Tailored reduced kinetic mechanisms for atmospheric chemistry modeling

L. M. T. Joelsson*, C. Pichler, E. J. K. Nilsson

Department of Physics, Combustion Physics, Lund University, Box 118, SE-221 00 Lund, Sweden

Abstract

Reduced chemical kinetic mechanisms are essential for atmospheric chemistry modeling where use of explicit kinetic schemes are too computationally demanding. By tailoring of mechanisms to specific cases, mechanism size can be kept small, without significant loss of accuracy in predictions of selected species' concentrations. In the present work we present small kinetic mechanisms tailored using a novel method.

The reduced mechanisms are generated by applying the method to several cases previously described in the literature and their performance in box model simulations are evaluated. The characteristics of the reduced mechanisms are examined. In addition, the method’s sensitivity towards time scales, choice of trace gas species of interest; and NOx regime are investigated.

The reduced mechanisms include 10 %–30 % of all the reactions in the relevant subset of the detailed chemical mechanism. Simulations with the reduced mechanisms typically yield no loss in accuracy of ozone concentration predictions and less than a 10 % accuracy loss for the concentration predictions of nitrogen oxides for the cases over as long as five simulated days.

Mechanisms generated to predict the concentrations of few species, over short time scales, high NOx conditions with no isoprene generally include fewer reactions than mechanisms generated to predict the concentrations of several

*Corresponding author
Email address: magnus.joelsson@forbrf.lth.se (E. J. K. Nilsson)
species, over long time scales, in isoprene rich, low NO\textsubscript{x} conditions.

Keywords: Box modeling, air pollution, reduced chemical kinetic mechanism, ant colony optimization

1. Introduction

Growing concern for emissions of air pollutants deteriorating local and regional air quality as well as greenhouse gases altering the Earth’s radiation budget, has spurred development of computational modeling of the atmosphere (e.g. Ginnebaugh et al. 2010; Naik et al. 2013). Modeling is a tool to understand atmospheric processes and a means of predicting trends in climate and air quality by extrapolation into the future. Accurate predictions of concentrations of various trace gases are important in order to provide proper decisions basis for policy-makers, both on local and regional air quality and on global climate issues (IPCC 2013).

Coupled atmospheric chemistry-transport modeling is conducted at a wide range of spatial scales, from global (e.g. Emmons et al. 2010) and regional scales (Monks et al. 2009) to the street scale (Zhong et al. 2016a). The scale of the model domain put requirements on the chemical kinetic mechanism, since the (advection) time scale and spatial scale of a chemistry-transport system are coupled. In the present study, time scales of up to five days are considered and extra attention is paid to the urban local scale (i.e. street canyon) application, since the coupled chemistry-transport modeling in this setting is a rather new research topic with high demands on the chemical mechanisms. Also, local systems under short periods of time will experience a narrower span of conditions than a global system under long periods of time. A local scale model will therefore be especially suitable for a tailored reduction of its chemical description.

Reduction of kinetic mechanisms is commonly achieved via structural lumping (Gery et al. 1989), intermediate species lumping (Jenkin et al. 2008), emission lumping (Stockwell et al. 1997; Watson et al. 2008; Bright et al. 2013) or sensitivity analysis (present study). Several reduced chemical mechanisms have
been presented in the literature, some described in a review of coupled street
canyon modeling (Zhong et al., 2016a), some described in a comparison study of
chemical mechanisms used in global models (Emmerson and Evans 2009). The
level of detail on the mechanisms vary from simple O$_3$–NO$_x$ chemistry (nitrogen
oxides: $[\text{NO}_x] = [\text{NO}] + [\text{NO}_2]$) to inclusion of a range of hydrocarbons.

Some street canyon air quality studies develop or use reduced mechanisms
based on the Master Chemical Mechanism (MCM) family of mechanisms (Bright
et al., 2013; Zhong et al., 2016b). MCM is an attempt to describe tropospheric
chemistry explicitly (Saunders et al., 2003; Jenkin et al., 2003; MCM, 2018).
The latest MCM version 3.3.1 (Jenkin et al., 2015) follow the photooxidation
path of methane and 142 additional VOCs adding up to 16 701 reactions and
5 832 species. Other extensive mechanisms are the National Center for At-
mospheric Research Master Mechanism (NCAR-MM) (Madronich and Calvert
1989; NCAR, 2018) and the Statewide Air Pollution Research Center Atmo-
spheric Chemical Mechanisms (SAPRC) (Carter, 2010; Carter and Heo, 2013;
SAPRC, 2013). These mechanisms and more are briefly reviewed in Zhong
et al. (2016a) and compared in Chen et al. (2010). The results of Chen et al.
(2010) as well as of other studies (e.g. Emmerson and Carslaw 2009; Whalley
et al., 2011) indicate that no mechanism thus far is able to perfectly replicate
field measurement data in any given settings nor is there necessarily always
a negative correlation between deviation from measurement and mechanism
size. For example, hydrogen radical concentrations in low NO$_x$ environments
have proved elusive. The limitation of the parent mechanism will presumably
be inherited in any reduced mechanism. Most of the street-scale simulations
use mechanisms either originally developed for regional or global applications,
such as the GEOS-Chem mechanism (Kim et al., 2012), or derived from such
mechanisms, e.g. Reduced Chemistry Scheme (RCS) (Bright et al., 2013; Zhong
et al., 2016b) and Complex Chemical Mechanism (CCMCFD) (Sanchez et al.
2016) which are derived from the Common Representative Intermediate (CRI)
(Jenkin et al., 2008) and Regional Atmospheric Chemistry Mechanism (RACM)
(Stockwell et al., 1997), respectively.
When reducing mechanisms, there will always be a trade-off between accuracy and computational speed (which depend on the number of reactions and species included). A way to solve the need for accuracy but still keep the number of reactions and species low is to tailor mechanisms for a limited set of conditions with respect to emissions, concentrations, etc. Other important aspects of the tailoring procedure are the time scales for which the reduced mechanism is to be used and the compounds for which the concentrations are considered important to predict (target compounds). To our knowledge, the first automatically tailored mechanism to be used in a street canyon simulation, was CCMCFD, developed in by Sanchez et al. (2016) with the software CHEMATA (CHEmical Mechanism Adaptation to Tropospheric Applications) (Kirchner, 2005; Junier et al., 2005). CHEMATA takes species, their source strength, and kinetic data as input to generate an explicit or lumped reduced mechanism. CHEMATA does not, however, consider other conditions such as time frames, solar radiation, and temperature (solar radiation and temperature is implicitly included in the kinetic data input, but does not, to our understanding, influence the selection of reactions or species) nor does it consider the interest of the user in terms of predictions of certain compounds. These conditions constrain the degree to which a mechanism can be reduced with utility as will be shown below. Moreover, advances in kinetic research (e.g. Yarwood et al., 2010; Carter and Heo, 2013; Jenkin et al., 2015) calls for continuous updating of the detailed mechanisms, eventually making the older versions and thus their reduced offspring outdated. The tailored approach will enable the reduced mechanisms to be in pace with the most recent detailed version of its parent mechanism franchise.

The aim of the present work is to evaluate the performance and describe the characteristics of tailored kinetic mechanisms for modeling of atmospheric chemistry. Reduced mechanisms generated for cases with different compositions of trace gases, values of temperature, relative humidity, and solar radiation influx, along with various time scales and sets of target compounds are evaluated and characterized. Differences among the reduced mechanisms, which presumably reflect their cases’ NO$_x$ regime, are given special attention. From evaluation
of the mechanisms performance and characteristics, conclusions can be made on the need for chemical detail in modeling of atmospheric chemistry. In the current study, chemical kinetics mechanisms are tailored for six cases originally presented by Emmerson and Evans (2009) plus one high NO$_x$ case (see Section 2.2) along with a mechanism tailored for all six cases combined. Mechanisms are also tailored for three time scales (see Section 2.3) and two target compound sets (see Section 2.4). Their performance (ability to accurately predict target compound concentrations), sizes (number of reactions), and characteristics (composition of reactions) are discussed (see Section 3).

2. Methodology

2.1. Mechanism reduction and box modeling

The kinetic mechanisms employed in the current study, are generated by reducing a detailed mechanism (henceforth called base mechanism) while limiting the consequential loss of precision of relevant predictions. Here, the base mechanism is MCM v3.3.1. The reduction method, denoted Ant Colony Reduction (ACR), is a semi-stochastic, statistical method based on the heuristic Ant Colony Optimization (ACO) concept (Dorigo et al., 1996; Dorigo and Birattari, 2011) and was recently developed for combustion physics applications (Pichler and Nilsson, 2018). The main idea behind the ACO algorithms is to mimic biological ant colonies’ ability to find optimal trails between their anthill and some food resource by communications via the distribution of pheromones. Similarly, within ACR, simulated ants are set out to find optimal oxidation paths in a kinetic mechanism from an emitted compound (e.g. VOC or NO$_x$) to an oxidation end product (e.g. water vapor, carbon dioxide, or aqueous phase nitric acid). A large number of functional reduced mechanisms are generated for each application of the method which partly allows the users to select the most suitable mechanism for their demands, partly allows the method to be improved recursively. The reduced mechanisms are evaluated via box model simulations.
The reduction process is designed as such: All reactions in the base mechanism with one particular species (initially, this can be an emitted hydrocarbon) as reactant are listed. The reactions are ascribed weights calculated from a combination of static rate of production values and non-static “pheromone”-values. The pheromone-value mimic the ant’s pheromone trails, which intensities are used to communicate the utility of a certain path from the anthill to a food resource between individual ants and the ant colony. Thus, the artificial pheromone-value in the method is continuously re-calculated based on feedback data from the method itself (e.g. reduced mechanism performance and size).

Reactions important for an accurate description on the chemical system will hence gain more weight through the reduction process compared to less important reactions. A reaction is semi-stochastically selected according to their weight; this way an entire oxidation path is built up. The set of reactions collected through the process makes up the reduced mechanism. The reduced mechanism is evaluated by a box model simulation and is given an (average) root-mean-square score, see Eq. (1).

The accuracy (or score) of the mechanisms is defined as:

\[
\text{score} \equiv \frac{1}{n} \sum_{A=X_1, X_2, \ldots, X_n} 1 - \sqrt{\left( \frac{[A]_{\text{reduced}}}{[A]_{\text{base}}} - 1 \right)^2}
\]

(1)

where \([A]\) is the concentration of target compound A. The subscript reduced refers to predictions obtained with a simulation using the reduced mechanism, in this case the subscript base refers to predictions (base predictions) obtained with a simulation using the base mechanism, but can also be concentrations obtained with measurements.

The box model used in the current study is a version of the chemical module of the Aerosol Dynamics, gas- and particle-phase chemistry model for laboratory CHAMber studies (ADCHAM) model (Roldin et al., 2014), where the aerosol sub-module is omitted. The model uses the Kinetic Pre-Processor (KPP) software (Damian et al., 2002). The photolysis constants are calculated with the Tropospheric Ultraviolet and Visible (TUV) Radiation Model (NCAR, 2018).
In the process, a large number of reduced mechanisms (here, 6,000) are constructed and evaluated before one final reduced mechanism is selected. Note that all the constructed reduced mechanisms are functional kinetic mechanisms even though the primary role of this abundancy in mechanism generation and scoring is to refine the overall reduction process. The reduced mechanisms span a range of sizes and corresponding accuracy, such that either a sufficiently small (inexpensive) or sufficiently accurate mechanism for the demand of the application in question can be chosen. In the current study, the smallest (including fewest reactions) reduced mechanism scoring higher than 0.9 (0.7 for the biogenic case, see below) is selected. This reduced mechanism is called A0.90 (A0.70). The entire process takes a few hours on the working desk-top machine used in the present work (15.7 GB memory, eight-core processor ×16), depending on the complexity of the case.

Example of full selections of accepted reduced mechanisms generated by entire reduction processes and the selected reduced mechanisms are depicted in Fig. 1.

2.2. Cases: Different pollution scenarios

Mechanisms are generated for the prediction of the target compound sets described below (see Section 2.4) in six cases, previously described by Emmerson and Evans (2009).

The initial conditions for the six cases are derived from an annual simulation of the GEOS-CHEM composition transport model (Bey et al., 2001). The six cases take on values from grid boxes which reach extremes in typical tracer concentration patterns representing six types of environments: Industrial, clean, cold & dry, hot & wet, biogenic, and non-biogenic. The initial values of the six cases are tabulated in Table 1. The cases were used to study the six chemistry mechanisms’ ability to predict the concentrations of ozone, NO$_x$, nitrate, hydroxyl radical, and PAN for five simulated days (120 hour), starting at midnight local time, in a box model setting. Emmerson and Evans’ idea is to test the mechanisms in the wide range of condition which are likely to occur in a global
Figure 1: The full selection of accepted mechanisms generated by six entire reduction processes of the hot & wet case, see Table I. Mechanisms tuned to the three different time scale are depicted in the three panels (from left to right): Five-day, one-day, and one-hour. Mechanisms tuned to the two target compound sets are depicted with colored dots: Basic (blue) and Emmerson (red). The A0.90 mechanisms are encircled, the grey dotted lines correspond to the cut-off for the score (0.90).

model. In the current study, the idea is to test the method’s ability to tailor mechanisms for this wide range of realistic (but simplified) conditions, and to evaluate the inter-variability of the produced mechanisms for the six cases. The five-day time scale and the target compounds are retained in the current study. Emmerson and Evans (2009) use MCM v3.1 as the benchmark. The mean deviation of the target compounds between MCM v3.1 and MCM v3.3.1 formulated as a score with the MCM v3.3.1 used as the base mechanism for all the cases lie between 0.44 and 0.89, reflecting the development of the MCM mechanism. Direct comparisons between the current simulation results and the benchmark simulation of Emmerson and Evans (2009) are thus not relevant. The mean deviation of the target compounds between MCM v3.1 and MCM v3.3.1 formu-
lated as a score with the MCM v3.3.1 used as the base mechanism for all the cases are presented in Section S.1 and the time resolved predictions are plotted in Figs. S.1–S.6 in the Supplementary Material.

Two cases include isoprene (C$_5$H$_8$, industrial and biogenic) and four do not. The four non-isoprene cases all share the same initial compound setup, only the initial concentrations of the different compounds are varied. Similarly, the two isoprene cases share the same initial compound setup. The four non-isoprene cases will thus be reduced from (and tested against) one particular subset of the full MCM mechanism (296 reactions, 99 species), and the two isoprene cases will be reduced from another particular subset (2016 reactions, 638 species). The non-isoprene base mechanism corresponds to a MCM subset with methane, ethane, propane, formaldehyde, acetaldehyde, and acetone as parent compounds including inorganic species as can be downloaded from the MCM website [MCM 2018]. All reaction including sulphur are removed. The isoprene base mechanism corresponds to a MCM subset which includes isoprene as well as all the other parent compounds listed above. There is a substantial complexity of the isoprene chemistry (Jenkin et al., 2015; Wennberg et al., 2018); the isoprene chemistry subset covers 1 900 reactions, which is about 10 % of the size of the full MCM mechanism. Furthermore, isoprene’s two olefinic bonds warrant high reactivity and thus a significant role in ozone chemistry.

The NO$_x$ regime of a system can be indicated by whether the dominant sink of radicals (hydroxyl-, hydroperoxyl-, and organic peroxy radicals) is reactions with NO$_x$ or not (Jacob, 1999). Kleinman et al. (1997) introduces the measure $L_N/Q$ as an indicator for the NO$_x$ regime of a system, where $L_N$ represents the total rate of all reactions where a radical reacts with either nitric oxide or nitrogen dioxide and $Q$ the total rate of all radical loss reactions. A high NO$_x$ system is defined as a system where $L_N/Q > 0.5$, a system with $L_N/Q < 0.5$ is defined as a low NO$_x$ system. Consequently, a system commonly shifts from one regime to another under the course of a day. The average ratios, $\mu(L_N/Q)$, for the cases are tabulated in Table 1. It can be noted that three cases are (on average) in the high NO$_x$ regime: Industrial, cold & dry, and non-biogenic and
three cases are in the low NO\textsubscript{x} regime: Clean, hot \& wet, and biogenic. The time resolved \( L_N/Q \) ratios for the cases are plotted in Figs. S.7–S.13 in the Supplementary Material.

In order to isolate the chemistry’s sensitivity of \( L_N/Q \), mechanisms are reduced for the hot \& wet case with increased levels of nitrogen dioxide, in addition to the cases represented in (Emmerson and Evans, 2009), see the high NO\textsubscript{x} rows in Table 1. The initial concentration of 80 ppb nitrogen dioxide is chosen to be comparably high, but not unrealistic. The value is below the official 1-hour health thresholds for nitrogen dioxide, but slightly above the annual mean threshold: The WHO 1-hour average nitrogen dioxide standard is set to \( 200\mu\text{gm}^{-3} \approx 100\text{ppb} \) and the annual nitrogen dioxide standard is set to \( 40\mu\text{gm}^{-3} \approx 20\text{ppb} \) (WHO, 2006), the EPA 1-hour average nitrogen dioxide standard is set to 100 ppb and the annual average nitrogen dioxide standard is set to 53 ppb (EPA, 2011).

Finally, one mechanism is generated for the purpose of predicting the target compound concentrations with (on average) high accuracy for all Emmerson and Evans six original cases. This mechanism is named the all-round mechanism.

2.3. Time scales

To investigate the methods sensitivity to time scales, mechanisms are tailored to the cases described in Section 2.2 over shorter time scales. The underlying assumption is that shorter time scales offer less time for the chemistry to evolve and therefore the selection of chemical reactions may differ. Furthermore, the exclusion of a period without photolysis (night) is expected to influence the size and characteristics of a reduced mechanism.

Mechanisms are generated for time scales of one day (24 hours) and one hour in addition to the default time scale of five days. One hour corresponds to the time scales of residence time in a confined urban environment that is not efficiently ventilated to the free boundary layer. An hour in the middle of the day is selected. The day time simulations are initialized at 11:30 local time such that solar zenith of the simulations will occur at the midpoint of the simulation.
time, as for the simulations with longer time scales. The one-day and five-day simulations will be initialized at midnight.

When considering time scales, also the spin-up time of the model should be taken into account. The spin up allows the concentrations of all uninitialized compounds to build up to realistic levels. Reasonable spin up time depend on the spatial scale of the model: For regional and global models, the spin-up time can be on the order of days. For street canyon modelling, on the other hand, 30 minutes have been considered conservative (Bright, 2012).

2.4. Target compound sets

Depending on the goal of a simulation, different compounds are of interest. In this study we perform mechanism reduction constrained to two target compound sets, to investigate the influence on the mechanism size and its composition of reactions. The two sets of target compounds are:

- **Emmerson**: Emmerson and Evans (2009) studied the concentrations of ozone, \( \text{NO}_x \), nitrate, hydroxyl radical, and PAN for a number of mechanisms. In the present study, these compounds make up the Emmerson target compound set with the expansion of \( \text{NO}_x \) into nitric oxide and nitrogen dioxide. Nitric oxide and nitrogen dioxide are thus targeted individually in the reduction process, even though occasionally represented together as \( \text{NO}_x \).

- **Basic**: Ozone, nitric oxide, and nitrogen dioxide are arguably the compounds of most interest in the air pollution community, partly due to their environmental and health impacts, partly to the extensive monitoring of these compounds in urban settings. These compounds constitute the Basic target compound set.

2.5. Reaction categories

In the analysis of the generated mechanisms seven mutually exclusive categories of reactions are used. There is a hierarchy of the categories, such that
those reactions that meet the criteria of several categories, fall in the first cat-
gegory for which these criteria is met, as they are listed below:

1. \(RO_2 + NO\): All the reactions in the form \(RO_2 + NO \rightarrow RO + NO_2\), where an organic peroxy radical reacts with a nitric oxide to produce a nitrogen dioxide.

2. \(RH + OH\): All the reactions in the form \(RH + OH \rightarrow RO_2 + H_2O\), where an organic compound reacts with a hydroxyl radical to eventually produce an organic peroxy radical.

3. other \(NO_x\): Other reactions that have nitric oxide or nitrogen dioxide either as a reactant or a product.

4. other \(NO_y\): Other reactions that have any nitrogen containing compound (predominantly oxidized nitrogen, commonly defined as \([NO_y] \equiv [NO_x] + [HNO_3] + [HONO] + [N_2O_5] + [ClONO_2] + [NO_3] + [HOONO_2] + [BrONO_2]\), either as a reactant or a product. However, all reactions involving nitric oxide or nitrogen dioxide fall into the other \(NO_x\) category and are not included here. This reaction category is especially associated with night time chemistry.

5. other \(HO_x\): Other reactions that have hydroxyl radical or hydroperoxyl radical either as a reactant or a product.

6. other \(RO_2\): Other reactions that have an organic peroxy radical either as a reactant or a product (predominantly peroxy-peroxy reactions).

7. other: All other reaction (\(O_x\) reactions and unimolecular decomposition of hydrocarbons).

The reaction categories are designed to capture the characteristics of mechanisms beyond size.

3. Results and discussion

3.1. Different pollution scenarios

The size and the score of all simulations with the A0.90 (A0.70) mechanism of all the cases, as described in Sections 2.1 and 2.2 are tabulated in Table
The extent of reduction in number of reactions and species for the reduced mechanisms, including the all-round mechanism, are presented in Table 3. All reduced mechanisms are developed for five simulated days using the Emmerson target compound set except where otherwise noted. The threshold for the accuracy based mechanism in the biogenic case is lowered to 0.70 (A0.70), since the method does not return useful mechanisms with accuracy above 0.90 with the current settings. The smallest A0.90 mechanism for the biogenic case generated thus far includes 1734 reactions and 633 species. The partial scores of the A0.90 (A0.70) mechanisms are presented in see Table 4.

Since common approaches to chemistry simulations of urban street canyon air quality models are either to use a minimal O₃–NOₓ-mechanism (Zhong et al., 2016a) or simply regard all compounds as unreactive (no chemistry) (Vardoulakis et al., 2003), the cases are tested with these approaches. Scores obtained by simulations with an O₃–NOₓ mechanism, covering only three reactions, and scores calculated by keeping the concentrations constant (no chemistry) are tabulated in Table 2.

It can be deduced from Tables 2–4 that the method can successfully generate reduced mechanisms for simple non-isoprene or isoprene lean atmospheric chemistry cases, down to a third or even a tenth the size of a near-explicit chemistry subset without losing more than 10% accuracy on average of predictions of a set of relevant compounds over at least as long as five days, even if the chemistry is in the NOₓ-limited regime. Isoprene rich chemistry proved to require larger numbers of reactions to accurately predict the target compound concentrations, especially PAN and hydroxyl radicals (both with partial scores of 0.54 for the A0.70). The all-round mechanisms scored 0.98 or higher for all non-isoprene cases, 0.90 for the industrial case, and 0.56 for the biogenic case.

Generally, the score of the cases with $\mu(L_N/Q) < 0.5$ (hot & wet, clean, and biogenic) are mostly held back by the low accuracy of the PAN prediction, while this is not the case for the cases with higher $\mu(L_N/Q) > 0.5$, where the PAN score does not stand out from the other trace gas species prediction scores.
3.2. Non-isoprene cases

3.2.1. Cases

Figure 2: Details of the simulation of the clean (upper panels) and cold & dry (lower panels) over five days: MCM (green color) and A0.90 mechanisms (blue) broken up compound by compound as (from left) OH, O\textsubscript{3}, NO\textsubscript{x}, and PAN. All mechanisms are optimized to simulate the Emmerson target compound set. The scoring is described in Eq. (1).

The result of all non-isoprene cases, five-day simulations with the A0.90 mechanism of all the cases are depicted along with the results of the simulation using the non-isoprene MCM subset in Figs. 2 and 3 all developed using the Emmerson target compound set. The result of the high NO\textsubscript{x} alteration of the hot & wet case five-day simulation is depicted in Fig. 4. Additionally, the scores of the prediction of peroxy radical concentrations ([HO\textsubscript{2}] and [RO\textsubscript{2}]) of the five-day Emmerson non-isoprene mechanism simulations are added to Table 4. The time resolved concentration predictions are plotted in Figs. S.14–S.18 in the Supplementary Material.

Figs. 2 and 3 show very small deviations between the reduced mechanisms and the full MCM predictions. The reactions included in the A0.90-mechanisms,
Figure 3: Details of the simulation of the hot & wet (upper panels) and non-biogenic (lower panels) over five days: MCM (green color) and A0.90 mechanisms (blue) broken up compound by compound as (from left) OH, O₃, NOₓ, and PAN. All mechanisms are optimized to simulate the Emmerson target compound set. The scoring is described in Eq. (1).

divided into the reaction categories as defined in Section 2.5 are depicted as bars in Fig. 5, the number of reactions of each category in the MCM subset are depicted as envelope bars. For all the cases the largest absolute reduction is in the other HOₓ category (where 73–94 reactions are removed from the MCM subset corresponding to 36 %–39 % of the total reduction), followed by the other NOₓ (53–61 reactions corresponding to 23 %–28 %), other RO₂ (31–40 reactions, corresponding to 15 %–18 %), RH + OH (19–30 reactions corresponding to 15 %–12 %), RO₂ + NO (10–13 reactions, corresponding to 4 %–5 %), other NOₙ (8–10 reactions, corresponding to about 4 %), and other (3 reactions, corresponding to 1 %–2 %) categories. About a third of the reduction in any of the cases investigated are thus made in the categories concerning hydrocarbons (RO₂ + NO, RH + OH, and other RO₂), about a third in the category concerning HOₓ reactions without hydrocarbons (other HOₓ), and about a third
in the categories concerning reactions including reactive nitrogen without hydrocarbons (other NO\textsubscript{x} and other NO\textsubscript{y}). Only a small reduction is made in the other category. The absolute reduction scales quite well with the size of the category in the MCM subset: The more reactions that are included in the category, the more reactions are removed by the reduction process. It can be noted, however, that the other NO\textsubscript{y} (9 \%-27 \% of the reactions are left), other HO\textsubscript{x} (11 \%-31 \%), and other RO\textsubscript{2} (2 \%-24 \%) categories are generally reduced to a higher degree than the RO\textsubscript{2} + NO (18 \%-37 \%), RH + OH (14 \%-45 \%), and other NO\textsubscript{x} (22 \%-32 \%) categories for the selected mechanisms. All the A0.90 mechanism have the same set of other reactions, which are the oxygen/ozone regeneration reactions and the decomposition of formaldehyde. The oxygen/ozone regeneration reactions have in the current reduction processes been included in
the mechanisms automatically and were therefore not explicitly selected by the reduction process. The relatively small size of the non-biogenic mechanism implies that the general level of initial concentrations of the reactants, not only their relative abundance, influence the extent of reduction. This could be the result of smaller variation in reaction channels.

Indication on how the NO$_x$ regime affects the reduction process can be easiest found by comparing the hot & wet and the hot & wet, high NO$_x$ cases since only the NO$_x$ content differs between the two. The reduction process did render a smaller A0.90 mechanism for the hot & wet, high NO$_x$ than the default hot & wet case (57 reactions, 38 species versus 96 reactions, 57 species). The partial scores (Table 4) give relatively better PAN scores (0.92 for the high NO$_x$ versus 0.80 for the default hot & wet case). Regarding the composition of reaction categories, Fig. 5 shows that the largest relative difference between hot & wet and hot & wet, high NO$_x$ are in the other RO$_2$ (24 % versus 4 %), RH + OH (45 % versus 20 %), and other HO$_x$ (31 % versus 11 %) categories, where the high NO$_x$ case is more reduced. The reduction rate is identical for the RO$_2$ + NO (37 %), other NO$_x$ (29 %), and other (62 %) categories. The default hot & wet case is slightly less reduced for the other NO$_y$ category (27 % versus 18 %) than the high NO$_x$ case. HO$_x$ and hydrocarbon chemistry is thus less influential on the chemistry controlling the concentration of the target compounds in the high NO$_x$ regime than in the low NO$_x$ regime, in agreement with established literature (Jacob, 1999).

3.2.2. Time scales

To investigate the influence of time scale on the reduction process, two additional reduction processes are run for the Emmerson target compound set, hot & wet case with reduced times scales of one simulated day and one simulated hour, as described in Section 2.3, and the resulting predictions are depicted in Fig. 6. Additionally, the scores of the prediction of peroxy radical concentrations of the one-day and one-hour Emmerson hot & wet simulations are added to Table 4. The time resolved concentration predictions are plotted in Figs. S.19
Figure 5: Number of reactions of the A0.90 mechanisms of the non-isoprene cases: Clean (blue color), cold & dry (red), hot & wet (light green), and non-biogenic (cyan) including the high NOx alteration of the hot & wet case (dark green) five-day simulations generated by ACR for each reactions category with the Emmerson target compound set, the numbers above the bars represent the fraction of the numbers of reactions in the reduced mechanisms to the numbers of reactions in the MCM subset of each category, expressed in percent.

The one-hour A0.90 mechanism is smaller (61 reactions, 36 species) than both the one-day mechanism (82 reactions, 49 species) and the five-day mechanism (96 reactions, 57 species). Averaged over all the four non-isoprene cases, generated one-day A0.90 mechanisms are reduced 11 % (three percentage points) more than corresponding generated five-day mechanisms (Emmerson target compound set). Generated one-hour A0.90 mechanisms are reduced 27 % (seven percentage points) more than the corresponding five-day mechanisms.

The largest difference in partial scores between the one-hour and one-day mechanisms of the target compounds are PAN where the one-day mechanism scores are better than the one-hour (0.79 versus 0.64), and the nitric oxide where
the one-hour mechanism scores higher than the one-day mechanism (0.96 versus 0.88). Both mechanisms score worse than the five-day mechanism for nitrate (0.85 versus 0.93). It should be noted, however, that nitrate is associated with night time chemistry and is therefore not particularly relevant for the one-hour case. The mechanisms, split up according to the reaction categories as defined in Section 2.5, are depicted as bars in Fig. 7. The one-day mechanism include a larger fraction of other NOx and other NOy reactions than the one-hour mechanism (26 % versus 21 % and 27 % versus 9 % respectively), reflecting the need for a working night time chemistry in the one-day mechanism. Between the five-day mechanisms and the one-day mechanisms, the largest relative difference is in the RO2 + NO reactions (37 % versus 18 %). This is presumably due to the twelve percentage points larger contribution of organic peroxy radicals from the oxidation of the more long lived organic carbons especially with life-
Figure 7: Number of reactions of the A0.90 mechanisms of the hot & wet case over three different time scales: Five-day (light blue color), one-day (red), one-hour (green) for each reactions category with the Emmerson target compound set along with the five-day Basic target compound set mechanism (dark blue), the numbers above the bars represent the fraction of the numbers of reactions in the reduced mechanisms to the numbers of reactions in the MCM subset of each category, expressed in percent.

3.2.3. Target compounds

To test the influence of the choice of target compounds on the reduction process, a reduction was made for the five-day hot & wet case with the Basic target compound set in addition to the Emmerson target compound set, as described in Section 2.4 and the resulting predictions depicted in Fig. 4. Additionally, the scores of the prediction of peroxy radical concentrations of the five-day Basic hot & wet mechanism simulations are added to Table 4. The time resolved concentration predictions are plotted in Fig. S.21 in the Supplementary Material.
The Basic A0.90 mechanism is substantially smaller (61 reactions, 36 species) than the corresponding Emmerson mechanism (96 reactions, 57 species). Averaged over all the four non-isoprene cases, generated Basic A0.90 mechanisms are reduced 18 % (five percentage points) more than the corresponding Emmerson mechanisms (five-day).

The largest difference between the two mechanisms of the Emmerson target compounds are nitrate (0.93 versus 0), for which the concentrations collapses in the Basic mechanisms. The hydroxyl radical concentrations are quite well represented in the Basic mechanism (0.89) even if it is not included in the target compound sets. The most visually obvious deviation between the curves in Fig. 4 is arguably the night time behavior of $\text{NO}_x$, which is probably connected to the missing nitrate chemistry. It can be noted that the method seems guided by the inclusion of nitrate in the target compound set towards better $\text{NO}_x$
concentration predictions. The number of reactions in each of the reaction categories as defined in Section 2.5 included in the five-day hot & wet Basic mechanism are plotted as a barplot in Fig. 7. The use of the Basic target compound set result in mechanisms most reduced in the other NO\(_x\) and the other HO\(_x\) (both 17% of the MCM subset) and the RO\(_2\) + NO and other NO\(_y\) categories (both 18%). It is less reduced for the RH + OH categories (28%). The mechanism is not further reduced in the other category (predominantly O\(_x\) chemistry) than any other mechanism (62%). Relative to the corresponding Emmerson target set mechanism the Basic mechanism is most reduced in the RO\(_2\) + NO (19 percentage points lower than the Emmerson mechanism) and RH + OH (17 percentage points lower). The Basic mechanism is relative to the corresponding Emmerson mechanism less reduced in the other RO\(_2\) (five percentage points) and other NO\(_y\) (nine percentage points) categories.

The results from the reductions of the two different target set mechanisms imply that the size of a reduced mechanism can depend on the compounds of interest; if only ozone and NO\(_x\) concentrations are of interest, parts of the chemistry can be left out without substantially compromising the accuracy of the predictions of these compounds’ concentrations.

3.3. Isoprene cases

The result of the isoprene case simulations (five-day, Emmerson target compound set) along with the results of the corresponding simulations using the MCM subset including isoprene are plotted in Fig. 9. Additionally, the scores of the prediction of peroxy radical concentrations of the five-day Emmerson industrial and biogenic mechanism simulations are added to Table 4. The time resolved concentration predictions are plotted in Figs. S.22 and S.23 in the Supplementary Material.

The A0.90 (industrial) and the A0.70 (biogenic) mechanisms are split up according to the reaction categories as defined in Section 2.5 and are depicted as bars in Fig. 10 along with the all-round mechanism and the hot & wet mechanism, which represents a non-isoprene mechanism. The largest relative differ-
ence between the biogenic case (isoprene rich) and industrial (isoprene lean) is in the $RO_2 + NO$ category where the biogenic case mechanism include 45% of the $RO_2 + NO$ type reactions, while the industrial case mechanism includes 10%. Even the large all-round mechanism does not include more than 27%. The reason for this is probably the elevated levels of isoprene yielding more organic peroxy radicals. The difference in composition of reaction categories between the industrial case and the hot & wet case are small (0–10 percentage points).

Not only the compositions of reactants, but also their initial concentration will thus influence the reduction.
4. Conclusions and Outlook

Reduced mechanisms generated by the Ant Colony Reduction (ACR) method are here proven able to successfully predict ozone, nitrogen oxides, and other important compounds’ concentrations in simulations of several cases up to five simulated days. The mechanisms typically include 10 %–30 % of all reactions in the relevant subset of the detailed chemical kinetic mechanism (MCM v3.3.1).

The extent of the reduction depends on the time scale, the composition and initial concentration of reactants, NO\(_x\) regime, and the compounds of interest. Smallest mechanisms are obtained for cases on shorter time scales with fewer compounds (especially reactive hydrocarbons such as isoprene), lower initial
concentrations, and fewer compounds of interest. High NO\textsubscript{x} cases result in smaller mechanisms compared to low NO\textsubscript{x} cases. It is also shown here that these different conditions require different parts of the chemistry; e.g. daytime simulations deselects NO\textsubscript{y} reactions to a larger degree than simulations with time scales on the order of days, longer time scales require more RO\textsubscript{2} + NO \rightarrow RO + NO\textsubscript{2} type reactions, and higher NO\textsubscript{x} cases require less hydrocarbon and HO\textsubscript{x} chemistry.

Future developments include optimization of reaction rates and emission-, intermediate species-, and reaction lumping. Optimization of reaction rates will compensate loss of reactivity in deselected reactions by turning up the rate of other reactions which have a similar role in the chemistry. Emission lumping will enable reduced mechanisms for large number of hydrocarbons by joining groups of hydrocarbon into surrogate species. Intermediate species lumping will decrease the size of the mechanisms by joining intermediate species into surrogate species and reaction lumping by bypassing fast reaction steps.

The reduction method is very useful for time consuming simulations, e.g. street canyon CFD, where only a limited set of chemical reactions can be included. These environments have a limited complexity and therefore small mechanisms can be tailored without significant loss of accuracy. For climate modeling, where a wide range of species and conditions need to be included, the method extracts larger mechanisms. The use of the method for creating mechanisms for a wide range of conditions will significantly benefit from implementation of further reduction strategies like reaction lumping.

Acknowledgements

The authors would like to thank Dr. Pontus Roldin for the help with and the permission to use the ADCHAM chemistry module, Dr. Jian Zhong for sharing the box model script used in their work, and Dr. Dennys Angove for sharing measurement data useful in the development of the current method. This work was supported by the Swedish Energy Agency through the project GRECOP.
under the project number 38913-2 and by Crafoordska stiftelsen.


EPA, 2011. Air quality index for nitrogen dioxide. [ONLINE].
URL https://www3.epa.gov/airnow/no2.pdf


URL www.climatechange2013.org


MCM, 2018. The Master Chemical Mechanism. [ONLINE]. URL http://mcm.leeds.ac.uk/MCMv3.3.1/home.htm


29


Sanchez, B., Santiago, J.-L., Martilli, A., Palacios, M., Kirchner, F., 2016. CFD modeling of reactive pollutant dispersion in simplified urban configurations with different chemical mechanisms. Atmospheric Chemistry and Physics 16 (18), 12143–12157.


Stockwell, W. R., Kirchner, F., Kuhn, M., Seefeld, S., 1997. A new mecha-


Table 1: Initial values of the test cases as described previously (Emmerson and Evans, 2009). Initial concentrations are given in ppb.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Lon. /°E</td>
<td>100</td>
<td>-120</td>
<td>-5</td>
<td>-140</td>
<td>-145</td>
<td>-160</td>
</tr>
<tr>
<td>Lat. /°N</td>
<td>18</td>
<td>-30</td>
<td>-6</td>
<td>-10</td>
<td>26</td>
<td>-75</td>
</tr>
<tr>
<td>Date (mm-dd)</td>
<td>4-14</td>
<td>2-14</td>
<td>10-11</td>
<td>12-10</td>
<td>7-13</td>
<td>12-31</td>
</tr>
<tr>
<td>Press. /hPa</td>
<td>982.6</td>
<td>941.6</td>
<td>1036.6</td>
<td>982.6</td>
<td>982.6</td>
<td>1036.6*</td>
</tr>
<tr>
<td>Temp. /K</td>
<td>299.7</td>
<td>299.4</td>
<td>214.4</td>
<td>302.7</td>
<td>302.5</td>
<td>214.3</td>
</tr>
<tr>
<td>Rel. hum. /%</td>
<td>46</td>
<td>71</td>
<td>152</td>
<td>71</td>
<td>57</td>
<td>154</td>
</tr>
<tr>
<td>CH₄</td>
<td>1700.0</td>
<td>1700.0</td>
<td>1700.0</td>
<td>1700.0</td>
<td>1700.0</td>
<td>1700.0</td>
</tr>
<tr>
<td>CO</td>
<td>956.5</td>
<td>58.4</td>
<td>87.6</td>
<td>56.9</td>
<td>217.7</td>
<td>56.1</td>
</tr>
<tr>
<td>NO₂</td>
<td>3.6</td>
<td>0.003</td>
<td>0.58</td>
<td>0.002</td>
<td>0.12</td>
<td>0.14</td>
</tr>
<tr>
<td>(high NOₓ)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>80.0</td>
</tr>
<tr>
<td>O₃</td>
<td>63.3</td>
<td>19.0</td>
<td>86.3</td>
<td>13.3</td>
<td>10.5</td>
<td>93.9</td>
</tr>
<tr>
<td>H₂O₂</td>
<td>11.0</td>
<td>1.7</td>
<td>0.05</td>
<td>1.5</td>
<td>8.5</td>
<td>0.02</td>
</tr>
<tr>
<td>HNO₃</td>
<td>2.8</td>
<td>0.003</td>
<td>0.58</td>
<td>0.002</td>
<td>0.12</td>
<td>0.14</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>5.6</td>
<td>0.2</td>
<td>0.9</td>
<td>0.2</td>
<td>0.6</td>
<td>0.3</td>
</tr>
<tr>
<td>C₃H₈</td>
<td>1.4</td>
<td>0.003</td>
<td>0.2</td>
<td>0.002</td>
<td>0.09</td>
<td>0.02</td>
</tr>
<tr>
<td>C₅H₈</td>
<td>0.3</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>6.7</td>
<td>–</td>
</tr>
<tr>
<td>HCHO</td>
<td>6.0</td>
<td>0.4</td>
<td>0.06</td>
<td>0.4</td>
<td>4.8</td>
<td>0.02</td>
</tr>
<tr>
<td>CH₃CHO</td>
<td>3.0</td>
<td>0.004</td>
<td>0.007</td>
<td>0.004</td>
<td>3.8</td>
<td>0.0006</td>
</tr>
<tr>
<td>CH₃COCH₃</td>
<td>17.9</td>
<td>1.5</td>
<td>2.0</td>
<td>1.5</td>
<td>15.4</td>
<td>0.36</td>
</tr>
<tr>
<td>PAN</td>
<td>1.0</td>
<td>0.00008</td>
<td>0.2</td>
<td>0.0003</td>
<td>0.04</td>
<td>0.03</td>
</tr>
<tr>
<td>μ(LN/Q)</td>
<td>0.52</td>
<td>0.34</td>
<td>0.66</td>
<td>0.34</td>
<td>0.40</td>
<td>0.55</td>
</tr>
<tr>
<td>(high NOₓ)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.98</td>
</tr>
</tbody>
</table>

*The original pressure values are treated as misprint.
Table 2: Size (number of reactions) and score of the A0.90 mechanisms, the $O_3$–NO$_x$ column reflect the corresponding score obtained with a minimal photostationary state scheme, the No chem. column reflect the corresponding score obtained with constant concentrations. The scoring is described in Eq. (1).

<table>
<thead>
<tr>
<th>Case</th>
<th>A0.90 Size</th>
<th>A0.90 Score</th>
<th>$O_3$–NO$_x$ Score</th>
<th>No chem. Score</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-isoprene</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Clean</td>
<td>85</td>
<td>0.91</td>
<td>-0.14</td>
<td>-0.22</td>
</tr>
<tr>
<td>Non-biogenic</td>
<td>49</td>
<td>0.93</td>
<td>0.06</td>
<td>0.15</td>
</tr>
<tr>
<td>Cold &amp; dry</td>
<td>80</td>
<td>0.91</td>
<td>-0.17</td>
<td>0.15</td>
</tr>
<tr>
<td>Hot &amp; wet</td>
<td>96</td>
<td>0.94</td>
<td>-0.07</td>
<td>-0.2</td>
</tr>
<tr>
<td>high NO$_x$</td>
<td>57</td>
<td>0.97</td>
<td>-0.11</td>
<td>-0.41</td>
</tr>
<tr>
<td>basic</td>
<td>61</td>
<td>0.90</td>
<td>-0.15</td>
<td>-0.13</td>
</tr>
<tr>
<td>one-day</td>
<td>82</td>
<td>0.91</td>
<td>0.37</td>
<td>0.08</td>
</tr>
<tr>
<td>one-hour</td>
<td>63</td>
<td>0.90</td>
<td>0.37</td>
<td>0.23</td>
</tr>
<tr>
<td>Isoprene</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Industrial</td>
<td>183</td>
<td>0.95</td>
<td>-0.21</td>
<td>-0.21</td>
</tr>
<tr>
<td>Biogenic</td>
<td>657*</td>
<td>0.74*</td>
<td>-0.19</td>
<td>-0.21</td>
</tr>
<tr>
<td>All-round</td>
<td>760</td>
<td>0.90</td>
<td>-0.12</td>
<td>-0.09</td>
</tr>
</tbody>
</table>

*A0.70
Table 3: Number of reactions (Reac.) and species (Spec.) of the A0.90 mechanisms and of their corresponding base mechanism (Base mech.), and the fraction $n_{A0.90}/n_{base}$ in % (Rel. size), where $n$ either is the number of reactions (Reac.) or the number of species (Spec.) for the A0.90 and the base mechanism respectively.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-isoprene</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Clean</td>
<td>85</td>
<td>46</td>
<td>296</td>
<td>99</td>
<td>28.7</td>
<td>46.5</td>
</tr>
<tr>
<td>Non-biogenic</td>
<td>49</td>
<td>33</td>
<td>296</td>
<td>99</td>
<td>16.6</td>
<td>33.3</td>
</tr>
<tr>
<td>Cold &amp; dry</td>
<td>80</td>
<td>49</td>
<td>296</td>
<td>99</td>
<td>27.0</td>
<td>49.5</td>
</tr>
<tr>
<td>Hot &amp; wet</td>
<td>96</td>
<td>57</td>
<td>296</td>
<td>99</td>
<td>32.4</td>
<td>57.6</td>
</tr>
<tr>
<td>high NO$_x$</td>
<td>57</td>
<td>38</td>
<td>296</td>
<td>99</td>
<td>19.3</td>
<td>38.4</td>
</tr>
<tr>
<td>basic</td>
<td>61</td>
<td>36</td>
<td>296</td>
<td>99</td>
<td>20.6</td>
<td>36.4</td>
</tr>
<tr>
<td>one-day</td>
<td>82</td>
<td>49</td>
<td>296</td>
<td>99</td>
<td>27.7</td>
<td>49.5</td>
</tr>
<tr>
<td>one-hour</td>
<td>63</td>
<td>38</td>
<td>296</td>
<td>99</td>
<td>21.2</td>
<td>38.4</td>
</tr>
<tr>
<td>Isoprene</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Industrial</td>
<td>183</td>
<td>111</td>
<td>2016</td>
<td>638</td>
<td>9.1</td>
<td>17.4</td>
</tr>
<tr>
<td>Biogenic</td>
<td>657*</td>
<td>398*</td>
<td>2016</td>
<td>638</td>
<td>32.5</td>
<td>62.4</td>
</tr>
<tr>
<td>All-round</td>
<td>760</td>
<td>380</td>
<td>2016</td>
<td>638</td>
<td>37.7</td>
<td>59.6</td>
</tr>
</tbody>
</table>

*A0.70
Table 4: Partial and total score of the A0.90 (A0.70) mechanisms for the different cases. The scoring is described in Eq. (1).

<table>
<thead>
<tr>
<th>Case</th>
<th>O₃</th>
<th>NO</th>
<th>NO₂</th>
<th>NO₃</th>
<th>OH</th>
<th>PAN</th>
<th>Tot.</th>
<th>HO₂</th>
<th>RO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-isoprene</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Clean</td>
<td>1.00</td>
<td>0.91</td>
<td>0.91</td>
<td>0.90</td>
<td>0.98</td>
<td>0.78</td>
<td>0.91</td>
<td>0.75</td>
<td>0.64</td>
</tr>
<tr>
<td>Non-biogenic</td>
<td>1.00</td>
<td>0.96</td>
<td>0.96</td>
<td>0.80</td>
<td>0.89</td>
<td>0.99</td>
<td>0.93</td>
<td>0.94</td>
<td>-1.0</td>
</tr>
<tr>
<td>Cold &amp; dry</td>
<td>1.00</td>
<td>0.87</td>
<td>0.88</td>
<td>0.89</td>
<td>0.84</td>
<td>1.00</td>
<td>0.91</td>
<td>0.84</td>
<td>-1.0</td>
</tr>
<tr>
<td>Hot &amp; wet</td>
<td>1.00</td>
<td>0.99</td>
<td>0.99</td>
<td>0.93</td>
<td>0.99</td>
<td>0.80</td>
<td>0.95</td>
<td>0.99</td>
<td>0.99</td>
</tr>
<tr>
<td>High NOₓ</td>
<td>0.99</td>
<td>0.99</td>
<td>1.00</td>
<td>0.97</td>
<td>0.95</td>
<td>0.92</td>
<td>0.97</td>
<td>0.70</td>
<td>-1.0</td>
</tr>
<tr>
<td>Basic</td>
<td>0.97</td>
<td>0.87</td>
<td>0.86</td>
<td>0.00</td>
<td>0.89</td>
<td>0.40</td>
<td>0.67</td>
<td></td>
<td>-0.42</td>
</tr>
<tr>
<td>One-day</td>
<td>1.00</td>
<td>0.88</td>
<td>0.96</td>
<td>0.85</td>
<td>0.97</td>
<td>0.79</td>
<td>0.91</td>
<td>0.63</td>
<td>0.69</td>
</tr>
<tr>
<td>One-hour</td>
<td>1.00</td>
<td>0.96</td>
<td>0.99</td>
<td>0.85</td>
<td>0.97</td>
<td>0.64</td>
<td>0.90</td>
<td>0.99</td>
<td>0.89</td>
</tr>
<tr>
<td>Isoprene</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Industrial</td>
<td>0.99</td>
<td>0.97</td>
<td>0.97</td>
<td>0.94</td>
<td>0.91</td>
<td>0.96</td>
<td>0.96</td>
<td>0.85</td>
<td>0.67</td>
</tr>
<tr>
<td>Biological*</td>
<td>0.96</td>
<td>0.83</td>
<td>0.79</td>
<td>0.79</td>
<td>0.54</td>
<td>0.54</td>
<td>0.74</td>
<td>0.65</td>
<td>0.35</td>
</tr>
<tr>
<td>All-round</td>
<td>0.97</td>
<td>0.92</td>
<td>0.92</td>
<td>0.79</td>
<td>0.88</td>
<td>0.93</td>
<td>0.90</td>
<td>0.90</td>
<td>0.46</td>
</tr>
</tbody>
</table>

†The score is the average of all the partial scores, except HO₂ and RO₂
*A0.70