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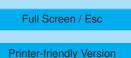
Interactive comment on "Detailed heterogeneous chemistry in an urban plume box model: reversible co-adsorption of O₃, NO₂, and H₂O on soot coated with benzo[a]pyrene" by M. Springmann et al.

Anonymous Referee #2

Received and published: 15 May 2009

General Comments:

The paper by Springmann and coworkers is another step in better understanding the factors that govern heterogeneous chemistry and the chemical aging of aerosol. Specifically, the paper highlights the impact of co-adsorbing species on gas-phase feedback and the lifetime of surface-bound species. To achieve this, the authors combined the dynamic uptake coefficient method developed by Pöschl, Rudich and Ammann (PRA; Pöschl et al., 2007, Ammann and Pöschl, 2007) with a gas-phase chemical mechanism, RADM2 (Stockwell et al., 1990) and applied it to a broader context by



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integrating it into a tropospheric urban plume box model. The hetereogeneous reactions of benzo[a]pyrene, a PAH, with ozone and NO2 in both the presence and absence of water on soot particles was used as the model aerosol surface reaction.

The methodology for investigating the impact of each additional co-adsorbing species on surface and gas-phase composition was systematic and logical. The conclusions presented were based on reasonable interpretations of the results presented. However, the authors are weak in articulating the additional insight gained by coupling the PRA mechanism with the gas-phase mechanism and they do not clearly provide insights for future modelling or laboratory studies of heterogeneous reactions on atmospheric aerosol based on their investigations. However, the paper does provide a link between experimental observations and theoretical models of heterogeneous chemistry and begins to highlight some of the limitations of both modelling these complex systems and performing experiments of increasing complexity.

This paper is recommended for publication in Atmospheric Chemistry and Physics once the following comments have been addressed.

Specific comments:

Comment 1: In Section 3: Model approach, the authors should provide some justification or explanation for the chosen gas-phase mechanism and box model. For example, what is the authors' justification for using RADM2 (Stockwell et al., 1990) as their chemical gas-phase mechanism? Stockwell and co-workers have published an updated version of this model, RACM (Stockwell et al., 1997), with more up-to-date rate constants and product yields. Why wasn't RACM or another more recent model used? Further, could the authors provide some justification for using PLUME 1 by Kuhn et al., 1998.

Comment 2: Section 4: One of the major limitations with this paper is that it does not go far enough in distinguishing some of the observations that are made in this work from those that are made in Pöschl et al. (2007) and Pöschl and Ammann (2007). The

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PRA already provides a link between the gas-phase and surface reactions. Therefore, how has the addition of the gas-phase chemical mechanism made a difference? A comparison of Model System Solid 1 (Pöschl and Ammann, 2007) and Scenario A of this manuscript would help address this. The authors claim one of the aims of the paper is to show for the first time the application of PRA with a gas-phase chemical mechanism but the authors do not highlight in sufficient depth the additional information gained by this exercise.

Comment 3: In both the abstract and in the conclusions, the authors suggest that the results of their work should guide future modelling and experimental investigations of the heterogeneous chemistry and chemical ageing of aerosol, however, they do not expand on this point. In Section 4.2 (BaP lifetime) page 10076, after observing differences in the simulated lifetimes and the lifetimes observed from the experimental data of Pöschl et al. (2001) the authors merely state that "Reasons for the longer simulated lifetimes in scenario P could be due to parameter sensitivity or physio-chemical processes that were not accounted for in the model approach." There should be a more extensive discussion of what the extent of these parameters could be as well as further description of the processes that were not accounted for in the model approach, why they were not accounted for and if they should be accounted for in future studies. For example, the authors suggest that physio-chemical changes such as changes to the soot particle's hydrophilicity could result in longer residence times. Could the authors have not varied the desorption time for water on the surface in a few model runs to get an appreciation of the impact of this parameter on their results as well as exploring the effects of other parameters?

Comment 4: Many of the initial experiments performed in this work used the same gas-phase and surface concentrations as well as uptake coefficients as those used in Ammann and Pöschl (2007). There should be a further exploration of the effects of changing some of these parameters, by way of sensitivity runs, to extend the previous work in the literature. For example, there is a wide range of known uptake coefficients

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for NO2 on soot (Aubin and Abbatt, 2007, see references therein), how would varying the gamma affect the results? What are the effects of changing other parameters such as ozone, NO and NO2 gas-phase concentrations over wider atmospherically relevant concentration ranges?

Comment 5 The derivations outlined in Sections 2.1 and 2.2 should be more strongly attributed to Ammann and Pöschl (2007) and Pöschl et al. (2007). Further, the authors should state more clearly that what is presented in the paper is a condensed version highlighting the key points of the derivation that are relevant to coupling the gas-phase chemical mechanism to the PRA.

Comment 6: The authors go into great detail describing the pertinent features of the PRA mechanism (section 2.1) and provide details of the tropospheric box model (section 3.1) but they do not highlight some of the key reactions of RADM that may be particularly relevant to this study and are therefore relevant in affecting the results compared to running the PRA on its own.

Technical comments:

*Pg 10056 line 17: Delays should be replaced with "reduces," i.e., "Physisorption of water vapour reduces the half life of the coating substance BaP."

*Pg 10056 lines 19-21: Lines 19-21 of the abstract should be re-written to read: Soot emissions modelled by replenishing reactive surface sites lead to maximum gas-phase O3 depletions of 41 ppbv and 7.8 ppbv for an hourly and six-hourly replenishment cycle, respectively.

*Pg 10062 line 18: The period after "for the scenarios considered here." should be a comma.

*Pg10069 line 1: Initial experiments are performed with a BaP surface coverage of 1 \times 10¹⁴ molecules cm-2. The authors should mention that this corresponds to a full monolayer of BaP surface coverage and therefore the entire surface of the particle is

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covered.

*Pg 10077 title of Section 4.3 Title of Section 4.3 should be more descriptive similar to that of Section 4.4, i.e., Feedback on the gas-phase O3 concentration with differing emission scenarios

*Pg 10091 lines 6-7: Fuchs and Sutugin (1970) reference is not in the right location. It is out of alphabetical order.

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