

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 (O₃) 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 (CO₂). This series of further reactions can involve photolysis steps, further loss and/or regeneration of OH and hydroperoxy radicals (HO₂), and conversion of nitric oxide (NO) to nitrogen dioxide (NO₂). The conversion of NO to NO₂ leads subsequently via photolysis of NO₂ to the production of O₃, 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 (CH₄), the simplest and longest lived VOC in the atmosphere, can contribute to tropospheric ozone formation far away from its source regions. The reactions involved in the OH-initiated oxidation of CH₄ are shown in Table 1. After the initial attack by OH and subsequent formation of the methyl peroxy radical (Reaction R1), the peroxy radical may react in seven different ways (R2–R9), some of which ultimately lead to production of NO₂, and some of which do not. The products of this second step may themselves be oxidised via a number of different pathways. Each of these possibilities has a different impact on the atmospheric budgets of radicals and NO_x (collectively NO and NO₂ are known as NO_x), and therefore also on the amount of ozone formed.

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 CH₄ may degrade to carbon monoxide (CO), and derived analytic equations for the combined effect of all of these sequences of CH₄



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Table 1. Listing of reactions involved in oxidation of CH₄.

CH ₄ + OH	→	CH ₃ O ₂	R1
CH ₃ O ₂ + NO	→	CH ₃ O + NO ₂	R2
CH ₃ O ₂ + NO	→	CH ₃ NO ₃	R3
CH ₃ O ₂ + NO ₃	→	CH ₃ O + NO ₂	R4
CH ₃ O ₂ + HO ₂	→	CH ₃ OOH	R5
CH ₃ O ₂ (+ RO ₂)	→	CH ₃ O	R6
CH ₃ O ₂ (+ RO ₂)	→	HCHO	R7
CH ₃ O ₂ (+ RO ₂)	→	CH ₃ OH	R8
CH ₃ O ₂ + NO ₂	→	CH ₃ O ₂ NO ₂	R9
CH ₃ O ₂ NO ₂	→	CH ₃ O ₂ + NO ₂	R10
CH ₃ O	→	HCHO + HO ₂	R11
CH ₃ NO ₃ + OH	→	HCHO + NO ₂	R12
CH ₃ NO ₃ + <i>hν</i>	→	CH ₃ O + NO ₂	R13
CH ₃ OOH + OH	→	CH ₃ O ₂	R14
CH ₃ OOH + OH	→	HCHO + OH	R15
CH ₃ OOH + <i>hν</i>	→	CH ₃ O + OH	R16
CH ₃ OH + OH	→	HCHO + HO ₂	R17
HCHO + OH	→	CO + HO ₂	R18
HCHO + <i>hν</i>	→	CO + HO ₂ + HO ₂	R19
HCHO + <i>hν</i>	→	CO + H ₂	R20
HCHO + NO ₃	→	CO + HNO ₃ + HO ₂	R21

oxidation on the formation and loss of OH and O₃ in the atmosphere. In principle, such an analytic approach to the determination 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 CH₄ 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.

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. This approach differs from the “history matrix” approach of Tonneson (1995) in that it analyses a single set of averaged or steady state reaction rates, rather than following the time steps of a time-dependant model simulation. 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.net/2/145/2009/gmd-2-145-2009-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 destruction 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 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

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SEQUENCE(species, rate)
1  return if (rate/root_destruction) < min_rate
2  fraction ← rate/total_production(species)
3  for consumer ← consuming(species)
4    do
5      reaction_rate ← rates(consumer) × fraction
6      for species ← effect_list(consumer)
7        do
8          rate ← stoichiometry(consumer, species) × reaction_rate
9          contribution(consumer, species) ← contribution(consumer, species) + rate
10         SEQUENCE(species, rate) if is_intermediate(species)

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Fig. 1. Pseudocode description of the sequence algorithm.

contribution. Each of the products of the consumption reactions is itself the subject of a call to SEQUENCE if it is an intermediate product.

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 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 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 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, HO₂, 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. CO₂) and there may be nett production or loss of radical and NO_x species.

The performance of the algorithm is dependant on its implementation, the choice of *min_fraction*, and also on the complexity of the chemical mechanism under analysis. 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 in the electronic supplement <http://www.geosci-model-dev.net/2/145/2009/gmd-2-145-2009-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 CH₄ 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 CH₄ 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, HO₂, NO_x and O₃, 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 CH₄, CO, O₃ and NO are held constant at 1.75 mmol mol⁻¹, 200 nmol mol⁻¹, 40 nmol mol⁻¹, and 100 pmol 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 CH₄ chemistry, with no deposition processes. The DEP simulation is the same as the BASE simulation but with deposition velocities for formaldehyde (HCHO), methyl hydroperoxide (CH₃OOH) and methyl nitrate (CH₃NO₃) 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 × 10⁹ 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 CH₄

Despite being the simplest of the VOC, the MCM still requires 21 reactions to oxidise CH₄ 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 CH₄ 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 the fact that the CH₄ oxidation mechanism listed in Table 1 is carbon conserving shows us that the algorithm is correctly following the reaction sequences leading from CH₄ 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 CH₄ can be obtained by inspection of Table 3. For example, most CH₃O₂ is lost by reaction with NO in Reaction (R2), with the majority of the remainder reacting with HO₂ via Reaction (R5) to form CH₃OOH, and a smaller amount reacting with the general pool of organic peroxy (RO₂) radicals (which in the BASE model run consists only of the methyl peroxy radical, CH₃O₂) via Reactions (R6), (R7), and (R8). Most HCHO is formed by decomposition of the alkoxy radical CH₃O. This process also forms approximately half of the HO₂, 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 CH₃OOH.

As CH₄ 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 CH₄ oxidation is shown at the bottom line of Table 3. The oxidation of one mole of CH₄ produces one mole of CO and 0.26 mol of H₂. Along the way, 1.7 mol of OH are converted to 1.7 mol of HO₂, and 0.93 mol of NO are converted to 0.93 mol of NO₂. In principle, in a steady-state system with no loss of intermediate products, the nett effect of CH₄ oxidation on the intermediate species (CH₃O₂, HCHO, etc.)

Table 5. The output of the SEQUENCE algorithm for CH₄, in the MIX run, including 117 other VOC. All rates have been normalised to the loss rate of CH₄.

	CH ₄	OH	HO ₂	<i>hν</i>	CH ₃ O ₂	CH ₃ O	CH ₃ OOH	CH ₃ OH	HCHO	CH ₃ NO ₃	CH ₃ O ₂ NO 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

The output of the SEQUENCE algorithm from the DEP run with CH₄ as the root species is shown in Table 4. With deposition of intermediates, the yield of CO from CH₄ oxidation is no longer 1, but rather 0.96. For each mol of CH₄ 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, CH₃OOH, and CH₃NO₃) has changed from a small fraction of the total production (as seen in Tables 3 and 5) to 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 reaction 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 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 VOC in the MCM (Sect. 3). All of these species share common intermediates with CH₄ (CH₃O₂, 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. If this were to be done, then the total production of CO would be greater than the total consumption of CH₄. The output of the SEQUENCE algorithm from the MIX run with CH₄ 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 CH₄, and CO produced from oxidation of all other species.

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 (RO₂) by about threefold. This changed chemical environment has led to changes in the CH₄ oxidation sequences, which are visible in Table 5. The lower concentration of OH has led to a greater importance for photolysis reactions, in 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 RO₂ concentration is noticeable in the approximate threefold increases in the contribution of RO₂ reactions (Reactions R6, R7, and R8) to the loss of CH₃O₂. This extra competition from RO₂ leads to a smaller contribution from NO to the removal of CH₃O₂ (Reaction R2), and thus also to a slightly reduced total yield of NO₂ from CH₄ oxidation compared with the BASE run.

5 Application to ozone production potential

The amount of NO₂ produced during the atmospheric oxidation of VOC is closely related to the amount of O₃ 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 incremental reactivity methods (Sect. 1), which do not explicitly account for this production of NO₂, but rather relate incremental changes in O₃ to incremental changes in VOC. By allowing the computation of NO₂ yields from VOC oxidation, the SEQUENCE algorithm potentially represents an alternative method for the calculation of ozone production potentials of VOC.

The NO₂ yields from the oxidation of the emitted VOC in the MIX run (Sect. 3) are shown in Fig. 2. As for CH₄

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