**Geoscientific
Model Development
Discussions**

Automated sequence analysis of atmospheric oxidation pathways: SEQUENCE version 1.0

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Abstract

An algorithm for the sequential analysis of the atmospheric oxidation of chemical species using output from a photochemical model is presented. Starting at a "root species", the algorithm traverses all possible reaction sequences which consume this species, and lead, via intermediate products, to final products. The algorithm keeps track of the effects of all of these reactions on their respective reactants and products. Upon completion, the algorithm has built a detailed picture of the effects of the oxidation of the root species on its chemical surroundings. The output of the algorithm can be used to determine product yields, radical recycling fractions, and ozone production potentials of arbitrary chemical species.

1 Introduction

The chemistry of reactive trace gasses in the atmosphere of the Earth is a highly complex, nonlinear system. The many thousands of volatile organic compounds (VOC) in the troposphere are generally removed by initial attack from the hydroxyl radical (OH), which is formed primarily by photolysis of ozone (O_3) and subsequent reaction of an excited oxygen atom ($O(^1D)$) with water vapour. The resulting partially oxidised species may be deposited to surfaces, condense into the aerosol phase, or undergo further reactions until they ultimately form unreactive carbon dioxide (CO_2). This series of further reactions can involve photolysis steps, further loss and/or regeneration of OH and hydroperoxy radicals (HO_2), and conversion of nitric oxide (NO) to nitrogen dioxide (NO_2). The conversion of NO to NO_2 leads subsequently via photolysis of NO_2 to the production of O_3, which in turn influences the atmospheric radical budget, acts as greenhouse gas, and is an important component of photochemical smog.

For decades, numerical models of this system have been used in order to improve our understanding of these processes. Unfortunately these models are often so complex that it can be difficult to understand why they produce the results they do; analysis

of the output of atmospheric chemical models remains challenging. Lehmann (2004) describes an algorithm for the automatic determination of dominant pathways in chemical systems. The algorithm of Lehmann (2004) can detect cyclic sequences which yield net production or loss of a species of interest, and as such is especially well suited to the discovery of catalytic cycles of ozone depletion in the stratosphere.

A different approach has been used for the analysis of the effects of specific chemical species on their environment during their degradation, for example the calculation of total ozone yields due to the oxidation of individual VOC. Methane (CH_4), the simplest and longest lived VOC in the atmosphere, can contribute to tropospheric ozone formation far away from its source regions. In order to analyse the effects of methane oxidation on atmospheric chemistry, Johnston and Kinnison (1998), building on earlier work done by Crutzen (1973), identified 34 possible reaction sequences by which CH_4 may degrade to carbon monoxide (CO), and derived analytic equations for the combined effect of all of these sequences of CH_4 oxidation on the formation and loss of OH and O_3 in the atmosphere.

In principle, such an analytic approach to the determination of of the effects of individual VOC on the atmosphere is possible for any VOC. In practice, the very large number of possible reaction sequences for VOC other than CH_4 makes this approach too complicated. Instead, incremental reactivity methods (e.g. Carter, 1994; Derwent et al., 1998) have been used to estimate the effects of higher-order VOC on ozone production, particularly in the context of urban photochemical smog. Using these methods, several runs of a photochemical model are performed, each with a slight perturbation to the amount of a particular target VOC. The change, or increment, in the amount of ozone produced by the model is then used to determine the incremental reactivity of each VOC under consideration. Disadvantages of the incremental reactivity approach compared with the sequence approach are that a model run must be performed for each individual VOC under consideration, and that the resulting incremental reactivities contain no information about the underlying mechanisms of ozone production (or removal) due to each VOC and all intermediate oxidation products.

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In this paper a numerical implementation of the sequence method is presented, which, given a list of chemical reactions and their reaction rates, automatically traverses all degradation sequences for any given VOC, keeping track of radical and NO_x conversions (collectively NO and NO_2 are known as NO_x). It is shown how the output of this algorithm can be used to provide information on the effects of a target VOC on atmospheric budgets of radicals and NO_x. Applications of this information are discussed. This algorithm has already been applied in the literature to determine the yields of product species from isoprene (Taraborrelli et al., 2009), and the amount of radical recycling during isoprene oxidation (Lelieveld et al., 2008; Butler et al., 2008), although the algorithm itself was not described in this previous work. This paper provides the first detailed description and evaluation of the algorithm, and makes a sample implementation available as an electronic supplement http://www.geosci-model-dev-discuss.net/2/1001/2009/gmdd-2-1001-2009-supplement.zip. Section 2 describes the algorithm and its implementation, Sect. 3 describes our modelling approach, Sect. 4 evaluates the algorithm with some relatively simple chemical systems, Sect. 5 explores a potential application of the algorithm (calculation of ozone production potentials).

2 Automating the sequence method

The sequence algorithm is presented in pseudocode in Fig. 1. The basic idea behind the algorithm is to start at a "root species", and determine its oxidation products and the side effects of its oxidation reactions. Each of the oxidation products is then treated as an intermediate product for which the process is repeated.

The algorithm is recursive, and is initially called with the root species and the total rate of production of this root species as arguments. All rates of production and loss within the algorithm are specified in $mol\, cm^{-3}\, s^{-1}$. The first action performed is a check that the production rate of *species* as a fraction of the total rate of consumption of the root species is greater than *min_rate*. In this way, minor reaction sequences are not computed. The next step is the calculation of *fraction*, which represents the fraction

of the total production of *species* traceable back to the root species at the current stage of the current sequence. The effective rates at the current stage of the current sequence of each of the reactions consuming *species* are the reaction rates from the model output multiplied by *fraction*. The contribution of each of these consumption
5 reactions to each species on which the given reaction has an effect (the list of affected species is read from the array *effect_list*) is calculated based on these effective rates and the reaction stoichiometry (read from the array *stoichiometry*), and accumulated in the global variable *contribution*. Each of the products of the consumption reactions is itself the subject of a call to SEQUENCE if it is an intermediate product.

10 As the reaction sequence is followed through the recursive subroutine calls past more and more intermediate products, the rate gets progressively smaller. Recursion is terminated either when the sequence reaches its end, or when the rate falls below *min_rate* and the remainder of the sequence is ignored.

The algorithm makes use of a number of read-only global variables which must be
15 initialised before the SEQUENCE subroutine is called.

– The *rates* array contains the rates of each reaction in the system, and is initialised from the output of a photochemical model.

– The *total_production* array contains an entry for each species consisting of the sum of any emissions and the rates of all chemical reactions which produce that
20 species. This array is also initialised from the output of a photochemical model.

– *root_destruction* is a scalar variable containing the sum of the rates of all chemical reactions which consume the root species. This is initialised from model output.

– The *consuming* array contains an entry for each species comprising of a list of reactions which consume that species. This array is initialised from the specification
25 of the chemical system used by the photochemical model.

– The *effect_list* and *stoichiometry* arrays, containing the list of reactants and products of each reaction and their stoichiometric coefficients, respectively, are also

initialised from the chemical system specification.

- – The *is_intermediate* array is a boolean array containing an entry for each species, which is true if the species is an intermediate product, and false otherwise. In order to compute all sequences of a complex chemical system, it is easier to specify as false which species are not intermediates (e.g. OH, HO_2, etc. . .), rather than to explicitly set all potential intermediate products to true. The true entries in this array may however be specified manually if the user is interested in computing only certain reaction sequences.

- – *min_fraction*, as described above, is used to decide when the rate of the remainder of a sequence is small enough to be ignored. The value of this variable is specified by the user. When using the algorithm to analyse a chemical system, several runs should be performed using progressively smaller values of *min_fraction* as a test of the potential contribution of uncomputed sequences to the final result.

The algorithm does not count individual sequences, but rather integrates the effects of all significant sequences on all relevant species in the chemical system. The final result of the algorithm is stored in the global array *contribution*. For each species in the chemical system, the array contains a list of all reactions which contribute to the budget of that species, along with the rates of these contributions due ultimately to the oxidation of the root species. The nett effect of the oxidation of the root species on each of the other species in the system can be determined by summing the rates (positive for production, negative for loss) of the contributions to each species. When the chemical system is in steady state, the production and loss of the intermediate oxidation products of the root species (e.g. alkyl peroxy radicals) should approximately balance, there should be nett production of chain termination species (e.g. CO_2) and there may be nett production or loss of radical and NO_x species.

An implementation of the SEQUENCE algorithm in the Perl 5 programming language, complete with self-contained input from the BASE model run (Sect. 3) is available

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in the electronic supplement http://www.geosci-model-dev-discuss.net/2/1001/2009/gmdd-2-1001-2009-supplement.zip to this article.

3 Modelling approach

To investigate the performance of the SEQUENCE algorithm, simulations are performed with the photochemical box model MECCA (Module Efficiently Calculating the Chemistry of the Atmosphere, Sander et al., 2005), which is based on a version of KPP (Kinetic Pre-Processor, Damian et al., 2002) modified to produce FORTRAN 90 code. All model runs in this study are performed using the near-explicit Master Chemical Mechanism (MCM) v3.1 (Saunders et al., 2003). The specification of the chemical reactions for the MCM was downloaded from http://mcm.leeds.ac.uk/MCM. Photolysis rates are parameterised as a function of solar zenith angle.

The atmospheric oxidation of CH_4 to CO is chosen as the process used to validate the SEQUENCE algorithm. The reactions involved in this process are shown in Table 1. For clarity, only the reactions directly involved in transformation of CH_4 and its oxidation intermediates to CO are shown. The MCM also includes explicit representations of other atmospheric processes such as the inorganic reactions involving OH, HO_2, NO_x and O_3, as well as near-explicit representations of the reactions of over 100 primary VOC and their oxidation products.

The model is run in a perpetual midday state, in which photolysis rates are kept constant at those calculated for local midday at 45° latitude for the equinox. Mixing ratios of CH_4, CO, O_3 and NO are held constant at $1.75\,\text{mmol}\,\text{mol}^{-1}$, $200\,\text{nmol}\,\text{mol}^{-1}$, $40\,\text{nmol}\,\text{mol}^{-1}$, and $100\,\text{pmol}\,\text{mol}^{-1}$, respectively. Temperature is held constant at 293 K, pressure at 101 325 Pa, relative humidity at 81%, and all species are assumed to be well mixed up to an altitude of 1000 m. Three different model simulations are performed. The BASE simulation contains only CH_4 chemistry, with no deposition processes. The DEP simulation is the same as the BASE simulation but with deposition velocities for formaldehyde (HCHO), methyl hydroperoxide (CH_3OOH) and

methyl nitrate (CH_3NO_3) of $0.33\,cm\,s^{-1}$, $0.55\,cm\,s^{-1}$, $1.1\,cm\,s^{-1}$, respectively. The MIX simulation is the same as the BASE simulation, but includes constant emissions of $1\times10^9\,mol\,cm^{-2}\,s^{-1}$ of each of the non-halogenated primary VOC in the MCM (117 species in all, which are set to zero during the BASE and DEP runs). For all runs the model timestep is 20 min, and a run time of 30 d is sufficient to ensure that all species are near steady state. Proximity to steady state is not a strict requirement of the SEQUENCE algorithm, but is desirable for validation purposes.

The SEQUENCE algorithm is run on output from the last timestep of each simulation. A value for the parameter *min_fraction* of 1×10^{-9} is sufficient to ensure that uncomputed reaction sequences do not significantly affect the output of the algorithm; a value of 1×10^{-10} produces a change in the order of 0.001% in the results.

4 Validation with CH_4

Despite being the simplest of the VOC, the MCM still requires 21 reactions to oxidise CH_4 to CO (Table 1). There are many different possible sequences of different length through these 21 reactions, some of which potentially involve cycles (e.g. R9 followed by R10 followed by R9 etc...). At first the use of the SEQUENCE algorithm is demonstrated using a simpler case, the oxidation of HCHO to CO. This process has four possible sequences (R18, R19, R20, and R21 from Table 1) each consisting of a single step. Using the output of the model at the last timestep of the BASE simulation, the SEQUENCE algorithm is run with HCHO as the root species. The output is summarised in Table 2. The algorithm correctly identifies the four sequences, and assigns rates to the *contribution* array which are equal to the rates of the reactions from the model. In this simple case, the SEQUENCE algorithm has not told us anything which could not have been learnt by simply inspecting the output of the model. It shows, however, that the algorithm provides a sensible result for this simple case.

The output of the SEQUENCE algorithm with CH_4 specified as the root species (BASE simulation) is shown in Table 3. The CO yield of 0.9994 (rounded to 1 in Table 3), and

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the fact that the CH_4 oxidation mechanism listed in Table 1 is carbon conserving shows us that the algorithm is correctly following the reaction sequences leading from CH_4 to CO. The algorithm does not explicitly give the sequences as lists of reactions, but an idea of the relative importance of various sequences in the oxidation of CH_4 can be obtained by inspection of Table 3. For example, most CH_3O_2 is lost by reaction with NO in reaction R2, with the majority of the remainder reacting with HO_2 via reaction R5 to form CH_3OOH, and a smaller amount reacting with the general pool of organic peroxy (RO_2) radicals (which in the BASE model run consists only of the methyl peroxy radical, CH_3O_2) via reactions R6, R7, and R8. Most HCHO is formed by decomposition of the alkoxy radical CH_3O. This process also forms approximately half of the HO_2, the other half coming from HCHO photolysis. The magnitude of the R9–R10 cycle can also be seen. There is a small amount of OH regeneration through photolysis of CH_3OOH.

As CH_4 is the only VOC present in this model run, Table 3 can be reproduced by simply substituting the reaction rate output of the model for the output of the SEQUENCE algorithm. The result (not shown) is an exact copy of Table 3, again confirming that the SEQUENCE algorithm has found the correct sequences. A summary of the nett effect of CH_4 oxidation is shown at the bottom line of Table 3. The oxidation of one mole of CH_4 produces one mole of CO and 0.26 mol of H_2. Along the way, 1.7 mol of OH are converted to 1.7 mol of HO_2, and 0.93 mol of NO are converted to 0.93 mol of NO_2. In principle, in a steady-state system with no loss of intermediate products, the nett effect of CH_4 oxidation on the intermediate species (CH_3O_2, HCHO, etc...) should be zero. As seen in Table 3, this is not the case. The fact that Table 3 can be reproduced by simply substituting the reaction rate output from the photochemical model shows that these nonzero terms in Table 3 are not artifacts introduced by the SEQUENCE algorithm, but rather result directly from the output of the photochemical model. They could be due to minor deviations from steady state, or small numerical inaccuracies in the reaction rate output from the photochemical model.

The output of the SEQUENCE algorithm from the DEP run with CH_4 as the root species is shown in Table 4. With deposition of intermediates, the yield of CO from

CH$_4$ oxidation is no longer 1, but rather 0.96. For each mol of CH$_4$ oxidised, 0.04 mol of carbon are lost via deposition. It can be seen at the bottom line of Table 4 that the residual production of the three deposited species (HCHO, CH$_3$OOH, and CH$_3$NO$_3$) has changed from a small fraction of the total production (as seen in Tables 3 and 5) to
5 a significant fraction of the total production of each of those intermediate species. This is because the SEQUENCE algorithm does not explicitly follow deposition as part of re-action sequences. Any molecules which are deposited are subsequently unavailable to continue reacting in the chemical system. The chemical production rate of deposited species is larger than their chemical loss rate. This is reflected in the rate output of
10 the chemical model, and subsequently also in the *rates* array used by the SEQUENCE algorithm (Sect. 2).

The SEQUENCE algorithm is also capable of correctly following reaction sequences when the intermediate species have other production mechanisms. This is illustrated by analysis of the MIX run, which includes emissions of all non-halogenated primary
15 VOC in the MCM (Sect. 3). All of these species share common intermediates with CH$_4$ (CH$_3$O$_2$, HCHO, etc. . .), and most of the carbon which they contain ultimately forms CO. The total chemical production rate of CO from this new run increases by 2.2 times compared with the BASE run. It is therefore no longer possible to duplicate the output of the SEQUENCE algorithm solely from inspection of the photochemical model output.
20 If this were to be done, then the total production of CO would be greater than the total consumption of CH$_4$. The output of the SEQUENCE algorithm from the MIX run with CH$_4$ specified as the root species is shown in Table 5. The CO yield is still 1, indicating that the algorithm is capable of differentiating between CO produced due to oxidation of CH$_4$, and CO produced from oxidation of all other species.
25 The addition of the other VOC to the model in the MIX run has the effect of reducing the modelled OH concentration by about 40%, and increasing the total concentration of organic peroxy radicals (RO$_2$) by about threefold. This changed chemical environment has led to changes in the CH$_4$ oxidation sequences, which are visible in Table 5. The lower concentration of OH has led to a greater importance for photolysis reactions, in

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particular for HCHO. In the BASE run, 58% of HCHO was removed by OH, in this run that amount has decreased to 44%. The threefold increase in RO_2 concentration is noticeable in the approximate threefold increases in the contribution of RO_2 reactions (reactions R6, R7, and R8) to the loss of CH_3O_2. This extra competition from RO_2
5　leads to a smaller contribution from NO to the removal of CH_3O_2 (reaction R2), and thus also to a slightly reduced total yield of NO_2 from CH_4 oxidation compared with the BASE run.

5   Application to ozone production potential

The amount of NO_2 produced during the atmospheric oxidation of VOC is closely re-
10　lated to the amount of O_3 which can be formed (Sect. 1). The current state of the art for the determination of ozone production potentials of VOC is the use of incremen- tal reactivity methods (Sect. 1), which do not explicitly account for this production of NO_2, but rather relate incremental changes in O_3 to incremental changes in VOC. By allowing the computation of NO_2 yields from VOC oxidation, the SEQUENCE algorithm
15　represents an alternative method for the calculation of ozone production potentials of VOC.

The NO_2 yields from the oxidation of the emitted VOC in the MIX run (Sect. 3) are shown in Fig. 2. As for CH_4 (Table 3), most of the NO_2 produced during the oxidation of other VOC is formed from reaction of RO_2 with NO. Larger VOC molecules can poten-
20　tially produce more RO_2 fragments during their oxidation chain than smaller molecules. The ozone production potential is thus expected to be higher for larger molecules. To illustrate the relationship between molecular size and NO_2 production, the bars rep- resenting the emitted VOC in Fig. 2 have been coloured according to the number of carbon atoms in the molecule. In general, larger molecules produce more NO_2 during
25　their oxidation than smaller molecules, but there are exceptions. For example, ethyl glyoxal produces about half as much ozone as methane despite having twice as many carbon atoms, and benzaldehyde and styrene, despite having only seven and eight

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carbon atoms, respectively, produce more NO_2 during their oxidation than n-dodecane, which has twelve carbon atoms. Other factors such as molecular structure and functionality clearly influence the production potential of NO_2, and thus also of O_3. The SEQUENCE algorithm provides a method with which to understand the mechanistic dif-

5 ferences between ozone production potentials of various VOC by providing information about the contribution of individual reactions to the overall yield of products from those VOC (e.g. Table 3).

A full application of the SEQUENCE algorithm to the determination of ozone production potentials of all VOC in the MIX run under realistic scenarios is beyond the scope

10 of this paper. Such a determination must take into account the variability of chemical regimes in the real world, the different timescales involved in the oxidation of these VOC, and the indirect role of HO_2 radicals in the production of NO_2, among other factors. A manuscript examining the ozone production potentials of these VOC is currently in preparation.

15 **6 Discussion and conclusions**

Sequential analysis of atmospheric oxidation pathways has been a part of the scientific literature for several decades, but has until now been performed "by hand". Its application was therefore limited to simple cases such as the oxidation of CH_4. This paper presents the first detailed description and evaluation of the SEQUENCE algorithm, which

20 is capable of extending the sequential analysis concept to oxidation systems with arbitrary levels of complexity, such as VOC oxidation in the state of the art near-explicit MCM. The output of the algorithm for each VOC is a matrix showing the effects of all reactions involved in the oxidation of that VOC on all chemical species involved in that oxidation.

25 The correctness of the algorithm has been verified for the simplest of cases, the oxidation of HCHO to CO, and it has been shown that this also extends to the oxidation of CH_4. It has also been shown that the algorithm can distinguish between the

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effects of individual VOC present in mixtures, calculating product yields, OH regeneration efficiencies, and NO_2 yields. Results for many of the VOC in the MCM have been presented. A potentially interesting application of the Sequence algorithm is the calculation of ozone production potentials of VOC. Work is currently underway exploring the potential of the algorithm for this application.

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Table 1. Listing of reactions involved in oxidation of CH_4.

$CH_4 + OH$	$\longrightarrow$ CH_3O_2	R1
$CH_3O_2 + NO$	$\longrightarrow$ $CH_3O + NO_2$	R2
$CH_3O_2 + NO$	$\longrightarrow$ CH_3NO_3	R3
$CH_3O_2 + NO_3$	$\longrightarrow$ $CH_3O + NO_2$	R4
$CH_3O_2 + HO_2$	$\longrightarrow$ CH_3OOH	R5
$CH_3O_2 (+ RO_2)$	$\longrightarrow$ CH_3O	R6
$CH_3O_2 (+ RO_2)$	$\longrightarrow$ $HCHO$	R7
$CH_3O_2 (+ RO_2)$	$\longrightarrow$ CH_3OH	R8
$CH_3O_2 + NO_2$	$\longrightarrow$ $CH_3O_2NO_2$	R9
$CH_3O_2NO_2$	$\longrightarrow$ $CH_3O_2 + NO_2$	R10
CH_3O	$\longrightarrow$ $HCHO + HO_2$	R11
$CH_3NO_3 + OH$	$\longrightarrow$ $HCHO + NO_2$	R12
$CH_3NO_3 + h\nu$	$\longrightarrow$ $CH_3O + NO_2$	R13
$CH_3OOH + OH$	$\longrightarrow$ CH_3O_2	R14
$CH_3OOH + OH$	$\longrightarrow$ $HCHO + OH$	R15
$CH_3OOH + h\nu$	$\longrightarrow$ $CH_3O + OH$	R16
$CH_3OH + OH$	$\longrightarrow$ $HCHO + HO_2$	R17
$HCHO + OH$	$\longrightarrow$ $CO + HO_2$	R18
$HCHO + h\nu$	$\longrightarrow$ $CO + HO_2 + HO_2$	R19
$HCHO + h\nu$	$\longrightarrow$ $CO + H2$	R20
$HCHO + NO_3$	$\longrightarrow$ $CO + HNO_3 + HO_2$	R21

Table 2. The output of the SEQUENCE algorithm using HCHO as the root species. The numbers in the table are rates in molecules $cm^{-3} s^{-1}$.

	HCHO	hv	OH	NO_3	HO_2	HNO_3	H_2	CO
R18	−1.2e+06	−	−1.2e+06	−	1.2e+06	−	−	1.2e+06
R19	−3.3e+05	−3.3e+05	−	−	6.6e+05	−	−	3.3e+05
R20	−5.6e+05	−5.6e+05	−	−	−	−	5.6e+05	5.6e+05
R21	−12	−	−	−12	12	12	−	12
Nett effect	−2.1e+06	−8.9e+05	−1.2e+06	−12	1.9e+06	12	5.6e+05	2.1e+06
Normalised effect	−1	−0.42	−0.58	−5.7e−06	0.89	5.7e−06	0.26	1

Table 3. The output of the SEQUENCE algorithm for CH_4 in the BASE run. All rates have been normalised to the loss rate of CH_4.

	CH_4	OH	HO_2	hv	CH_3O_2	CH_3O	CH_3OOH	CH_3OH	$HCHO$	CH_3NO_3	$CH_3O_2NO_2$	NO	NO_2	NO_3	HNO_3	H_2	CO
R1	−1	−1	–	–	1	–	–	–	–	–	–	–	–	–	–	–	–
R2	–	–	–	–	−0.93	0.93	–	–	–	–	–	−0.93	0.93	–	–	–	–
R3	–	–	–	–	−0.00093	–	–	–	–	0.00093	–	−0.00093	–	–	–	–	–
R4	–	–	–	–	−8.2e−05	8.2e−05	–	–	–	–	–	–	8.2e−05	−8.2e−05	–	–	–
R5	–	–	−0.16	–	−0.16	–	0.16	–	–	–	–	–	–	–	–	–	–
R6	–	–	–	–	−0.0019	0.0019	–	–	–	–	–	–	–	–	–	–	–
R7	–	–	–	–	−0.0019	–	–	–	0.0019	–	–	–	–	–	–	–	–
R8	–	–	–	–	−0.0019	–	–	0.0019	–	–	–	–	–	–	–	–	–
R9	–	–	–	–	−1.4	–	–	–	–	–	–	1.4	−1.4	–	–	–	–
R10	–	–	–	–	1.4	–	–	–	–	–	–	−1.4	1.4	–	–	–	–
R11	–	–	0.94	–	−0.94	–	–	–	0.94	–	–	–	–	–	–	–	–
R12	–	−0.00077	–	–	–	–	–	–	0.00077	−0.00077	–	–	0.00077	–	–	–	–
R13	–	–	–	−0.00016	–	0.00016	–	–	–	–	−0.00016	–	0.00016	–	–	–	–
R14	–	−0.1	–	–	0.1	–	−0.1	–	–	–	–	–	–	–	–	–	–
R15	–	–	–	–	–	–	−0.052	–	0.052	–	–	–	–	–	–	–	–
R16	–	0.013	–	−0.013	–	0.013	−0.013	–	–	–	–	–	–	–	–	–	–
R17	–	−0.0019	0.0019	–	–	–	–	−0.0019	0.0019	–	–	–	–	–	–	–	–
R18	–	−0.58	0.58	–	–	–	–	–	−0.58	–	–	–	–	–	–	–	0.58
R19	–	0.31	−0.15	–	–	–	–	–	−0.15	–	–	–	–	–	–	–	0.15
R20	–	–	−0.26	–	–	–	–	–	−0.26	–	–	–	–	–	–	0.26	0.26
R21	–	–	5.7e−06	–	–	–	–	–	−5.7e−06	–	–	–	–	−5.7e−06	5.7e−06	–	5.7e−06
Nett effect	−1	−1.7	1.7	−0.43	−6e−05	−6.3e−05	−0.00048	−5.2e−06	0.0014	9.5e−07	−0.00016	−0.93	0.93	−8.7e−05	5.7e−06	0.26	1

Table 4. The output of the SEQUENCE algorithm for CH_4, in the DEP run, with deposition of intermediates. All rates have been normalised to the loss rate of CH_4.

	CH_4	OH	HO_2	$h\nu$	CH_3O_2	CH_3O	CH_3OOH	CH_3OH	HCHO	CH_3NO_3	$CH_3O_2NO_2$	NO	NO_2	NO_3	HNO_3	H_2	CO
R1	−1	−1	–	–	1	–	–	–	–	–	–	–	–	–	–	–	–
R2	–	–	–	–	−0.92	0.92	–	–	–	–	–	−0.92	0.92	–	–	–	–
R3	–	–	–	–	−0.00092	–	–	–	–	0.00092	–	−0.00092	–	–	–	–	–
R4	–	–	–	–	−5.8e−05	5.8e−05	–	–	–	–	–	–	5.8e−05	−5.8e−05	–	–	–
R5	–	–	−0.16	–	−0.16	–	0.16	–	–	–	–	–	–	–	–	–	–
R6	–	–	–	–	−0.0019	0.0019	–	–	–	–	–	–	–	–	–	–	–
R7	–	–	–	–	−0.002	–	–	–	0.002	–	–	–	–	–	–	–	–
R8	–	–	–	–	−0.002	–	–	0.002	–	–	–	–	–	–	–	–	–
R9	–	–	–	–	−1.4	–	–	–	–	–	–	1.4	−1.4	–	–	–	–
R10	–	–	–	–	1.4	–	–	–	–	–	–	−1.4	1.4	–	–	–	–
R11	–	–	0.93	–	–	−0.93	–	–	0.93	–	–	–	–	–	–	–	–
R12	–	−0.0002	–	–	–	–	–	–	–	0.0002	−0.0002	–	0.0002	–	–	–	–
R13	–	–	–	−4.2e−05	–	4.2e−05	–	–	–	–	−4.2e−05	–	4.2e−05	–	–	–	–
R14	–	−0.089	–	–	0.089	–	−0.089	–	–	–	–	–	–	–	–	–	–
R15	–	–	–	–	–	–	−0.047	–	0.047	–	–	–	–	–	–	–	–
R16	–	0.012	–	−0.012	–	0.012	−0.012	–	–	–	–	–	–	–	–	–	–
R17	–	−0.002	0.002	–	–	–	–	−0.002	0.002	–	–	–	–	–	–	–	–
R18	–	−0.55	0.55	–	–	–	–	–	−0.55	–	–	–	–	–	–	–	0.55
R19	–	–	0.3	−0.15	–	–	–	–	−0.15	–	–	–	–	–	–	–	0.15
R20	–	–	–	−0.26	–	–	–	–	−0.26	–	–	–	–	–	–	0.26	0.26
R21	–	–	3.8e−06	–	–	–	–	–	−3.8e−06	–	–	–	–	−3.8e−06	3.8e−06	–	3.8e−06
Normalised	−1	−1.6	1.6	−0.42	0.00016	−0.00017	0.015	−6.9e−06	0.025	0.00068	−0.0003	−0.92	0.92	−6.1e−05	3.8e−06	0.26	0.96

Table 5. The output of the SEQUENCE algorithm for CH_4, in the MIX run, including 117 other VOC. All rates have been normalised to the loss rate of CH_4.

	CH_4	OH	HO_2	hv	CH_3O_2	CH_3O	CH_3OOH	CH_3OH	HCHO	CH_3NO_3	$CH_3O_2NO_2$	NO	NO_2	NO_3	HNO_3	H_2	CO
R1	−1	−1	–	–	1	–	–	–	–	–	–	–	–	–	–	–	–
R2	–	–	–	–	−0.92	0.92	–	–	–	–	–	−0.92	0.92	–	–	–	–
R3	–	–	–	−0.00093	–	–	–	–	–	0.00093	–	−0.00093	–	–	–	–	–
R4	–	–	–	–	−6.5e−05	6.5e−05	–	–	–	–	–	–	6.5e−05	−6.5e−05	–	–	–
R5	–	–	−0.14	–	−0.14	–	0.14	–	–	–	–	–	–	–	–	–	–
R6	–	–	–	–	−0.0056	0.0056	–	–	–	–	–	–	–	–	–	–	–
R7	–	–	–	–	−0.0057	–	–	–	0.0057	–	–	–	–	–	–	–	–
R8	–	–	–	–	−0.0057	–	–	0.0057	–	–	–	–	–	–	–	–	–
R9	–	–	–	–	−1.5	–	–	–	–	–	–	1.5	–	−1.5	–	–	–
R10	–	–	–	–	1.5	–	–	–	–	–	–	−1.5	–	1.5	–	–	–
R11	–	–	0.95	–	–	−0.95	–	–	0.95	–	–	–	–	–	–	–	–
R12	–	−0.00067	–	–	–	–	–	–	0.00067	−0.00067	–	–	0.00067	–	–	–	–
R13	–	–	–	−0.00025	–	0.00025	–	–	–	−0.00025	–	–	0.00025	–	–	–	–
R14	–	−0.077	–	–	0.077	–	−0.077	–	–	–	–	–	–	–	–	–	–
R15	–	–	–	–	–	–	−0.041	–	0.041	–	–	–	–	–	–	–	–
R16	–	0.017	–	−0.017	–	0.017	−0.017	–	–	–	–	–	–	–	–	–	–
R17	–	−0.0056	0.0056	–	–	–	–	−0.0056	0.0056	–	–	–	–	–	–	–	–
R18	–	−0.44	0.44	–	–	–	–	–	−0.44	–	–	–	–	–	–	–	0.44
R19	–	–	0.41	−0.21	–	–	–	–	−0.21	–	–	–	–	–	–	–	0.21
R20	–	–	–	−0.35	–	–	–	–	−0.35	–	–	–	–	–	–	0.35	0.35
R21	–	–	6.3e−06	–	–	–	–	–	−6.3e−06	–	–	–	–	−6.3e−06	6.3e−06	–	6.3e−06
Normalised	−1	−1.5	1.7	−0.57	−4.6e−05	−4.7e−05	−0.00018	2.4e−05	0.0013	9.2e−06	−8.1e−05	−0.93	0.93	−7.1e−05	6.3e−06	0.35	1

Automated sequence analysis of atmospheric oxidation pathways

T. M. Butler

Full Screen / Esc

SEQUENCE($species, rate$)

1   **return if** $(rate/root\_destruction) < min\_rate$

2   $fraction \leftarrow rate/total\_production(species)$

3   **for** $consumer \leftarrow consuming(species)$

4   **do**

5        $reaction\_rate \leftarrow rates(consumer) \times fraction$

6   **for** $species \leftarrow effect\_list(consumer)$

7   **do**

8            $rate \leftarrow stoichiometry(consumer, species) \times reaction\_rate$

9            $contribution(consumer, species) \leftarrow contribution(consumer, species) + rate$

10   SEQUENCE($species, rate$) **if** $is\_intermediate(species)$

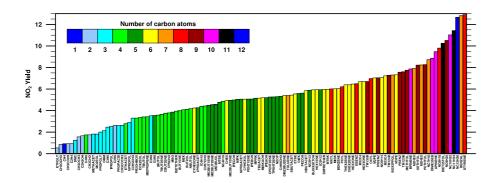**Fig. 1.** Pseudocode description of the sequence algorithm.

Fig. 2. The NO_2 yields from oxidation of emitted VOC species. Bars are coloured according to the number of carbon atoms in each species. Only species with a yield of more than 0.5 mol of NO_2 are shown.