The Influence of Temperature on Ozone Production under varying NO_x Conditions – a modelling study

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Abstract

Surface ozone is a secondary air pollutant produced during the atmospheric photochemical degradation of emitted volatile organic compounds (VOCs) in the presence of sunlight and nitrogen oxides (NO_x). Temperature directly influences ozone production through speeding up the rates of chemical reactions and increasing the emissions of VOCs, such as isoprene, from vegetation. In this study, we used an idealised box model with different chemical mechanisms (MCMv3.2, CRIv2, MOZART-4, RADM2, CB05) to examine the non-linear relationship between ozone, NO_x and temperature, and compared this to previous observational studies. Under high-NO_x conditions, an increase in ozone from 20 °C to 40 °C of up to 20 ppbv was due to faster reaction rates while increased isoprene emissions added up to a further 11 ppbv of ozone. The largest inter-mechanism differences were obtained at high temperatures and high-NO_x emissions. CB05 and RADM2 simulated more NO_x-sensitive chemistry than MCMv3.2, CRIv2 and MOZART-4 which could lead to different mitigation strategies being proposed depending on the chemical mechanism. The increased oxidation rate of emitted VOC with temperature controlled the rate of O_x production, the net influence of peroxy nitrates increased net O_x production per molecule of emitted VOC oxidised. The rate of increase in ozone mixing ratios with temperature from our box model simulations was about half the rate of increase in ozone with temperature observed over central Europe or simulated by a regional chemistry transport model. Modifying the box model setup to approximate stagnant meteorological conditions increased the rate of increase of ozone with temperature as the accumulation of oxidants enhanced ozone production through the increased production of

peroxy radicals from the secondary degradation of emitted VOCs. The box model simulations approximating stagnant conditions and the maximal ozone production chemical regime reproduced the 2 ppbv increase in ozone per °C from the observational and regional model data over central Europe. The simulated ozone-temperature relationship was more sensitive to mixing than the choice of chemical mechanism. Our analysis suggests that reductions in NO_x emissions would be required to offset the additional ozone production due to an increase in temperature in the future.