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Global modelling of secondary organic aerosol from α-pinene oxidation using a parameterization based on a detailed chemical mechanism

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Monoterpenes are oxidized in the atmosphere by ozone and the hydroxyl and nitrate radicals. The condensable products resulting from these reactions contribute to Secondary Organic Aerosol (SOA). We have developed a detailed α-pinene chemical mechanism BOREAM (Capouet et al. 2008), in which the primary gas phase chemistry is based on quantum-chemical results, structure activity relationships and experimental data. The secondary chemistry of the most important products is treated explicitly, while further chemistry is reduced by the aid of generic species classes. The partitioning between gas phase and SOA is modeled using Pankow's partitioning approach (Pankow 1994), with vapor pressures (Capouet and Müller 2006) and activity coefficients (Compernolle et al. 2009) obtained from group contribution methods.

We will discuss the performance of BOREAM through comparison of model predictions for SOA formation with experimental SOA yields for a large number (>150) of photo-oxidation and dark ozonolysis experiments (Ceulemans et al. 2009). Although the BOREAM SOA yields are significantly higher than in several previous box modeling studies, a reasonable agreement is found in comparison with most laboratory measurements.

For use in a global model, the detailed BOREAM chemistry is replaced by a parameterized scheme based on the two-product approach (Odum et al. 1996) with parameters obtained through regressions of full model simulations. The reduced scheme accounts for the dependence of SOA yield on the oxidant (ozone, OH or NO_3) and the NOx regime. For example, the reaction of alpha-pinene with OH generates a peroxy radical which, upon reaction with either NO or HO_2 leads to the formation of two condensable products. The branching ratios and partitioning coefficients are temperature dependent.

We inserted the obtained parameterized scheme in the global model IMAGES, where it is used to represent the SOA formation due to the monoterpenes. For aromatics, isoprene and sesquiterpenes we use two-product parameterizations based on smog chamber studies. Irreversible SOA formation due to polymerization of short-chained aldehydes (glyoxal, methylglyoxal, etc.) and direct emission of POA are also considered. Monoterpenes are estimated to contribute about 20-40 TgOA/year globally, i.e. a factor 2-4 higher than in previous modeling studies. This large contribution stems from the high SOA yields (of the order of 50% in atmospheric conditions) obtained using BOREAM at low NOx in the the oxidation of α-pinene by OH. These high yields result from the predicted formation of highly condensable polyfunctional compounds (e.g. hydroxy-dihydroperoxides). Possible uncertainties on these estimates will be discussed on the basis of sensitivity tests with the full mechanism.

The calculated OA concentrations are compared with a large number of ground-based (IMPROVE, CARBOSOL, etc.) and aircraft (INTEX-A and ACE-1) measurements. Whereas a relatively good agreement is found over both Eastern and Western US, large OA underestimations are generally found over Europe, Africa and Asia. Possible causes will be discussed.

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