Estimating biogenic contributions to ozone production at continental scale

S. Moukhtar¹, B. Bessagnet¹, P. Carlier², J.F. Doussin², L. Rouil¹ & V. Simon³
¹ INERIS, France  
² LISA, France  
³ ENSIACET, France

Abstract

Recent studies about urban plume pollution have highlighted the obvious role of strongly reactive biogenic hydrocarbons on secondary gaseous pollutants and aerosols formation. They have confirmed that looking for air pollution control strategies, these components have to be correctly considered.

Photochemical processes modelling, which describes the relationships between primary compounds emissions and airborne concentrations, allows to realize these analyses. However, in current tools, the role of biogenic volatile organic compounds is often represented through a very simplified approach.

The main purpose of this study is to analyse the sensitivity of biogenic VOCs modelling in the global process of secondary pollutants formation. A new chemical mechanism including a more realistic description (related to the state of the art) of biogenic processes has been developed in a continental scale model called CHIMERE. More precisely, new monoterpenes have been introduced in the primary pollutant classes, and some of the associated secondary products have been isolated. The new mechanism induces a significant effect on PAN and formaldehyde concentrations. Variations from 10% to 20% are observed. However, no important variations on ozone concentrations are noted.

This fact points out difficulties encountered to assess objectively the performance of a photochemical model. If ozone concentrations are only considered, an unsuitable interpretation of the chemical regime could be given. Indeed this work is also oriented towards the determination of significant indicators of photochemical models quality.
1 Introduction

Statistics on ozone concentrations are often used as indicators of photochemical models accuracy. The good representation of other secondary pollutants as HCHO (formaldehyde) and PAN ( Peroxy Acetyl Nitrate) is often neglected. Nevertheless, these two secondary pollutants have a strong impact on air quality, and more precisely from a human health point of view. Moreover the numerous sources of ozone formation decrease the sensitivity of this pollutant. This paper proposes an assessment, using modelling tools, of the impact of biogenic VOCs on air quality, related to ozone, formaldehyde and PAN concentrations.

CHIMERE which has been used in this study, is a large scale Chemistry Transport Model (CTM). It is an Eulerian code covering the western part of Europe with 0.5°*0.5° grid. The CHIMERE chemistry reductions are based on the method developed in the “Statewide Air Pollution Research Center” (SAPRC) mechanism [1]. Intermediary species like radicals or nitrate compounds are represented by chemical operators applied to all reactions. In the base reduced CHIMERE model, each functional group is represented by well documented model species. The aldehydes, for example, are represented by one compound CH3CHO (acetaldehyde), the ketones are represented by CH3COE (methyl ethyl ketone). The biogenic species emitted in the troposphere are represented by two compounds: “isoprene” and “α-pinene”. The “α-pinene” specie includes all the monoterpenes compounds.

New chemical schemes have been developed, taking into account two specific monoterpenes: β-pinene and D-limonene, in addition to α-pinene already present. They have been chosen because of their natural abundance above forests. Moreover, the three monoterpenes classes implemented in the code are representative of most of the monoterpenes. α-pinene is used to define all monoterpenes with endocyclic alkene, β-pinene for monoterpenes with exocyclic alkene and limonene for monoterpenes with exocyclic and endocyclic alkene.

Their contribution has been studied through the analysis of three modelled chemical mechanisms implemented in CHIMERE:
- a reduced one, similar to the initial model with some modifications related to the state of the art for the isoprene and α-pinene chemistry
- a semi-developed one, with the introduction of the secondary products of the oxidation of “new modelled” monoterpenes (pinonaldehyde, nopinone, limona and limonon)
- a developed one, based on the MCM (Master Chemical Mechanism) [2,3], for isoprene, α-pinene and β-pinene - D-limonene is not introduce in the MCM. The intermediate reactions are taken into account.

This analysis is supposed to give answers to several questions:
- What is the impact of the emission of main monoterpenes on the concentrations of secondary pollutants ?
- What is the contribution of a detailed biogenic mechanism in a chemistry transport model ?
- Is it necessary to develop biogenic chemistry in a reduced model ?
In a first step, the basic chemistry implemented in CHIMERE is described and the references we used to develop new mechanisms are presented. Then, some results obtained after introducing in the code “new” monoterpenes and oxidation products are commented.

2 Monoterpenes chemistry

2.1 Monoterpenes chemistry in CHIMERE

The monoterpene chemistry in the initial model includes oxidation of α-pinene by hydroxyl radical (OH), ozone (O₃) and nitrate radical (NO₃). Tropospheric oxidation of monoterpenes mainly produces carbonyls: aldehydes and ketones. To describe the reactivity of all monoterpenes, the oxidation of α-pinene in the initial model produces aldehyde (CH₃CHO) and ketone (CH₃COE) at once. This assumption leads to overestimation of the carbonyles number, and thus of the number of final secondary pollutants. The addition of β-pinene and limonene avoids this overestimation.

2.2 Representation and degradation of monoterpenes

2.2.1 Isoprene

The mechanisms proposed in [4,5] have been used for the oxidation of isoprene by OH. Moreover, mechanisms proposed in [5,6] for the oxidation of isoprene by NO₃ and mechanism proposed in [7] for the reaction of isoprene with ozone have also been considered. Isoprene chemistry implemented in CHIMERE has just been up-dated considering recent papers. No more development are proposed.

2.2.2 α-pinene

Reaction of α-pinene with OH has been implemented following recommendations in [8]. The results show a yield of 0,87-0,09 for pinonaldehyde and acetone. [9] proposed a lower yield of pinonaldehyde (0,34). The reaction of α-pinene with NO₃ is less documented. [10] gives a yield of 0,62 for the pinonaldehyde, which has been chosen. The production of nitrate compounds (yield of 0,14) has been measured by [10] for the first time. The reaction of α-pinene with O₃ has been studied by [9], they report a yield of 0,19 for pinonaldehyde. More recently, [11,12] report a yield of respectively 0,175 and 0,23 for pinonaldehyde. The yield of OH produces during this ozonolysis is 0,7–0,8 [11,13].

The reactivity of pinonaldehyde has been recently described in [14]. H-abstraction from pinonaldehyde by OH is mainly on H-aldehyde (0,59). The main products of this reaction are acylperoxy radicals and aldehydes.

2.2.3 β-pinene

To our knowledge, the reaction between β-pinene and NO₃ has not been studied. For this reaction, the mechanism described in the MCM with an important formation of nopinone and HCHO, has been considered. Reactivity of the secondary compound, nopinone, has neither been studied. The MCM mechanism and the current knowledge about ketone degradation, give aldehyde as the main product.

2.2.4 Limonene
Only [17] introduces limonene in a model, - the RACM (Regional Atmospheric Chemistry Mechanism). Oxidation of limonene mainly produces two compounds: limona and limonon. Limona compound presents an endocyclic alkene and a ketone function. In such a case, the alkene function is the more reactive. Limonon compound has three different functional groups: an aldehyde, a ketone and an exocyclic alkene. The exocyclic alkene and the aldehyde are the most reactive functions, much more than ketone. For these two secondary products, the known reactivity of the main functional group and the mechanism described by [17] have been used.

3 Results

A pollution event occurring on the 11th of August 1998 in the afternoon has been simulated. Representations below show the situation at 3pm. During this episode, the initial version of the CHIMERE model gives maxima ozone concentrations around 350 μg/m³ and peaks for HCHO and PAN concentrations around 15 and 35 μg/m³ respectively.

3.1 Addition of β-pinene

3.1.1 Impact on HCHO concentrations
Differences obtained applying new chemical mechanisms are presented below.

![Image of maps showing HCHO concentrations](a) and (b)

Figure 1: difference between the HCHO concentrations (μg/m³) with and without β-pinene: (monoterpenes = α-pinene + β-pinene) - (monoterpenes = α-pinene ), in a semi-developed (a) and a developed mechanism (b).
Figure 1 shows an increase of HCHO concentrations when β-pinene is introduced in both mechanisms. This trend is the same in the reduced mechanism (not shown here). Maximum increase is about 2 μg/m³ for all the mechanisms. The larger are the initial (in base model) HCHO concentrations and monoterpenes emissions, the larger is the increase.

### 3.1.2 Impact on PAN concentrations

![PAN concentration maps](image)

Figure 2: difference between the PAN concentrations (μg/m³) with and without β-pinene: (monoterpenes = α-pinene + β-pinene) - (monoterpenes = α-pinene), in a semi-developed (a) and a developed mechanism (b).

The addition of β-pinene in the semi-developed mechanism (a) and in the complete mechanism (b) induces an increase of PAN (figure 2). Maximum increase is around 3 μg/m³ for these two mechanisms but the semi-developed mechanism shows peaks of PAN a little bit higher than the developed scheme. The reduced mechanism (not shown here) gives a small increase (maximum 1 μg/m³). Maximal increases are correlated with the initial maximal concentrations of PAN and with the maximal emission of monoterpenes.

### 3.1.3 Impact on ozone concentration

Results on ozone concentrations depend clearly on the chemical scheme used and are not always correlated with the maximal emission of monoterpenes. In the reduced model (figure 3, a), β-pinene induces very little changes (a maximum of 3 μg/m³ increase on ozone concentrations), negligible in the case of this pollution episode. In the semi-developed and developed model (figure 3, b), β-pinene leads to a more important increase, respectively +15 and +10 μg/m³ max. These variations are relatively weak compared to the high ozone concentrations registered, ozone peaks reaching 350 μg/m³ in this case. Addition of β-pinene implies an increase less than 10% of the initial ozone concentrations.
Figure 3: difference between the O₃ concentrations (µg/m²) with and without β-pinenene: (monoterpenes = α-pinene + β-pinene) - (monoterpenes = α-pinenene), in a reduced (a) and a developed mechanism (b).

3.2 Addition of D-limonene

Impact of the addition of D-limonene in a model where α- and β-pinene represent all the monoterpenes species and in a model only with α-pinene has been assessed.

3.2.1 Impact on HCHO concentrations

The impact of limonene on formaldehyde concentrations is negligible when β-pinene is already present in the model. When α-pinene is the only monoterpenes (not shown here), addition of D-limonene induces an increase of HCHO concentration. This increase reach a maximum closed to 1 µg/m³, correlated with the initial maximal concentrations of HCHO and with the maximal emission level of monoterpenes.

3.2.2 Impact on PAN concentration

The impact of the addition of D-limonene on PAN concentrations is weaker in a model where β-pinene is already present (figure 4, a) than in a model taking only into account α-pinene (figure 4, b). The increase is about 2 µg/m³ when α-pinene is the only monoterpenes and about 1.4 µg/m³ when β-pinene is already present. These increases are correlated with the initial maximal concentrations of PAN and with the maximal emission of monoterpenes. It should be noted that the calculated effect is greater with the reduced scheme.
3.2.3 Impact on ozone concentration
Addition of D-limonene in the model with β-pinene induces a weak variation of ozone concentration. The maximal variation represents less than 10% of the initial ozone concentration. The same phenomena, when α-pinene class includes all the monoterpens, is observed.

4 Discussion
The addition of β-pinene in the chemical scheme has an obvious impact (figure 1 and figure 2). In fact, increase of PAN and HCHO concentrations reach respectively 10 and 20% for the peak concentrations. Moreover, addition of β-pinene avoids the carbonyls overestimation caused by the presence of only one monoterpene. The addition of D-limonene induces weak variations in a model with α- and β-pinene (SEQARABIC and figure 4). In fact, the D-limonene structure is very close to the ones of α- and β-pinene. The most reactive functional group of limonene is the endocyclic alkene. This alkene reacts in a first step like the α-pinene alkene. Primary products of the reaction between limonene exocyclic alkene and tropospheric oxidants are HCHO and ketone, the same as in the case of β-pinene reactions. In a scheme with α-pinene as only monoterpene, D-limonene has a more important effect. Variations induced by addition of D-limonene are similar and a little bit lower than the variations due to addition of β-pinene. In fact, reaction between D-limonene and tropospheric oxidant produces less PAN and HCHO than β-pinene oxidation, when looking at stochiometric coefficient. But D-limonene is more reactive than α- and β-pinene. For example, the reaction rate of α-pinene, β-pinene and D-limonene ozonolysis are respectively $8.5 \times 10^{-17}$, $1.34 \times 10^{-17}$, $2.10 \times 10^{-16}$ cm$^3$ mol$^{-1}$ s$^{-1}$ [17,18].
When α-pinene is the only monoterpene, addition of β-pinene or limonene has a significant impact on PAN and HCHO concentrations whatever the model used (reduced, semi-developed or developed). No significant effect on ozone concentrations is noted. Variations represent less than 10% of the initial ozone concentrations.

The variations resulting from the introduction of new monoterpens have the same general characteristics (increase or decrease, localisation of maximum) whatever the model used. However, the reduced scheme still presents a good sensitivity for the detection of variation of PAN and HCHO. This sensitivity seems decreasing for the ozone variation (figure 3). The reduced model does not take into account the amplitude of the variations of ozone in the case of addition of β-pinene (figure 3), of D-limonene and in the case of update of isoprene and α-pinene reactivity.

5 Conclusion

It has been shown in this work that the impact of the addition of β-pinene and D-limonene is important in a Chemistry Transport Model similar to CHIMERE, even using a reduced chemical scheme. The representation of monoterpens by the three species: α-pinene, β-pinene and D-limonene gives a good representation of the biogenic chemistry and avoids the initial overestimation of carbonyls concentrations. Moreover, oxidation of D-limonene produces numerous biogenic particles. This compound is very important taking into account particles chemistry.

This study allows us to conclude in favour of a low sensitivity of ozone concentrations, in particular in a reduced model. So ozone may not be a significant indicator of photochemical models quality, especially in a simplified chemistry scheme. Secondary pollutants like PAN and HCHO seem to be more sensitive and may constitute useful complementary indicators to assess the performance of air quality simulation tools.

References


