REFEREE #1

This technical note explains a method for inference of chemical and physical parameters relevant to atmospheric processes. As explained in the note, it could be of use to multiple types of atmospherically-relevant experiments investigating different parameters. It is therefore relevant to the journal and of importance to the research community.

I recommend publication pending minor revisions. Below are a description of these revisions (numbered). On the whole the note is very well written and presented, and I think goes into sufficient depth without being overbearing (as would be possible due to the relatively complicated nature of the method in question).

We thank the reviewer for their effort and comments. The comments will be addressed individually, below.

1) The sentence spanning lines 103-106 is both complicated and elongated. Could it be made more readable?

The sentence has been adjusted. It originally read:

*For cloud-aerosol interaction models, inverse modeling techniques using evolutionary algorithms as global optimization technique in Monte-Carlo Markov Chain (MCMC) algorithms were developed previously to determine parametric uncertainties.*

it now reads:

*A related technique (Monte-Carlo Markov Chain algorithm) has been used to determine parametric uncertainties in cloud-aerosol interaction models.*

2) In sect. 3 (around the genetic algorithm explanation) I am left unsure how homogenisation of the population is achieved. My interpretation of the text and Fig. 1 is that some set of the population with a satisfactorily high correlation survives and is not further changed. The remaining population of parameter sets (children) changes through recombination and mutation of extant children or through replacement of these children with new ones. How does this child population homogenise to a population with high correlation? Are their parameter values informed by the parent population (as the family names suggest)? If so, this needs to be made clearer I think.

The reviewer correctly notes that 5 % of the individuals with the best goodness of fit survive and are passed directly to the next generation of the model as so-called elites (which we previously called parents), whereas the remaining 95 % of individuals of the next generation are created by recombination and mutation (80% vs. 20% respectively), this has

been made clearer in the revised manuscript. Homogenization is achieved not only through survival of elites, but also through the parent selection process: the likeliness of contributing as a parent to a child for the next generation depends on the goodness-of-fit of the individuals. We have adjusted the statement in section 3 to make it clear how generations are formed. It originally read:

*The remaining population is generated using combinations of parameters from the individuals in the previous generation with moderate or better goodness-of-fit, forming the children for the next generation. To further ensure genetic variability, a mutation scheme alters parameters in a stochastic manner.*

It now reads:

*The remaining population is generated using combinations of parameters from the individuals in the previous generation with moderate or better goodness-of-fit (the parents), forming the children for the next generation. In this study, 5% of the next generation are elite individuals, which are transferred with no changes, while 80 % of the children is created by randomly choosing individual parameters (genes) from two selected parents with equal weighting. The higher the goodness-of-fit of a certain individual, the higher is its likeliness to be selected as parent. This way, parameters leading to high goodness-of-fit are positively reinforced, leading to improvement and slow homogenization of the population. Finally, 20 % of children are created by applying a mutation scheme that alters parameters in a stochastic manner within the prescribed bounds to enhance genetic variability.*

Figure 1 was modified to reflect these changes:

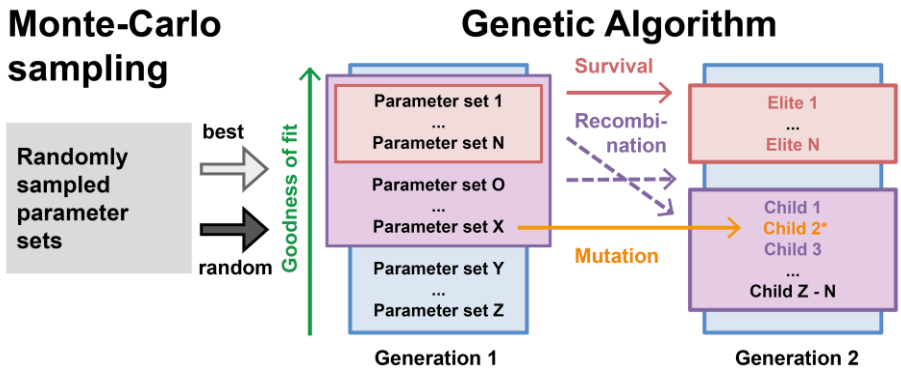


**Figure 1.** Schematic representation of the MCGA optimization method consisting of a Monte-Carlo sampling, which feeds into a genetic algorithm. *Populations* of model input parameter sets (blue boxes) are iteratively improved over several generations through survival of *elites* (red boxes) and recombination and mutation of *parents* to create *children*

(purple boxes), until a sufficient correlation to the experimental data (goodness of fit) is obtained.

An alternative process that comes to mind is that the size of the parent population increases as more children meet the correlation criteria (i.e. a satisfactorily high correlation). They achieve this through the random process of parameter change (recombination etc) rather than through any inheritance from parents. Again, if this (or any other) process causes homogenisation then it needs to be explained more clearly in the text (and possibly in Fig. 1).

This is an interesting idea to consider for future work. The current genetic algorithm operates with a fixed population size; this allows variables to be preallocated for computational efficiency.

3) On lines 144-150 can some additional information be provided as to the relative pros and cons (if any) of the reseeding and migration approach vs. repetition of the MCGA approach? Furthermore, can statistical bounds be determined using the former approach as it is stated they can be for the latter?

The reseeding / migration mechanisms were not used in this data presented in this manuscript and our informal tests indicate that it is not significantly faster to optimize using reseeding / migration than the repeated execution approach. We have removed the reference to reseeding and migration in the manuscript to reflect the work that we present and eliminate this point of confusion.

4) In Fig. 1, I suggest making the distinction between the Monte-Carlo step and the genetic algorithm step clearer. From reading of the main text the difference is clear, however, the names of the two steps are combined in Fig. 1, and they could be separate and placed distinctly above their respective schematic representation. I only suggest this because it may make the concept of the approach easier to appreciate (I got confused with when the Monte-Carlo usage stopped due to the random nature of mutations and introductions of new parameter sets in new generations of the genetic- algorithm step).

The figure has been adjusted according to the reviewer's suggestion.

5) I ask the authors to consider expanding on their description of model development in the introduction to further emphasise the importance of the MCGA method. The increased model complexity they describe does allow for inference of parameter values from increasingly complex measurement setups. However, this is only possible through methods like MCGA. As atmospheric science tries to bridge the divide between laboratory

measurements and the real atmosphere and simplified models and global ones, it seems that methods like the MCGA will be very important.

We are delighted that the reviewer finds the MCGA method worthwhile and wishes us to further highlight its utility. We have added the following statement to the end of the introduction (lines 101-104 of revised manuscript):

*The MCGA algorithm presented here is able to overcome the difficulty of a complex optimization hypersurface with many local minima while providing the user with a realistic assessment of how well-constrained the model input parameters are by the experimental data.*

6) Typos: Should "similar model output" on line 27 be "similar model input"?

The phrase should be "similar model output." There is some potential confusion between the kinetic model and the optimization algorithm. The MCGA algorithm optimizes "input parameters" while the kinetic model produces "output" for comparison to experimental data. We added the following paragraph to the introduction and hope this clarifies our nomenclature:

*We will use the term "input parameters" to address the prescribed model parameters (thermodynamic, kinetic, or physical) that are optimized in this study so that kinetic model output matches experimental data, a process that we will refer to as "fitting the kinetic model". Note that this definition excludes model parameters that are clearly defined by physical laws or the experiment (e.g. physical constants, experimental conditions) or are of purely technical nature (e.g. integration time steps).*

Should "breath" on line 92 be "breadth"?

Yes, the referee is correct. However, we decided that the sentence does not add much to the discussion at this point and removed it for simplification.

Should "as heuristic" on line 110 read "as a heuristic"?

Yes, it has been adjusted.

REFEREE #2

The manuscript describes the principles of the Monte-Carlo genetic algorithm (MCGA) and how it can be used to constrain various model input parameters for multiphase chemical kinetic systems.

The manuscript is very well written and it is relatively straightforward to understand the general idea, advantages and limitations of the MC genetic algorithm despite the complex topic. I especially like the examples given in Figure 3 concerning why model input parameter can remain unconstrained. I have very little additional to add apart from what reviewer 1 already pointed out. I recommend the manuscript to be published after a minor revision where you consider the comments from reviewer 1, which I fully agree with, and my very minor additional comments given below.

We thank the reviewer for their effort and comments. The specific comments will be addressed below.

On p. 2, L33-34: Do you really mean that the MCGA algorithm itself should be portable to any numerical model with similar computational expense and extent of the fitting parameter space or do you mean that the results (the constrained parameters) can be implemented in these models?

In this instance, we would like to express that MCGA can also be used with other numerical models. The abstract has been adjusted to reflect that we are using it for aerosol science, but that the method is portable to any process that can be numerically modeled. The constrained parameters generated by the MCGA should be portable to other models (e.g. of aerosol science), as long as the other model does not make other base assumptions.

On p. 5, L87-90: This sentence is long and I had to read it several times before I understood the full meaning of it. Is it possible to reformulate it? Maybe: Furthermore, experiments covering a broad range of conditions must be conducted to achieve observables that are controlled by (a) as many model input parameters as possible across all experimental conditions, but (b) by as few model input parameters as possible for a specific experimental condition (i.e. limiting cases).

The sentence has been adjusted using the suggestion of the reviewer with minor modification. It originally read:

*Furthermore, experiments must be conducted by covering broad ranges of experimental conditions to achieve that the observables are controlled by (a) as many model input*

*parameters as possible across all experimental conditions, but (b) by as few model input parameters as possible for a specific experimental condition (i.e. limiting cases).*

It now reads:

*Furthermore, experiments covering a broad range of conditions must be conducted to ensure that the observables are controlled by (a) as many model input parameters as possible across all experimental conditions, but (b) by as few model input parameters as possible for a specific experimental condition (i.e. limiting cases).*

On p. 5, L92: I am not sure if I understand what you want to say with "in the required breath". Do you mean that because of technical limitations or transient behaviour it may not be possible to sample all required input parameters at the same time?

We have adjusted the discussion of limitations on lines 90-95. What this statement meant is that it may not be physically possible to fully constrain all parameters, e.g., if a bulk reaction happens so "fast" that it is never the limiting process in experimental data, the corresponding parameter will have a lower limit set by experiment and an upper limit set by diffusion. However, we decided that the sentence does not add much to the discussion at this point and removed it for simplification.

I agree with referee 1 that some additional information needs to be provided about the advantages of the reseeding and migration approach vs. repetition of the MCGA approach? Have you used the reseeding and migration approach for any of the results presented in the article? If I understand it correctly you used the repeated execution approach when you generated the results presented in Figure 3.

Please see comments to reviewer 1. To answer the specific questions raised by reviewer 2: we have not used the reseeding and migration approach for the results in this article; as such, those statements have been removed from the article. The reviewer is correct in stating that the results in Figure 3 were generated via the repeated execution approach.

REFEREE #3

The authors present a Monte-Carlo Genetic Algorithm tool for fitting large sets of input parameters of kinetic multiphase atmospheric chemistry box models using multiple experimental data sets. The manuscript is well written and is recommended for publication in ACP after the authors address the following minor comments.

We thank the reviewer for their effort and comments. The specific comments will be addressed below.

1) Line 73: Please define the term "non-orthogonal input parameters".

We have changed the manuscript to include "(coupled)" following "non-orthogonal input parameters. A more thorough definition of the term "non-orthogonal parameters" is given in Sect. 3, line 193 and an example given on lines 207-213.

2) Line 80-82: While I generally understand what the authors are trying to say here, it would be useful to elaborate a bit on what the term "the most limiting processes" exactly means in this context. It would be great to briefly illustrate it with an example, if possible.

We have added more details and an example to the paper (lines 90-95 of revised manuscript). The text now reads:

*For example, if a model is trained using data that is exclusively limited by a single process, it will constrain the parameters that represent that specific process while the other parameters remain nearly unconstrained even if multiple data sets are used. This means that a parameter set were optimized using data from surface film experiments, the bulk diffusion coefficients would likely be poorly constrained regardless of how many different experimental datasets of that type were used.*

3) While MCGA will prove to be a powerful tool in interpreting experimental data, I appreciate the discussion of its limitations in section 3. This is not presently reflected in the abstract. I suggest adding a sentence in the abstract that cautions the future users of such a tool to its limitations as well as potential solutions to overcome them (e.g., broader range of experimental techniques and approaches, etc.).

We have adjusted the abstract to note that the MCGA is "allowing users to design experiments that should be particularly useful to constrain model parameters" (line 29-30 of revised manuscript).

# *Technical Note:* Monte-Carlo genetic algorithm (MCGA) for model analysis of multiphase chemical kinetics to determine transport and reaction rate coefficients using multiple experimental data sets

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## Abstract

We present a Monte-Carlo Genetic Algorithm (MCGA) for efficient, automated and unbiased global optimization of model input parameters by simultaneous fitting to multiple experimental data sets. The algorithm was developed to address the inverse modelling problems associated with fitting large sets of model input parameters encountered in state-of-the-art kinetic models for heterogeneous and multiphase atmospheric chemistry. The MCGA approach utilizes a sequence of optimization methods to find and characterize the solution of an optimization problem. It addresses an issue inherent to complex models whose extensive input parameter sets may not be uniquely determined from limited input data. Such ambiguity in the derived parameter values can be reliably detected using this new set of tools, allowing users to design experiments that should be particularly useful to constrain model parameters. We show that the MCGA algorithm has been used successfully to constrain parameters such as chemical reaction rate coefficients, diffusion coefficients and Henry's law solubility coefficients in kinetic models of gas uptake and chemical transformation of aerosol particles as well as multiphase chemistry at the atmosphere-biosphere interface. While this study focuses on the processes outlined above, the MCGA approach should be portable to any numerical process model with similar computational expense and extent of the fitting parameter space.

## 1. Introduction

Atmospheric aerosols play a key role in climate, air quality and public health. Heterogeneous reactions and multiphase processes alter the physical and chemical properties of organic aerosol particles, but the effects of these reactions are not fully elucidated (e.g. Finlayson-Pitts, 2009;George and Abbatt, 2010;Abbatt et al., 2012;Pöschl and Shiraiwa, 2015). While multiphase chemistry in aerosols and clouds can be described by a sequence of well-understood physical and chemical elementary processes in kinetic models (Hanson et al., 1994;Pöschl et al., 2007;George and Abbatt, 2010), the deduction of parameters or rate coefficients of the individual elementary processes is severely complicated by the inherent coupling of chemical reactions and mass transport processes (Kolb et al., 2010;Berkemeier et al., 2013;Shiraiwa et al., 2014).

Heterogeneous chemical reactions on aerosol particles are traditionally described using so-called "resistor" models, which represent parallel and sequential physical or chemical processes in analogy to electrical circuits. These models have typically been used to derive analytical expressions for simplified limiting cases (e.g. Hanson et al., 1994;Worsnop et al., 2002;Hearn et al., 2005). Recently, numerical models have been developed that allow a more complete consideration of the time- and depth-resolved chemical and physical behaviour of aerosol particles, leading to a better understanding of these reaction systems, especially under conditions where the steady-state assumptions underlying the resistor models are not valid (Smith et al., 2003;Pöschl et al., 2007;Steimer et al., 2015;Berkemeier et al., 2016). Kinetic multi-layer models describe single particles or thin films by division into compartments such as near-surface gas phase, surface and particle bulk, and further subdivision of the particle bulk into thin layers to achieve depth-resolution. Specific models provide a focus on chemistry such as KM-SUB (Shiraiwa et al., 2010), on gas-particle partitioning such as KM-GAP (Shiraiwa et al., 2012) and ADCHAM (Roldin et al.,

2014), or on water diffusion such as the ETH Diffusion Model (Zobrist et al., 2011). For simplicity, throughout this manuscript we refer to a "kinetic model" as any computational model that is used to simulate a system's behaviour. We will use the term "input parameters" to address the prescribed model parameters (thermodynamic, kinetic, or physical) that are optimized in this study so that kinetic model output matches experimental data, a process that we will refer to as "fitting the kinetic model". Note that this definition excludes model parameters that are clearly defined by physical laws or the experiment (e.g. physical constants, experimental conditions) or are of purely technical nature (e.g. integration time steps).

Ideally, fitting a kinetic model to experimental data would return all chemical and physical parameters necessary to understand the importance of the processes at work and to predict the outcome of future experiments, even if conducted under experimental conditions not part of the training data set, i.e. all experimental data used during the fitting process. However, kinetic models often require a multitude of input parameters, some of which are not constrained well experimentally or are merely effective parameters combining a sequence of inherently coupled processes. In general, two main difficulties arise when optimizing complex models to experimental data:

(1) The optimization hyper surface is often non-convex, i.e., it will not have only a single minimum due to interactions between non-orthogonal (coupled) input parameters and/or scatter in the experimental data. Hence, steepest descent methods fail since they get trapped easily in local minima. Brute-force or exhaustive searches, where an $n$-dimensional grid is applied to the input parameter space and the fit quality evaluated for every grid point in all $n$ dimensions, are often not computationally feasible.

(2) If too little or too similar experimental data is used during the fitting process or input parameters are allowed to move in a large range, the optimization problem can be underdetermined (ill-defined) and multiple solutions may exist. In this case, even though a good agreement between model output and training data set is obtained, it is likely that only the model input parameters corresponding to the most limiting processes will be physically meaningful. Extrapolation of the model outside its training range can then lead to strong discrepancies between modelled and measured data. For example, if a model is trained using data that is exclusively limited by a single process, it will constrain the parameters that represent that specific process while the other parameters remain nearly unconstrained even if multiple data sets are used. This means that a parameter set were optimized using data from surface film experiments, the bulk diffusion coefficients would likely be poorly constrained regardless of how many different experimental datasets of that type were used.

Hence, sophisticated optimization methods are needed, which quickly and reliably determine the model input parameters that lead to the best correlation between kinetic model and experiment. Furthermore, experiments covering a broad range of conditions must be conducted to ensure that the observables are controlled by (a) as many model input parameters as possible across all experimental conditions, but (b) by as few model input parameters as possible for a specific experimental condition (i.e. limiting cases). The MCGA algorithm presented here is able to overcome the difficulty of a complex optimization hypersurface with many local minima while providing the user with a realistic assessment of how well-constrained the model input parameters are by the experimental data.

## 2. Monte-Carlo Genetic Algorithm (MCGA)

In many modelling applications, methods are needed that reliably find the optimum in non-convex optimization problems and detect underdetermined optimization problems. Global optimization methods have been subject of extensive research in the past (Arora et al., 1995) and provide means of approximating non-convex optimization problems without premature convergence to local optima. Examples for these methods are simulated annealing methods and evolutionary algorithms. In atmospheric chemistry, simple optimization techniques are commonly used to determine kinetic parameters by fitting of rate equations to experimental data sets, but to our knowledge no global optimization technique diligently designed for the determination of atmospheric reaction rate coefficients from multiple data sets was described thus far. A related technique (Monte-Carlo Markov Chain algorithm) has been used to determine parametric uncertainties in cloud-aerosol interaction models (Partridge et al., 2012;Lowe et al., 2016). Global optimization was also used to calculate thermodynamic equilibria for phase separation of aqueous multicomponent solutions (Zuend and Seinfeld, 2013).

In this study, we present the Monte-Carlo Genetic Algorithm (MCGA), a method combining direct Monte-Carlo sampling with a genetic algorithm as a heuristic global optimization method that approximates the global optimum for input parameter sets of computational models. Repeated execution of the search algorithm can be used to test for uniqueness or to provide statistical bounds on the model input parameters. The MCGA algorithm utilizes a two-step approach to find minima on non-convex hyper surfaces. First, a Monte-Carlo (MC) sampling is performed in the large space of possible model input parameters to narrow down the possible solution to smaller areas of interest. The parameter sets are evaluated using a goodness-of-fit expression of the user's choice, such as the root-mean-square (RMS) error between kinetic model output and experimental data.

In the examples presented here, the RMS error or logarithmic RMS error was used. When multiple datasets were fitted, a weighting factor was introduced to prevent bias due to the number of data points in different experimental datasets. An additional optional weighting factor allows the user to assign priority to experimental data with lower statistical error or scatter. The parameter sets for the MC sampling are generated randomly from a distribution of the model input parameters. Each parameter was sampled using a logarithmically spaced distribution of values to provide uniform sampling over the large ranges most input parameters can possibly adopt. Note that, depending on the problem, different distributions and sampling strategies (e.g. Latin hypercube sampling) could be applied.

The genetic algorithm (GA) uses survival of the fittest to optimize an ensemble (the *population)* of parameter sets (the *individuals*) over several iterations (the *generations*). Processes known from natural evolution such as survival, recombination, mutation and migration are mimicked to optimize a population. The initial population is formed by the parameter sets with the best goodness-of-fit obtained in the MC sampling step. An equal number of random parameter sets are added to ensure diversity within the pool of parameter sets and counteract sampling bias from shallow local minima (Fig. 1).

During execution of the GA, a number of model input parameter sets with the highest correlation between model output and experimental data (goodness-of-fit) are directly transferred into the next generation by the survival mechanism (the *elites*). The remaining population is generated using combinations of parameters from the individuals in the previous generation with moderate or better goodness-of-fit (the *parents*), forming the *children* for the next generation. In this study, 5% of the next generation are elite individuals, which are transferred with no changes, while 80 % of the children is created by randomly choosing individual parameters (*genes*) from two selected parents

with equal weighting. The higher the goodness-of-fit of a certain individual, the higher is its likeliness to be selected as parent. This way, parameters leading to high goodness-of-fit are positively reinforced, leading to improvement and slow homogenization of the population. Finally, 20 % of children are created by applying a mutation scheme that alters parameters in a stochastic manner within the prescribed bounds to enhance genetic variability. Collectively, these mechanisms enable the MCGA to overcome local minima, a crucial feature of a global optimization method. Iteration of these steps eventually results in a homogeneous, optimized population and the common parameter set is taken as result. The MCGA can be run multiple times to generate a set of representative solutions, which has been the default approach in previous applications of MCGA (cf. Sect. 4). With only few (~5-10) repetitions, this procedure allows the user to assure full convergence to the global optimum. In addition, the random sampling of optimization space between different executions of MCGA will generate statistical bounds on the parameters if a sufficiently large number of repetitions is computationally feasible.

In this study we used the genetic algorithm provided by MathWorks® (Matlab® Global Optimization Toolbox) and developed a routine for parallel computation on computer clusters. In a typical setting, the MC step and GA step of the optimization occupied an approximately equal amount of computation time. Figure 2 describes the implementation of the parallel MCGA optimization method. The *N* parallel threads share common populations of parameter sets that are iteratively optimized by extracting a subset of parameter sets and performing the genetic algorithm on this subset. Once a sub-evaluation of the genetic algorithm has finished, the parameter sets are mixed into the population, and after randomization, a different subset of parameter sets is extracted and their optimization is immediately continued. Since the parallel threads will run

asynchronously, a fraction of individuals must remain in the population to be mixed with, to enable continuous operation without waiting times.

## 3. Implications for modelling and measuring chemical kinetics

Although models may possess a multitude of kinetic and thermodynamic input parameters that represent the many possible sequential and/or concurrent processes occurring in the system, their behaviour is often driven by only a single or at most a few processes at a certain point in time. In chemical kinetics, the behaviour of the system can often be characterized by a kinetic regime, which may change during the course of the reaction and with experimental conditions (Berkemeier et al., 2013). If a set of model input parameters can be uniquely determined (by MCGA or another means) and results in a high-fidelity fit of model output to experimental data, the parameters then would be regarded as correct within the approximations of the underlying model and uncertainties of the experimental data. This is a convenient way to assimilate data from multiple previous studies; data sets can be weighted to reflect confidence in their results, and the final range of accepted parameters then represents a consensus from the fitted data. However, it may not always be possible to fully constrain the input parameters, even using multiple experimental datasets. In general, there are two reasons that a model input parameter can remain unconstrained after optimization:

(i) the parameter is non-influential, or

(ii) the parameter is inherently coupled to another one, forming a non-orthogonal parameter pair under all experimental conditions.

Fig. 3 illustrates both cases in an example taken from atmospheric multiphase chemistry, using the benchmark system of ozone + oleic acid and data adopted from Hearn *et al.* (2005). The original data was converted from ozone exposure to a time series using an ozone concentration of $2.76\times10^{15}$ $cm^{-3}$. The MCGA algorithm was executed under a constrained parameter set, in which only desorption lifetime and surface reaction rate coefficient were allowed to vary. In this scenario, repeated execution of MCGA returned multiple solutions, for which the model output had nearly equivalent goodness-of-fit with only slight variance between them (Fig. 3A). In stark contrast to the uniform correlation between model output and experimental data, Fig. 3B shows the high variance within the model parameters yielding these solutions (red markers) which scatter across a narrow valley of the optimization hypersurface (contour lines). In the upper portion of the figure, i.e. above a desorption lifetime of $10^{-4}$ s, a vertical relationship between both parameters indicates that the desorption lifetime is a non-influential parameter and can take on any value in this interval, corresponding to case (i) above. In the lower portion of the figure, i.e. below a desorption lifetime of the diagonal relationship indicates that an increase in one parameter can be compensated with a decrease in the other parameter and both form a non-orthogonal pair, corresponding to case (ii) above. For comparison, Figs. 3C and 3D show examples of optimization hypersurfaces from Berkemeier et al. (2016), who studied multiphase ozonolysis of shikimic acid and investigated the existence of non-orthogonal parameter pairs by varying optimized parameters ($\lambda_i$) by a factor $f(\lambda_i)$ to depict the total residual as a 2D contour map. Fig. 3C shows that the Henry's law coefficient for ozone ($H_{cp,O3}$) and the product of the bulk reaction rate coefficient ($k_{BR}$) with the bulk diffusivity of ozone ($D_{b,O3}$) and the bulk-to-surface transport coefficient of ozone ($k_{bs,O3}$) are fully non-orthogonal. Figure 3D shows a single, well-defined optimum parameter set for the effective

molecular cross section of ozone ($\sigma_{O3}$) and the desorption lifetime of ozone ($\tau_{d,O3}$), indicating that these parameters are fully orthogonal for the experimental data fit in that study.

The prerequisite of a successful optimization is to fit a sufficiently broad experimental data set so that a unique and accurate set of fitting parameters is obtained. Thus, both of the above conditions must be avoided. This may be achieved by including additional experimental data, especially from a different experimental technique or over a different timescale so that the system might sample another limiting behaviour. In the data given in Fig. 3 above, for example, measuring full time series at different oxidant concentrations may help to constrain the oxidant's desorption lifetime. However, if a model has too many free parameters (or especially parameters that are not well-constrained by experimental data), it may be necessary to reduce the model complexity or fix some of the parameters. We therefore recommend using data sets obtained from a range of different experimental techniques to ensure this variability if they are available, and using models with as few free parameters as possible.

In the example above, it was possible to use brute-force sampling to determine the true optimization hypersurface (contour lines) for comparison to the MCGA results. Of course, in typical applications, the number and range of input parameters makes such a search prohibitive. The computational feasibility of an optimization depends crucially on the size of the input parameter space, i.e. number and possible range of all parameters. Using an unreasonably large range for input parameters increases the possibility of finding non-physical solutions that fit the experimental data. The input parameter space can be reduced based on *a priori* knowledge from laboratory experiments and theoretical calculations. Parameters can be narrowed down by laboratory experiments (e.g. bulk experiments for derivation of trace gas solubility), by physics (e.g. the upper limit of the accommodation coefficient at unity), or by simulations (e.g., molecular

dynamics simulations to estimate the surface accommodation coefficient and desorption lifetime as in Vieceli et al. (2005) and Julin et al. (2013)). Note that in the example given in Fig. 3b, the two parameters were not truly independent, so that constraining either model parameter from *a priori* information would constrain the other parameter. In multi-parameter optimizations, where many such dependencies might exist, this can lead to a significant reduction in solution space.

## 4. Application of MCGA in atmospheric multiphase chemistry

The MCGA algorithm has been applied previously to chemical reaction systems of atmospheric relevance (Table 1). The essential parameters we use to describe an atmospheric multiphase chemical kinetic system of reactive trace gases X and bulk material Y include chemical reaction rate coefficients at the surface ($k_{SLR}$) and in the bulk ($k_{BR}$) of aerosol particles; bulk diffusion coefficients of reactive trace gases ($D_{b,X}$) and the bulk matrix ($D_{b,Y}$); accommodation coefficients ($\alpha_{s,X}$) and desorption lifetimes ($\tau_{d,X}$) of trace gases to the particle surface to determine transient and equilibrium adsorption behavior; and equilibrium constants for the solubility of reactive trace gases ($K_{sol,cc,X}$), typically expressed in terms of Henry's law coefficients ($H_{cp,X}$) (Pöschl et al., 2007;Ammann and Pöschl, 2007;Shiraiwa et al., 2010;Berkemeier et al., 2013).

In its first application the MCGA algorithm was used to fit individual data sets of the decay of oleic acid upon ozonolysis (Berkemeier et al., 2013), highlighting the need of fitting to multiple experimental data sets to constrain kinetic parameters. This was done in further studies that investigated gas uptake to (semi-)solid organic material in coated-wall flow-tube reactors (Arangio et al., 2015;Berkemeier et al., 2016), ozone-induced protein oligomerization in bulk solutions (Kampf et al., 2015), viscosity change upon alkene ozonolysis as measured with fluorescence

microscopy (Hosny et al., 2016), the redox-cycling reactions in the human lung lining fluid (Lakey et al., 2016a) as well as ozonolysis of squalene contained in human skin lipids (Lakey et al., 2016b). In each of these studies, a large set of model input parameters was optimized to several experimental data sets to constrain the input parameter space. In the following, we review results previously obtained by the MCGA algorithm to demonstrate its utility in determining kinetic parameters, assimilating large datasets, and detecting ill-defined problems.

In Berkemeier et al. (2016), 11 parameters were varied simultaneously to fit the ozone uptake to shikimic acid films over many hours, under 12 distinct experimental conditions, and using a single set of kinetic parameters (Fig. 4). The model was found to accurately describe the humidity- and concentration-dependence of ozone uptake and a high correlation between model output and experimental data was achieved. During optimization, a subset of six parameters, including diffusivity coefficients and trace gas solubility, was allowed to increase or decrease monotonically over 6 steps in relative humidity, resulting in a total of 41 optimized parameter values. Despite this large number of optimization parameters, a well-constrained parameter set could be obtained due to the large depth in training data and by applying *a priori* information.

In another study investigating the oxidation of biomass burning tracers with hydroxyl radicals (Arangio et al., 2015), repeated execution of MCGA revealed a remaining uncertainty in the kinetic parameters obtained from optimization to the two experimental data sets (Fig. 5). While some parameters could be narrowly constrained (diffusion coefficient of the organic matrix, $D_{org}$), others were subject to larger uncertainties (surface layer reaction rate constant $k_{SLR}$, desorption lifetime $\tau_d$). Note that while these parameters seem almost unconstrained in Fig. 5, this uncertainty is due to the presence of non-orthogonal parameter pairs. As detailed in Fig. 3 and in Arangio et al. (2015), only specific combinations of the non-orthogonal parameters will lead to agreement

between model and experiment. This knowledge can be used to constrain these parameters in further experiments.

## 5. Conclusions

The MCGA algorithm addresses the problem of extracting physical and chemical parameters from experimental data. The algorithm allows the user to assimilate multiple datasets and its random sampling approach reduces the bias which may arise in more user-directed optimization methods. Unlike simple gradient-based optimization methods, MCGA can thus be used as a statistical tool that not only detects unconstrained parameters, but also finds dependencies between unconstrained parameters. The results can be applied in process models and may serve to direct future experimental studies, e.g. to drive a reaction system into regimes in which the remaining unconstrained parameters have high sensitivity. MCGA could also be used to constrain chemical reaction systems in the post-analysis of field and laboratory studies: starting with a large set of model input parameters (i.e. chemical reactions, physical processes), data from various measurement campaigns could be combined, reconciled and in a further step used to reduce the number of model input parameters to the key processes necessary to describe all measurement data. MCGA may be a powerful and useful tool to constrain kinetic parameters and reaction rate coefficients in models that study the formation of secondary organic aerosol in reaction chambers (Chan et al., 2007;Shiraiwa et al., 2013;Cappa et al., 2013;Riedel et al., 2016). It could be suitable for fine-tuning of reaction rates in large reaction mechanisms of atmospheric chemistry, such as the Master Chemical Mechanism (MCM; Jenkin et al., 1997;Saunders et al., 2003), the Gas-Aerosol Model for Mechanism Analysis (GAMMA; McNeill et al., 2012) or the Chemical Aqueous Phase Radical Mechanism (CAPRAM; Herrmann et al., 1999). Multiple experimental data sets from a broad range of techniques could be used with the algorithm to narrow down

difficult-to-measure reaction rate coefficients, provide uncertainty estimates and reconcile experiments across different research groups and facilities.

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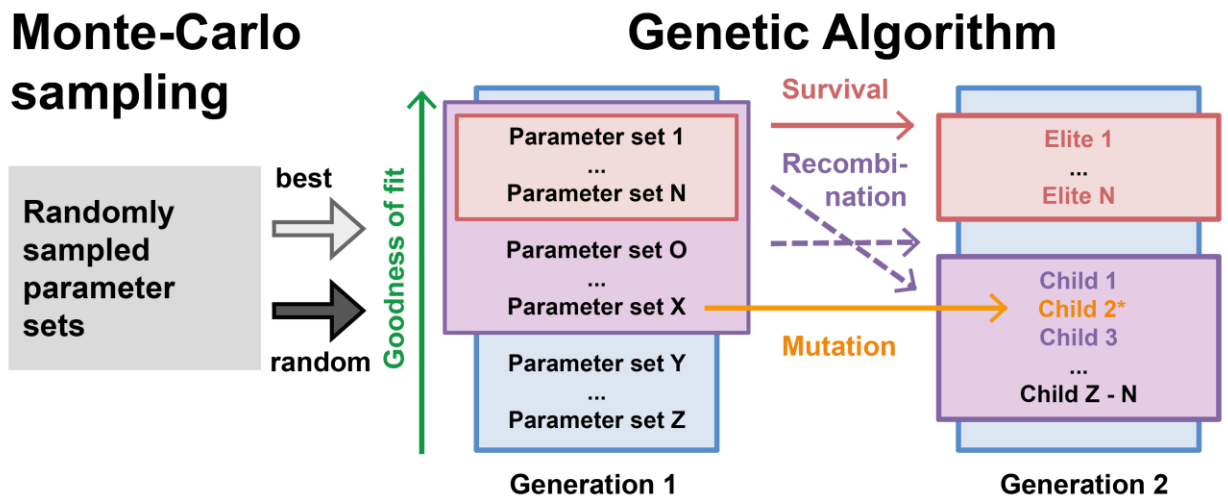
**Table 1.** Previous studies applying the MCGA algorithm.

| Study | Reaction system |
|---|---|
| Berkemeier et al. (2013) | oleic acid + $O_3$ |
| Arangio et al. (2015) | levoglucosan and abietic acid + OH |
| Kampf et al. (2015) | protein + $O_3$ |
| Hosny et al. (2016) | oleic acid + $O_3$ |
| Berkemeier et al. (2016) | shikimic acid + $O_3$ |
| Tong et al. (2016) | OH formation by SOA decomposition in water |
| Lakey et al. (2016a) | reactive oxygen species and PM2.5 in lung lining fluid |
| Lakey et al. (2016b) | skin lipid (squalene) + $O_3$ |




321

322 **Figure 1.** Schematic representation of the MCGA optimization method consisting of a Monte-Carlo
323 sampling, which feeds into a genetic algorithm. *Populations* of model input parameter sets (blue boxes) are
324 iteratively improved over several generations through survival of *elites* (red boxes) and recombination and
325 mutation of *parents* to create *children* (purple boxes), until a sufficient correlation to the experimental data
326 (goodness of fit) is obtained.

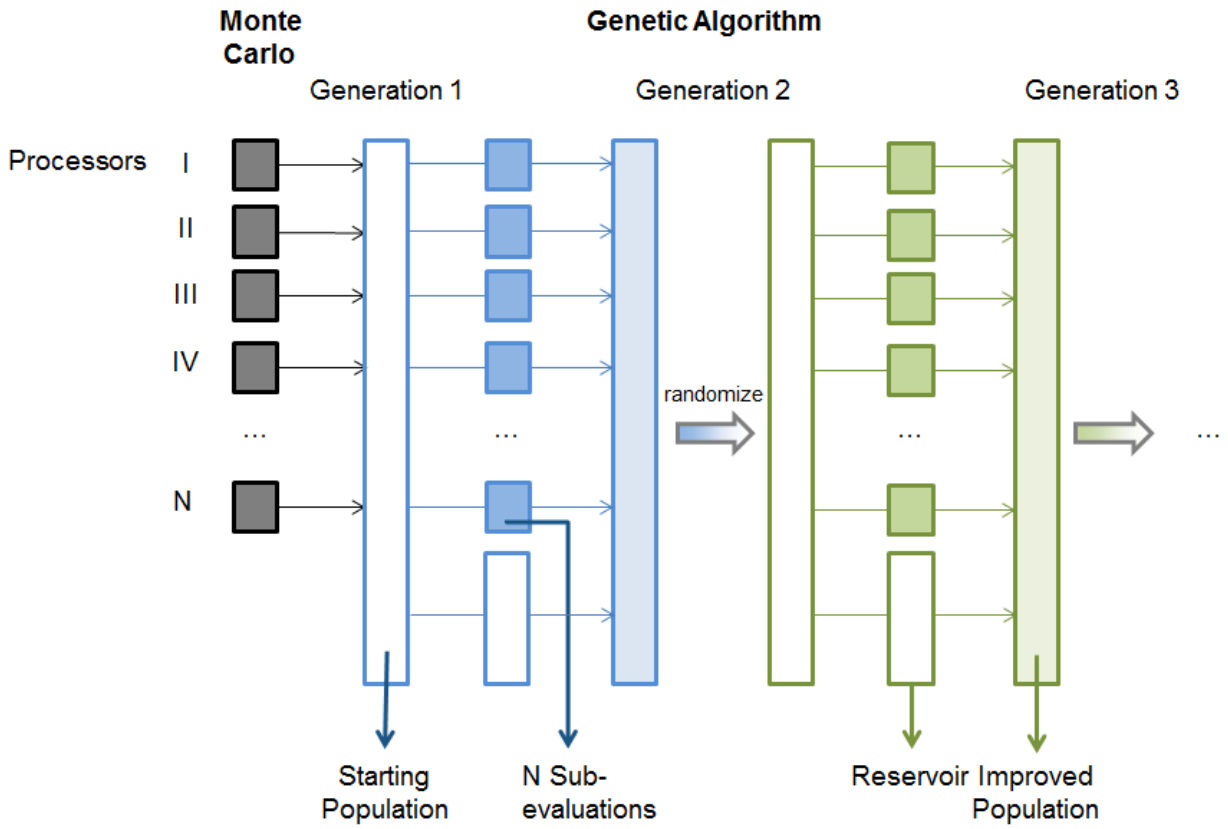



**Figure 2.** Schematic visualization of the parallelized MCGA optimization method. The Monte Carlo step is performed independently on *N* processors and the best fitting parameter sets are fed along with random parameter sets into the starting population. During the genetic algorithm step, each processor extracts a number of parameter sets from the collective pool and performs a sub-evaluation of the genetic algorithm on these parameter sets. After completion, the optimized parameter sets are fed back into the pool, which always contains a non-zero number of parameter sets as reservoir. After randomization, a different combination of parameter sets is extracted and the process repeated.

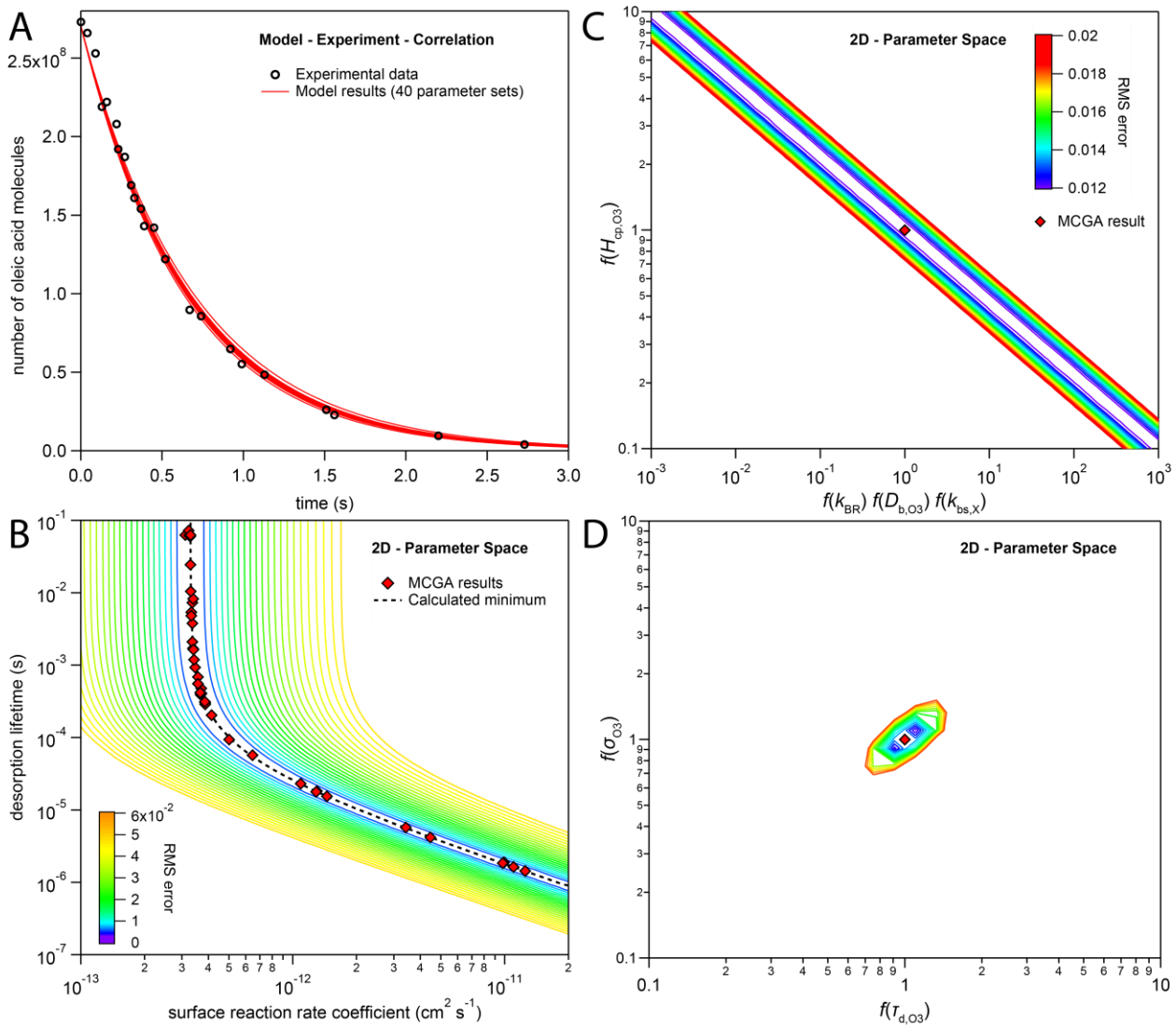



**Figure 3.** (A) Results from repeatedly fitting a kinetic model to a single experimental decay curve (adopted from Hearn et al., 2005). MCGA was used to optimize two model parameters, a surface reaction rate coefficient and the desorption lifetime of the gas phase oxidant. All other model parameters remained fixed. (B) Visualization of MCGA algorithm's findings on the 2-dimensional optimization hypersurface. The hypersurface (contour lines represent the root mean square deviances) exhibits no unique minimum due to insufficiently broad experimental data and optimization results (red diamonds) scatter along the extended minimum (black dashed line). (C) and (D) show exemplary optimization hypersurfaces with two parameters

showing an elongated (C) or a distinct minimum (D). Panels C and D are reproduced from Berkemeier et al. (2016) with permission from the PCCP Owner Societies.

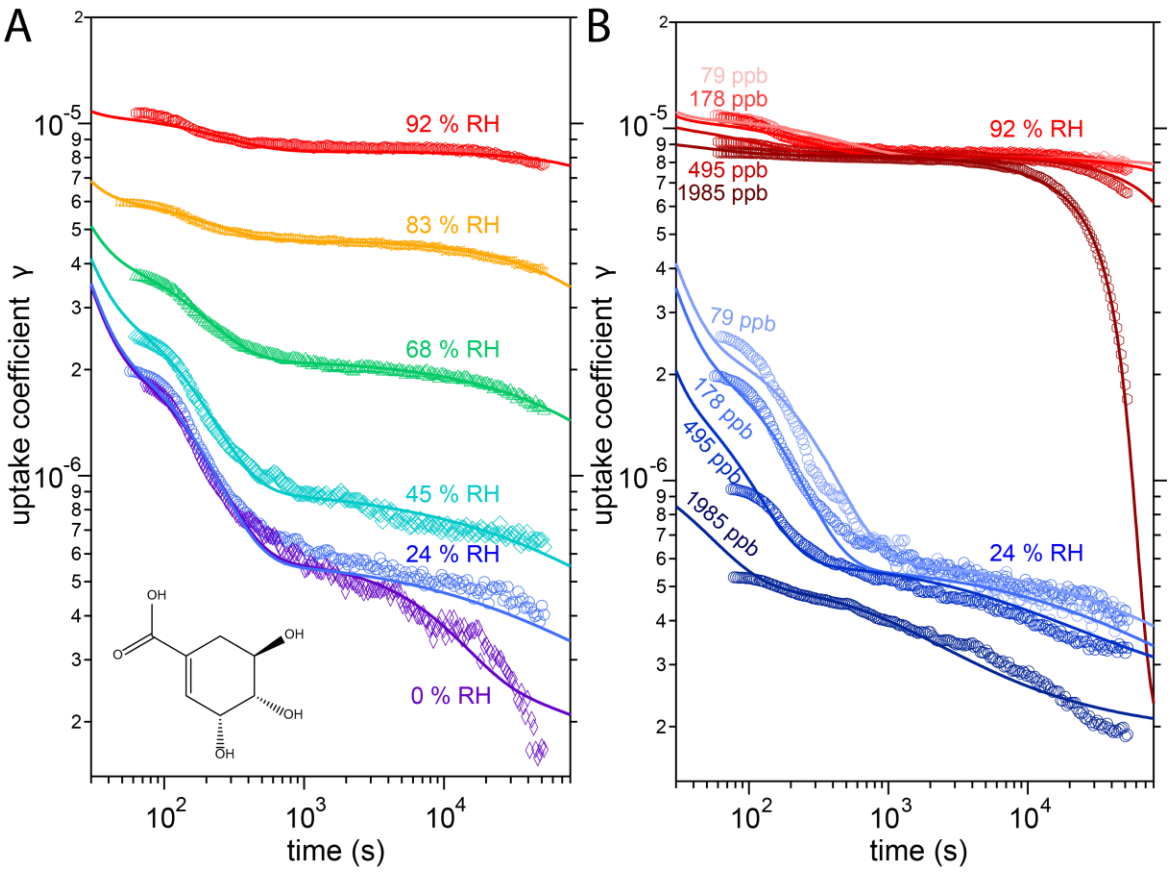
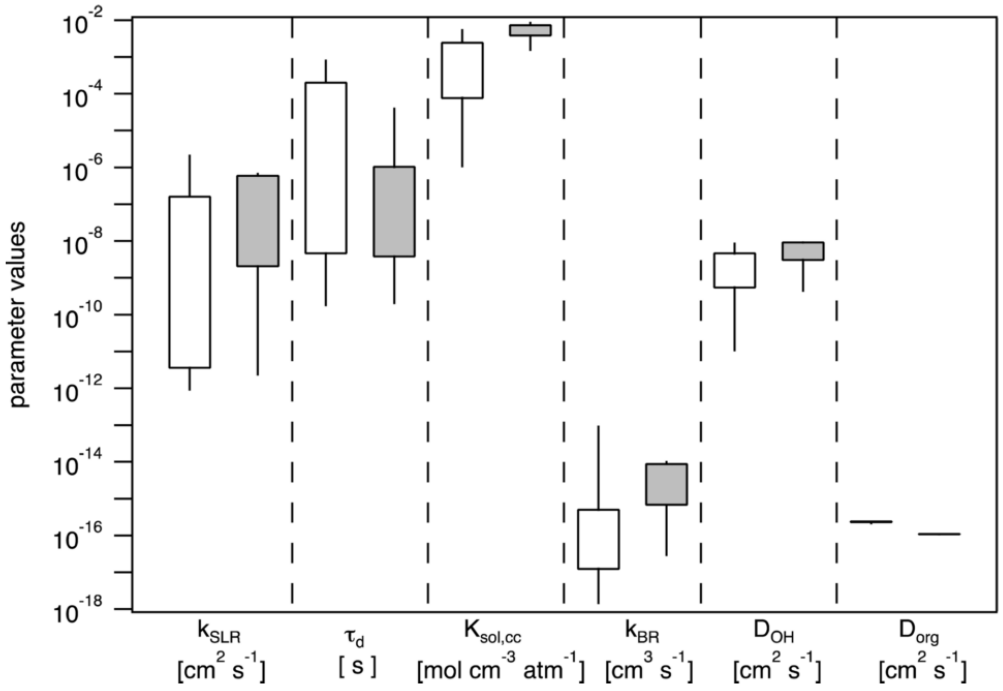



**Figure 4.** Observed (markers) and modelled (lines) uptake coefficients of ozone onto a thin film of shikimic acid as a function of exposure time. (A) Uptake coefficients at 178 ppb ozone gas phase concentration $[O_3]_g$ at different relative humidities of 0, 24, 45, 68, 83, and 92%. The structural formula of shikimic acid is displayed in the left bottom corner. (B) Uptake coefficients at 24% RH (blue solid lines) and 92% RH (red solid lines) with different $[O_3]_g$ of 79, 178, 495, and 1985 ppb. Reproduced from Berkemeier et al. (2016) with permission from the PCCP Owner Societies.




352

353 **Figure 5.** Kinetic parameters for multiphase chemical reactions of OH with levoglucosan (white) and
354 abietic acid (gray) determined by the MCGA method of fitting the experimental data with the KM-GAP
355 model. The ranges of parameters are depicted as a box−whisker plot (the percentiles of 10, 25, 75, and 90%
356 are shown). Reprinted with permission from Arangio et al. (2015). Copyright 2015 American Chemical
357 Society.

# References


Abbatt, J. P. D., Lee, A. K. Y., and Thornton, J. A.: Quantifying trace gas uptake to tropospheric aerosol: recent advances and remaining challenges, Chem. Soc. Rev., 41, 6555-6581, 2012.

Ammann, M., and Pöschl, U.: Kinetic model framework for aerosol and cloud surface chemistry and gas-particle interactions - Part 2: Exemplary practical applications and numerical simulations, Atmos. Chem. Phys., 7, 6025-6045, 2007.

Arangio, A. M., Slade, J. H., Berkemeier, T., Pöschl, U., Knopf, D. A., and Shiraiwa, M.: Multiphase Chemical Kinetics of OH Radical Uptake by Molecular Organic Markers of Biomass Burning Aerosols: Humidity and Temperature Dependence, Surface Reaction, and Bulk Diffusion, J. Phys. Chem. A, 119, 4533–4544, 10.1021/jp510489z, 2015.

Arora, J. S., Elwakeil, O. A., Chahande, A. I., and Hsieh, C. C.: Global optimization methods for engineering applications: A review, Structural optimization, 9, 137-159, 10.1007/bf01743964, 1995.

Berkemeier, T., Huisman, A. J., Ammann, M., Shiraiwa, M., Koop, T., and Pöschl, U.: Kinetic regimes and limiting cases of gas uptake and heterogeneous reactions in atmospheric aerosols and clouds: a general classification scheme, Atmos. Chem. Phys., 13, 6663-6686, 10.5194/acp-13-6663-2013, 2013.

Berkemeier, T., Steimer, S. S., Krieger, U. K., Peter, T., Poschl, U., Ammann, M., and Shiraiwa, M.: Ozone uptake on glassy, semi-solid and liquid organic matter and the role of reactive oxygen intermediates in atmospheric aerosol chemistry, Phys. Chem. Chem. Phys., 18, 12662-12674, 10.1039/C6CP00634E, 2016.

Cappa, C. D., Zhang, X., Loza, C. L., Craven, J. S., Yee, L. D., and Seinfeld, J. H.: Application of the Statistical Oxidation Model (SOM) to secondary organic aerosol formation from photooxidation of C12 alkanes, Atmos. Chem. Phys., 13, 1591-1606, 10.5194/acp-13-1591-2013, 2013.

Chan, A. W. H., Kroll, J. H., Ng, N. L., and Seinfeld, J. H.: Kinetic modeling of secondary organic aerosol formation: effects of particle- and gas-phase reactions of semivolatile products, Atmos. Chem. Phys., 7, 4135-4147, 10.5194/acp-7-4135-2007, 2007.

Finlayson-Pitts, B. J.: Reactions at surfaces in the atmosphere: integration of experiments and theory as necessary (but not necessarily sufficient) for predicting the physical chemistry of aerosols, Phys. Chem. Chem. Phys., 11, 7760-7779, 10.1039/b906540g, 2009.

George, I. J., and Abbatt, J. P. D.: Heterogeneous oxidation of atmospheric aerosol particles by gas-phase radicals, Nat. Chem., 2, 713-722, 10.1038/nchem.806, 2010.

Hanson, D. R., Ravishankara, A. R., and Solomon, S.: Heterogeneous reactions in sulfuric acid aerosols - A framework for model calculations, Journal of Geophysical Research-Atmospheres, 99, 3615-3629, 10.1029/93jd02932, 1994.

Hearn, J. D., Lovett, A. J., and Smith, G. D.: Ozonolysis of oleic acid particles: evidence for a surface reaction and secondary reactions involving Criegee intermediates, Phys. Chem. Chem. Phys., 7, 501-511, 10.1039/b414472d, 2005.

Herrmann, H., Ervens, B., Nowacki, P., Wolke, R., and Zellner, R.: A chemical aqueous phase radical mechanism for tropospheric chemistry, Chemosphere, 38, 1223-1232, http://dx.doi.org/10.1016/S0045-6535(98)00520-7, 1999.

Hosny, N. A., Fitzgerald, C., Vysniauskas, A., Athanasiadis, A., Berkemeier, T., Uygur, N., Poschl, U., Shiraiwa, M., Kalberer, M., Pope, F. D., and Kuimova, M. K.: Direct imaging of

changes in aerosol particle viscosity upon hydration and chemical aging, Chem. Sci., 10.1039/C5SC02959G, 2016.
Jenkin, M. E., Saunders, S. M., and Pilling, M. J.: The tropospheric degradation of volatile organic compounds: a protocol for mechanism development, Atmos. Environ., 31, 81-104, http://dx.doi.org/10.1016/S1352-2310(96)00105-7, 1997.
Julin, J., Shiraiwa, M., Miles, R. E. H., Reid, J. P., Pöschl, U., and Riipinen, I.: Mass Accommodation of Water: Bridging the Gap Between Molecular Dynamics Simulations and Kinetic Condensation Models, The Journal of Physical Chemistry A, 117, 410-420, 10.1021/jp310594e, 2013.
Kampf, C. J., Liu, F., Reinmuth-Selzle, K., Berkemeier, T., Meusel, H., Shiraiwa, M., and Pöschl, U.: Protein Cross-Linking and Oligomerization through Dityrosine Formation upon Exposure to Ozone, Environ. Sci. Technol., 49, 10859-10866, 10.1021/acs.est.5b02902, 2015.
Kolb, C. E., Cox, R. A., Abbatt, J. P. D., Ammann, M., Davis, E. J., Donaldson, D. J., Garrett, B. C., George, C., Griffiths, P. T., Hanson, D. R., Kulmala, M., McFiggans, G., Pöschl, U., Riipinen, I., Rossi, M. J., Rudich, Y., Wagner, P. E., Winkler, P. M., Worsnop, D. R., and O' Dowd, C. D.: An overview of current issues in the uptake of atmospheric trace gases by aerosols and clouds, Atmos. Chem. Phys., 10, 10561-10605, 10.5194/acp-10-10561-2010, 2010.
Lakey, P. S. J., Berkemeier, T., Tong, H., Arangio, A. M., Lucas, K., Pöschl, U., and Shiraiwa, M.: Chemical exposure-response relationship between air pollutants and reactive oxygen species in the human respiratory tract, Sci. Rep., 6, 32916, 10.1038/srep32916, 2016a.
Lakey, P. S. J., Wisthaler, A., Berkemeier, T., Mikoviny, T., Pöschl, U., and Shiraiwa, M.: Chemical kinetics of multiphase reactions between ozone and human skin lipids: implications for indoor air quality and health effects, Indoor Air, Accepted Manuscript, 10.1111/ina.12360, 2016b.
Lowe, S., Partridge, D. G., Topping, D., and Stier, P.: Inverse modelling of Köhler theory – Part 1: A response surface analysis of CCN spectra with respect to surface-active organic species, Atmos. Chem. Phys., 16, 10941-10963, 10.5194/acp-16-10941-2016, 2016.
McNeill, V. F., Woo, J. L., Kim, D. D., Schwier, A. N., Wannell, N. J., Sumner, A. J., and Barakat, J. M.: Aqueous-phase secondary organic aerosol and organosulfate formation in atmospheric aerosols: A modeling study, Environ. Sci. Technol., 46, 8075-8081, 10.1021/es3002986, 2012.
Partridge, D. G., Vrugt, J. A., Tunved, P., Ekman, A. M. L., Struthers, H., and Sorooshian, A.: Inverse modelling of cloud-aerosol interactions – Part 2: Sensitivity tests on liquid phase clouds using a Markov chain Monte Carlo based simulation approach, Atmos. Chem. Phys., 12, 2823-2847, 10.5194/acp-12-2823-2012, 2012.
Pöschl, U., Rudich, Y., and Ammann, M.: Kinetic model framework for aerosol and cloud surface chemistry and gas-particle interactions - Part 1: General equations, parameters, and terminology, Atmos. Chem. Phys., 7, 5989-6023, 2007.
Pöschl, U., and Shiraiwa, M.: Multiphase Chemistry at the Atmosphere–Biosphere Interface Influencing Climate and Public Health in the Anthropocene, Chem. Rev., 115, 4440–4475, 10.1021/cr500487s, 2015.
Riedel, T. P., Lin, Y. H., Zhang, Z., Chu, K., Thornton, J. A., Vizuete, W., Gold, A., and Surratt, J. D.: Constraining condensed-phase formation kinetics of secondary organic aerosol components from isoprene epoxydiols, Atmos. Chem. Phys., 16, 1245-1254, 10.5194/acp-16-1245-2016, 2016.
Saunders, S. M., Jenkin, M. E., Derwent, R. G., and Pilling, M. J.: Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part A): tropospheric degradation of non-aromatic volatile organic compounds, Atmos. Chem. Phys., 3, 161-180, 10.5194/acp-3-161-2003, 2003.

Shiraiwa, M., Pfrang, C., and Pöschl, U.: Kinetic multi-layer model of aerosol surface and bulk chemistry (KM-SUB): the influence of interfacial transport and bulk diffusion on the oxidation of oleic acid by ozone, Atmos. Chem. Phys., 10, 3673-3691, 2010.
Shiraiwa, M., Pfrang, C., Koop, T., and Pöschl, U.: Kinetic multi-layer model of gas-particle interactions in aerosols and clouds (KM-GAP): linking condensation, evaporation and chemical reactions of organics, oxidants and water, Atmos. Chem. Phys., 12, 2777-2794, 10.5194/acp-12-2777-2012, 2012.
Shiraiwa, M., Yee, L. D., Schilling, K. A., Loza, C. L., Craven, J. S., Zuend, A., Ziemann, P. J., and Seinfeld, J. H.: Size distribution dynamics reveal particle-phase chemistry in organic aerosol formation, Proc. Natl. Acad. Sci. USA, 110, 11746-11750, 10.1073/pnas.1307501110, 2013.
Shiraiwa, M., Berkemeier, T., Schilling-Fahnestock, K. A., Seinfeld, J. H., and Poschl, U.: Molecular corridors and kinetic regimes in the multiphase chemical evolution of secondary organic aerosol, Atmos. Chem. Phys., 14, 8323-8341, 10.5194/acp-14-8323-2014, 2014.
Smith, G. D., Woods, E., Baer, T., and Miller, R. E.: Aerosol uptake described by numerical solution of the diffusion - Reaction equations in the particle, Journal of Physical Chemistry A, 107, 9582-9587, 10.1021/jp021843a, 2003.
Steimer, S. S., Berkemeier, T., Gilgen, A., Krieger, U. K., Peter, T., Shiraiwa, M., and Ammann, M.: Shikimic acid ozonolysis kinetics of the transition from liquid aqueous solution to highly viscous glass, Phys. Chem. Chem. Phys., 17, 31101-31109, 10.1039/C5CP04544D, 2015.
Vieceli, J., Roeselova, M., Potter, N., Dang, L. X., Garrett, B. C., and Tobias, D. J.: Molecular dynamics simulations of atmospheric oxidants at the air-water interface: Solvation and accommodation of OH and $O_3$, Journal of Physical Chemistry B, 109, 15876-15892, 10.1021/jp051361+, 2005.
Worsnop, D. R., Morris, J. W., Shi, Q., Davidovits, P., and Kolb, C. E.: A chemical kinetic model for reactive transformations of aerosol particles, Geophys. Res. Lett., 29, 57, 10.1029/2002gl015542, 2002.
Zobrist, B., Soonsin, V., Luo, B. P., Krieger, U. K., Marcolli, C., Peter, T., and Koop, T.: Ultra-slow water diffusion in aqueous sucrose glasses, Phys. Chem. Chem. Phys., 13, 3514-3526, 10.1039/c0cp01273d, 2011.
Zuend, A., and Seinfeld, J. H.: A practical method for the calculation of liquid–liquid equilibria in multicomponent organic–water–electrolyte systems using physicochemical constraints, Fluid Phase Equilibria, 337, 201-213, 2013.