

Home

Online Library ACP

- Recent Final Revised Papers
- Volumes and Issues**
- Special Issues
- Library Search
- Title and Author Search

Online Library ACPD

Alerts & RSS Feeds

General Information

Submission

Review

Production

Subscription

Comment on a Paper

Impact
Factor
4.865

ISI
indexed



[Volumes and Issues](#) [Contents of Issue 7](#)

Atmos. Chem. Phys., 4, 2025-2056, 2004

www.atmos-chem-phys.net/4/2025/2004/

© Author(s) 2004. This work is licensed under a Creative Commons License.

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

L. E. Whitehouse¹, A. S. Tomlin¹, and M. J. Pilling²

¹Energy and Resources Research Institute, University of Leeds, Leeds LS2 9JT, UK

²School of Chemistry, University of Leeds, Leeds LS2 9JT, UK

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)

Citation: Whitehouse, L. E., Tomlin, A. S., and Pilling, M. J.: Systematic reduction of complex tropospheric chemical mechanisms, Part I: sensitivity and time-scale analyses, Atmos. Chem. Phys., 4, 2025-2056, 2004. [Bibtex](#) [EndNote](#) [Reference Manager](#)

Search ACP

Library Search

Author Search

News

- [Sister Journals AMT & GMD](#)
- [Financial Support for Authors](#)
- [Journal Impact Factor](#)
- [Public Relations & Background Information](#)

Recent Papers

01 | ACPD, 06 Mar 2009: Lightning characteristics observed by a VLF/LF lightning detection network (LINET) in Brazil, Australia, Africa and Germany

02 | ACP, 06 Mar 2009: Summertime PM_{2.5} ionic species in four major cities of China: nitrate formation in an ammonia-deficient atmosphere

03 | ACPD, 05 Mar 2009: A~model study of the January 2006 low total ozone episode over Western Europe and comparison with ozone

