Local and global uncertainty analysis of complex chemical kinetic systems

J. Zádor*, I.Gy. Zsély, T. Turányi

Department of Physical Chemistry, Eötvös University (ELTE), H-1518 Budapest, P.O. Box 32, Hungary

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Abstract

Computer modelling plays a crucial part in the understanding of complex chemical reactions. 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.
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1. Uncertainty analysis methods

Uncertain parameters used in a model may 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 pdfs 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

$$\sigma_j^2(c_i) = \sigma^2(\ln k_j)\left(\frac{\partial c_i}{\partial \ln k_j}\right)^2, \tag{1}$$

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:

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

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

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

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

*Corresponding author. Fax: +36 1 372 2592.
  E-mail address: zador@chem.elte.hu (J. Zádor).

model. The main advantage is the low computational cost that is gained in turn.

1.2. Morris method

Morris method is a screening method [1,4]. Screening methods are relatively cheap, compared to Monte Carlo (MC) type methods, but also investigate 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 of the results 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. In this work we have used the improved Morris method, where the absolute values of the effects are considered [5]. 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 provided, since it is possible to distinguish parameters with linear effects from parameters with nonlinear or interaction effects. The drawback of this method is that it cannot quantify the uncertainty of the results because it does not take the pdfs 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 [6] 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 each calculation.

1.4. Assignment of uncertainties to parameters

Great attention was paid to the careful selection of input uncertainties, which is often one of the most time-consuming parts of the analysis, and where the judgement of professionals of the field plays a crucial role. Uncertainty factors for the rate coefficients and for the enthalpy-of-formation data were collected from chemical kinetic and thermodynamic databases [7–10], which were critically evaluated and are frequently updated. These factors were converted to the variance of the parameters using the method described in the 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 pdfs of the parameters were also established; lognormal distribution was assumed for rate coefficients, normal distribution for the enthalpy-of-formation data, and uniform distribution for parameters of other type (e.g. channel ratios of reactions).

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 had been implemented in the Master Chemical Mechanism version 3 (MCMv3) [11]. The MCMv3 is an explicit chemical mechanism, containing the photochemical degradation scheme of more than 120 volatile organic compounds (VOCs), and incorporating approximately 10,000 reactions of 2500 species. The initial compounds in the submechanism used in this article are ethene (C_2H_4) and nitrogen oxides (NO, NO_2), and this model contains 141 reactions of 45 chemical species. The rate coefficient of each reaction was treated as uncertain. For brevity, in this paper only the results concerning the uncertainty of ozone (O_3) and formaldehyde (HCHO) concentrations are discussed.

Ozone is one of the most important photochemical pollutants and the prediction of its concentration from the initial concentrations of VOCs and nitrogen oxides is crucial. Formaldehyde also plays a very important role in the oxidation scheme of many VOCs. It is responsible for several chemical processes, in which it accelerates the chain reaction of VOC degradation, through the recycling of radicals that are formed during the photolysis of formaldehyde. In this paper we briefly describe the uncertainty analysis of this model, with some representative results. More detailed results and further discussions are presented in a recently submitted paper [12].

2.2. Experimental results

Uncertainty analysis for tropospheric ethene oxidation was developed for the interpretation of 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 various analytical instrumentation. The volume of the chamber is approximately $200 \, m^3$. 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 by means of finding those parameters, which have the highest contribution to the overall uncertainty of the most important variables, such as the concentrations of ozone and formaldehyde.

2.3. Results for the atmospheric chemical model

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 calculated maximal ozone concentration depends on the initial ethene and NO_x concentrations in a nonlinear manner. It can be seen that the gradient of the ozone surface is qualitatively different at high and at low ethene-to-NO_x ratios, so the two selected cases represent two fundamentally different regions according to this plot. In the low NO_x case, changing the initial ethene concentration does not affect the maximal ozone concentration, while in the other case ozone increases with increased initial ethene concentration.

In the low NO_x experiment the initial concentrations of NO, NO_2, and C_2H_4 were 39, 9, and 1259 ppb, respectively. In the high NO_x case the initial concentrations of NO, NO_2, and C_2H_4 were 175, 23, and 613 ppb, respectively. Temperature and pressure in the chamber were monitored, and the corresponding values were about 30 °C and 10^5 Pa, respectively. Each experiment lasted for 6 h. The calculations were done with program FACSIMILE [13], and with purpose written Fortran programs.

2.3.1. Local uncertainty analysis

Fig. 2 shows reactions with the highest uncertainty contribution s_{ij} % (see Eq. (3)) to the calculated final HCHO concentration at the end of the experiment. The sensitivity coefficients were calculated by the brute force method [2], by increasing each rate coefficient by 1% of the nominal value. The cut-off criterion on the figures was 10% 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 formaldehyde concentration.

In the low NO_x case reactions $HCHO = H_2 + CO$, $HCHO = 2HO_2 + CO$ and $C_2H_4 + OH = HOCH_2CH_2O_2$

Fig. 1. Simulated maximal ozone concentrations as a function of the initial concentrations of C_2H_4 and NO_x. The * signs show the initial concentrations for the two investigated experiments.

(a) **Contribution to the total uncertainty %**

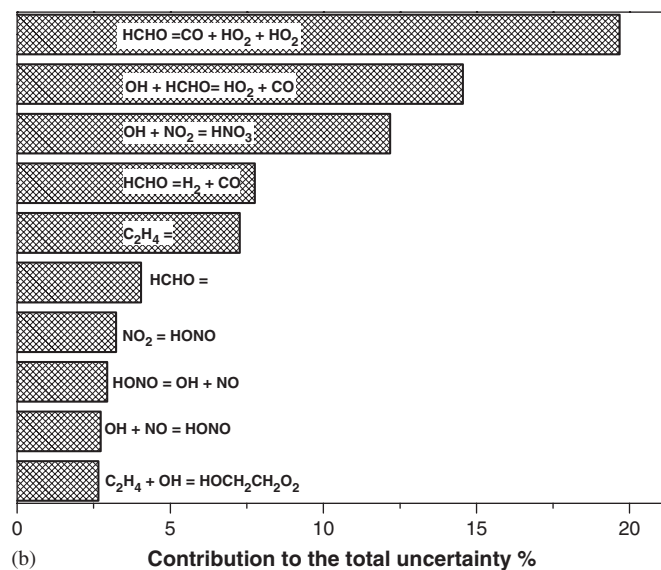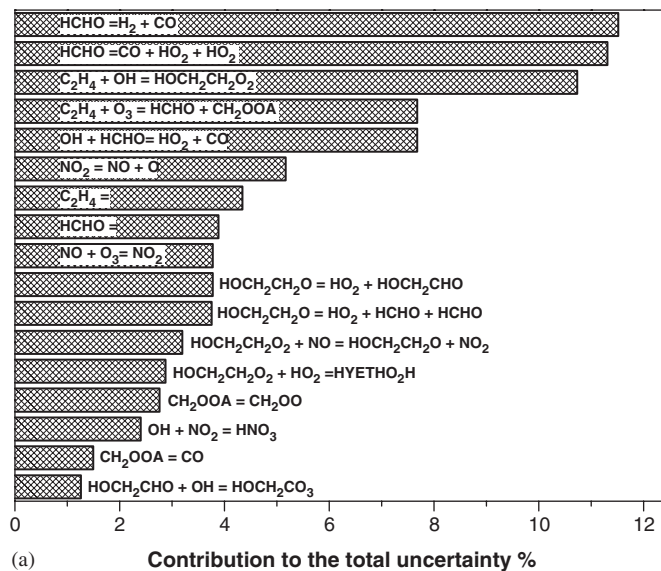(b) **Contribution to the total uncertainty %**

Fig. 2. Contribution of the uncertainty of the rate coefficients to the uncertainty in the calculated formaldehyde concentration at the end of the experiment at (a) low and (b) high NO_x conditions as determined by local uncertainty analysis.

account for well above 30% of the total HCHO uncertainty. The overall 2σ uncertainty for formaldehyde, calculated by Eq. (2), is 20%. In the high NO_x case, more than 20% of the total uncertainty in formaldehyde originates from reactions $HCHO = 2HO_2 + CO$ and $OH + NO_2 = HNO_3$. The overall uncertainty of the calculated formaldehyde concentration at the final time was found to be 30%. Results for ozone concentration were similar to those of formaldehyde: in the high NO_x case significantly fewer reactions have substantial contribution to the ozone uncertainty than in the low NO_x case.

2.3.2. Morris analysis

Fig. 3 shows the results of the Morris analysis for formaldehyde. The mean values are usually in fairly good
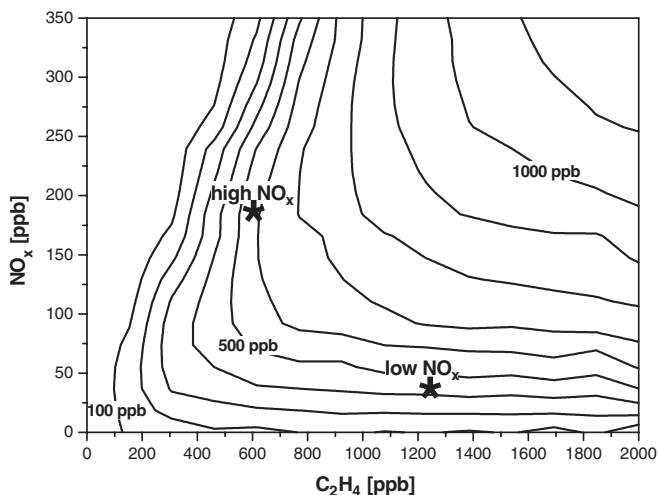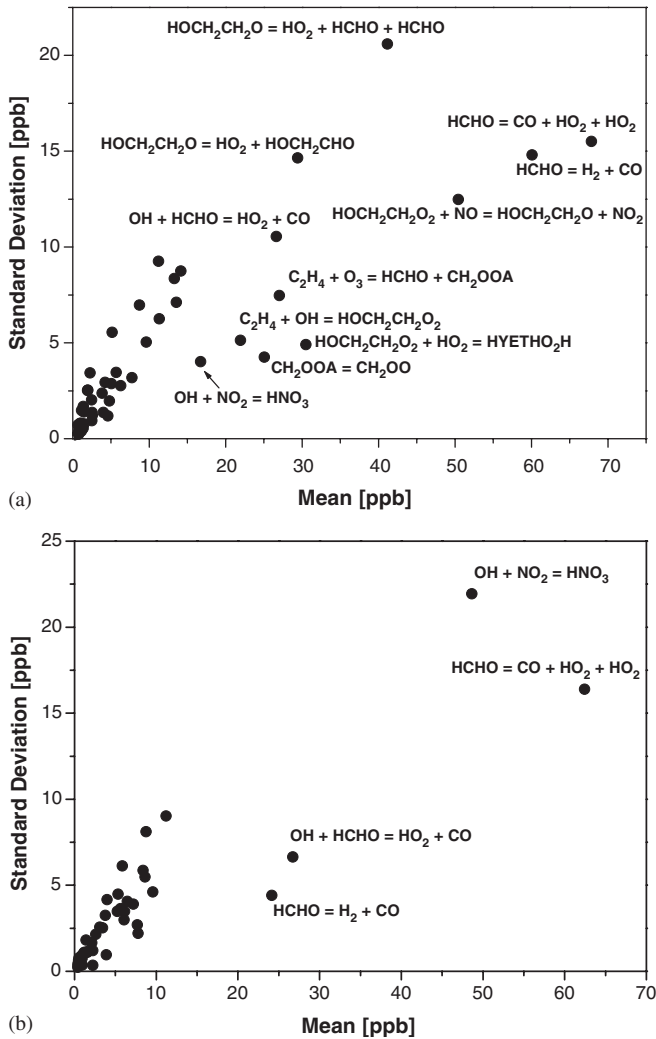
(a)

(b)

Fig. 3. The mean and the standard deviation effects, calculated with the Morris method for formaldehyde in the (a) low and (b) high NO_x case.

accordance with the results of the local uncertainty analysis. The ranking based on the mean values differ in some cases significantly from the ranking obtained from the local analysis. For example, in the low NO_x case reaction $C_2H_4 + OH = HOCH_2CH_2O_2$ was the third most influential in the local analysis, while the Morris analysis shows only a medium importance for this reaction. 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 high NO_x 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. In the high NO_x case, reaction $OH + NO_2 = HNO_3$ has a very high nonlinear or interaction characteristic in its contribution to the uncertainty.

In the low NO_x case approximately 10, and in the high NO_x case only 4 reactions out of the 141 reactions are responsible for most of the uncertainties in the final

formaldehyde concentration. The mean values and the standard deviations of the effects are about the same for both cases, 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 [1].

2.3.3. Monte Carlo simulations

Fig. 4 compares the uncertainty ranges of the measurements with that of the MC analysis results. MC estimates of the uncertainties in the calculated formaldehyde concentrations were determined in every exact hour of the experiments. The MC calculations indicated that the distribution of the calculated formaldehyde concentration is always nearly lognormal, while measurement uncertainties were assumed to be normally distributed. The overlap of the 2σ uncertainty limits of the experimental values and the model results is marginal, which suggests a systematic
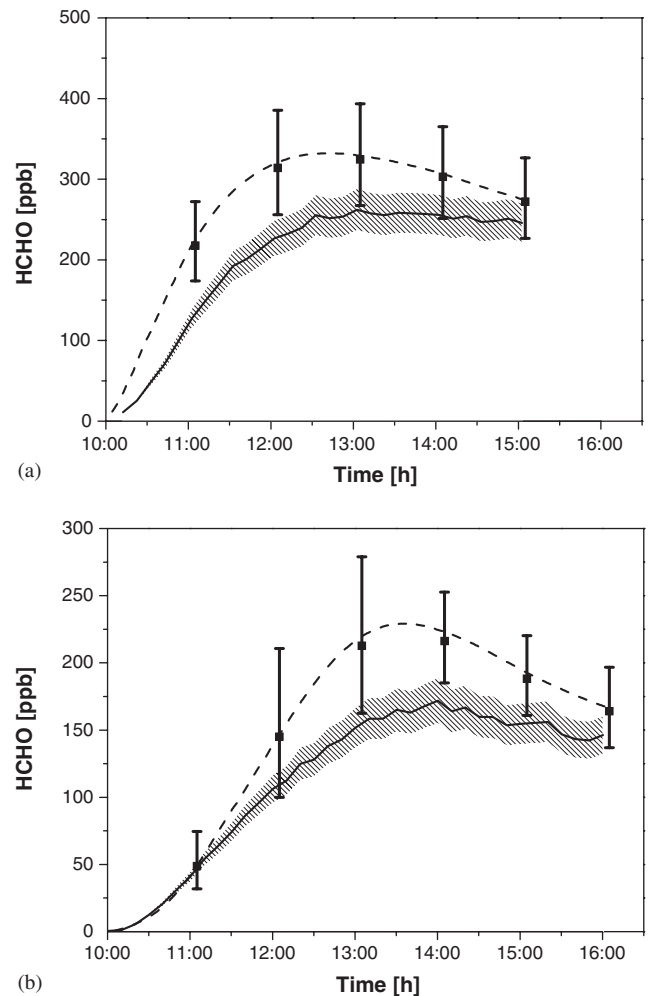

(a)

(b)

Fig. 4. Comparison of modelled and measured concentrations of formaldehyde and their associated uncertainties. Measured values and their associated uncertainty (2σ): straight line with striped band; calculated mean and its 2σ uncertainty: dots and error bars; simulation results with the nominal parameter values: dashed line.

over-prediction of formaldehyde concentration. There are difficulties in simulating both the rise time and the peak formaldehyde concentration. The uncertainty contribution of reaction $OH + NO_2 = HNO_3$ is high to the formaldehyde concentration uncertainty, especially in the high NO_x case (see Figs. 2 and 3). The rate coefficient of this reaction has been extensively studied recently [7], therefore it is expected that the uncertainty of the rate coefficient of this reaction will decrease significantly in the near future. If this happens, uncertainty in the high NO_x case will drop significantly and consequently the overlap is likely to disappear.

3. Uncertainty analysis of a methane flame

3.1. Brief description of a methane oxidation mechanism

Until recently, there have been only few applications of uncertainty analysis to the investigation of complex combustion mechanisms [3,14–20]. In our calculations, a stoichiometric, stationary, laminar, freely propagating methane flame was investigated and the simulations were performed with the Leeds Methane Oxidation Mechanism [21,22]. This mechanism contains 175 reversible chemical reactions and 37 species. Our aim was to determine the uncertainty of the simulation results caused by the uncertainty of thermodynamic and kinetic parameters; it means that the uncertain parameters in the mechanism were the 175 rate coefficients and the 37 enthalpy-of-formation data, which adds up to 212 uncertain parameters in total.

The investigated results were the concentration maxima of some important species (OH, H, O, CH_2, CH), the maximum temperature, and the laminar flame velocity (v_L); the latter number is characteristic to a freely propagating flame [23] and is often used when modelling and measurement results are compared [22].

The simulations were carried out with program PRE-MIX [24] of the CHEMKIN-II package [25] and with program KINALC [21]. The calculations were done at atmospheric pressure; the cold boundary temperature was 298.15 K. The uncertainties of the parameters were the same as in the paper of Turányi et al. [3].

3.2. Results for the combustion model

3.2.1. Local uncertainties

The results of the local uncertainty analysis are summarised on a blob graph, shown in Fig. 5. It can be seen that only 33 out of the 212 parameters contribute at least with 1% to the total uncertainty of any of the monitored results. Moreover, there are only few really important contributors; the most important is reaction $O_2 + H = OH + O$. This reaction is responsible for about 60% of the uncertainty in the laminar flame velocity. From the thermodynamic parameters, the enthalpy-of-formation of OH has a significant contribution to the uncertainty in
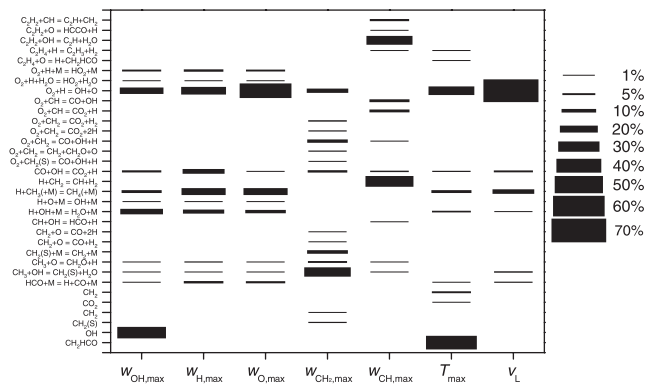

Fig. 5. The percentage contributions are shown for those input parameters (rate coefficients of reactions and enthalpy-of-formation of species), which contribute at least by 1% to the uncertainty of at least one investigated result (see the horizontal axis). Uncertainty contributions are expressed in percentages, and the thickness of the line is proportional to the percentage value (see scale).
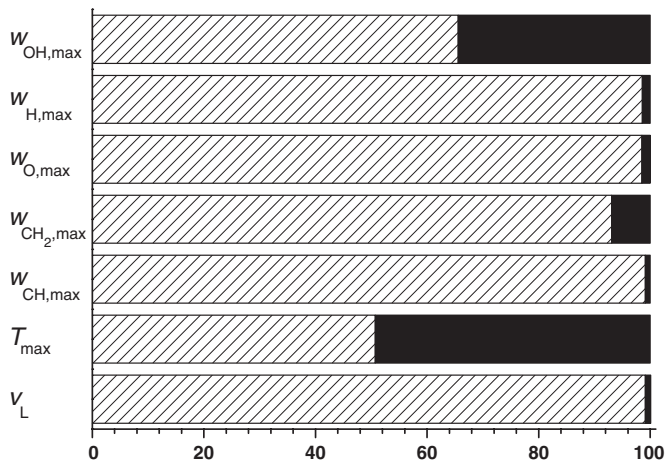

Fig. 6. Kinetic (striped) and thermodynamic (black) contributions to the total uncertainty of the monitored parameters as calculated from local uncertainty analysis and expressed in percentages.

the maximum OH concentration, while the enthalpy-of-formation of CH_2CO has approximately 40% contribution to the uncertainty of the maximum flame temperature. It can be seen from the figure, that there are relatively few reactions having significant uncertainty contributions, especially compared to the total number of uncertain parameters (212).

In Fig. 6, the contributions of the kinetic and thermodynamic parameter uncertainties are compared. These results should be handled with some precaution, because these are valid only if the values of the parameters are not correlated, as it was assumed in our calculations. Also, there is an inherent nonlinearity in this chemical kinetic system, and therefore these results are semi-quantitative only. Our calculations show that for most of the monitored variables, 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 the Morris method are shown in Fig. 7. In this analysis, the significant parameters in the Morris figures are the same as those that have a great uncertainty contribution in the local analysis. However, there are changes in the order of reactions when looking at their mean effect. For example, in the case of the maximum temperature, the $H + CH_3 (+M) = CH_4 (+M)$ precedes reaction $H + OH + M = H_2O + M$, while the order is the opposite according to the local analysis. In the case of maximum flame temperature, the enthalpy-of-formation of CH_2CO cannot be found in the Morris plot, unlike in the local analysis.

It had been observed [1] in other models that greater standard deviation in the Morris plot belonged to greater mean effect and it was found also in this case. One exception is the maximum temperature, where the enthalpy-of-formation of some species (H_2O, OH, CO, CO_2 and CH_4) affects the resulting temperature uncertainty significantly, but in a purely linear way, according to the Morris analysis. This is an interesting result, which shows that thermodynamic parameters have a somewhat different behaviour in the methane oxidation mechanism, compared to the kinetic ones.

3.2.3. Monte Carlo analysis

The MC simulations resulted in the pdfs of the monitored results. Fig. 8 shows the histograms of the flame velocity, maximal H concentration and maximal temperature. 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 H radical is 13%. The uncertainty of some other species (like the CH radical) can be as high as about 50%.

The results of the MC analysis enable the comparison of the experimental and modelled results. In this way, it is possible to judge the simulation results not only by the mean values, but also by taking the uncertainties in to account. Model validation experiments can also be justified. The uncertainty of the measured peak flame temperature was reported to be around ± 100 K [26,27] and this uncertainty limit is much higher than the uncertainty in the computed temperature of ± 2 K. It means that it is not possible to validate flame models by investigating experimentally the maximum flame temperature.

On the other hand, the uncertainty of the measured laminar flame velocity is relatively small, it is about $1 \, cm \, s^{-1}$ [28,29]. This is much smaller than the intrinsic uncertainty of the model, which is about $6 \, cm \, s^{-1}$. It means that the good agreement between the calculated and the measured flame velocity values in methane flame models are only a matter of good luck and maybe the fine-tuning of some model parameters.
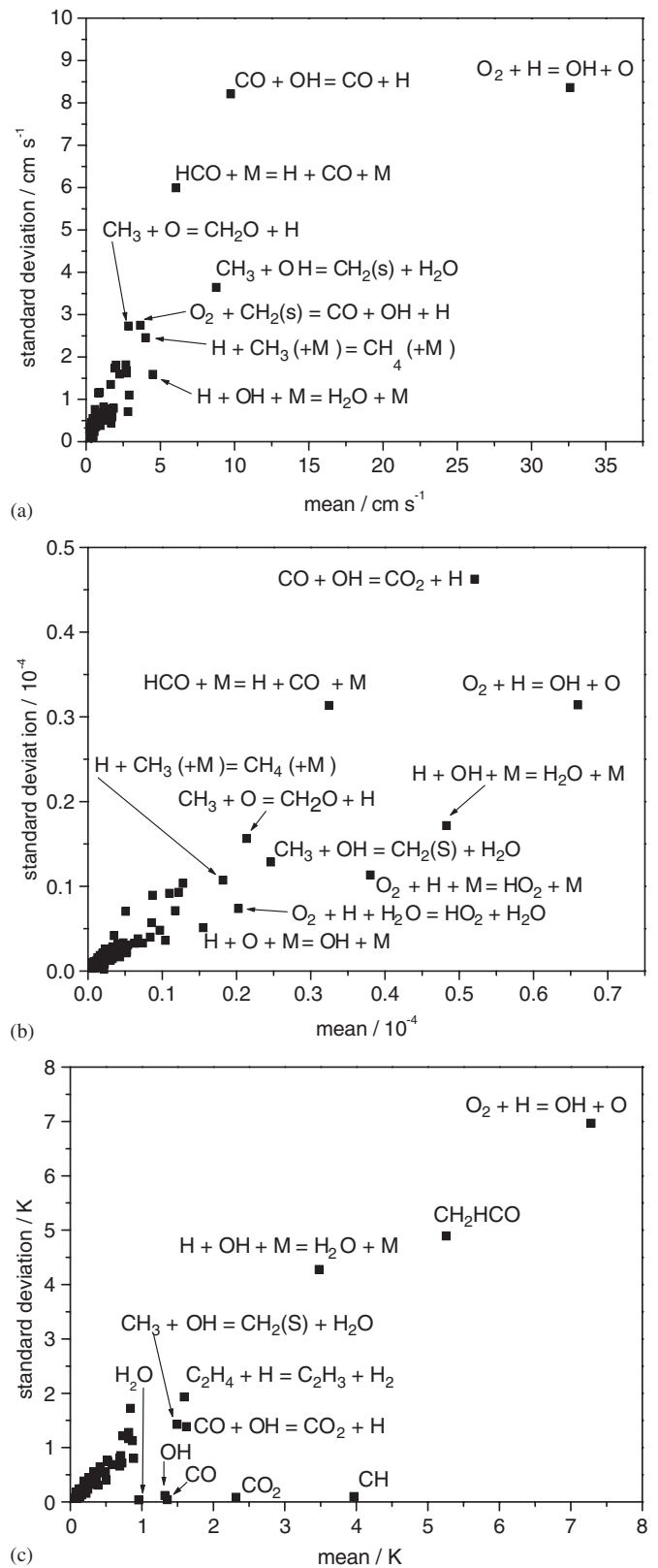

Fig. 7. Results of the Morris analysis for (a) laminar flame velocity, (b) maximum hydrogen radical concentration, (c) maximum adiabatic flame temperature.
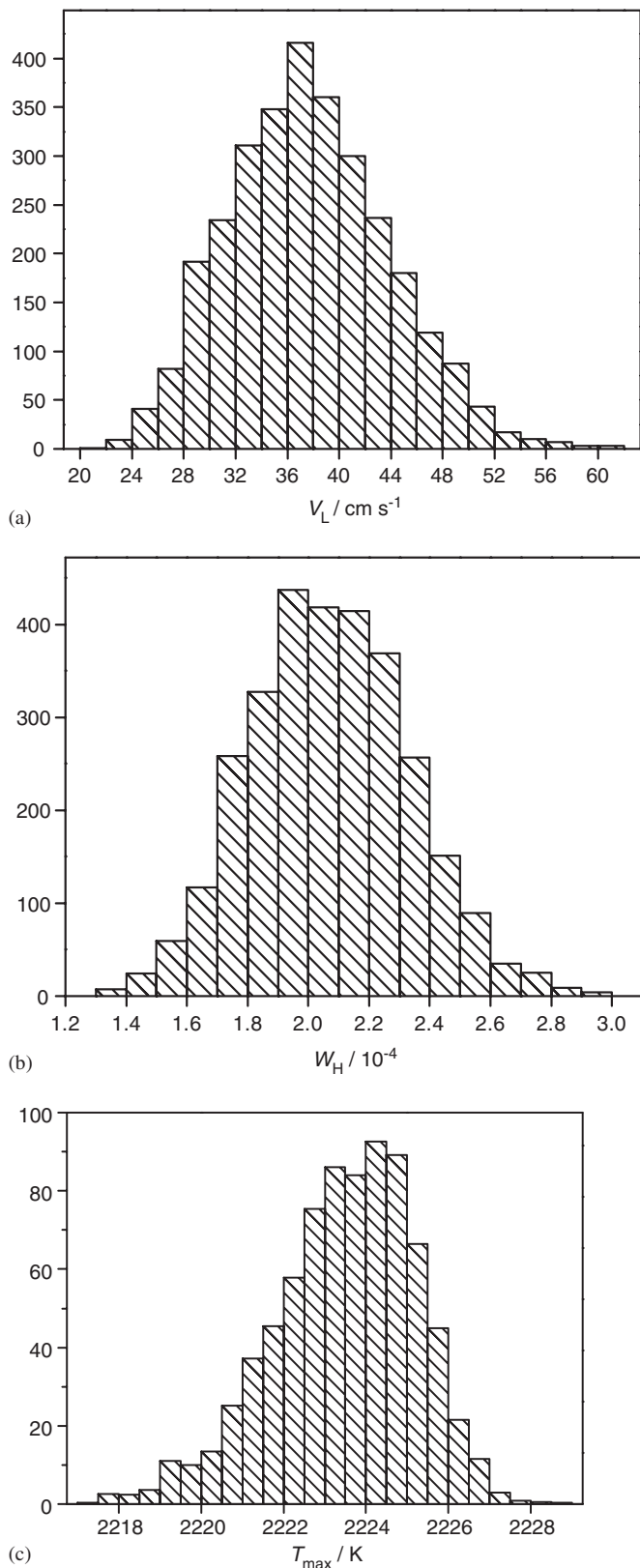
(a)

(b)

(c)

Fig. 8. Distribution of some selected results in a stoichiometric methane flame, as obtained from MC simulations: (a) laminar flame velocity, (b) maximum hydrogen radical concentration, (c) maximum adiabatic flame temperature.

3.3. Global uncertainty of local sensitivity coefficients: a numerical approach

Local sensitivities are often used in chemical kinetics as indicators of reaction importance. However, these are almost exclusively calculated at the nominal values of the parameters. Therefore, the robustness of local sensitivity coefficients to great parameter changes in chemical kinetic systems has to be investigated. During the MC simulations, all parameters were varied simultaneously within their uncertainty limits and the first-order local sensitivity coefficients of rate parameters were also calculated in each run. By processing the results, the global uncertainties of the local sensitivities were obtained.

Fig. 9 shows the results for the laminar flame velocity, for the maximum concentration of hydrogen atom and for the maximum temperature. The cut-off criterion for the figure was 10% of the highest sensitivity coefficient. Figs. 9a and b show that for the laminar flame velocity and maximum hydrogen atom concentration sensitivities, respectively, 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 1σ 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. Their order can change when taking the extreme values into account; however, the qualitative information obtained from local sensitivity analysis remains identical if the order of the most important reactions alters due to the change of the parameter values within their uncertainty limits. In the case of the local sensitivity coefficients of the maximal flame temperature, the 1σ uncertainty limits are also relatively narrow, but the attainable extremes are somewhat wider. These figures show only representative examples, but very similar figures were obtained for the other variables as well.

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 hydrocarbon flames. In this paper, we presented uncertainty analysis results for models of both types. Uncertainties of simulation results were calculated by local uncertainty methods and Monte Carlo analysis, and also contribution of the various parameters to the uncertainty of the results were investigated by local uncertainty analysis and the Morris method. The surprising joint experience from the analyses of the two chemical kinetic models is that few parameters cause most of the
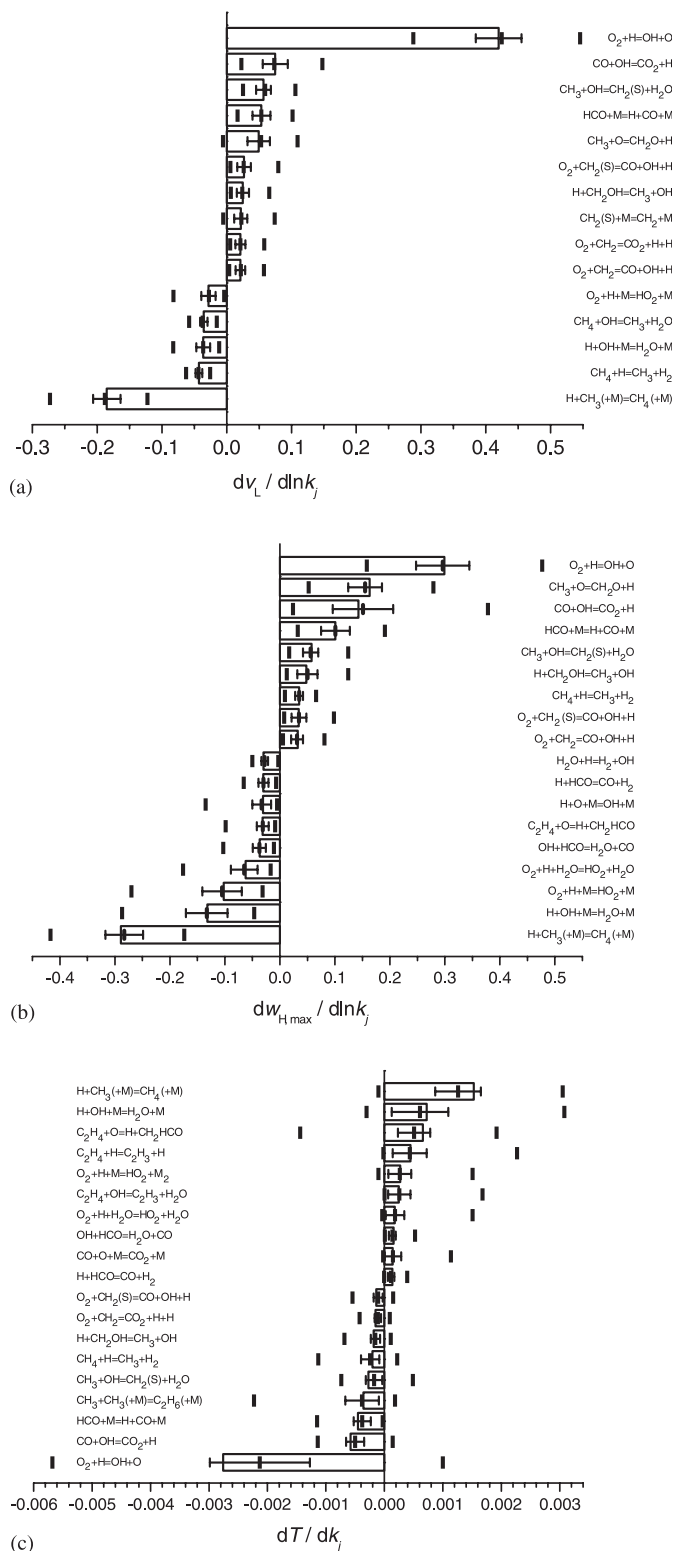
uncertainties. The atmospheric chemical and the combustion models contained 141 and 212 uncertain parameters, respectively, and only about 30 parameters had noticeable contribution to the uncertainty of any of the important results. This means that knowing better a few parameters only may significantly improve the quality of simulations both in atmospheric chemistry and combustion science, which are among the most important fields of application of complex reaction mechanisms.

Acknowledgements

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Fig. 9. Results of global uncertainty analysis of local sensitivity coefficients for (a) laminar flame velocity, (b) maximum hydrogen radical concentration, (c) maximum adiabatic flame temperature of the stoichiometric methane–air flame. Only those reactions are shown, for which the corresponding sensitivities are greater than 10% of that of the highest sensitivity one. Bars refer to the local sensitivity coefficients at the nominal parameter set, ticks interconnected with a vertical line indicate the 1σ uncertainty interval, and the outer stripes show the attainable minimum and maximum sensitivity coefficients at any parameter set within the uncertainty limits of parameters.

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