Local and Global Uncertainty Analysis
of Complex Chemical Kinetic Systems

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Abstract: Computer modelling plays a crucial part in the understanding of complex chemical processes. Parameters of elementary chemical and physical processes are usually determined in independent experiments and are always associated with uncertainties. Two typical examples of complex chemical kinetic systems are the combustion of gases and the photochemical processes in the atmosphere. In this study, local uncertainty analysis, the Morris method, and Monte Carlo analysis with Latin hypercube sampling were applied to an atmospheric and to a combustion model. These models had 45 and 37 variables along with 141 and 212 uncertain parameters, respectively. The toolkit used here consists of complementary methods and is able to map both the sources and the magnitudes of uncertainties. In the case of the combustion model, the global uncertainties of the local sensitivity coefficients were also investigated and the order of parameter importance based on local sensitivities were found to be almost independent of the parameter values within their range of uncertainty.

Keywords: local uncertainty analysis, Morris method, Monte Carlo method, atmospheric chemistry, combustion modelling, mechanism validation

1. UNCERTAINTY ANALYSIS METHODS

Uncertain parameters used in a model give rise to uncertainties in simulation results. Highly nonlinear models tend to magnify the uncertainty of some parameters and damp the uncertainty of others. There is a wide range of methods for uncertainty analysis [1], which differ from each other in their applicability to different types of models, in the scope of information provided, and in the level of sophistication and computational demand. For chemical kinetic models, the most comprehensive task is the conversion of the joint probability density function (*pdf*) of the parameters into the *pdf*'s of the simulation results. A more modest request is the estimation of the variance of results from the variance of parameters. In this work, several types of uncertainty methods were used and the uncertainty indicators obtained from them were compared.

1.1. Local Uncertainty Analysis

Local uncertainties were calculated by combining local sensitivity coefficients s_{ij} [2] with uncertainty estimates of the input parameters [3]. An individual contribution $\sigma_j^2(c_i)$ of rate coefficient k_j to the total uncertainty of concentration c_i can be expressed as:

$$\sigma_j^2(c_i) = \sigma^2(\ln k_j)\left(\frac{\partial c_i}{\partial \ln k_j}\right)^2,$$

(1)

where $\sigma^2(\ln k_j)$ is the variance of the logarithm of rate coefficient k_j. The overall variance $\sigma^2(c_i)$ of the output concentration c_i is:

$$\sigma^2(c_i) = \sum_j \sigma_j^2(c_i).$$ (2)

The individual contribution of k_j can be expressed as percentage s_{ij} %:

$$s_{ij}\% = \sigma_j^2(c_i)/\sigma^2(c_i) \times 100.$$ (3)

The main drawback of this method is that the linearity assumption is applied for a highly nonlinear chemical kinetic model.

1.2. Morris Method

Morris method is a screening method [1]. Screening methods are relatively cheap, compared to Monte Carlo (MC) type methods, but are investigating the model on a global range, i.e. the input parameters are varied over the whole range of their possible values. In the Morris method, the uncertainty is characterised by a value called *effect*, which is assigned to each uncertain parameter for each investigated output result. This effect is calculated several times, by varying the input parameter set according to a given algorithm. The results of the Morris analysis are usually shown on a graph, where the horizontal axis refers to the mean of the calculated effects, while the vertical axis represents the standard deviation of the effects.

This procedure enables the selection of important parameters, by evaluating the model with various input parameter sets. Besides importance, information on the type of the effect of the parameter is also obtained: it is possible to distinguish parameters with linear effects from parameters with nonlinear or interaction effects. The drawback of this method is that it does not provide information on the magnitude of the uncertainty of the output variables. The other weakness of this method is that it does not take the shape of the *pdf* of the parameters into account.

1.3. Monte Carlo Simulations with Latin Hypercube Sampling

The above methods are computationally cheap, but are not able to provide the exact and unbiased *pdf* of the output values. For this reason, Monte Carlo type simulations were also carried out. To keep the number of runs as low as possible, Latin hypercube sampling was applied. This sampling covers the parameter space with minimal sample size and in an unbiased manner [1]. The number of runs was 3000 in all calculations.

1.4. Assignment of Uncertainties to Parameters

Great attention was paid to the careful selection of input uncertainties. Uncertainty factors were collected from chemical databases [4-7], which are critically evaluated and are frequently updated. These factors were converted to the variance of the parameters using the method described in article [3]. If no uncertainty factor was found for a reaction, then a thorough literature search was carried out and this factor was estimated. The *pdf* of the parameters were also established; lognormal distribution was assumed for rate coefficients, normal distribution for heat-of-formation data, and uniform distribution for parameters of other type (e.g. channel ratios).

2. UNCERTAINTY ANALYSIS OF A PHOTOCHEMICAL AIR POLLUTION MODEL

2.1. Brief Description of the Model

Detailed uncertainty analysis was carried out on the photochemical degradation model of ethene that is implemented in the Master Chemical Mechanism version 3 (MCMv3) [8]. The MCMv3 is an explicit chemical mechanism, containing the photochemical degradation scheme of more than 120 volatile organic compounds, and incorporating approximately 10000 reactions of 2500 species. The initial compounds in our model were ethene (C_2H_4) and nitrogen oxides (NO_x). The submechanism of ethene degradation contains 141 reactions of 45 chemical species. For brevity, in this paper the results concerning the uncertainty of ozone (O_3) concentration are discussed only. Ozone is one of the most important photochemical pollutants and the prediction of its concentration from the initial concentration of pollutants is crucial. More results are presented in a recently submitted paper [9].

2.2. Experimental Results

The methods of uncertainty analysis were developed for comparison with measurements made in the European Photoreactor (EUPHORE) at Valencia, Spain. This is a so-called smog chamber, where the chemical compounds are injected into a tent having Teflon walls, and their concentration–time profiles are followed by state-of-the-art analytical instrumentation. There are three sources of error when chemical models are tested against smog chamber measurements: (i) measurement errors, (ii) errors introduced by chamber specific effects and (iii) errors and uncertainties in the model itself. Our work aimed to reveal the significance of the various error sources.

The ethene oxidation model was tested at two experimental circumstances: one with a high, the other with a low initial NO_x concentration. Fig. 1 shows that the slope of the calculated maximal ozone concentration depends on the ratio of the initial ethene and NO_x concentration. The two cases that we selected represent two fundamentally different regions according to this plot. In the low NO_x case, changing the initial ethene concentration does not effect the maximal ozone concentration, while in the other case ozone increases with increased initial ethene concentration.
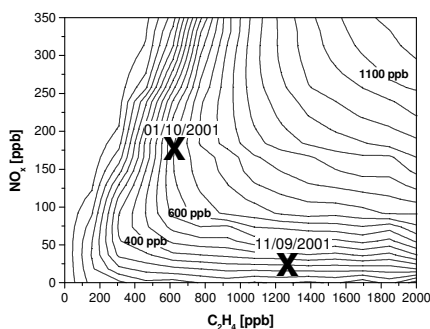

Figure 1. Simulated maximal ozone concentrations as a function of initial concentrations. The 'X' signs show the initial concentrations for the two investigated experiments.
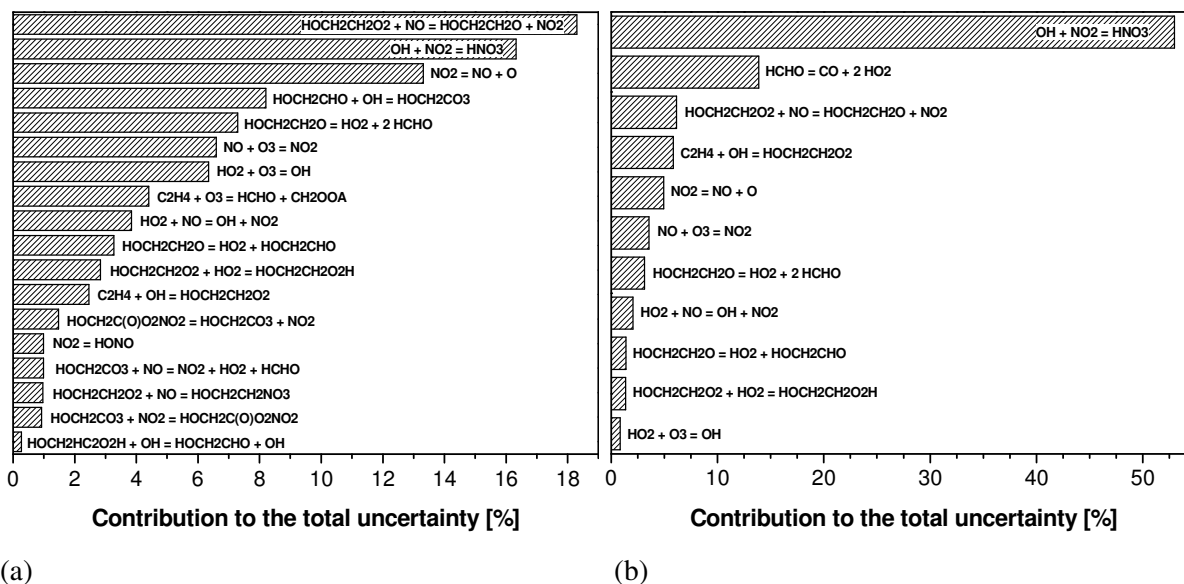
Figure 2. Contribution of the uncertainty of the rate coefficients to the uncertainty in the calculated ozone concentration at the end of the experiment at (a) low and (b) high NO_x conditions as determined by local uncertainty analysis.

2.3. Results for the Atmospheric Chemical Model

2.3.1. Local uncertainty analysis

Fig. 2 shows reactions with the highest uncertainty contribution s_{ij} % (see Equation (3)) to the calculated final O_3 concentration. The cut-off criterion was 1 % compared to the reaction having the highest uncertainty contribution. It is well visible that in the low NO_x case more reactions have significant contribution to the uncertainty of the ozone concentration.

In the low NO_x case reactions $HOCH_2CH_2O_2 + NO = HOCH_2CH_2O + NO_2$, $OH + NO_2 = HNO_3$ and $NO_2 = NO + O$ account for about 50 % of the total O_3 uncertainty. The overall 2σ uncertainty for ozone, calculated by Equation (2), is 20 %. In the high NO_x case, more than 50 % of the total uncertainty in ozone originates from reactions $HCHO + h\nu = 2HO_2 + CO$ and $OH + NO_2 = HNO_3$. The overall uncertainty of calculated ozone concentration at the final time was found to be 29 %.

2.3.2. Morris analysis

Fig. 3 shows the results of the Morris analysis for ozone. The mean values are in excellent accordance with the results of the local uncertainty analysis. The standard deviations provide interesting insights into the linearity assumption used, because ranking the rate coefficients according to their standard deviation differs from the ranking that results from the means. Under both conditions, the reactions of the $HOCH_2CH_2O_2$ and $HOCH_2CH_2O$ molecules are ranked higher on the standard deviation scale than on the mean scale. This can be due to the fact, that these parameters are important only in a period of the oxidation.
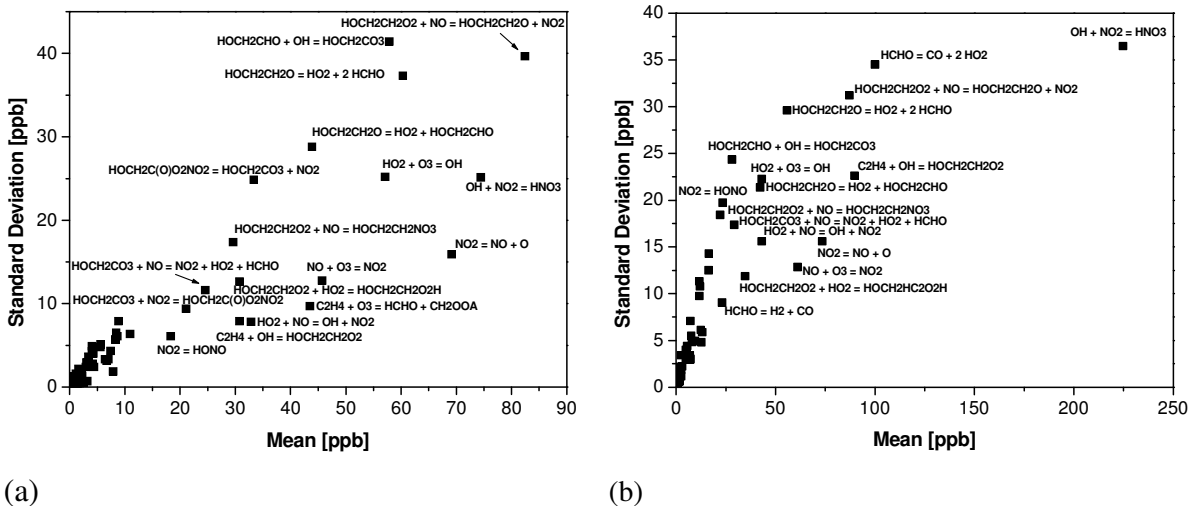
Figure 3. The mean and the standard deviation effects, calculated with the Morris method for O_3 in the (a) low and (b) high NO_x case.

In both cases, less than 20 out of the 141 reactions are responsible for most of the uncertainties in the final ozone concentration. The mean values of the effects in the high NO_x case are twice those in the low NO_x case. However, the standard deviations are about the same, which suggests that the nonlinear behaviour is about the same for the two experiments. There is a significant correlation between the mean and the standard deviation: rate coefficients with great absolute effects tend to have high nonlinear effects as well.
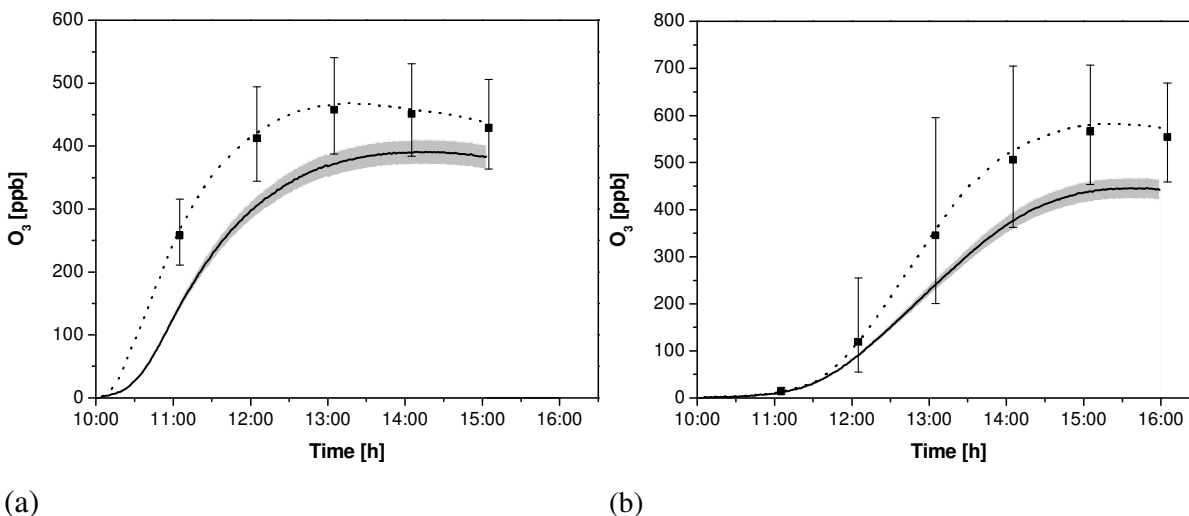

Figure 4. Comparison of modelled and measured concentrations of ozone and their associated uncertainties. Measurement and associated uncertainty (2σ): black line with grey band; model mean and its uncertainty (2σ): black dots and error bars; simulation with nominal parameter values: dotted line.

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2.3.3. Monte Carlo simulations

Fig. 4 compares the uncertainty ranges of the measurements with that of the MC analysis results. The latter indicated that the distribution of the calculated ozone concentration is always nearly lognormal, while measurement uncertainties were assumed to be normally distributed. The overlap of the 2σ uncertainty limits of the measurement and model calculation is marginal, which suggests a systematic over-prediction of ozone concentration. There are difficulties in simulating both the rise time and the peak O_3 concentration. The uncertainty contribution of reaction $OH + NO_2 = HNO_3$ is high to the ozone concentration uncertainty (see Figs. 2 and 3). The rate coefficient of this reaction has been extensively studied recently [4], therefore it is expected that the uncertainty of the rate coefficient of this reaction will decrease significantly in the near future. In this case, uncertainty in the high NO_x case will drop significantly and consequently the overlap is likely to disappear.

3. UNCERTAINTY ANALYSIS OF A METHANE FLAMES

3.1. Brief Description of the Methane Oxidation Mechanism

Until recently, there are only few applications of uncertainty analysis to the investigation of complex combustion mechanisms. In our combustion calculations, a stationary, laminar methane flame was investigated and the simulations were performed with the Leeds Methane Oxidation Mechanism [10]. This chemical mechanism contains 175 chemical reactions and 37 chemical species. Our aim was to determine the uncertainty of simulation results caused by the uncertainty of thermodynamic and kinetic parameters. The investigated results included the concentration maximum of some important species (H, O, OH, CH, CH_2), the maximum temperature, and the laminar flame velocity (v_L); the latter number is characteristic to a freely propagating flame and is often used when model and measurement are compared [11]. The simulations were carried out with the CHEMKIN-II package [12] and with program KINALC [10]. In this paper results only for the stoichiometric case are presented.
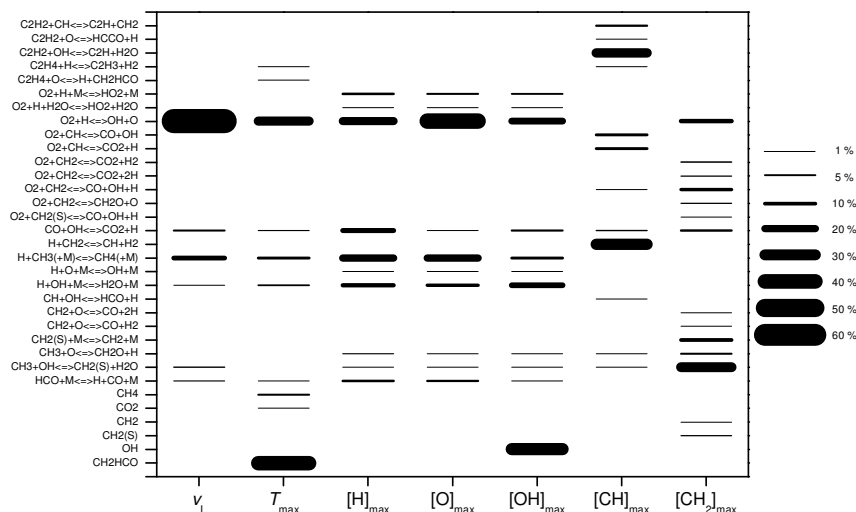

Figure 5. The percentage contributions are shown for those input parameters (rate coefficients of reactions and heat-of-formation of species), which contribute at least by 1 % to the uncertainty of at least one investigated result (see the horizontal axis). Uncertainty contributions are expressed in percentages, and the thickness of the line is proportional to the percentage value (see scale).
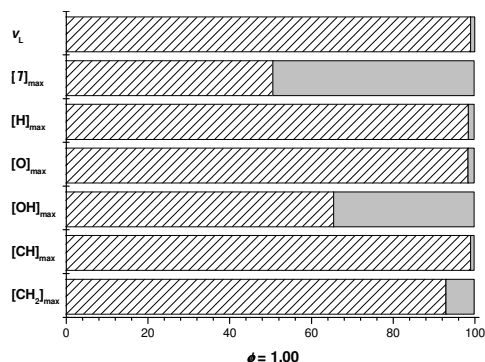
Figure 6. Kinetic (striped) and thermodynamic (grey) contributions to the total uncertainty of the monitored parameters calculated from local uncertainty analysis and expressed as percentages.

3.2. Results for the Combustion Model

3.2.1. Local Uncertainties

The results of the local uncertainty are summarised on a blob graph, show in Figure 5. It can be seen that only 33 out of the 212 parameters contribute at least with 1 % to the total uncertainty to any of the investigated parameters. Moreover, there are only few really important contributors, from which the most important is reaction of $O_2 + H = OH + O$.

In Figure 6, the contributions of the kinetic and thermodynamic parameter uncertainties are compared. For most of the investigated outputs, the effect of kinetic uncertainties is much greater than that of the thermodynamic ones. The two exceptions are the calculated flame temperature and the calculated OH concentration. Therefore, uncertainties arising from thermodynamic data cannot be neglected in a mechanism validation procedure.

3.2.2. Morris Method

Results of Morris method are in accordance with the local uncertainty analysis. The tendency that greater standard deviation belongs to greater mean effect is also observed in this case.

3.2.3. Monte Carlo Analysis

As a result of MC simulations, *pdf*s of the monitored output variables were obtained, from which a selection can be seen in Figure 7. These distributions have a high variability in both shape and width. The overall 1σ standard deviation for the laminar flame velocity is 12 %, for the temperature 0.1 %, while for the concentration of the CH radical is 46 %.
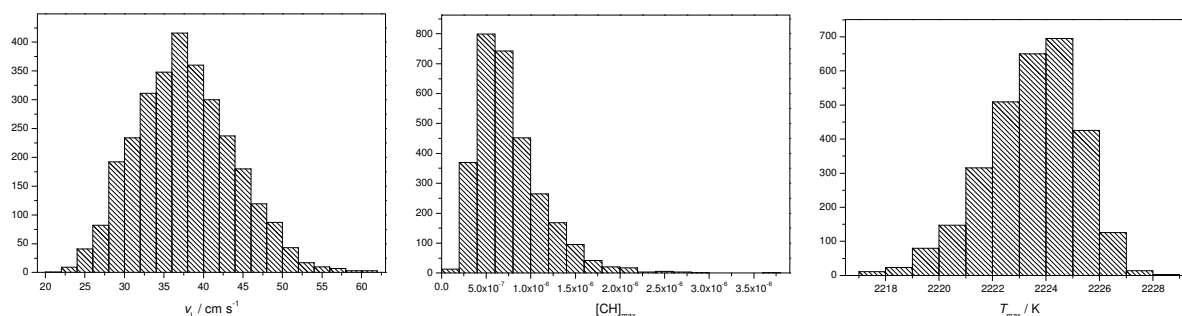

Figure 7. Distribution of some selected results in a stoichiometric methane flame, as obtained from MC simulations.
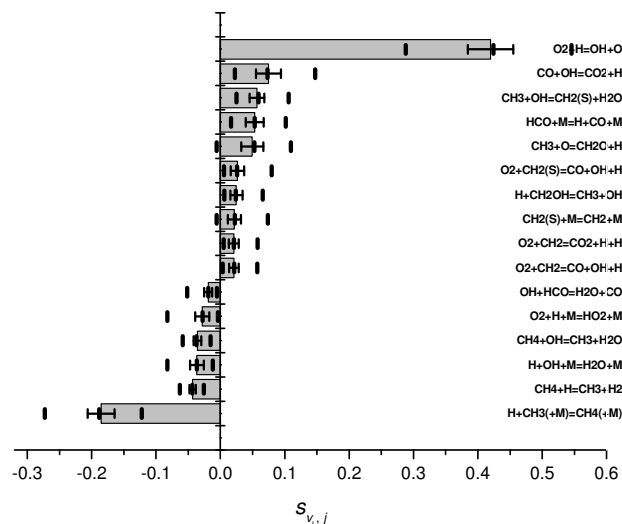
Figure 8. Result of global sensitivity analysis of the local sensitivity coefficients for the laminar flame velocity of a stoichiometric methane–air flame. Only those reactions are shown, whose rate parametric sensitivities are greater than 5% of that of the highest sensitivity one. Grey stripes refer to the local sensitivity coefficients at the nominal parameter set, small bars interconnected with a vertical line indicate the 1σ uncertainty interval of local sensitivity coefficients, and outer larger bars show the attainable minimum and maximum sensitivity coefficients at any parameter set within the uncertainty limits of parameters.

3.3. Global Uncertainty of Local Sensitivity Coefficients: A Numerical Approach

During the MC simulations, all parameters were varied simultaneously within their uncertainty limits and the first-order local sensitivity coefficients of rate parameters were calculated in each run. By processing the results, the global uncertainties of the local sensitivities were obtained. Figure 8 shows that for the laminar flame velocity sensitivities the 1σ uncertainty limits are relatively narrow. Looking at the possible extremes of the calculated local sensitivity coefficients, it can be seen that the sensitivity coefficients almost never change their sign. The small variation of the calculated sensitivity coefficients within the uncertainty range of parameters means that the rank order of importance of kinetic parameter as deduced by the local sensitivity coefficients is basically independent of the values of parameters within their range of uncertainty. This figure shows only a representative example, but very similar figures were obtained for the other variables and at other fuel-to-air ratios.

4. CONCLUSIONS

The two most significant areas of applications of large reaction mechanisms are the simulation of tropospheric chemical systems and the combustion of fuels. In these fields, the most important topics include the prediction of maximum generated ozone concentration at given conditions, and the simulation of methane flames. In this paper, we presented uncertainty analysis results for models of both types. Uncertainties of simulation results were calculated by local methods and Monte Carlo analysis, and also contribution of the various parameters to the uncertainty of the results were investigated by local sensitivity analysis and the Morris method. The surprising joint experience from the two calculations is that few parameters cause most of the uncertainties. The atmospheric chemical and the combustion models contained 141 and 212 uncertain parameters, respectively, and only about 30 parameters had noticeable

contribution to the uncertainty of any of the important results. This means that knowing better a few parameters only may significantly improve the quality of simulations in atmospheric chemistry and combustion science, which are among the most important fields of application of complex reaction mechanisms.

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