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Systematic reduction of complex tropospheric chemical mechanisms, Part I: sensitivity and time-scale analyses

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Abstract. Explicit mechanisms describing the complex degradation pathways of atmospheric volatile organic compounds (VOCs) are important, since they allow the study of the contribution of individual VOCS to secondary pollutant formation. They are computationally expensive to solve however, since they contain large numbers of species and a wide range of time-scales causing stiffness in the resulting equation systems. This paper and the following companion paper describe the application of systematic and automated methods for reducing such complex mechanisms, whilst maintaining the accuracy of the model with respect to important species and features. The methods are demonstrated via application to version 2 of the Leeds Master Chemical Mechanism. The methods of Jacobian analysis and overall rate sensitivity analysis proved to be efficient and capable of removing the majority of redundant reactions and species in the scheme across a wide range of conditions relevant to the polluted troposphere. The application of principal component analysis of the rate sensitivity matrix was computationally expensive due to its use of the decomposition of very large matrices, and did not produce significant reduction over and above the other sensitivity methods. The use of the quasi-steady state approximation (QSSA) proved to be an extremely successful method of removing the fast time-scales within the system, as demonstrated by a local perturbation analysis at each stage of reduction. QSSA species were automatically selected via the calculation of instantaneous QSSA errors based on user-selected tolerances. The application of the QSSA led to the removal of a large number of alkoxy radicals and excited Criegee bi-radicals via reaction lumping. The resulting reduced mechanism was shown to reproduce the concentration profiles of the important species selected from the full mechanism over a wide range of conditions, including those outside of which the reduced mechanism was generated. As a result of a reduction in the number of species in the scheme of a factor of 2, and a reduction in stiffness, the computational time required for simulations was reduced by a factor of 4 when compared to the full scheme.

Final Revised Paper (PDF, 2806 KB) Discussion Paper (ACPD)

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