**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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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.

We thank the referee for the comments and suggestions regarding our manuscript. The main criticism concerning the weakness in articulating the additional insight gained by coupling the PRA mechanism with the gas-phase mechanism and lack of insights for future modeling or laboratory studies will be addressed within the answers for the specific comments below.

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.

As numerous model intercomparison studies in the literature show, the choice of a chemical mechanism when modeling atmospheric chemistry is a general problem. We used RADM2, since it is still widely used in regional atmospheric chemistry model systems, e. g. in the community model WRF-chem (Weather Research and Forecasting model including emission, turbulent mixing, transport, transformation, and fate of trace gases and aerosols) (e.g., Grell et al., 2005; Tie et al., 2007). Both RADM2 and RACM have been evaluated with environmental chamber studies (Stockwell et al., 1990, 1997), and the comparison in Stockwell et al. (1997) shows that both predict similar O_3 and NO_2 concentrations for typical atmospheric conditions. Regarding aromatic compounds and biogenically emitted compounds, RACM does provide more detail, however this was not the focus of our conceptual study presented in this paper.

We used the urban plume scenario PLUME 1 by Kuhn et al. (1998), since this case was designed to represent the chemistry in the polluted boundary layer, which is consistent

with our urban plume scenario where emissions of soot occur.

We add the following sentences to the manuscript:

On page 10067, line 17: "RADM2 is widely used in atmospheric models to predict concentrations of oxidants and other air pollutants (e.g., Grell et al., 2005; Tie et al., 2007)."

On page 10067, line 19: "This case was designed to represent the chemistry in the polluted boundary layer, which is consistent with an urban plume scenario where emissions of soot occur."

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 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.

On page 10060, line 13 we state "The new contributions of this study are the coupling of the PRA framework to the gas-phase chemistry and the co-adsorption of multiple gas-phase species with coupled surface reactions. By including the competing effects of O_3, NO_2, and water vapor, the model complexity goes beyond current laboratory experiments, which consider two co-adsorbing gas-phase species at most (e.g., Pöschl et al., 2001). It also places the heterogeneous reactions into a more realistic atmospheric context with atmospheric humidity levels, gas-phase and soot emissions, and diurnal photolysis patterns."

To further highlight the advances compared to the PRA framework, we changed Fig. 2 by adding a panel showing corresponding variations in gas phase concentrations.

We made the following changes to the text to accommodate the new figure (the figure captions have been changed accordingly):

We add the following sentence on page 10073, line 23: "This is shown in Fig. 2G, which presents the gas-phase concentrations and diurnal cycles of O_3, NO_2, NO, and HONO corresponding to scenario A. Since the effect of the surface chemistry on the gas phase is negligible in scenario A, B, and C, the temporal evolution of the gas-phase concentrations in scenarios A, B, and C are identical."

On page 10074, line 5 we replaced "This results in negative γ_{O_3}-values which are indicated by the discontinuations along the abscissa in Fig. 2."

by

"This results in negative γ_{O_3}-values which represent the direct response to the diurnal cycle of gas-phase O_3 as depicted in Fig. 2G and are indicated by the discontinuations along the abscissa in Fig. 2A."

On Page 10074, line 11 we changed "The initial NO_2 uptake exceeds that of O_3 due to a larger accommodation coefficient for NO_2 of $\alpha_{s,0,NO_2} = 0.14$ compared to $\alpha_{s,0,O_3} = 0.001$ for O_3."

to

"Although, NO_2 gas-phase concentrations are lower, the initial NO_2 uptake exceeds that of O_3 due to a larger accommodation coefficient for NO_2 of $\alpha_{s,0,NO_2} = 0.14$ compared to $\alpha_{s,0,O_3} = 0.001$ for O_3."

On Page 10074, line 26 we replaced "O_3 and NO_2 surface concentrations exhibit the same evolution as the corresponding gas-phase concentrations (not shown in Fig. 2B). As O_3 and NO_2 gas-phase concentrations alternate via the tropospheric NO_x-O_3 cycle,

this also induces an alternating evolution of O_3 and NO_2 surface concentrations and uptake coefficients. The resulting maxima of uptake coefficients range from 1×10^{-5} to 1×10^{-4} for γ_{NO_2}, and from 5×10^{-8} to 3×10^{-7} for γ_{O_3} on days two to five."

by

"Since the NO_2 adsorption flux initially exceeds that of O_3, more NO_2 molecules than O_3 molecules are occupying surface sites. Therefore the NO_2 surface concentration exhibits the same temporal evolution as the NO_2 gas-phase concentration, as can be seen by comparing Fig. 2B to Fig. 2G. The O_3 surface concentration increases when surface sites become available from a decrease in the NO_2 surface concentration due to a decrease in the NO_2 gas-phase concentration. The resulting alternating evolution of O_3 and NO_2 surface concentrations also induces an alternating evolution of O_3 and NO_2 uptake coefficients, with maxima ranging from 1×10^{-5} to 1×10^{-4} for γ_{NO_2}, and from 5×10^{-8} to 3×10^{-7} for γ_{O_3} on days two to five."

On Page 1075, line 14 we replaced "As a result, surface concentrations and uptake coefficients of O_3 and NO_2 are reduced by one order of magnitude in comparison to scenario B, as can be seen in Fig. 2C. Lower surface concentrations of O_3 and NO_2 result in slower surface reactions, thereby delaying the production of higher order surface components by over half an order of magnitude. For this reason the uptake coefficients exhibit only two plateaus on the first day, one due to the initial uptake and one governed by the reactions of O_3 with BaP and NO_2 with Y2. On days two to five, the γ_{NO_2} evolution is similar to the one in scenario B, but maximum γ_{NO_2}-values are reduced by over half an order of magnitude in comparison to scenario B. Thus, the NO_2 uptake is too little to considerably alter the gas-phase NO_2 concentration and a feedback on the gas-phase O_3 concentration of the same magnitude as in scenario B does not occur. Therefore, the O_3 surface concentration shows a similar temporal evolution as the one in scenario A where NO_2 adsorption is absent. The H_2O co-adsorption also reduces the maximum γ_{O_3}-values on days two to five by almost one order of magnitude in comparison to scenario B."

by

"This reduces the adsorption fluxes of O_3 and NO_2 and results in a decrease in the surface concentrations and uptake coefficients of O_3 and NO_2 by almost one order of magnitude and half an order of magnitude, respectively, as can be seen by comparison with Fig. 2B. Since O_3 and NO_2 adsorption have little influence on the total surface coverage, their gas-phase uptakes and surface concentrations are not as interdependent as in scenario B. Consequently, both the O_3 and the NO_2 surface concentrations mimic closely their respective gas-phase concentrations, which are depicted in Fig. 2G. Lower surface concentrations of O_3 and NO_2 also result in slower surface reactions, thereby delaying the production of higher order surface components by over half an order of magnitude. For this reason, the uptake coefficients exhibit only two plateaus on the first day, one due to the initial uptake and one governed by the reactions of O_3 with BaP and NO_2 with Y2. On days two to five, the evolution of O_3 and NO_2 uptake coefficients is similar to the one in scenario B, but in comparison to scenario B, maximum γ-values are reduced by up to one order of magnitude."

We add the following sentence on Page 10075, line 28: "The variations in the adsorbents' surface concentrations and uptake coefficients after the first day of the simulation period exemplify the differences to uptake scenarios that do not account for a dynamic gas-phase chemistry, such as the Models Systems Solid 1 and 2 discussed in Ammann and Pöschl (2007). However, as shown in Fig. 2, variations in the adsorbents' gas-phase concentrations have a direct effect on the adsorbents' surface concentrations and, consequently, on their uptake coefficients. By accounting for variable gas-phase concentrations in our coupled PRA framework, we can resolve variations in the uptake coefficient over atmospherically relevant time scales and study the effect of different gas-phase scenarios on the particle surface chemistry."

We add the following sentence on page 10077, line 25 "The diurnal cycle of gas-phase

O$_3$ and the potential decreases in the gas-phase O$_3$ concentration due to the heterogeneous reactions implemented in our model scenarios can be clearly identified."

We add the following sentence on page 10081, line 9: "This allowed us to study, in detail, the heterogeneous kinetics and its dependency on diurnal changes in gas-phase composition due to photochemical processes."

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?

The last sentence of the abstract is changed to the following:

"It yields further insight into the atmospheric importance of the chemical oxidation of particles and emphasizes the necessity to implement detailed heterogeneous kinetics

C1449

in future modeling studies."

Concerning the BaP lifetime, please see also answers to referee 1. We changed the desorption time of H$_2$O to determine its effect on the BaP lifetime. A change in τ_{H_2O} by $\pm$ 10% changes the BaP lifetime by about $\pm$ 5 min.

We add the following sentence on page 10077, line 20, after answer to referee 1: "A variation of the H$_2$O desorption time, τ_{H_2O}, of about $\pm$10% due to possible changes in particle hydrophilicity changes the BaP lifetime by about $\pm$5 min."

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 for NO$_2$ 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 NO$_2$ gas-phase concentrations over wider atmospherically relevant concentration ranges?

To address the points raised by the referee, we add a paragraph on page 10079, line 8: "Since there is a wide range of measured uptake coefficients for NO$_2$ on soot, ranging from smaller than 4×10^{-8} to 0.12 (Aubin and Abbatt, 2007), we also simulated the B-scenarios with accommodation coefficients of α_{NO_2}=10^{-6} (Kleffmann et al., 1999) and α_{NO_2}=10^{-3} (Kirchner et al., 2000). These lower initial uptake coefficients yield, within 1 ppbv, the same gas-phase feedback as the A-scenarios, which have no NO$_2$ co-adsorption implemented. Thus, the gas-phase feedback from the co-adsorption of NO$_2$ obeying an accommodation coefficient smaller than 10^{-3} is negligible."

To test the influence of different gas-phase scenarios on the surface chemistry, we implemented a high NO emission scenario for scenario B shown in the new Fig. 3. The only change to scenario B is a 10-fold increase in the NO emissions rate from

C1450

2.68 pptv min^{-1} to 26.8 pptv min^{-1}. The corresponding figure caption has been added.

We add the following text on page 10075, line 29:

"We investigated the effect of high NO-emissions on the gas phase and particle surface composition of scenario B. The only change to scenario B is a 10-fold increase in the NO emissions rate from 2.68 pptv min^{-1} to 26.8 pptv min^{-1}. The simulation results are shown in Fig. 3. Figure 3G shows the temporal evolution of the gas-phase concentrations of O_3, NO_2, NO, and HONO for this model scenario. While the NO gas-phase concentration increases from 0.2 ppbv to 97 ppbv during the five days simulation period, more NO can react with O_3 to produce NO_2 and O leading to a strong nighttime titration of O_3 from the second to the fifth day. Figure 3B* presents the soot particle's surface concentrations. As can be seen in Fig. 3B*, the O_3 gas-phase depletion is accompanied by a decrease in the O_3 surface concentration. During periods of O_3 depletion, γ_{O_3} becomes negative, since surface desorption exceeds the reduced adsorption from the gas phase. The overall decrease in the O_3 surface concentration delays the production of the surface component Y4 until the fifth day of the simulation period. The decrease in the O_3 surface coverage yields increases in the NO_2 surface concentration resulting in NO_2 saturation with a maximum surface concentration of $1/\sigma_{NO2} = 3 \times 10^{14}$ cm^{-2}. Although only the NO emission rate was changed compared to scenario B, the particle surface compositions of this scenario and of scenario B are significantly different. While in scenario B (see Fig. 2B) the O_3 surface concentration is almost double the amount of the NO_2 surface concentration at the end of the five day simulation period, the sorption layer surface in the high NO emission scenario is almost entirely filled with NO_2 molecules (see Fig. 3B*). This clearly demonstrates that temporal changes in the gas-phase composition can lead to large differences in the particle surface composition."

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). Fur-

ther, 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.

We add the following sentence on page 10062, line 2: "The presented derivations are relevant to couple the gas-phase mechanism RADM2 to the PRA framework (Pöschl et al., 2007; Ammann and Pöschl, 2007). The subsequent equations represent a condensed version of the PRA framework and follow closely its derivations outlined in Pöschl et al. (2007) and Ammann and Pöschl (2007)."

We change the sentence on page 10065, line 18 from "For the cases considered here, we focus on surface reactions between the sorption layer (s) and the quasi-static surface layer (ss) as suggested by previous studies (Pöschl et al., 2001; Ammann et al., 1998; Ammann and Pöschl, 2007)." to "For the cases considered here, we focus on surface reactions between the sorption layer (s) and the quasi-static surface layer (ss) following the derivations by Pöschl et al. (2007) and Ammann and Pöschl (2007)."

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.

We add the following sentence on page 10067, line 17:

"The main feature that RADM2 provides to this study is the NO_x-O_3 chemistry with its diurnal pattern. This results in continuous changes in the O_3 and NO_2 gas-phase concentrations throughout the simulation period.These variations in gas-phase concentrations subsequently affect the magnitude of the individual and combined uptake of O_3 and NO_2 by the soot particles. This investigation of the gas phase-particle surface interrelationship under atmospherically relevant conditions is one of the main foci and and novelty of this study."

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."

Corrected.

*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.

Corrected.

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

Corrected.

*Pg10069 line 1: Initial experiments are performed with a BaP surface coverage of 1×10^{14} 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 covered.

We changed the sentence "While the surface concentration remains constant in this model, the passivation of the surface is introduced by the consumption of the BaP coating, which has initially a surface concentration of 1×10^{14} cm^{-2}." to "While the surface concentration remains constant in this model, the passivation of the surface is introduced by the consumption of the BaP coating, which has initially a surface concentration of 1×10^{14} cm^{-2} corresponding to a full monolayer coverage."

*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

C1453

We changed the title of section 4.3 to "Feedback on the gas-phase O$_3$ concentration with differing uptake and emission scenarios."

Due to the additional simulation results we changed the title of section 4.4 to "Gas-phase O$_3$ feedback for constant uptake parameterizations."

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

Corrected.

References

Ammann, M. and Pöschl, U.: Kinetic model framework for aerosol and cloud surface chemistry and gas-particle interactions - Part 2: Exemplary practical applications and numerical simulations, Atmos. Chem. Phys. , 7, 6025–6045, 2007.

Aubin, D. G. and Abbatt, J. P. D.: Interaction of NO$_2$ with hydrocarbon soot: Focus on HONO yield, surface modification, and mechanism, J. Phys. Chem. A, 111, 6263–6273, doi:10.1021/jp068884h, 2007.

Grell, G. A., Peckham, S. E., Schmitz, R., McKeen, S. A., Frost, G., Skamarock, W. C., and Eder, B.: Fully coupled "online" chemistry within the WRF model, Atmos. Env., 39, 6957–6975, 2005.

Kirchner, U. and Scheer, V. and Vogt, R.: FTIR spectroscopic investigation of the mechanism and kinetics of the heterogeneous reactions of NO$_2$ and HNO$_3$ with soot, J. Phys. Chem. A, 104, 8908–8915, 2000.

Kleffmann, J., Becker, K. H., Lackhoff, M., and Wiesen, P.: Heterogeneous conversion of NO$_2$ on carbonaceous surfaces, Phys. Chem. Chem. Phys., 1, 5443–5450, 1999.

Kuhn, M., Builtjes, P. J. H., Poppe, D., Simpson, D., Stockwell, W. R., Andersson-Skold, Y., Baart, A., Das, M., Fiedler, F., Hov, O., Kirchner, F., Makar, P. A., Milford, J. B., Roemer, M. G. M., Ruhnke, R., Strand, A., Vogel, B., and Vogel, H.: Intercomparison of the gas-phase chemistry in several chemistry and transport models, Atmos. Environ., 32, 693–709, 1998.

Pöschl, U., Rudich, Y., and Ammann, M.: Kinetic model framework for aerosol and cloud sur-

face chemistry and gas-particle interactions - Part 1: General equations, parameters, and terminology, Atmos. Chem. Phys., 7, 5989–6023, 2007.

Stockwell, W. R., Middleton, P., Chang, J. S., and Tang, X. Y.: The 2nd generation regional acid deposition model chemical mechanism for regional air-quality modeling, J. Geophys. Res-Atmos., 95, 16 343–16 367, 1990.

Stockwell, W. R., Kirchner, F., Kuhn, M. and Seefeld, S.: A new mechanism for regional atmospheric chemistry modeling, J. Geophys. Res.-Atmos., 102, 25847–25879, 1997.

Tie, X., Madronich, S., Li, G. H., Ying, Z., Zhang, R., Garcia, A. R., Lee-Taylor, J., and Liu, Y.: Characterizations of chemical oxidants in Mexico City: A regional chemical dynamical model (WRF-Chem) study, Atmos. Env., 41, 1989–2008, 2007.

Figure 2 (revised): The temporal evolution of gas-phase component concentrations (G), surface component concentrations, and uptake coefficients for the adsorption and surface reaction of O_3 (A), the co-adsorption of O_3 and NO_2 (B), and the co-adsorption of O_3, NO_2 and H_2O (C) following the surface reactions defined in Table 1 is plotted on a logarithmic timescale for day one (left panels) and on a linear timescale for the four following days (right panels).

Figure 3 (additional, Figure 4 in manuscript): The temporal evolution of gas-phase component concentrations (G), surface component concentrations, and uptake coefficients for scenario B* are shown and plotted on a logarithmic timescale for day one (left panels) and on a linear timescale for the four following days (right panels). Scenario B* corresponds to scenario B with a 10-fold increase of the NO emission rates.

C1455

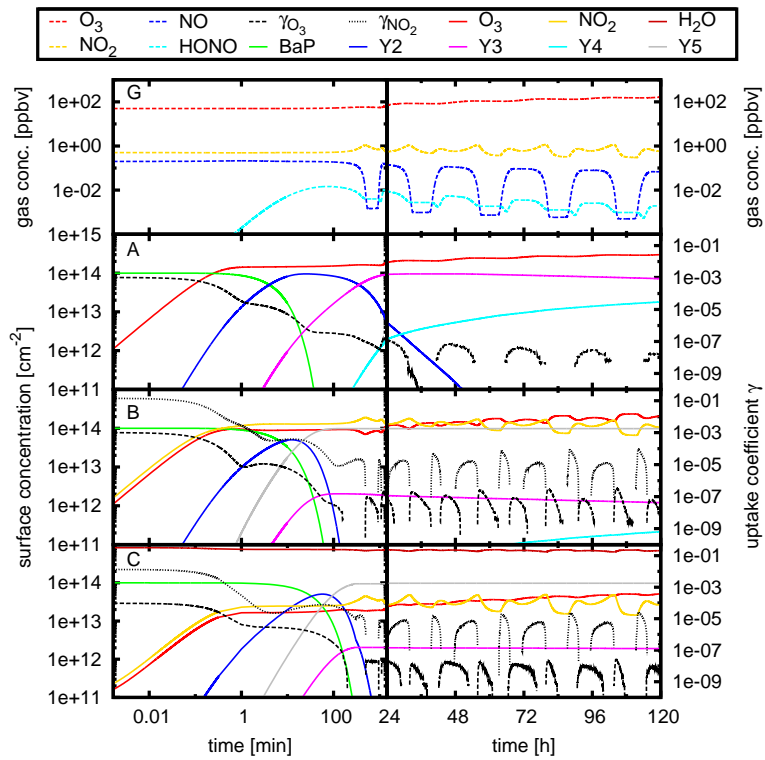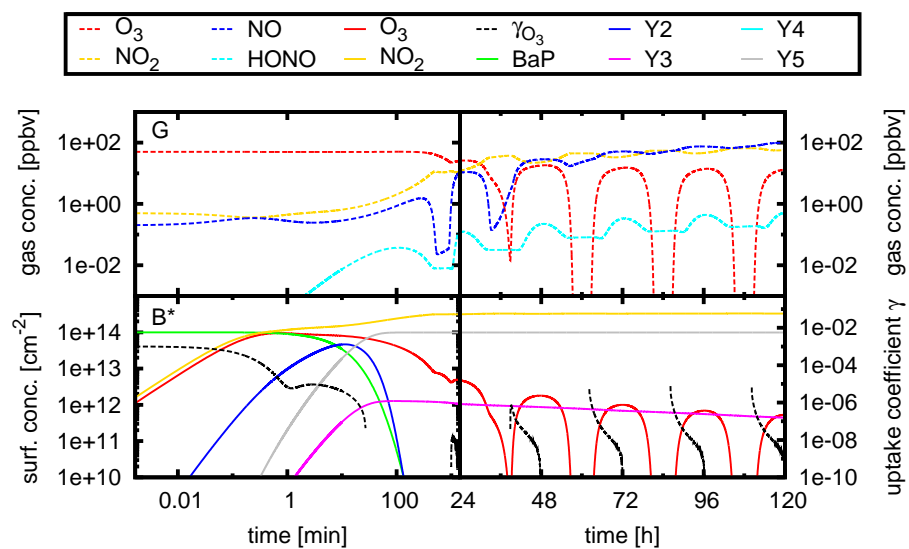springmann_fig2_revised.pdf

C1456

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Fig. 3. Figure 2 revised.

Fig. 4. Figure 3 addition.

C1459