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Effects of seasonal changes on the oxidation capacity of the city air of Santiago de Chile

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A strong seasonal dependence of the pollutant concentration in the city of Santiago de Chile has been previously reported in different studies. In this study the effects of seasonal changes on the oxidation capacity has been analysed during summer and winter. The oxidation capacity of the highly polluted urban area of Santiago de Chile has been evaluated during a winter measurement campaign from June 25 - July 07, 2005 and the results were compared with those previously evaluated during the summer campaign from March 8 – 20, 2005. The hydroxyl (OH) radical budget was evaluated in both campaigns employing a simple quasi-photostationary-state model (PSS) constrained with simultaneous measurements of HONO, HCHO, O_3, NO, NO_2, $j(O^1D)$, $j(NO_2)$, 13 alkenes and meteorological parameters. In addition, a zero dimensional photochemical box model based on the Master Chemical Mechanism (MCMv3.1) has been used to estimate production rates and total free radical budgets, including OH, HO_2 and RO_2. Besides the above parameters, the MCM model has been constrained by the measured CO and volatile organic compounds (VOCs) including alkanes and aromatics. The mixing ratios of the trace gasses were generally higher during the winter than the summer. The evaluated daytime peak OH radical concentration during winter was $\sim 3 \times 10^6$ which is about 5 times lower than that during the summer. However, both PSS and MCM models showed the same OH radical budget during daytime for both summer and winter which indicates that the primary OH sources and sinks included in the simple PSS model are predominant. On a 24-h basis, HONO photolysis was shown to be the most important primary OH radical source comprising alone more than $\sim$52%, $\sim$66% of the total initial production rate during summer and winter, respectively followed by alkene ozonolysis, $\sim$ 24%, 30% and photolysis of HCHO $\sim$ 16 %, 3% and O_3 $\sim$ 5 %, $<$1%, respectively. The impact of the seasonal change on the radical budgets has been discussed.