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Quantitative assessment of uncertainties for a model of tropospheric ethene oxidation using the European Photoreactor (EUPHORE)

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Abstract

Methods of uncertainty analysis were used for comparison of the Master Chemical Mechanism version 3 (MCMv3) with measurements made in the European Photoreactor (EUPHORE) at Valencia (Spain) to investigate model–measurement discrepancies and to obtain information on the importance of wall effects. Two EUPHORE smog chamber measurements of ethene oxidation, under high and low NO_x conditions were analysed by the following methods: (i) local uncertainty analysis, (ii) the global screening method of Morris and (iii) Monte Carlo (MC) analysis with Latin hypercube sampling. For both experiments, ozone (by 25% and 30%, respectively) and formaldehyde (by 34% and 40%, respectively) are significantly over-predicted by the model calculations, while the disagreement for other species is less substantial. According to the local uncertainty analysis and the Morris method, the most important contributor to ozone uncertainty under low NO_x conditions is $HOCH_2CH_2O_2 + NO \rightarrow HOCH_2CH_2O + NO_2$, while under high NO_x conditions $OH + NO_2 \rightarrow HNO_3$ is the main contributor. The MC simulations give an estimate of the 2σ uncertainty for ozone as ~20% in both scenarios at the end of the experiment. The results suggest systematic disagreement between measurements and model calculations, although the origin of this is not clear. It seems that chamber effects alone are not responsible for the observed discrepancies.

Keywords: Uncertainty analysis; European photoreactor; Master chemical mechanism; Ethene; Smog chamber; Wall effects; Monte Carlo; Morris method

1. Introduction

In the past decades, several detailed models have been developed to represent photochemical processes in the troposphere (Kerr and Calvert, 1985; Derwent et al., 1996; Jenkin et al., 1997). In spite of the huge efforts, both experimental and theoretical, tropospheric chemical mechanisms are still imperfect and remain under continuous development. The applicability of outdoor environmental chambers for the testing of the oxidation mechanism of volatile organic compounds (VOCs) is still not well-known, mainly because of the ill-defined wall effects (Dodge, 2000).

Measurement–model inconsistencies derive from three sources. (i) Measurement errors can be either statistical or systematic and the latter can be significant. (ii) Errors introduced by the operating conditions

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include heterogeneous reactions, such adsorption, desorption and transformation of molecules on the wall of the chamber or on aerosol particles. Some of these act as a continuous radical source and can thus strongly influence the overall chemistry. Poorly characterised solar radiation inside the chamber, uncertainties in the initial conditions and inhomogeneities (e.g., in temperature) inside the chamber provide further sources of error. (iii) Uncertainties are also present in the reaction mechanism. Rate coefficients always have associated uncertainties, which can lead to significant errors in the calculated concentration profiles.

In the recent review of Dodge (2000), the performance of various photochemical oxidation mechanisms was investigated in comparison with chamber experiments. Uncertainties in the peak ozone concentration were found to be as high as 30% due to the combination of uncertainties in the chemical kinetic data and uncertain chemical processes related to the chambers, such as heterogeneous reactions and photolysis rates.

In the present work, uncertainty analysis is applied for the degradation scheme of ethene in the Master Chemical Mechanism version 3 (MCMv3, Jenkin et al., 1997, 2003; Saunders et al., 2003) to reveal if model–measurement discrepancies are significant and to estimate the importance of chamber effects. Measurements of ethene oxidation in the European Photoreactor (EUPHORE) chambers in Valencia (Spain) were used to give more insight into chamber dependent processes (see also Bloss et al., 2005). The analysis was carried out for two particular measurements, one with a low and one with a high initial NO_x/ethene ratio.

After a brief description of the degradation of ethene in the troposphere, technical aspects of the MCMv3 are given, highlighting features which are important for the uncertainty analysis. A short description of the EUPHORE chambers, relevant to this work, is also provided. The mathematical–statistical background to the applied methods of uncertainty analysis is outlined in Section 3 along with the determination of uncertainty estimates and probability distribution functions (pdfs) of the model parameters. The significance of model–measurement discrepancies and the impact of wall effects are discussed in Section 4, which is followed by conclusions.

2. The model and the measurements

2.1. The chemical model

The MCM (Jenkin et al., 1997) is an explicit atmospheric kinetic model. The present work is based on the MCMv3, which is the latest version and is mounted on the Web (Saunders et al., 2003; Jenkin et al., 2003; http://mcm.leeds.ac.uk//MCM). The rate coefficients in the mechanism are based on kinetic and photochemical data evaluations (Atkinson et al., 2002; Sander et al., 2002; hereinafter these will be referred along with the past editions to as IUPAC and JPL compilations, respectively). If evaluated data are not available, unevaluated measurement data or estimates based on analogy, structure-activity relations (SAR) (Kwok and Atkinson, 1995) or ab initio calculations are used. Some groups of reactions are characterised by generic rate coefficients.

Photolysis rates in the MCMv3 protocol are parameterised functions of the solar zenith angle and are based on calculations with typical values of radiation parameters. Rate coefficients were originally calculated by the Fortran program UVFLUX (Hayman, 1997). In the present simulations, the time dependence of the formulae was corrected using the code of Giesen (2001) so as to have the maximum photolysis frequency at the exact noon by shifting the original curve (see Table 3). Complete agreement between calculated and measured photolysis rates cannot be expected, because the standard parameters used in the fitting procedure do not apply to the actual measurement conditions. Therefore, photolysis rate coefficients were scaled with respect to the measured $j(NO_2)$ values.

The mechanism of ethene oxidation consists of three parts. The first describes ethene oxidation pathways, the second the inorganic reactions, while the third characterises the chamber effects, such as wall reactions and dilution. The latter is referred to as the auxiliary mechanism and is not part of the MCMv3, but based on characterisation experiments. The mechanism contains 46 species and 141 chemical reactions. Details can be found at the MCM website. The key reactions, which are discussed in greater detail in Section 4 are presented in Table 1.

Table 1
Major reaction steps of ethene oxidation in the troposphere

Radical formation (initiation)	
$HONO + h\nu \rightarrow OH + NO$	(R1)
$HCHO + h\nu \rightarrow 2HO_2 + CO$	(R2)
Propagation	
$C_2H_4 + OH \rightarrow HOCH_2CH_2O_2$	(R3)
$HOCH_2CH_2O_2 + NO \rightarrow HOCH_2CH_2O + NO_2$	(R4)
$HOCH_2CH_2O \rightarrow 2HCHO + HO_2$	(R5)
$HO_2 + NO \rightarrow OH + NO_2$	(R6)
$HO_2 + O_3 \rightarrow OH$	(R7)
$OH + HCHO \rightarrow HO_2 + CO$	(R8)
Radical loss (termination)	
$OH + NO_2 \rightarrow HNO_3$	(R9)
$HOCH_2CH_2O_2 + HO_2 \rightarrow HOCH_2CH_2O_2H$	(R10)
$2HO_2 \rightarrow H_2O_2$	(R11)
NO_x chemistry	
$NO + O_3 \rightarrow NO_2$	(R12)
$NO_2 + h\nu \rightarrow NO + O_3$	(R13)