved fairly good results in capturing the $O_3$-depleting effect on the gas phase by imposing a much smaller constant uptake coefficient than the experimentally determined one. However, we found that this constant uptake coefficient could not be deduced from experimental studies but had to be fitted to the model results and thus is constrained to a certain time frame and boundary conditions, such as initial gas phase concentrations. Another problem with the application of such fitted constant uptake values was that they could not be superimposed, failing to mimic the $O_3$ depleting effect of more than one adsorbent. The parametrization of the uptake coefficient with two parameters as suggested, or even with three as could be deduced from Figure 2, was connected with the same set of problems, which clearly indicates the underlying complexity of physical-chemical processes governing the uptake. In account of this, we add the following on page 10081, line 4:

"In addition to using the initial uptake coefficients as constant uptake values, we also attempted to parameterize the uptake process by several time-specific uptake values

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modeled after the temporal evolution of the uptake coefficients as shown in Fig. 2. Neither a 3-step uptake parametrization, nor a 2-step one using an initial uptake value from laboratory measurements and subsequent values from our model was successful in capturing the $O_3$ depleting effect. Application of a single constant uptake value for each adsorbent yielded acceptable agreement with the gas-phase $O_3$ concentration of the respective model scenarios, if an uptake value was chosen significantly different from the laboratory measurements and model results. However, this approach is only successful for a certain time frame and certain boundary conditions, such as initial gas-phase concentrations. Furthermore, the adsorbent-specific uptake values determined in such a way, could not be used to capture the combined effect on the $O_3$ concentration of two or more adsorbents. Thus, the uptake values obtained in this manner are heavily scenario dependent and therefore of little use in general atmospheric models. These difficulties in obtaining a simplified and thus computationally more efficient description of the uptake process clearly indicate the underlying complexity of the involved physical-chemical mechanisms, emphasizing the need for a detailed modeling framework to accurately resolve the uptake process."

To address the computation time, we add the following sentence on page 10080, line 11:

"Application of constant uptake coefficients reduced the computation time by a factor of about 18 compared to a dynamic uptake approach and needed about the same time as a simulation without any heterogeneous reactions implemented."

**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.**

We change sentence on page 10083, line 29 to:

"In contrast, heterogeneous reactions following adsorption kinetics may predominantly occur at the surface of solid or crystalline particles (Rudich, 2003) and aqueous surfaces coated by an organic surfactant (Donaldson and Vaida, 2006)."

**Technical Corrections:**

**Page 10057, line 5: typo – change "are" to "is"**

Corrected.

**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.**

We changed the sentence on page 10058, line 26 to: "For these reasons, the uptake coefficient can not a priori be treated as a constant value."

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

We change the sentence to: "The value of $\gamma_{O_3}$ decreases by more than five orders of magnitude and then becomes negative."

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

Corrected.

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