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Evaluation of the volatility basis-set approach for the simulation of organic aerosol formation in the Mexico City metropolitan area

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Abstract. New primary and secondary organic aerosol modules have been added to PMCAMx, a three dimensional chemical transport model (CTM), for use with the SAPRC99 chemistry mechanism based on recent smog chamber studies. The new modelling framework is based on the volatility basis-set approach: both primary and secondary organic components are assumed to be semivolatile and photochemically reactive and are distributed in logarithmically spaced volatility bins. This new framework with the use of the new volatility basis parameters for low-NO_x and high-NO_x conditions tends to predict 4–6 times higher anthropogenic SOA concentrations than those predicted with the older generation of models. The resulting PMCAMx-2008 was applied in Mexico City Metropolitan Area (MCMA) for approximately a week during April 2003 during a period of very low regional biomass burning impact. The emission inventory, which uses as a starting point the MCMA 2004 official inventory, is modified and the primary organic aerosol (POA) emissions are distributed by volatility based on dilution experiments. The predicted organic aerosol (OA) concentrations peak in the center of Mexico City, reaching values above 40 μg m^{-3}. The model predictions are compared with the results of the Positive Matrix Factorization (PMF) analysis of the Aerosol Mass Spectrometry (AMS) observations. The model reproduces both Hydrocarbon-like Organic Aerosol (HOA) and Oxygenated Organic Aerosol (OOA) concentrations and diurnal profiles. The small OA underprediction during the rush-hour periods and overprediction in the afternoon suggest potential improvements to the description of fresh primary organic emissions and the formation of the oxygenated organic aerosols, respectively, although they may also be due to errors in the simulation of dispersion and vertical mixing. However, the AMS OOA data are not specific enough to prove that the model reproduces the organic aerosol observations for the right reasons. Other combinations of contributions of primary and secondary organic aerosol production rates may lead to similar results. The model results strongly suggest that, during

the simulated period, transport of OA from outside the city was a significant contributor to the observed OA levels. Future simulations should use a larger domain in order to test whether the regional OA can be predicted with current SOA parameterizations. Sensitivity tests indicate that the predicted OA concentration is especially sensitive to the volatility distribution of the emissions in the lower volatility bins.