Atmos. Chem. Phys. Discuss., 4, S2852–S2854, 2004
www.atmos-chem-phys.org/acpd/4/S2852/
European Geosciences Union

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Model-aided radiometric determination of photolysis frequencies in a sunlit atmosphere simulation chamber" *by* B. Bohn and H. Zilken

B. Bohn and H. Zilken

Received and published: 7 December 2004

We thank referee R. Scheirer for his favourable evaluation and his specific comments which are addressed in detail below.

1. The concept of SAPHIR is somewhat different compared to other simulation chambers (sometimes airily referred to as smog-chambers) many of which are used to study the degradation mechanisms of specific compounds in the atmosphere. The main focus of these studies is the detection and identification of primary and secondary degradation products. Therefore concentration levels and the type and strength of radical sources (including photolyses) are adjusted with respect to the feasibility of the

experiments. As a consequence conditions are often not representative for the atmosphere. In SAPHIR we want to study tropospheric chemistry by monitoring key species like HO_x, RO_x and NO_x in environments of varying complexity in order to understand the dynamics of the chemical system as a whole under conditions close to the natural atmosphere. In that sense SAPHIR experiments can be considered field experiments under conditions controlled with respect to trace gas concentrations and unaffected by transport. Although the advantage of an artificial light source would indeed be its constancy and availability at any time, it is difficult to simulate the spectral properties and intensity of natural sunlight by artificial light sources. For example it is hard to reproduce the typical ratio of photolysis frequencies found in the troposphere, e.g. the ratio $j(O^1D)/j(NO_2)$ which directly affects the relationship between the transient species mentioned above. Moreover, there is a variety of atmospheric photolysis processes not accounted for quantitatively because absorption cross sections and quantum yields are poorly known. Using natural sunlight at least makes sure that the net effect of these unaccounted processes is comparable to ambient conditions. A corresponding note will be added in the introduction.

2. The unknown distribution of sky radiance and possible effects of heterogeneous cloud cover are problems not yet solved. It is difficult to assess the influence of an unknown distribution and we don't think it useful to construct something considered extreme to quantify a possible error. For example, if clear sky conditions were treated as uniform overcast in the model, a relative error of the order 20-30% can be estimated assuming a 50% contribution of direct sunlight. This certainly is an overestimation of possible errors induced by clouds. The problem is also concerned with the final remark by the referee addressing our idea of monitoring sky radiance by a UV sensitive sky imager to create input for the model. We don't think this approach is unrealistic. The main problem will be a technical one, i.e. to set up a sky imager which can deliver a relative distribution of sky radiance in the UV (possibly in various wavelength bands). If an experimental radiance field $L(\vartheta, \varphi)$ were available, implementation into the chamber model merely means insertion into the relevant equations (e.g. Eqs. 18 and 24). The

ACPD

4, S2852–S2854, 2004

limitations of the current approach will be addressed more clearly in the results section.

3. We will try to condense the final procedure of deriving mean actinic flux spectra in a single formula and confine the corresponding explanations on page 23 accordingly.

4. The original calculations of the arrays of s and α for the selected 1400 ϑ, φ combinations (sections 3.1 and 3.2.1) took about two days. With the parameterisation then derived for the quantitiy f^{T} the time to calculate all necessary corrections for one day of spectroradiometer measurements is about 30 s on a personal computer (Pentium 4, 3.0 GHz). The most time-consuming step is the numerical calculation of shadow ring corrections for the time-dependent clear sky radiance distributions (about 0.03 s each).

Interactive comment on Atmos. Chem. Phys. Discuss., 4, 6967, 2004.