

# Reply to referees

We thank both referees for their useful suggestions how to improve our manuscript. Specific replies are embedded below. The changes we made to the manuscript are highlighted in the attached file diff.pdf.

## Referee #1

*The paper needs expand on its explanation of novel module (i.e. JVAL-13.99gmd) improvements, particularly on physical changes. It would be good to introduce the background of these changes and how to implement them. What scientific advantages would be expected due to these changes?*

As requested, more details are now presented in Sect. 2.2, which describes the physical changes implemented into JVAL.

*The paper would be improved if the authors add a description of how the upgraded photolysis module treats aerosol and cloud. Unlike those of tracer gases, the optical properties of aerosol and cloud depend on particle size distributions and other physical and chemical properties. What is the aerosol speciation considered in the module? Are the aerosols treated as internal mixed or external mixed? Is the cloud microphysics (i.e. cloud droplet size distribution and shape) considered in deriving its optical properties? A good representation of cloud and aerosol is a challenge for an online dynamics photolysis module.*

We apologize that the description of clouds and aerosols was not sufficient. We have now improved the text at three locations:

- We expanded the last paragraph of section 2.1, which summarizes the cloud and aerosol code by Landgraf and Crutzen (1998).
- The distinction between rural and maritime aerosol via the sea-land fraction was not available in the code of Landgraf and Crutzen (1998). This was changed, as described in the first item of section 2.2.
- Our future plans regarding aerosol coupling to other MESSy submodels are described in the second item of the outlook section.

*The paper needs in-depth evaluation and analysis of the module improvement. The authors need not only to show the changes of chemical fields due to the module upgrade, but also to explain the reasons for the changes. The authors could also explain the implication of the changes for air quality and climate. In addition, evaluation of the module improvement using observations is highly desirable. It may be difficult to evaluate the improvement of tracer mixing ratios using observations directly since atmosphere can be a buffer for its photolysis change. However, it is worth trying to evaluate photolysis rates directly using aircraft measurements.*

The full analysis of the impact of photolysis rates on air quality and climate would require several multi-year coupled chemistry-climate simulations (with interactive aerosol for air quality studies). As already mentioned in the text, several chemistry-climate-simulations with the new photolysis code are planned within the “Earth System Chemistry Integrated Modelling (ESCiMo)” initiative (<http://www.pa.op.dlr.de/~PatrickJoeckel/ESCiMo/>). Scientific results of these simulations will

be shown in upcoming publications in other journals. Here, we have specifically chosen the journal “Geoscientific Model Development” because the focus of our manuscript is on a detailed description of the new code, and not on the model results.

Moreover, we show that updating the photolysis rates does not dramatically alter the global model results compared to previous, well evaluated versions (Jöckel et al., 2010). Thus, we believe that other uncertainties in the complex model system are by far larger than the update of the photolysis rates. In other words: the uncertainty of the photolysis rates is not the major issue and therefore not the main reason for deviations between simulations and observations.

| *Please clearly indicate the novel module improvements of this work in abstract.*

The abstract has been extended accordingly.

| *Sections 4.1 and 4.2 seem unnecessary since the authors do not present any evaluations of the photolysis module using these two approaches.*

Indeed, sections 4.1 and 4.2 are not meant to be for evaluation but for different purposes:

In section 4.1, we offer the simple JVAL column model to members of the research community who want to implement their own photolysis reactions into our code.

Section 4.2 specifically addresses the users of the CAABA box model. CAABA is a widely used model of atmospheric chemistry (see e.g., Hosaynali Beygi et al., 2011; Lawler et al., 2011; Klippel et al., 2011; Trebs et al., 2012; van Eijck et al., 2013; Regelin et al., 2013; Hens et al., 2014). We think it is important to announce the updated photolysis module to the CAABA modeling community.

## Referee #2 (S. Madronich)

| *1. Which radiative transfer scheme is used for (a) the high-resolution calculation of the lookup tables, and (b) the lower-resolution on-line calculations?*

The lookup calculations are performed for a purely absorbing atmosphere using the Lambert-Beer absorption law. For the on-line calculations the two-stream Practical Improved Flux Method (PIFM) by Zdunkowski et al. (1980) is employed. We have added this information to the revised manuscript.

| *2. The absorption cross section data are from the MPI spectral data base (Keller-Rudeck et al. 2013). That data base contains multiple spectra measured by different groups, and it is not clear which spectra have been evaluated critically. How were the spectra selected for use in JVAL? Has a critical evaluation been done?*

For most photochemical reactions, we followed the latest JPL recommendations by Sander et al. (2011). If no recommendation was available, we used the most recent measurements, as listed in Table 2. In all cases, the cross section data files were downloaded from the UV/VIS Spectral Atlas by Keller-Rudek et al. (2013).

| *3. How good is the spherical parameterization? The paper by Lamago et al. is mostly for the stratosphere, where photolysis switches rapidly on/off, while in the troposphere one would expect lingering twilight effects. Depending on the radiative scheme, it may be quite easy to put in a pseudo-spherical calculation.*

Indeed, the spherical parameterization can be improved further, especially for solar zenith angles larger than 75°. In a study by Williams et al. (2006), a modified version of the band model by Landgraf and Crutzen (1998) was developed. It can be used for solar zenith angles up to 93°. Although the implementation of this approach into JVAL has not yet been completed, we mention the ongoing work in the outlook section.

| 4. *Is pressure dependence included, and if not, should it be planned for future improvements? It is significant for aldehydes and probably other organics (lower pressure -> less quenching -> larger quantum yields -> faster photolysis).*

Special functions for pressure-dependent cross sections are included for a few molecules (acetone, glyoxal, methacrolein, methyl glyoxal, and MVK). We have added this information to Table 2.

| 5. *Are wavelengths specified in air or vacuum?*

UV/visible cross sections for the chemical reactions were taken from the publications listed in Table 2. We have used the wavelengths as they were presented in these publications, without making any modifications. To determine if the wavelengths refer to air or vacuum, it would be necessary to check if this information can be found in those publications.

| *Related: Table 1 gives band boundaries to 6 significant figures, yet no data (O3 cross section, or extraterrestrial flux) is available with such wavelength accuracy.*

We now present the values with only 4 significant digits.

| *P.2504/L.15-16: The statement that "Absorption by aerosol and cloud particles and other gases play only a minor role..." is potentially misleading. Obviously scattering is very important, and the emphasis here is on absorption, which indeed is usually unimportant for clouds. But absorption can be significant for aerosols, esp. at UV wavelengths, and for gases in some specific situations, e.g. SO2 volcanic plumes.*

We agree that this sentence may be misleading and have removed it.

| *2504/15-16: Absorption ... play -> Absorption ... plays*

Corrected.

| *2504/20: adsorption -> absorption*

Corrected.

| *2504/21-22: The aerosol single scattering albedo is said to be from Table 1 of Slingo (1989) but that table refers to clouds, not aerosols. Can you explain?*

Indeed, the single scatter albedo from Slingo (1989) refers to clouds, not aerosols. For aerosols, we have used the corresponding values from Shettle and Fenn (1979). We have clarified this in the revised text.

2509/20-21: atmosphere well buffered against  $J$  changes?! I doubt that there is any evidence for that. There is a lot of evidence to the contrary, e.g. urban  $O_3$  production scales linearly with  $J$  values, while in cleaner atmospheres  $HO_x$  scales with the square root of  $J$  (due to the  $HO_2+HO_2$  quadratic termination), which is also hardly "buffered". I suggest putting in a citation or removing.

We have removed the remark about buffering. There are probably two main reasons why Fig. 4 only shows small changes in ozone:

1. The UV/VIS spectra did not change much when updating to the latest recommendations.
2. Our plots only show monthly and zonally averaged values. On shorter time scales larger and localized differences occur (not shown). Note, however, that a point-by-point comparison is not feasible here, since although we operated the EMAC Chemistry-Climate Model (CCM) in "nudged mode", the sub-synoptic meteorology is not constrained (different from a Chemical Transport Model, CTM). Thus, the interactive feedback from chemistry to dynamics causes deviating meteorological situations (basically noise) on the sub-synoptic scale. This also influences the calculation of the photolysis rates locally, for instance through differences in the cloud distributions.

| Table 2: is there a cleaner way of citing S.P. Sander et al., e.g. with footnote?

We are not sure what is meant by "cleaner way". If the referee refers to the initials "S. P.", these were added by the Copernicus publisher to distinguish between the authors R. Sander and S. P. Sander.

## References

- Hens, K., Novelli, A., Martinez, M., Auld, J., Axinte, R., Bohn, B., Fischer, H., Keronen, P., Kubistin, D., Nölscher, A. C., Oswald, R., Paasonen, P., Petäjä, T., Regelin, E., Sander, R., Sinha, V., Sipilä, M., Taraborrelli, D., Tatum Ernest, C., Williams, J., Lelieveld, J., and Harder, H.: Observation and modelling of  $HO_x$  radicals in a boreal forest, *Atmos. Chem. Phys.*, 14, 8723–8747, <http://www.atmos-chem-phys.net/14/8723>, 2014.
- Hosaynali Beygi, Z., Fischer, H., Harder, H. D., Martinez, M., Sander, R., Williams, J., Brookes, D. M., Monks, P. S., and Lelieveld, J.: Oxidation photochemistry in the Southern Atlantic boundary layer: unexpected deviations of photochemical steady state, *Atmos. Chem. Phys.*, 11, 8497–8513, <http://www.atmos-chem-phys.net/11/8497>, 2011.
- Jöckel, P., Kerkweg, A., Pozzer, A., Sander, R., Tost, H., Riede, H., Baumgaertner, A., Gromov, S., and Kern, B.: Development cycle 2 of the Modular Earth Submodel System (MESSy2), *Geosci. Model Dev.*, 3, 717–752, <http://www.geosci-model-dev.net/3/717>, 2010.
- Keller-Rudek, H., Moortgat, G. K., Sander, R., and Sörensen, R.: The MPI-Mainz UV/VIS spectral atlas of gaseous molecules of atmospheric interest, *Earth Syst. Sci. Data*, 5, 365–373, <http://www.earth-syst-sci-data.net/5/365>, 2013.

- Klippel, T., Fischer, H., Bozem, H., Lawrence, M. G., Butler, T., Jöckel, P., Tost, H., Martinez, M., Harder, H., Regelin, E., Sander, R., Schiller, C. L., Stickler, A., and Lelieveld, J.: Distribution of hydrogen peroxide and formaldehyde over Central Europe during the HOOVER project, *Atmos. Chem. Phys.*, 11, 4391–4410, <http://www.atmos-chem-phys.net/11/4391>, 2011.
- Landgraf, J. and Crutzen, P. J.: An efficient method for online calculations of photolysis and heating rates, *J. Atmos. Sci.*, 55, 863–878, 1998.
- Lawler, M. J., Sander, R., Carpenter, L. J., Lee, J. D., von Glasow, R., Sommariva, R., and Saltzman, E. S.: HOCl and Cl<sub>2</sub> observations in marine air, *Atmos. Chem. Phys.*, 11, 7617–7628, <http://www.atmos-chem-phys.net/11/7617>, 2011.
- Regelin, E., Harder, H., Martinez, M., Kubistin, D., Tatum Ernest, C., Bozem, H., Klippel, T., Hosaynali-Beygi, Z., Fischer, H., Sander, R., Jöckel, P., Königstedt, R., and Lelieveld, J.: HO<sub>x</sub> measurements in the summertime upper troposphere over Europe: A comparison of observations to a box model and a 3-D model, *Atmos. Chem. Phys.*, 13, 10 703–10 720, <http://www.atmos-chem-phys.net/13/10703>, 2013.
- Sander, S. P., Abbatt, J., Barker, J. R., Burkholder, J. B., Friedl, R. R., Golden, D. M., Huie, R. E., Kolb, C. E., Kurylo, M. J., Moortgat, G. K., Orkin, V. L., and Wine, P. H.: Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Evaluation No. 17, JPL Publication 10-6, Jet Propulsion Laboratory, Pasadena, <http://jpldataeval.jpl.nasa.gov>, 2011.
- Trebs, I., Mayol-Bracero, O. L., Pauliquevis, T., Kuhn, U., Sander, R., Ganzeveld, L., Meixner, F. X., Kesselmeier, J., Artaxo, P., and Andreae, M. O.: Impact of the Manaus urban plume on trace gas mixing ratios near the surface in the Amazon Basin: Implications for the NO-NO<sub>2</sub>-O<sub>3</sub> photostationary state and peroxy radical levels, *J. Geophys. Res.*, 117, D05307, doi:10.1029/2011JD016386, 2012.
- van Eijck, A., Opatz, T., Taraborrelli, D., Sander, R., and Hoffmann, T.: New tracer compounds for secondary organic aerosol formation from  $\beta$ -caryophyllene oxidation, *Atmos. Environ.*, 80, 122–130, 2013.
- Williams, J. E., Landgraf, J., Bregman, A., and Walter, H. H.: A modified band approach for the accurate calculation of online photolysis rates in stratospheric-tropospheric chemical transport models, *Atmos. Chem. Phys.*, 6, 4137–4161, 2006.
- Zdunkowski, W. G., Welch, R. M., and Korb, G.: An investigation of the structure of typical two-stream-methods for the calculation of solar fluxes and heating rates in clouds, *Beitr. Phys. Atmos.*, 53, 147–166, 1980.