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

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Introduction

A new parameterization for SOA formation due to α-pinene oxidation is developed for use in global CTMs. It is based on BOREAM, a detailed gas-phase chemical mechanism coupled to an SOA formation module. Evaluation of BOREAM against a large number of photo-oxidation experiments shows a fairly good agreement (factor of 2) in most cases. For use in a global CTM, a 10-product scheme is developed, with coefficients fitted to the full mechanism. Implementation into global CTM IMAGES results in a large estimated contribution of monoterpenes to the global organic aerosol (OA) budget, of the order of 50% overall, i.e. a factor of 4 higher than in previous model studies.

Detailed Mechanism for SOA formation

The detailed α-pinene mechanism of the BOREAM model (Capouet al., 2008), is based on advanced quantum chemical calculations, structure-activity relationships and experimental data. Secondary chemistry (i.e. further oxidation of the primary products) is treated using generic species classes. The partitioning between gas phase and SOA is modeled using Pankow’s partitioning approach (Pankow, 1994), with activity coefficients (Compernolle et al., 2009) obtained from group contribution methods.

Parameterization of SOA formation

For use in a global model, the detailed BOREAM chemistry is replaced by a parameterized scheme based on the number of photo-oxidation and dark ozonolysis smog chamber experiments were modeled (Capouet al., 2008, Ceulemans et al., 2010), and modeled and experimental SOA yields were found to agree within a factor 2 in most cases. The temperature dependence of modeled yields was too strong compared to experiment however, with underestimations at high temperatures. Yields in the low NOx photo-oxidation experiments of Ng et al. (2007) were slightly overestimated.

Global Modeling

The parameterization has been implemented in the global CTM IMAGESv2 (Stavracou et al., 2009), where it is used to represent SOA formation due to the monoterpenes. For isoprene, aromatics and sesquiterpenes/monoterpenes, we use two product parameterizations based on smog chamber studies. SOA formation resulting from the in-cloud oxidation and polymerization of short-chain aldehydes (glyoxal and methylglyoxal) as well as direct emission of Primary Organic Aerosols (POA) are also considered.

Monoterpenes are estimated to contribute to 40-50 Tg C/yr, i.e. a factor of 4 higher than in previous model studies. This contribution is particularly high over tropical and boreal forests, due to the high SOA yields estimated by BOREAM in low NOx conditions.

Comparisons with observations

Figure 6: Seasonal variation of modeled and observed OC concentrations averaged over 4 large sections (corresponding to the 4 colors on Figure 7) for 1999-2001. The overestimation in summer over the western US, and in autumn and winter over Europe, is due to an overestimation of SOA production in this region.

Figure 7: Vertical profiles of modeled and observed water-soluble organic carbon (WSOC) concentrations during the NEAQS campaign in NE U.S. (Jul-Aug 2004) and during the INTEX-B campaign over Mexico and the Western U.S. (Mar-Apr 2006). The observed profile shapes are well reproduced by the model, although large uncertainties in NEU.S. and underestimations in Mexico, (U.S.) are found.

References

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Figure 8: Annual averaged Organic Aerosol (OA) concentrations, estimated by IMAGES including the parameterization for monoterpane SOA. Large OA concentrations (10+ μg m⁻³) are generally associated with strong PGE emissions due to vegetation fires (e.g. in the Amazon basin) and anthropogenic activities (over India and China). SOA is especially significant over the Eastern U.S. and to a lesser extent over Boreal and Tropical forests.

Figure 9: Site locations