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HO_x Budgets during HO_xComp: a Case Study of HO_x Chemistry under NO_x limited Conditions

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Recent studies have shown that measured OH under NO_x limited, high isoprene conditions are many times higher than modelled OH. In this study, a detailed analysis of the HO_x radical budgets under low NO_x, rural conditions was performed employing a box model based on the Master Chemical Mechanism (MCMv3.2). The model results were compared with HO_x radical measurements performed during the international HO_xComp campaign carried out in Jülich, Germany during summer, 2005. Two different air masses influenced the measurement site denoted as high NO_x (NO: 1-3 ppbv) and low NO_x (NO: $<$1 ppbv) periods. Both modelled OH and HO_2 diurnal profiles lay within the measurement range of all HO_x measurement techniques, with correlation slopes between measured and modelled OH and HO_2 around unity. Recently discovered interference in HO_2 measurements caused by RO_2 cross-sensitivity was found to cause a 30 % increase in measured HO_2 during daytime on average. After correction of the measured HO_2 data, the model HO_2 is still in good agreement with the observations at high NO_x, but overpredicts HO_2 by a factor of 1.3 to 1.8 at low NO_x. In addition, for two different set of measurements, a missing OH source of 3.6$\pm$1.6 and 4.9$\pm$2.2 ppb h^{-1} was estimated from the experimental OH budget during the low NO_x period using the corrected HO_2 data. The measured diurnal profile of the HO_2/OH ratio, calculated using the corrected HO_2, is well reproduced by the MCM at high NO_x, but is significantly overestimated at low NO_x. Thus, the cycling between OH and HO_2 is better described by the model at high NO_x than at low NO_x. Therefore, similar comprehensive field measurements accompanied by model studies are urgently needed to investigate HO_x recycling under low NO_x conditions.