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Atmos. Chem. Phys., 9, 2257–2273, 2009

www.atmos-chem-phys.net/9/2257/2009/

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Oxidation capacity of the city air of Santiago, Chile

Y. F. Elshorbany^{1,2}, R. Kurtenbach¹, P. Wiesen¹, E. Lissi³, M. Rubio³, G. Villena³, E. Gramsch⁴, A. R. Rickard⁵, M. J. Pilling⁶, and J. Kleffmann¹¹Physikalische Chemie, FB C, Bergische Universität Wuppertal, Gaußstraße 20, 42119 Wuppertal, Germany²Environmental Sciences Division, National Research Center, Dokki, Giza, Egypt³Faculty of Chemistry and Biology, University of Santiago de Chile, USACH, Alameda L. Bernardo O'Higgins 3363, Santiago, Chile⁴Physics Department, Faculty of Science, University of Santiago de Chile, Alameda L. Bernardo O'Higgins 3363, Santiago, Chile⁵National Centre for Atmospheric Science, University of Leeds, Leeds, UK⁶School of Chemistry, University of Leeds, Leeds, UK

Abstract. The oxidation capacity of the highly polluted urban area of Santiago, Chile has been evaluated during a summer measurement campaign carried out from 8–20 March 2005. The hydroxyl (OH) radical budget was evaluated employing a simple quasi-photostationary-state model (PSS) constrained with simultaneous measurements of HONO, HCHO, O₃, NO, NO₂, $j(\text{O}^1\text{D})$, $j(\text{NO}_2)$, 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, HO₂ and RO₂. Besides the above parameters, the MCM model has been constrained by the measured CO and volatile organic compounds (VOCs) including alkanes and aromatics. Both models simulate the same OH concentration during daytime indicating that the primary OH sources and sinks included in the simple PSS model predominate. Mixing ratios of the main OH radical precursors were found to be in the range 0.8–7 ppbv (HONO), 0.9–11 ppbv (HCHO) and 0–125 ppbv (O₃). The alkenes average mixing ratio was ~58 ppbC accounting for ~12% of the total identified non-methane hydrocarbons (NMHCs). During the daytime (08:00 h–19:00 h), HONO photolysis was shown to be the most important primary OH radical source comprising alone ~55% of the total initial production rate, followed by alkene ozonolysis (~24%) and photolysis of HCHO (~16%) and O₃ (~5%). The calculated average and maximum daytime OH production rates from HONO photolysis was 1.7 ppbv h⁻¹ and 3.1 ppbv h⁻¹, respectively. Based on the experimental results a strong photochemical daytime source of HONO is proposed. A detailed analysis of the sources of OH radical precursors has also been carried out.

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Citation: Elshorbany, Y. F., Kurtenbach, R., Wiesen, P., Lissi, E., Rubio, M., Villena, G., Gramsch, E., Rickard, A. R., Pilling, M. J., and Kleffmann, J.: Oxidation capacity of the city air of Santiago, Chile, Atmos. Chem. Phys., 9, 2257–2273, 2009. [Bibtex](#) [EndNote](#) [Reference Manager](#)

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