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Assessment of the reduction methods used to develop chemical schemes: building of a new chemical scheme for VOC oxidation suited to three-dimensional multiscale HO_x-NO_x-VOC chemistry simulations

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Abstract

The objective of this work was to develop and assess an automatic procedure to write reduced chemical schemes for modeling gaseous photooxidant pollution at different scales. The method is based on (i) the development of a tool for writing the fully explicit schemes for VOC oxidation and (ii) the assessment of reduced schemes using the fully explicit scheme as a reference. The reference scheme contained ca. seventy emitted VOCs chosen to be representative of both anthropogenic and biogenic emissions, and their atmospheric degradation chemistry involving more than two million reactions and 350 000 species was written using an expert system generator approach.

Three methods were applied to reduce the size of chemical schemes: (i) use of operators, based on the redundancy of the reaction sequences involved in the VOC oxidation, (ii) lumping of primary species having similar reactivities and (iii) lumping of secondary products into surrogate species. The number of species in the final reduced scheme is 150, i.e. low enough for 3-D modeling purposes using CTMs. Comparisons between the fully explicit and reduced schemes, carried out with a box model for several typical tropospheric conditions, showed that the reduced chemical scheme accurately predicts ozone concentrations and some other aspects of oxidant chemistry for both polluted and clean tropospheric conditions.

1. Introduction

The atmospheric oxidation of volatile organic compounds (VOC) modifies the concentrations of key trace species (e.g. CH₄, CO, O₃ and OH) and has impacts at different scales. At urban and regional scales, VOC oxidation drives the production of high ozone concentrations close to the anthropogenic activities. At the global scale, the reactivity of the CO-NO_x-VOC system controls the abundance of ozone and OH and plays direct and indirect roles in radiative forcing.

Recent studies have shown the interactions of chemistry occurring at different scales.

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Variations of the background ozone concentrations can significantly impact the ozone values observed at regional scale (Fiore et al., 2002; Li et al., 2002; Längmann and Bauer, 2002). Furthermore, reactive species (radicals, NO_x) can form reservoir species near their sources, then be redistributed over large geographic scales by convective and advective transport. Alkyl nitrates and peroxyacetyl nitrates (PANs) may be particularly effective in supplying NO_x to the remote troposphere, with consequences for the net production of O_3 on hemispheric or even global scales (Moxim et al., 1996). Similarly, hydroperoxydes, ketones or aldehydes could be a significant source of radicals in free troposphere (Wennberg et al., 1998; Müller and Brasseur, 1999; Prather and Jacob, 1997).

The chemical schemes used in 3-D chemistry-transport models (CTM) attempt to reproduce the $\text{HO}_x/\text{NO}_x/\text{VOC}$ chemistry at local scale, i.e. with high concentrations of precursors (VOC and NO_x), as well as far from the sources, especially with very low NO_x concentrations. Chemical schemes must then be suited to the different chemical regimes as well as to formation of reservoirs and the release of reactive species from them.

The atmospheric chemistry of volatile organic carbon (VOC) involves many hundreds of initially emitted anthropogenic or natural compounds, as well as many thousands (or more) of potentially important intermediate partly oxidized species. Representation of the fully explicit VOC chemistry in chemistry transport models (CTMs) is not currently practical due to limited computer resources, so that reduced chemical schemes must be employed that contain typically only a few hundred species (for example, 33 species for Carbon Bond Mechanism CBM IV, Gery et al., 1989; 64 species for RACM, Stockwell et al., 1997 and 62 species for SAPRC99, Carter, 2000). The methods for developing these schemes have included, for example, use of surrogates or lumped species to represent a family of compounds or truncation of some peroxy radicals reactions. The accuracy of some reduction methods may actually depend on the particular case under consideration, in particular the chemical regime characterizing the relative importance of the different reactions involved during VOC oxidation. Consequently, the reduction

of the fully explicit VOC chemistry to a smaller mechanism often limits the validity of the smaller mechanism to a specific chemical regime, e.g., highly polluted, or pristine remote, but not both.

The objective of this work was to develop and assess a reduced chemical scheme suited to the study of gaseous photo-oxidant pollution at different scales, i.e. to different chemical regimes. The study therefore focuses on the $O_x/NO_x/HO_x$ chemistry and the reduction of the VOC oxidation schemes for that particular system. No attempt has been made in this study to keep in the reduced scheme the chemical information that may be required to deal with other aspect related to organic oxidation in the atmosphere (e.g. secondary organic aerosol formation or cloud chemistry).

Different methods exist to evaluate reduced chemical schemes (Calvert et al., 2002): inter-comparisons of existing chemical schemes, comparisons with measurements from smog-chambers, comparisons with in-situ data or comparisons with reference schemes that describe the chemistry as exhaustively as possible. The last approach is used here. In order to minimize the problems involved in the development of chemical schemes, an automatic generator of chemical schemes was developed for the tropospheric VOC oxidation. This generator is documented in a companion paper (Aumont et al., 2005) and fully described by Laval-Szopa (2003). This tool was used to build a quasi-explicit chemical scheme, then used as a reference to constrain the reduction methods. The reduction methods were also automated to allow fast updates of the schemes, modifications of reduction hypothesis and the “tagging” of some specific reactions to quantify chemical processes.

This paper first describes the reference chemical scheme (Sect. 2) and the various scenarios used to compare explicit and reduced schemes with a two-layer box model (Sects. 3 and 4). Secondly, the automatic procedures used to reduce the number of species and reactions in the chemical schemes are depicted (Sect. 5) and the biases induced by the reductions are assessed (Sects. 6 and 7). The reduced scheme finally obtained is provided in Appendix A (<http://www.copernicus.org/EGU/acp/acpd/5/755/acpd-5-755-sp1.pdf>).

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2. The reference scheme

As described in the companion paper (Aumont et al., 2005), the generator is a computer program that calculates and writes the fully explicit atmospheric degradation mechanism for an initially specified organic compound, down to the ultimate products CO₂ and H₂O. Reaction pathways (the products) and associated kinetics are taken from laboratory measurements when available, or otherwise assigned from structure-activity relations (SARs) derived by analogy with known reactions, based on data published before 2003 as described by Laval-Szopa (2003). An important advantage of the generator method is that as new laboratory data becomes available, the generator code is easily updated and a revised mechanism, fully consistent with the new information, is re-generated.

The inorganic chemistry and the chemistry of one-carbon species are relatively well known and do not require estimation of products or rate constant. This chemistry is added manually to the schemes from the generator. Reactions are those from the SAPRC99 mechanism updated with new data where available (Sander et al., 2000; Atkinson et al., 1999).

A reference chemical scheme was built using the generator for a set of emitted VOCs chosen to be representative of both anthropogenic and biogenic emissions. The anthropogenic species and their emission ratio are those selected in the EUROTRAC-2 protocol for intercomparison of multiphase tropospheric chemical schemes (Poppe et al., 2001). The VOC emission partitioning in this protocol is based upon the inventory developed by Derwent and Jenkin (1991). Modifications were made to keep only species containing less than ten carbon atoms. The emissions of longer carbon chain species were added to the emissions of species having the closest structure. Attention was paid to ensure mass conservation. In total, emissions of 64 anthropic emitted VOC were considered (Table 1), plus biogenic emission of isoprene, α -pinene and limonene.

The current version of the automatic generator does not allow the treatment of cyclic species. The initiation reactions of the oxidation for those species were written manu-

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ally using the schemes developed by Carter (2000). The non-cyclic secondary products from these reactions were then treated automatically by the generator.

A fully explicit description of the oxidation schemes for the 64 emitted VOC considered here would lead to chemical schemes too large to be resolved, even using a simple box model (see examples in Aumont et al., 2005). In order to decrease the dimension of the reference scheme, a pre-reduction was thus carried out. Some secondary species were replaced by isomers already treated during the writing of the scheme. Only isomers containing the same number of carbon atoms and bearing the same functional groups were grouped together. Attention was paid to the possible resonance between the functional groups, which implies different chemistry. The best compromise between bias and reduction efficiency was found when the species of third or higher generation of stable products were replaced. The loss of accuracy from this reduction was tested by comparing pre-reduced schemes with fully explicit schemes for hexane and for isoprene. Correlation coefficients were found to be greater than 0.9999 for O₃, NO_x, H₂O₂, OH and HO₂ when using this pre-reduction for these two species. After this pre-reduction, the scheme describes the oxidation of the 67 primary VOC through more than 2 million reactions and 350 000 species.

3. Scenarios

The effect of the reductions was tested using five scenarios representing various environmental conditions. Simulations were conducted for both summer and winter conditions. A two-layer box model was used to allow computation of the chemistry both with explicit and reduced chemical schemes.

3.1. Moderately and highly polluted scenarios

Two scenarios represent typical urban and polluted rural areas. The general conditions for these two scenarios are similar to those described by Aumont et al. (2003).

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Compounds are exchanged between the two layers (representing, respectively, the continental boundary layer and the residual layer) during the variation of the boundary layer height. The top of the lower layer varies from 150 m during the night to 1000 m in the afternoon for the summer conditions, and from 150 to 500 m for the winter conditions. The top of the upper layer is fixed at 2000 and 1000 m for the summer and winter scenarios, respectively. The residence time of the air over the area is assumed to be 6 and 36 h for the urban and polluted rural scenarios, respectively. Boundary conditions for both layers are from [Sillman et al. \(1990\)](#) and represent typical rural concentrations. The anthropogenic emissions of NO_x and VOC are based on [Sillman et al. \(1990\)](#) and [Bey et al. \(2001\)](#) and correspond to averaged values for typical urban and rural areas. As previously said, the distribution used for emission is based on the inventory provided by [Derwent and Jenkin \(1991\)](#). Diurnal variations of anthropogenic NO_x and VOC emissions were parameterized according to [Hough \(1986\)](#) and the corresponding profile can be found in [Bey et al. \(2001\)](#). Biogenic emissions of NO_x and VOC (isoprene and terpenes) were varied with temperature and with solar radiation (isoprene only) according to the parameterizations given by [Simpson et al. \(1995\)](#). Deposition velocities were computed for each scenario using the deposition model of [Wesely \(1989\)](#). Deposition was considered for SO_2 , O_3 , H_2O_2 , NO_2 , NO and HNO_3 . We used the categories 1 (i.e. “mid summer with lush vegetation”) and 3 (i.e. late autumn after frost, no snow”) provided by [Wesely \(1989\)](#) to estimate the deposition velocities for the summer and winter scenarios, respectively. Actinic fluxes were computed using the TUV model ([Madronich and Flocke, 1998](#)) in which we introduced the optical properties of aerosol mixtures recommended by the World Climate Research Program ([1986](#)). Photolysis rates were calculated for 45°N under clear sky conditions for a typical winter and summer day. Simulations were run over five days, corresponding to the time required to reach a steady state over a full diurnal cycle. The 24 h diurnal profiles presented below are given for the fifth day.

3.2. Free relaxation of air masses

Three other scenarios were built to test chemical schemes under low-NO_x conditions. In order to begin the simulations with a VOC speciation representative of an old air mass, these relaxation scenarios were built on the basis of the results simulated with the moderately polluted scenario. Thus, initial concentrations are taken at noon on the fifth day of the regional scenario. Neither emissions nor advection nor variation of the mixing height are considered in these scenarios. Deposition was also considered for SO₂, O₃, H₂O₂, NO₂, NO and HNO₃. Deposition velocities were computed with surface category 9, “water, both salt and fresh” (Wesely, 1989). Two scenarios, summer and winter, were considered for relaxation of air masses in the boundary layer. Another scenario was made to check the reductions at low pressure (540.5 mbar), low temperature (256 K) and low water vapor concentration. These values were taken from the US Standard Atmosphere 1976 for typical air mass at 5 km. No deposition is considered for this scenario.

4. Evaluation of the reference scheme

In order to test the basic realism of the model, some baseline comparisons with observations and with other chemical mechanism were performed. The reference scheme was used in polluted scenarios and the results were compared with typical diurnal profiles and with results obtained with the SAPRC 99 (Carter, 2000) scheme (with the same inorganic chemistry as the reference scheme, see Aumont et al., 2005). The objective of the scenarios was to test the chemistry in realistic and various environmental conditions rather than represent any particular location or time period. Nevertheless, the relevance of the results obtained with the reference scheme in the urban and polluted rural conditions was checked comparing the O₃ and NO_x diurnal concentration profiles simulated with the typical profiles monitored by the Paris air quality network (data available at <http://www.airparif.asso.fr>). Results of these comparisons are shown

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in Fig. 1 for O₃, NO and NO₂. Observations for the Paris area are represented by the percentile 5, 25, 75 and 95 computed with the data available since 1993. Data come from two locations: “Paris 18”, an urban station away from major traffic influence and chosen to be representative of the urban background atmosphere and “Rambouillet”, a rural station located 30 km south/west of Paris and experiencing high ozone concentrations during summertime when being downwind of Paris. Figure 1 shows that simulated concentrations match reasonably well the typical observed data. Furthermore, a very good agreement between the simulated concentrations with SAPRC 99 and the reference scheme is observed, thus providing confidence in the “reference” character of the explicit scheme.

5. Reduction methods

Reduction hypotheses tested in this work mainly come from the work of Carter for the development of SAPRC99. The SAPRC99 chemical scheme was developed to simulate ozone production in urban and regional atmospheres (Carter, 2000). In the present work, adaptations of some methods used in SAPRC were made to improve the simulation far from sources, i.e. in the low-NO_x regime. Furthermore, the reduction methods tested in this work were automated in order to allow a fast writing of reduced scheme and to facilitate quick modifications with future updates. The different levels of reduction are summarized on the Fig. 2. A short description of the methods is given hereafter. More details concerning the reductions are given by Laval-Szopa (2003).

5.1. Counter species for peroxy radical chemistry

The reference scheme takes into account nine reactivity classes for the RO₂+RO₂ recombination reactions (see Aumont et al., 2005) and uses the concept of counter species of Madronich and Calvert (1990) to represent them. Madronich and Calvert (1990) showed the importance of the representation of these reactions for low-NO_x

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conditions (e.g. marine boundary layer or Amazonian boundary layer), notably in the balance of radical species (HO_2 and RO_2), H_2O_2 , PAN, alcohols and organic acids. However, even with the use of the counter species, the representation of the RO_2+RO_2 reactions require numerous reactions (here 9 reactions per peroxy radical).

5 Different configurations for the reactivity classes of peroxy radicals were tested within conditions similar to those described by Madronich and Calvert (1990) for the marine boundary layer. The effect of this simplification was tested by comparing the results obtained with those simulated when using all nine reactivity classes. A good agreement was found when using only three different types of recombination reactivities instead
10 of nine in the explicit chemical scheme. These classes are:

- Acyl-peroxys which have a particularly high reactivity with themselves and other peroxy radicals. A cross-reaction rate constant of $10^{-11} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$ is assumed for all $\text{RCOO}_2+\text{RO}_2$ reactions.
- Peroxys having self-reaction rate constant greater than $10^{-13} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$ at 298 K are represented by a class of peroxy reacting with a self-reaction rate constant of $1.2 \times 10^{-12} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$ at 298 K. This rate constant corresponds to that recommended by Lesclaux (1997) for the primary peroxy radical with a branching in the alpha-position.
- Peroxys having a self-reactions rate constant less than $10^{-13} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$ at 298 K for which self-reactions and cross-reactions are neglected.

The regression parameters for key inorganic species and the deviations relative to the scheme involving nine classes of peroxys are presented for organic functional groups in the Tables 2 and 3. For inorganic species, the lumping of peroxys classes
25 has no significant impact on the simulated concentrations. For organic functions, maximums biases due to this reduction never exceed a few percent. Furthermore, this reduction decreases the number of reactions by about 20%.

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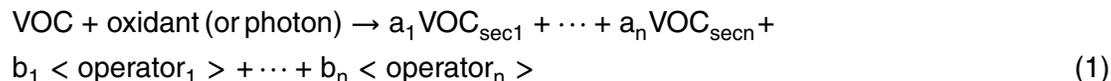
5.2. Operator species for peroxy radical chemistry

The “chemical operator” approach (Carter, 2000; Gery et al., 1989; Bey et al., 2001) was automated to reduce the organic radical chemistry. This method allows the writing of a generalized reaction with product yields to represent the organic sequence up to the secondary products resulting from the oxidation of an organic compound. In these generalized reactions, “chemical operators” are used to drive inorganic transformations, such as NO to NO₂ conversion or HO₂ radical regeneration.

This method relies on the following assumptions:

- the rate of the organic oxidation process is limited by the initiation of the organic radical chain
- the inorganic balances are redundant for various species in spite of their structural differences, except the organic nitrate yields

Each oxidation of an organic compound is then written by a global reaction as follows:



The various terms of the reaction are described below. The practical implementation of this method is illustrated in Figs. 3 and 4 for propane.

- The left side of the reaction describes the initiation of the oxidation of each explicit non-radical VOC. This VOC could be a primary (emitted) VOC or one formed in any of the subsequent generation (secondary species). The inorganic oxidant can be OH, O₃, NO₃ or the oxidation can be initiated by photons.
- VOC_{sec,1} through VOC_{sec,n} represent the secondary organic products created by the oxidation of the VOC. They are explicit non-radical VOCs, formed by the major reaction pathways of the peroxy radicals produced from the original VOC, followed by their reactions with NO. They are typically carbonyls (ketone or aldehyde). The

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coefficients a_1 - a_n are the production yields of each VOC as calculated from the branching ratio of the various organic radicals (peroxy and alkoxy) involved in the oxidation chain up to the formation of the considered VOC. Branching ratios (and therefore the $\text{VOC}_{\text{sec},i}$ yields) are estimated at a fixed temperature (here 298 K).

- The operators (noted operator_i) are surrogate peroxy radical species introduced to represent the contribution of the VOC oxidation to the inorganic balance. The same set of operators is used for several oxidation budgets. These species “operate” the inorganic chemistry (e.g. NO/NO₂ conversion or HO₂ regeneration) involved in the evolution of a peroxy and its descendant alkoxy radical. Different types of <peroxy> are built depending on the reactivity of their peroxy radical parent. These species are zero-mass species (mass being already taken into account in the $\text{VOC}_{\text{sec},n}$), except for <NITR>, which “operates” the NO uptake into a surrogate nitrate species (noted NITR in Appendix A: <http://www.copernicus.org/EGU/acp/acpd/5/755/acpd-5-755-sp1.pdf>). The b_1 - b_n are calculated on the same way as a_1 - a_n , that is to say multiplication of branching ratios (see coefficients a and b on the Figs. 3 and 4 for the oxidation of propane). Modifications were performed to adapt the Carter’s method to the various tropospheric conditions, especially low NO_x concentrations. Hence, new operators were introduced in order to regenerate NO₂ or OH (instead of HO₂) at the end of successive NO/NO₂ conversions. They correspond to the inorganic sequences of the oxidation of organic nitrates or the attack of OH on the hydrogen in alpha position of a carboxylic acid group, respectively, and are noted in the reduced scheme <2NO₂₂
- Additional surrogate non radical species must be introduced to take into account the formation of organic functionalities not generated by the RO₂+NO reactions, like hydroperoxides. Therefore, a surrogate hydroperoxide species (noted Hydroper_RO2 in Appendix A: <http://www.copernicus.org/EGU/acp/acpd/5/755/acpd-5-755-sp1.pdf>) is produced by the <peroxy>+HO₂ reactions. It is a

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zero-carbon species, mass being already represented in the budget equation (i.e. $\text{VOC}_{\text{sec},n}$). This zero-carbon species can react with OH or can be photodissociated and reform radical species (OH, HO_2 or $\langle \text{RO}_2 \rangle$) with the rate constant corresponding to that of the attack of OH on the -OOH function, much like explicit organic hydroperoxides. Similar to the SAPRC mechanism, organic nitrates are also not considered in the budget reaction, but are generated by the reaction of NO with the appropriate operator. This allows an accurate representation of the NO_x uptake even under low NO_x . The surrogate nitrate species (NITR) is therefore introduced as a product of the $\langle \text{NITR} \rangle + \text{NO}$ reaction, in order to maintain the NO_x budget in the reduced scheme. These surrogate species can impact the inorganic chemistry at a later stage, e.g. the NITR can be a source of remote NO_x and hydroperoxyde RO_2 can react with OH or photolyse. In the same way, other zero mass species were introduced in order to keep the specificity (e.g. reservoir species) of some organic products (PAN, carboxylic acids or peroxy acids).

The chemical pathways involving acylperoxy radicals are also replaced by a global budget with operators (see Fig. 5). The explicit organic products written in the global reaction of the reduced scheme are those arising from the reaction of $\text{RC}(=\text{O})\text{O}_2$ with NO in the explicit scheme. Nevertheless, in ambient air, the evolution of acyl peroxy depends notably on the NO/NO_2 ratio, which controls the formation of PAN-type species or the formation of an acyl-oxy radical (which decomposes rapidly to CO_2 and shorter alkyl radical which adds O_2 to form a shorter peroxy radical). Using this reduction method, the acyl-oxy products will then represent all the organic carbon and a zero carbon PAN like species is added to the mechanism to represent the other pathway. The PAN like species can regenerate NO_2 at the same rate as the peroxy acetyl nitrate (for decomposition and photolysis reaction).

When a species having a long carbon chain is oxidized, it leads to several successive NO/NO_2 conversions before reforming an inorganic radical fragment (i.e. OH, HO_2 , NO_2). The original operator method developed by Carter (1990, 2000) uses a parallel treatment for successive generations of peroxy radicals (see Fig. 6). For example, in

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the parallel treatment, a peroxy radical leading to 3 successive conversions of NO to NO₂ before giving HO₂ will be directly represented with an operator reacting with NO to give HO₂ and two operators allowing the conversion of NO to NO₂. Therefore, the RO₂ quantity at the nth generation is considered to be the same as that of the first generation. When competing reactions for RO₂ evolution are high (i.e. for low NO_x concentrations) this simultaneous treatment overestimates the NO to NO₂ conversion and the final HO₂ production. For NO_x limited regimes, this parallel approach also implies underestimations of the hydroperoxide formation and of the radical termination. In order to tailor the operator method to various conditions including low NO_x conditions, a sequential treatment of the different generations of peroxy radicals (Aumont et al., 1996) was retained instead of the parallel treatment (see Fig. 6). In the sequential treatment, the successive operators (i.e. peroxy radicals) are formed successively and their amount decreases at each generation due to reactions that compete with NO, such as RO₂+HO₂ and RO₂+R'O₂. The sequential treatment is a more accurate representation of the radical organic chains but requires an increased number of operators. To limit the number of these species, we chose to apply a parallel treatment for the operator forming a nitrate by reaction with NO. Four or more successive NO/NO₂ conversions occur only with very low yields (< few percent), even for molecules having a fairly long carbon chain (C>10). Including specific <peroxy> species to deal with these long reaction sequences would increase significantly the total number of species in the reduced scheme without significant improvement in accuracy. Therefore, when a sequence includes more than three generations of peroxy radicals, the first generations of NO/NO₂ conversions are arbitrarily treated in parallel and the last three generations are treated sequentially.

The writing of the global equation for each VOC, the creation of the appropriate operators and the writing of their chemistry are done automatically. The application of this method to the reference scheme results in a very large diminution of the number of species in the chemical scheme (1350 versus 3.6×10^5) using almost forty different operators.

5.3. Lumping of primary VOCs

Near anthropogenic sources, many primary VOCs must be taken into account to represent accurately the ozone production mechanisms. The oxidation sequences differ mainly by the rate of initiation step, the chemical nature of the secondary products, and the number of inorganic sequences that result (NO/NO₂ conversions, radical production or consumption, etc.). Nevertheless, some similarities exist for species of the same chemical family and with similar carbon chain length. These similarities are used to lump primary species together.

Primary species are separated by family and reactivity with OH (see Table 4). In the same group, the VOC + OH reaction rate cannot vary more than a factor 2. The thresholds for OH reaction rates are those from Middleton et al. (1990). Then, each group is represented by one of the species from the group which is used as surrogate for every VOC inside the group. Priority was given to the simplicity of the method and ease of implementation of the reduced chemical scheme in 3-D models. Consequently, the lumping used here can be applied independently of the emitted ratios of the primary species and no weighting by OH reactivity within each group is performed. For alkanes and aromatics, the mass of carbon emitted is conserved by multiplying the flux of the real species by the ratio of the number of carbon in the real species and the surrogate species. For some compounds with specific functional groups (e.g. alkenes, esters, aldehydes), the reactivity mainly comes from those functional groups. For these reasons, the number of emitted functional groups is conserved and the surplus of carbon is added to the butane emissions. Species containing 2 or 3 carbon atoms have low reactivity and the description of their chemistry does not require many species. This lumping method were therefore not applied to these species.

Due to its particularly long residence time (compared to the other oxygen containing secondary product), acetone is of some importance at global scales. Acetone can thus be affected by long range transport (Arnold et al., 1997; Jacob et al., 2002) and is suspected to be a significant source of radicals in the free troposphere (Wennberg

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et al., 1998; Jaegle et al., 2001). Jacob et al. (2002) estimate that oxidation of iso-alkanes represent about 20% of the global sources of acetone and could be the most important source in the extratropical areas during winter in the Northern Hemisphere. Consequently, the iso-structure (which can form acetone) is treated separately from the neo-structures.

The categories finally selected for this reduction of the chemical scheme are presented in the Table 4. The dimension of the scheme after this reduction is presented Fig. 2.

5.4. Lumping of secondary VOC

Secondary species having similar reactivities are also lumped into surrogate species. Criteria similar to those already applied for the primary species were used. Alcohols are produced in high quantity due to the isomerization of long chain alkoxy radicals. Their reaction with OH leads to the formation of a carbonyl compounds and the restitution of a radical species (HO_2). In the reduced chemical schemes using the lumping of secondary VOC, alcohol functional groups are directly replaced by carbonyl functional groups and a special zero-carbon surrogate species was created in order to allow an OH conversion into HO_2 . After this first substitution, the secondary VOC in the budget equation (Eq. 1) are essentially carbonyl species. The following 10 species were used as surrogate species to represent the various carbonyls: acetone; methyl ethyl ketone and methyl isobutyl ketone for higher linear and branched ketones, respectively; acetaldehyde and propanal for higher aldehyde; glyoxal; methyl glyoxal and biacetyl for higher α -dicarbonyls. Secondary species originating from aromatic oxidation (i.e. the unsaturated dicarbonyls DCB1, DCB2, DCB3) were kept just as they are in the explicit generator scheme. The number of species and reactions of the scheme after this reduction is presented Fig. 2.

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6. Results for the various scenarios

Reduction methods were applied successively to the explicit scheme, except that the operators and lumping of primary species were first tested independently before being combined. The order of application of the reduction methods and the numbers of species and reactions after each reduction step are presented in Fig. 2. The reduced schemes were then tested by comparison with reference scheme in a box model for the various conditions previously described.

For each scenario, a preliminary analysis using the reference scheme was first performed to characterize the dominant chemistry of the scenario and therefore to identify which aspects of the reduction methods would be tested by this scenario. For example, since VOCs react mainly with OH, the reactivity of the air masses was estimated by computing for all scenarios the term $\sum k_{(OH+VOC)_i} \times [VOC]_i$. In the same way, the contribution of primary and secondary species to the total reactivity were determined. The branching ratios for the reactions of peroxy radicals were also quantified to identify the importance of using reductions by the operator method. The main results of this preliminary analysis are briefly mentioned hereafter for each scenario and the results of reduction are then presented.

6.1. Polluted area (urban and regional scenarios)

The urban and regional scenarios are characterized by intense emissions of ozone precursors. Hence, primary VOC was found to play the main role in the reactivity (80% in the urban scenario and 40% to 80% in the regional scenario for summer and winter conditions, respectively). Furthermore, in these scenarios, the organic peroxy radicals react mainly with NO, except for the regional summer conditions in which the RO_2+RO_2 and RO_2+HO_2 reactions reach up to about 20% during the day and 60% during the night (other nighttime pathways being about 25% for reaction with NO and 15% with NO_3). The reduction of the primary VOC oxidation scheme is therefore most relevant in this scenario.

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Figure 7 shows diurnal profiles at different reduction levels by comparison with the explicit scheme for ozone, NO_x and RO_x ($\text{CH}_3\text{O}_2 + \text{HO}_2 + \text{OH} + \text{RO}_2$). For urban scenario (both summer and winter conditions) ozone and NO_x concentrations are well reproduced for all reduction levels, with relative errors of 1.4% for ozone and less than 1% for NO_x concentrations. The overall features of RO_x concentrations are also well reproduced, however with an overestimation of about 10% during the night. For the regional scenario, the reductions introduce errors in ozone concentrations of less than 1%. NO_x concentrations are also well simulated with reduced schemes for the winter conditions. For summertime, a bias induced by the use of operators is observed (up to 5%). This bias is related to the relatively low NO concentrations (a few hundred ppt) allowing radical recombination reactions. For both summer and winter conditions, reduction steps imply deviations of radical concentrations (RO_x), with an underestimation during the night and an overestimation during the day (see Fig. 7). The nighttime sources of radicals are the reactions of the VOC with NO_3 and O_3 . The deviation of radical concentrations is due to the aggregation of primary species. The daytime deviations of radical species are mainly due to the use of operators and, partly, to the aggregation of secondary species, which play a significant role in the organic reactivity with OH (10 to 30%).

These tests show that, in moderately to highly polluted conditions, chemistry is not very sensitive to the reductions. However, in these scenarios, the flushing time of the air in the box is shorter than the running time of the simulation. The simulated concentrations are therefore significantly influenced by boundary conditions. Impacts of the reduction are then attenuated, boundary conditions being not modified by them. In order to highlight the errors that may result from the reductions, a simulation in urban conditions was performed without any renewing of the air inside the box (i.e. no advection of air inside and outside the box is considered). This test leads to high ozone and NO_x concentrations (150–250 ppb). Results are shown Fig. 8 for ozone, NO_x , OH and HO_2 . As the two first days do not show significant deviations, they are not shown on this picture. Deviations between the different schemes increase

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substantially in these conditions. Ozone production is decreased by aggregating the primary species (−5% and −5.9% for fourth and fifth days, respectively) whereas it is increased by the use of operators (+6.4 and +10.8% for the same peaks). Chemical schemes combining both hypotheses provide the best results (2.4% and 3.7% for the last two peaks) due to error compensation. The OH concentration integrated over the whole last day is overestimated by 9% for the most reduced scheme. NO_x profiles are also well represented although the concentrations diverge slightly at the end of the simulation (6% for the most reduced scheme). This bias is due to the overestimation of OH levels, as NO₂ consumption is controlled by the OH+NO₂ reaction. Finally, the use of operators leads to an overestimation of HO₂ concentrations (up to 20% during the diurnal maximum). Overall, these comparisons show that even for very polluted scenarios (high NO_x levels), concentrations computed with reduced schemes are close to those obtained with explicit scheme.

6.2. Free relaxation of air masses in lower tropospheric conditions

These scenarios, with neither emission nor advection, are characterized by a fast up-take of NO_x. After two days, NO_x levels are relatively low: a few tens ppt for summer conditions, and less than 3 ppb for winter conditions. These tests are then highly sensitive to the competition between RO₂+NO reactions and RO₂+HO₂(or R'O₂) reactions, and therefore to the reduction assumptions involving operators.

Results are presented for ozone, NO_x and RO_x in Fig. 9. For summer conditions, net ozone destruction occurs after the second day. During the first day, it was found the RO₂+NO reactions contribute on average to about 50% of organic peroxy removal and the RO₂+HO₂ and RO₂+RO₂ reactions for 40% and 10%, respectively. The second to the fifth days are dominated by the RO₂+HO₂ and RO₂+RO₂ reactions (respectively 50% and 20%) and only about 30% of the removal of organic peroxy is due to the reaction with NO. For this scenario, concentrations of the inorganic species are relatively well reproduced although some growth of deviations with time is noted. However, even after five days, the relative error in ozone concentrations is less than 5% in this

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scenario. This error is mainly due to the operator reduction (see Fig. 9). The use of operators and the aggregation of secondary species lead to a decrease of NO_x concentrations, with a maximum bias at the end of the simulation of 8 ppt (20%) with the most reduced scheme. Biases in the daytime concentrations of RO_x are less than 5% but concentrations are underestimated by 10% during the night.

For winter conditions (see Fig. 9), ozone concentrations are affected only slightly by the reductions (bias <3%). Nevertheless, NO_x concentrations are underestimated by up to 0.26 ppb (i.e. a 33% bias) due to the use of operators. Radical species are underestimated somewhat (up to 10%) by the aggregation of the primary species. Operators lead to an overestimation of radicals (up to 30% during the night but less than 10% for diurnal values).

These tests show that for low NO_x conditions, ozone concentrations are well captured by the reduced chemical schemes. Nevertheless NO_x concentrations are biased with a systematic underestimation due to the use of operators.

6.3. Free relaxation of air masses in free tropospheric conditions

Results for these simulations at pressure (540.5 mbar) and temperature (256 K) corresponding to 5 km altitude are presented Fig. 10. The ozone profile is affected only slightly by the reductions. On the other hand, NO_x is underestimated significantly by the reduced schemes (about 40% after 24 h). It is nevertheless important to notice that this bias, which results from the use of operators, does not increase with time after 30 h. Furthermore this error is less than that of SAPRC which increases throughout the simulation (see Fig. 10). Thus, the modifications done to improve the suitability of reduction methods to low NO_x conditions seem to be efficient.

7. Summary of biases due to the reduction methods

Three methods were automated to decrease the size of chemical schemes describing the VOC oxidation in the troposphere: (1) The first one is the lumping of primary species into surrogate species. It does not lead to a significant bias for the key inorganic species (i.e. O_3 , OH, NO_x). This reduction is then suitable to a wide range of environmental conditions. (2) The second method is the use of operators which allow the treatment of redundant inorganic sequences with a few model species. This reduction induces no significant bias for high NO_x conditions. However, NO_x is systematically underestimated for low NO_x conditions because of the incomplete representation of the competition between the reaction of peroxy radicals with NO and with other peroxy radicals. This bias can reach 30% after five days for air masses having no injection of primary species. A bias in radical species is also observed after five days in winter conditions and free tropospheric conditions for the free relaxation of air masses scenario. (3) The last reduction is the replacement of secondary species by lumped species. This reduction does not influence concentrations for polluted conditions which are continuously subjected to fresh VOC emissions. Errors due to this reduction are then limited to situations not subjected to large VOC emission. The impact on RO_x and NO_x is small for the first three days but reaches ca. 10% after five days. For winter conditions, the lumping of secondary species induces an overestimation of RO_x , which compensates the underestimation due to operators.

After these reductions, the number of species in the scheme is sufficiently low to be implemented in a 3-D-chemistry transport model. The box model simulations showed that ozone concentrations are simulated well by the reduced scheme, with error (relative to the reference scheme) systematically less than 5% which, for the simulated conditions, corresponds to a maximum error of 1.5 ppb.

For all situations considered here, the reduced scheme reproduced the OH integral with less than 4% error, except for urban scenario without advection (10%), but these conditions are hardly realistic. General features of NO_x are well reproduced for urban to

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continental situation. However, a problem due to an overestimation of the NO_x storage in organic compounds is highlighted for long range transport of air masses. Nevertheless, these scenarios may be rather unrealistic because they consider air masses without any incorporation of new precursors during 5 days. Errors observed can then be viewed as upper limits for the biases.

Acetone is an ubiquitous compound in the troposphere, due to its low reactivity. In the urban and regional scenarios, the exportable amount of acetone (taken here as the integral of acetone concentrations over the fifth day) is underestimated by 0.3 to 11% with respect to the reference scheme. For the free relaxation air masses, acetone concentrations increase during the whole simulation. In these scenarios, acetone production in the most reduced scheme is underestimated by 20 to 30%.

H_2O_2 is one of the main oxidants in the aqueous phase. The good simulation of its concentrations is directly linked to the good representation of the HO_2 chemistry. H_2O_2 concentration is estimated with less than 10% of error. Finally, nitric acid is involved in the aerosol production and is scavenged by water droplets resulting in acidification of clouds and fogs. A good simulation of its concentration shows evidence of a good representation of the chemistry of OH and NO_2 . Biases on this species never exceed 6%.

In summary, all the tests performed so far show a fairly good agreement between the reduced chemical scheme and the reference scheme to reproduce the gaseous chemistry of the system $\text{O}_3/\text{NO}_x/\text{VOCs}$.

8. Conclusions

In order to evaluate the reduction methods typically used in the development of reduced schemes, a reference scheme was developed with the help of an expert system to generate reference scheme as explicitly as possible. The reference scheme describes the oxidation of 70 representative primary species, with about 350 000 species and 2 million reactions. Simulations of typical continental chemical conditions were carried

out with this reference scheme, showing that the simulated concentration agree with typical measured values as well as with concentrations simulated using the SAPRC chemical scheme.

Three methods were automated to reduce the size of an explicit chemical scheme: (i) use of operators, based on the redundancy of inorganic chemistry implied in the VOC oxidation, (ii) lumping of primary species having similar reactivities and (iii) lumping of secondary products into surrogate species.

The number of species in the final reduced scheme is 150, i.e. low enough for 3-D modeling purposes using CTM. The reduced scheme showed a fairly good accuracy in modeling the chemistry for conditions of continuous precursors emissions (urban or regional areas). For the conditions with lower NO_x concentrations, a systematic bias was noted during the transition from the regime where peroxy radicals react almost totally with NO to that where a significant concurrence of the combination reactions with RO_2 and HO_2 takes place. This bias is due to an overestimation of the storage of nitrogen in organic compounds. The error (maximum of 30 to 40% for tested conditions) first emerges during the transition between the two peroxy radicals regimes but then remains constant. Other key species involved in tropospheric chemistry (radicals and ozone) are very well simulated in the various conditions studied (respectively $\pm 10\%$ and $\pm 4\%$). This chemical scheme is therefore able to properly simulate the ozone and oxidant chemistry in various tropospheric situations, from polluted to remote conditions.

Furthermore, this work allowed the automation of reduction methods for chemical schemes coupled with an automatic generator of updated chemical schemes for the VOC tropospheric oxidation. This tool provides then an efficient way to build updated chemical schemes for various applications.

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Table 1. Anthropogenic VOC speciation at emission on the recommendations of the CMD-EUROTRAC-2 protocol (Poppe et al., 2001).

Species in the EUROTRAC inventory	Percentage of total emitted carbon	Species in the EUROTRAC inventory	Percentage of total emitted carbon
Alkanes	42	Aromatics	30.3
ethane	1.63	benzene	2.46
propane	0.4	toluene	10.43
n-butane	7.64	o-xylene	2.41
i-butane	4.15	m-xylene	3.12
n-pentane	2.87	p-xylene	3.12
i-pentane	4.44	ethylbenzene	1.98
n-hexane	1.97	n-propylbenzene	0.46
2-methylpentane	2.23	i-propylbenzene	0.24
3-methylpentane	1.57	1,2,3-trimethylbenzene	0.55
2,2-dimethylbutane	0.22	1,2,4-trimethylbenzene	2.11
2,3-dimethylbutane	0.71	1,3,5-trimethylbenzene	0.79
n-heptane	1.04	o-ethyltoluene	0.72
2-methylhexane	0.87	m-ethyltoluene	1.00
3-methylhexane	0.75	p-ethyltoluene	0.89
n-octane	0.76	Aldehydes	0.86
methylheptanes (1)	2.64	formaldehyde	0.47
n-nonane	1.58	acetaldehyde	0.09
methyloctanes (2)	0.65	propionaldehyde	0.11
n-decane (3)	1.32	butyraldehyde	0.08
methylnonanes (4)	0.85	i-butyraldehyde	0.07
n-undecane (3)	1.85	valeraldehyde	0.00436
n-duodecane (3)	1.86	benzaldehyde	0.05
Alkenes	8.5	Ketones	5.8
ethylene	3.09	acetone	1.65
propylene	1.11	methyl-ethyl-ketone	3.03
but-1-ene	0.70	methyl-isobutyl-ketone	1.12
but-2-ene	1.29	Alcohols	8.8
pent-2-ene	0.97	methanol	0.50
pent-1-ene	0.38	ethanol	8.33
2-methylbut-1-ene	0.21	Esters	1.7
3-methylbut-1-ene	0.25	methyl-acetate	0.12
2-methylbut-2-ene	0.47	ethyl-acetate	0.53
Alkynes	2.1	i-propyl-acetate	0.26
butylene	0.20	n-butyl-acetate	0.35
acetylene	1.88	i-butyl-acetate	0.44

(1) equally splitted between the 2-methylheptane, the 3-methylheptane and the 4-methylheptane

(2) equally splitted between the 2-methyloctane, the 3-methyloctane and the 4-methyloctane

(3) emission reported on the n-nonane

(4) emission reported on the methyl-octanes

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Table 2. Biases due to the reduction by decreasing the number of peroxy recombination reactivity: regression parameters for inorganic species.

Regression parameters		
Species	Slope	R ²
O ₃	1.0001	1.0000
H ₂ O ₂	0.99983	
CO	1.0021	1.0000
CO ₂	0.99890	1.0000
HNO ₃	0.99190	0.99996
HNO ₂	0.98982	0.99998
OH+HO ₂	1.0008	0.99992
NO _x	0.99452	0.99997

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Table 3. Biases due to the reduction by decreasing the number of peroxy recombination reactivity: maximum relative deviations for the organic functions.

Function	Maximum relative deviation (%)
Hydroperoxyde	-3.9
Alcohol	5.9
Aldehyde	1.2
Nitrate	2.3
Peroxy acid	3.5
Carboxylic Acid	-3.8

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Table 4. Primary species lumping: on the left, lumping criteria for each species family (kinetic rates and structural particularities), on the right, the retained surrogate species and the species lumped into these surrogate species.

Reactivity (k in molecule ⁻¹ cm ³ s ⁻¹)		Lumping criteria	Particular distinction *	Surrogate species	Species lumped into surrogate species	
Alkanes						
3.33×10^{-12}	k_{OH}	i	3.33×10^{-12}	n-alkanes i-alkanes	n-butane i-butane	n-butane i-butane, 2,2-dimethylbutane
	k_{OH}	i	6.66×10^{-12}	n-alkanes i-alkanes	n-hexane 2-methylpentane	n-pentane, n-hexane i-pentane, 2-methylpentane, 2,3-dimethylpentane
6.66×10^{-12}	k_{OH}	i	1.33×10^{-11}	n-alkanes	n-octane	n-heptane, 3-methylhexane, n-octane, 4-methylheptane, 3-methylheptane, n-nonane, 3-methyloctane, 4-methyloctane
				i-alkanes	2-methylheptane	2-methylhexane, 2-methylheptane, 2-methyloctane
Alkenes						
5×10^{-11}	k_{OH}	i	5×10^{-11}	$CH_2=CH-R$	but-1-ene	but-1-ene, pent-1-ene 3-methylbut-1-ene
				$R-CH=CH-R'$	but-2-ene, 2-methylbut-1-ene 2-methylbut-2-ene	but-2-ene, pent-2-ene 2-methylbut-1-ene 2-methylbut-2-ene
				$CH_2=C_i$ $R-CH=C_i$		
Aromatics						
6×10^{-12}	k_{OH}	i	6×10^{-12} 1.33×10^{-11}	toluene	toluene	toluene, n-propyl-benzene
				ethyl-toluene	ethyl-toluene	ethylbenzene, i-propylbenzene, o-ethyltoluene, p-ethyltoluene
1.33×10^{-11}	k_{OH}	i		1,2,4-trimethylbenzene	1,2,4-trimethylbenzene	o-xylene, m-xylene, p-xylene, 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene
Aldehydes						
				butyraldehyde	butyraldehyde	butyraldehyde, valeraldehyde
Esters						
3.33×10^{-12}	k_{OH}	i	3.33×10^{-12} 6.66×10^{-12}	n-acetates	ethylacetate	ethylacetate
				n-acetates	n-butyacetate	n-butyacetate
				i-acetates	i-propylacetate	i-propylacetate, i-butyacetate

* for alkanes, distinction between species capable to produce acetone or not

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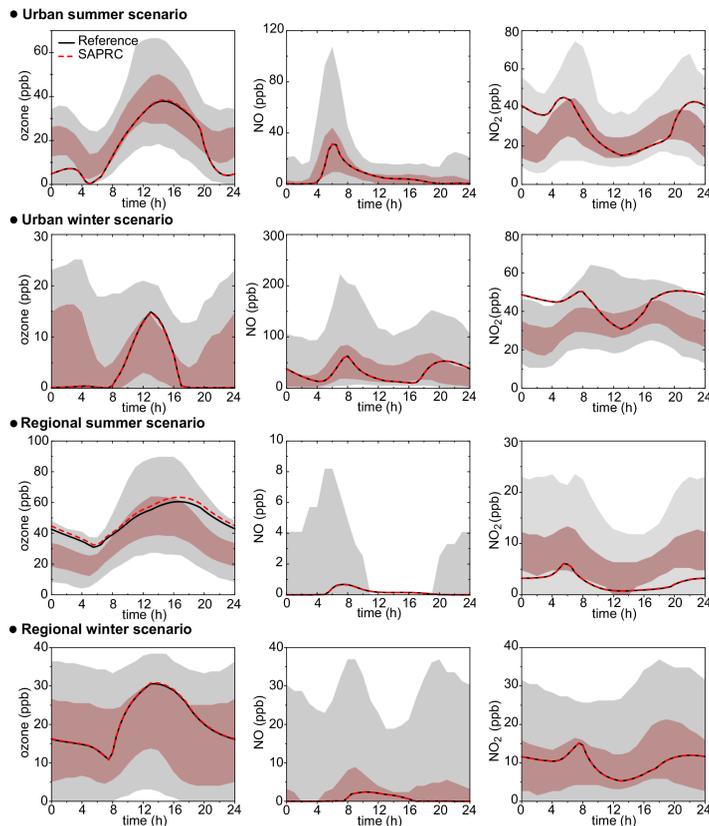


Fig. 1. Simulated mixing ratios of O₃, NO and NO₂ for the highly to moderately polluted scenarios simulated with the reference scheme (black line) and the SAPRC99 scheme (long dashed red line). The shaded regions are measurements (respectively in a Paris urban station and in a rural station in the suburb of Paris, averaged over 1993–2001 period). The pale gray zones represent the 5 and 95 percentiles. The dark zones represent the 25 and 75 percentiles. In the regional winter scenario, the 5, 25, 50 and 75 percentiles are below the detection limit (2.5 ppb) for NO. These percentiles are not represented on the concerned graphic.

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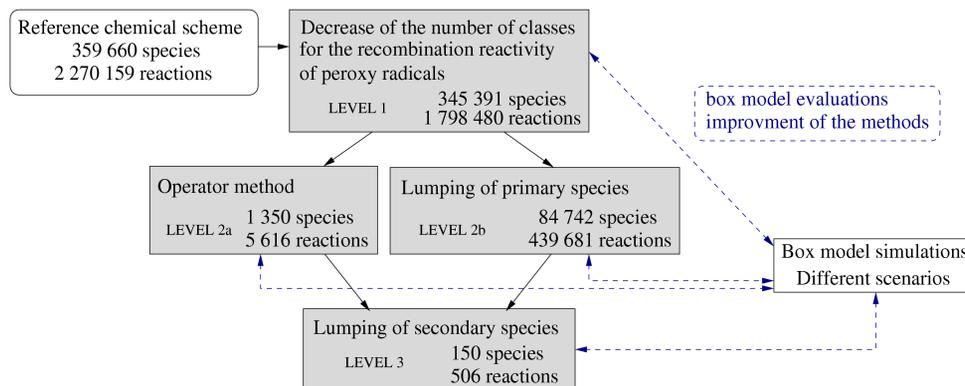
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**Fig. 2.** Number of species and reactions in the schemes at the different levels of reduction.[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)

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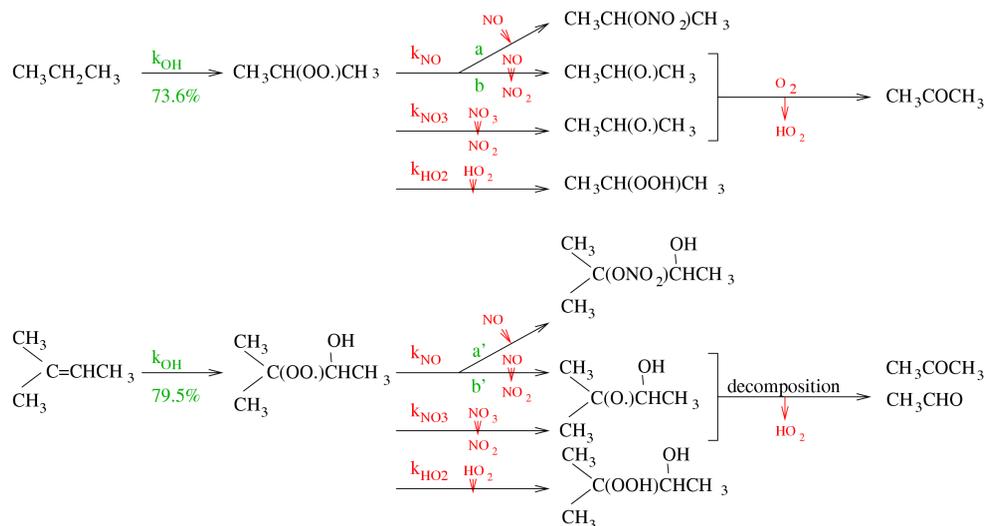


Fig. 3. Comparison of the oxidations of 2 VOC of different structures (the recombination reactions are not represented) – in green, kinetic elements differing in the two chains; in red, redundant elements in the two chains.

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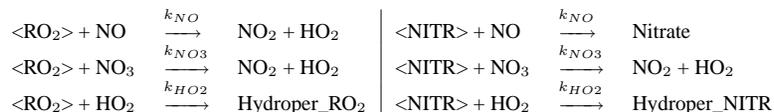
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with $\langle \text{RO}_2 \rangle$, the operator representing the NO to NO₂ conversion and the formation of HO₂ at the end of the chain
 $\langle \text{NITR} \rangle$, the operator which represents the consumption of NO by the pathway giving a nitrate

Their chemistry is then written as follow :



NB : Hydroper_RO₂ and Hydroper_NITR are surrogate hydroperoxydes (described in the text).

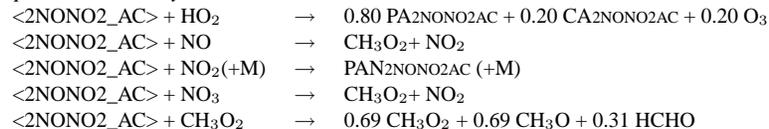
Fig. 4. Writing of the chemistry of propane using chemical operators.

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*Operator chemistry*

NB: other recombination reaction pathways are not written here but are included in the reduced chemical scheme.

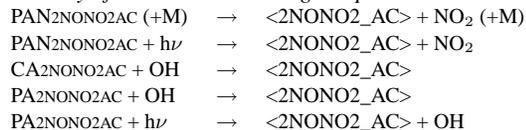
Chemistry of the zero mass surrogate species

Fig. 5. Writing of the chemistry of acetaldehyde using chemical operators for acyl peroxy chemistry.

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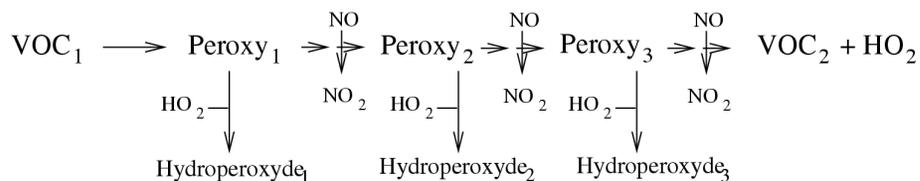
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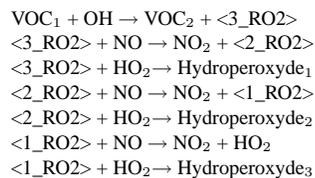
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SEQUENTIAL TREATMENT



PARALLEL TREATMENT

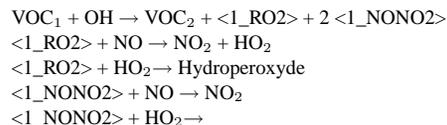


Fig. 6. Parallel and sequential treatments in the operator reduction method.

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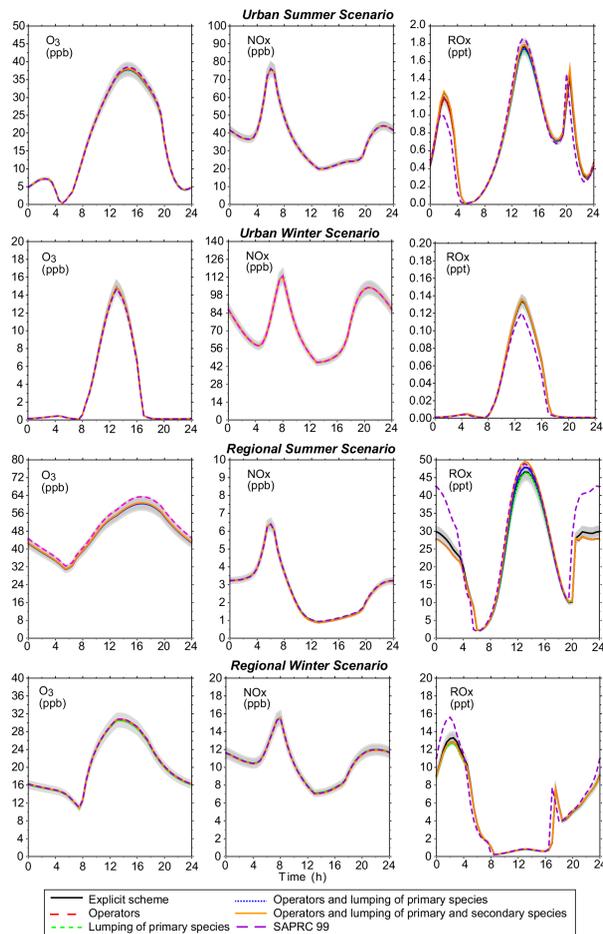


Fig. 7. Ozone, NO_x and RO_x (CH₃O₂+HO₂+OH+RO₂) mixing ratios simulated with the reference scheme and relative deviations of the reduced schemes with respect to that reference, for the polluted scenarios. The pale gray zones represent a deviation of 5% around the explicit scheme results.

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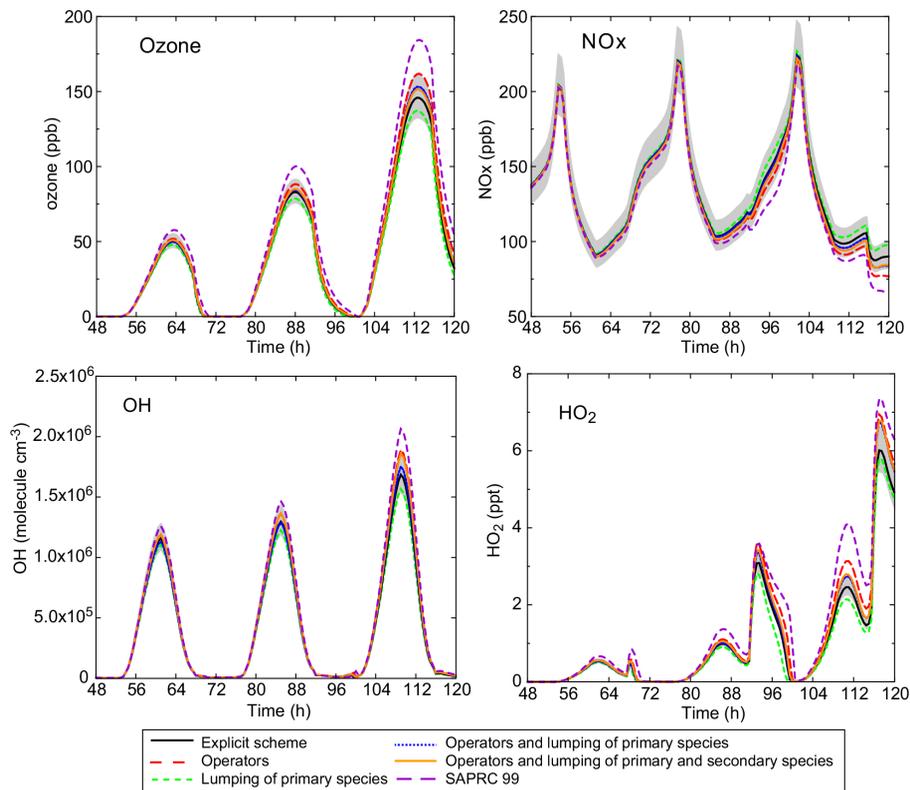


Fig. 8. Ozone, NO_x and HO₂ mixing ratios and OH concentrations simulated using schemes built with different levels of reduction for the urban summer scenario, without advection. The pale gray zones represent a deviation of 10% around the explicit scheme results.

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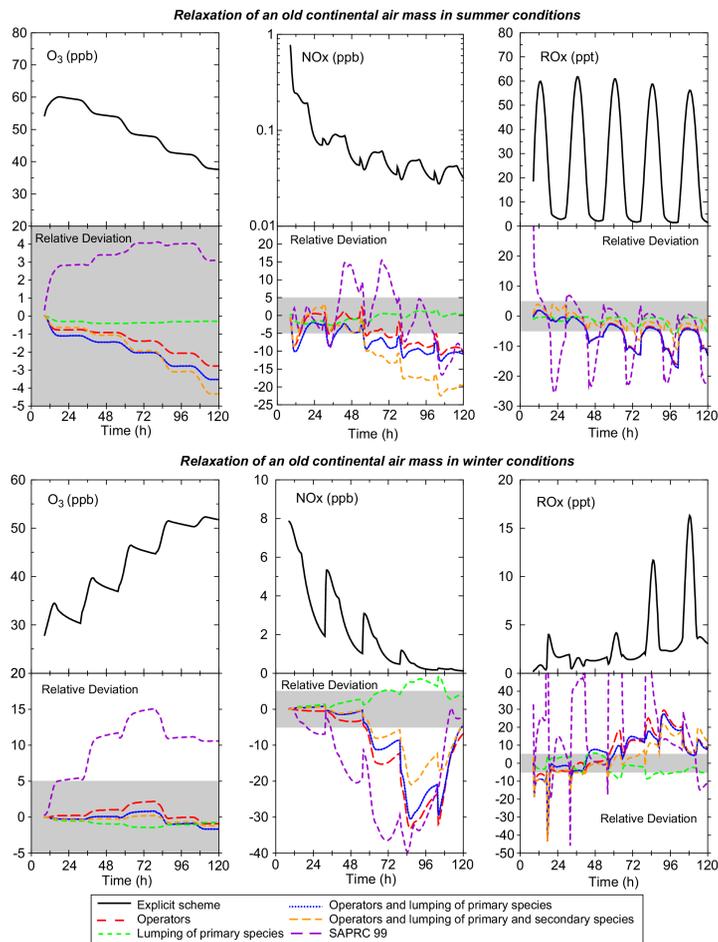


Fig. 9. Ozone, NO_x et RO_x ($\text{CH}_3\text{O}_2 + \text{HO}_2 + \text{OH} + \text{RO}_2$) mixing ratios simulated for the relaxation scenarios without emission, using schemes built with different levels of reduction. The pale gray zones represent a deviation of 5% around the explicit scheme.

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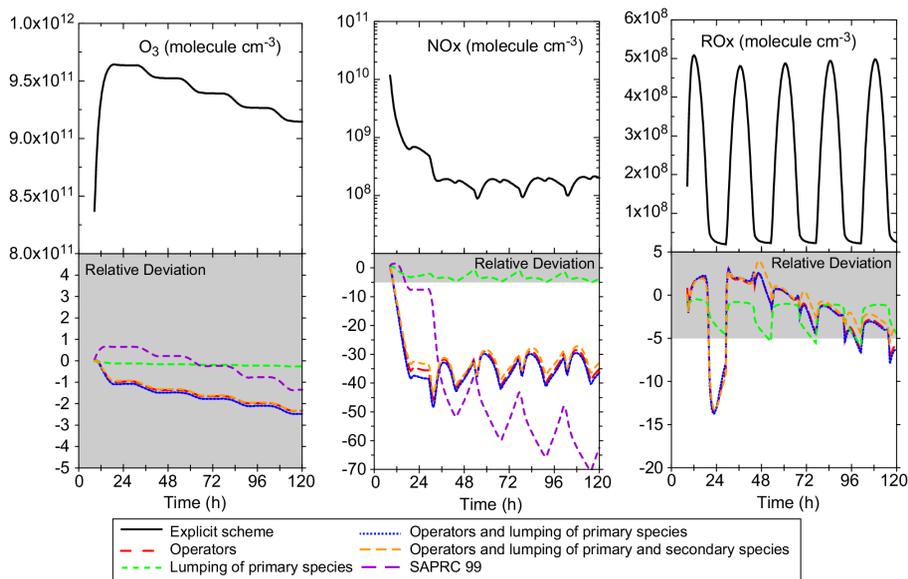


Fig. 10. Ozone, NO_x et RO_x (CH₃ O₂+HO₂+OH+RO₂) concentrations simulated for the relaxation scenarios at 5 km, using schemes built with different levels of reduction. The pale gray zones represent a deviation of 5% around the explicit scheme.

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