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

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Recent studies have shown that measured OH radical concentrations under low NO_x, rural conditions are many times higher than modelled OH, from which NO independent OH regeneration pathways were proposed. In this study, a detailed analysis of the HO_x radical budgets under low NO_x, rural conditions were investigated employing a zero dimensional photochemical box model based on the Master Chemical Mechanism (MCMv3.1). The model results were compared and contrasted with highly reliable HO_x radical measurements performed during the international HO_xComp campaign carried out in Jülich, Germany during summer, 2005. Two different air masses were experienced by the measurement site denoted as high NO_x (1-3 ppbv) and low NO_x (<1 ppbv) periods. Excellent agreement was obtained between measured and modelled OH radical levels, while HO_2 was slightly overestimated with measured to model ratio of 0.98 and 0.85, respectively. Average modelled reactivities during the high and low NO_x periods of 8.0 s^{-1} and 8.6 s^{-1} were also in excellent agreement with that measured. A balance ratio (BR) between the secondary radical production and destruction near unity was obtained during the high NO_x period owing to the high recycling efficiency. However, during the low NO_x period, a BR ratio of only 0.75 was obtained indicating net secondary radical loss owing to the low recycling efficiency. In addition, under low NO_x condition, significant fraction of the OH radical recycling processes occur without NO through P_{OH}(ROOH+hv) and P_{OH}(HO_2+O_3). During the high and low NO_x periods, O_3 had the highest contribution of 48 % and 57 % to the OH initiation sources followed by HONO (46 %, 34 %) and alkene ozonolysis (6 %, 9 %), respectively.