

3D ozone production in relation to VOC emission and oxidation, and the assessment of 2010 ozone control strategies

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Abstract

In order to efficiently reduce the number and intensity of ozone regional peaks, a regulation centered on the diminution of VOC and NO_x emissions was promoted for 2010 in many European countries. In this paper we present a study of the respective role of anthropogenic and biogenic VOCs on regional ozone production, in order to determine the species most involved in local ozone production and their geographical and temporal impact on ozone production rates. Through a 3D-modelling case study, we derived the participation in ozone production of the main precursor species (VOCs, CO) from the chemical scheme by the use of inert tracers. The results highlight the important role of biogenic emissions as expected, but also the strong participation of CO, and that of aromatic species and light alkenes as initiators of ozone production close to sources. This study is part of a larger project aiming to simulate 2010 regional scenarios. The same tracer studies will be conducted on 2010 projected emissions to evaluate from a detailed analysis of the ozone production mechanisms the efficiency of the engaged regulation.

Keywords: ozone production, VOC, CO, emissions, inert tracers, legislation.

1 Introduction

The effectiveness of ozone control strategies has been punctually investigated with 3D air quality models through case studies using both present and 2010-projected



emissions, for specific cities and polluted days. Anyway, a global understanding of the effects of the proposed emission strategies on ozone can only be reached through a temporal and geographical analysis setting the relationships between precursor emissions, VOC oxidation and ozone production within an air mass. This paper is based on a 3D-modelling case study of fast ozone production in the South of France, and presents a quantitative analysis of ozone production as a function of space, time and precursor emissions over the region. The participation of the main precursor species in ozone production (VOCs, CO) is derived from the chemical scheme in each grid cell and for each hour of the simulation. Then, the temporal evolution of ozone production rates is plotted against CO and VOC degradation and ozone yield, from various emission points towards the regional ozone maxima. The results of these analyses will allow us to define how species are involved in fast ozone production over the domain, but above all to spatialize their impact on ozone with regards to fast ozone production areas.

2 Strategy

The purpose of this work is to highlight the way VOC families and species are involved in regional ozone build-up, and how much this role is influenced by the intensity, location and time of their emissions. The final objective is to bring new elements for the analysis and proposal of efficient emission reductions for air quality at the regional scale. The chosen strategy is the use of 3D modelling which offers the possibility to follow the chemical transformation of primary species into oxidant species, through the use of specific indicators in the chemical scheme. Several polluted events, corresponding to a wide variety of dynamical situations and emission mixtures, were selected and simulated in order to obtain a mean estimate of the role of each VOC in the development of an oxidant plume, but also to quantify the variability of this role on a given site.

2.1 Presentation of the simulation domain and episodes

The simulation site is the Berre-Marseilles area, a 140x140km domain located on the French border of the Mediterranean sea, submitted to strong anthropogenic impacts and meteorological specificities (such as land-sea breeze recirculations) that reinforce the intensity of summer pollution events. The western part of this domain (shown in Figure 1) is characterized by the presence of the largest national industrial, chemical and petrochemical center, located around the Berre pond. At the same time, this tourist region presents a very dense road traffic network, large urban areas along the coast, but also forested areas in the North which give rise to extremely strong biogenic VOC emissions. This site was also chosen because it was the place of the large ESCOMPTE measurement campaign in summer 2001 [1], which provided a detailed 3D documentation of 4 pollution episodes for model validation. We focused on the two most severe Intensive Observation Periods (IOPs) of the campaign, but also on ozone pollution events that occurred in the first two weeks of August 2003, as they presented particularly elevated ozone con-





Figure 1: Map of the simulated domain, located on the French Mediterranean coast.

centrations lasting over the whole region for several days. The simulations were conducted using the transport-chemistry model CHIMERE [2]. Chemical boundary conditions were provided by the same model running at European scale. The CHIMERE horizontal resolution at regional scale is 4km, and the model includes 15 vertical levels from the ground to 3km. The comparison of model outputs to existing measurements was systematically conducted at ground level for NO_x, VOCs, ozone and oxidized nitrogen species, but also in altitude using vertical profiles provided by LIDARS or airplane measurements crossing altitude plumes. The general good agreement of the experimental and simulated values led us to the validation of the model results, configuration, input data and specific modules (meteorology, chemistry...). The work presented here will focus on a specific day of the ESCOMPTE IOP2 that occurred on 25 June 2001 (2001, [1]), and which is representative of some polluted breeze days. Systematic analysis over the whole selected period is part of this project and is currently conducted.

2.2 Realization of specific simulations with focus on reactive VOCs

The modelling strategy first led us to select the VOC most implicated in the formation of the ozone regional peaks, to further provide a spatial and temporal analysis of their individual impact on ozone production. The selection of the most highly reactive VOC species was done using the Reactivity Increment approach. It consists in simulations with modulated emissions - of about 5% - of each individual VOC species (including modelled species from the chemical scheme, such as the several classes of alkanes and alkenes). The resulting impacts on the regional ozone peak value are calculated by the model and classified from the highest to



the less significant one. The particularity of this study is that this approach was conducted with 3D Eulerian modelling, which allows to take also into account the time and location of VOC emissions in relation to mixing and transport of pollutants in the boundary layer along the day. The results of this VOC ranking highlight the determining role of biogenic VOC emissions as the first VOCs participating in ozone production on this domain. This role may result both from their fast reaction rates with OH and their large emissions spread out all over the northern part of the inland domain, especially because these emissions are located downwind the main anthropogenic areas initiating ozone photochemistry. Indeed, during episodes when the wind is blowing from the North or West of the domain and brings low polluted air masses, we observed no ozone production over these forested areas. The results confirm the importance of aromatic species, light alkenes and formaldehyde on ozone production, but also reveal a strong effect of carbon monoxide oxidation, that may be due to its large anthropogenic emissions. We will mainly focus here on CO, light alkenes and aromatic compounds.

In order to get an insight into ozone photochemistry on the site, we conducted simulations using tracers of VOC degradation for the 12 COV having the largest IR indexes. The implementation of the tracers was done as follows:

1. Two kinds of inert tracers were produced by the reaction of OH with the considered VOC. The first one, simulating the initial oxidation of the VOC has been called OXVOC, and was set to zero at each new time step. Its concentration fields thus indicate the exact location of the VOC when it first participates in local photochemistry and the number of molecules oxidized at this time step. The second tracer is also emitted by the OH attack on the VOC but its concentration fields are not reinitialized. This tracer, called TSPVOC, is dedicated to the identification of the zones impacted by the transport of all secondary species issued from this VOC photochemistry.
2. All species resulting from the initial VOC attack were marked in the chemical scheme. The evolution of all these species in the troposphere was followed by marking also their further oxidation or transformation, using reaction coefficients to evaluate as close as possible the quantity of products issued from the original VOC. A specific tracer called DEGRADVOC was produced when marked species oxidize other primary VOCs. Its concentration fields, set to zero at each time step, will indicate where and how the considered species in turn participates in VOC degradation in the troposphere. Ozone molecules finally produced as well as instantaneous rates of ozone production from the marked species were calculated in the model.
3. The evolution of marked species at ground level was followed along tracks going from the industrial and urban source areas to the center of the ozone plumes, from 8:00 AM to 15:00 PM on all days. Some of the obtained results are presented in the next section, with a special focus on 25 June 2001.

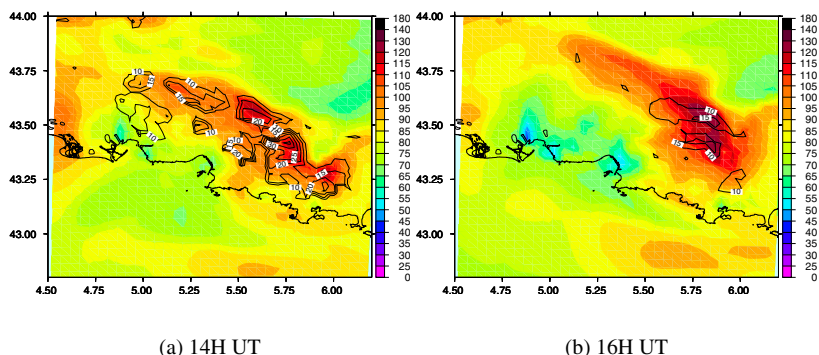


Figure 2: Simulated ozone concentrations (ppbv) and production rates (ppbv/h-lines) for 25/06/01.

3 Results: comparative analysis of VOC chemistry on the domain

3.1 Description of the photochemical event of 25 June 2001

The pollution event that occurred on 25 June 2001 is characterized by weak winds over the domain, leading to the establishment of a land-sea breeze cycle during the day. The anthropogenic emissions, mainly located along the coast, are then brought back inland by efficient breeze winds from 10H UT to the end of the afternoon. As can be seen from CHIMERE modelling outputs in Figure 2, ozone production rates are estimated to range between 15 and 30 ppbv/h on a thick line located 30 km inland at 14H UT. Two hours later, the maximum ozone concentrations are observed inland, in a plume pushed to the South-East of the inland domain by synoptic winds, and exceed 120 ppbv.

3.2 Geographical analysis of VOC participation to regional photochemistry

The participation of a VOC to the regional production of oxidant species is directly linked to its lifetime and oxidation pathways, but also to the specificities of its emissions into the atmosphere. Hourly emissions of aromatic species and CO are presented in Figure 3 (left graphs). We can observe the same order of magnitude of emissions for ethylene (thus not shown here) and aromatic compounds with a strong diurnal cycle, while their emission location is rather urban for ethylene and industrial for the aromatic species. Carbon monoxide emissions on the contrary are more than 50 times higher than the precedent ones, remain elevated at night, and CO is strongly emitted both by urban and industrial activities. Anyway, for all these compounds, emissions remain located punctually along the coast and on the northwestern to southeastern traffic axis. Only biogenic VOCs are emitted

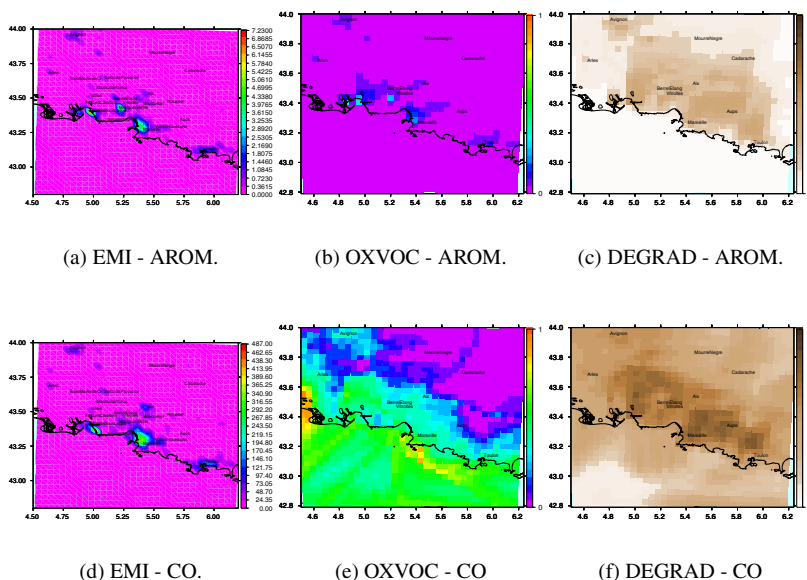


Figure 3: 12H-UT 2D visualisation of emissions, OXVOC tracers and diurnal maximum DEGRADVOC tracers (same color scale) from CHIMERE simulations for aromatic compounds, ethylene and carbon monoxide.

all around the northern and northeastern parts of the domain. Furthermore, their emissions are one order of magnitude larger than the main anthropogenic VOC species. Figure 3 (center) shows - on a non regular scale - the concentration fields of OXVOC at 12H UT for June 25 for these 2 species. We can see that the degradation of aromatics (as that of ethylene) occurs on the coast and very close to the sources. The two species show a very similar behavior and no significant oxidation signals are reported further than 20km from the sources. Anyway, their impact on the ozone event development is not restricted to ozone transport out of this area: indeed we can see on the right figures that secondary species issued from ethylene and aromatic compounds oxidation will in turn oxidize other VOCs on a large domain downwind the sources. These species may thus play a geographical role of initiators of ozone photochemistry.

Important results about carbon monoxide (Figure 3 upper part) concern the fact that the most intense CO oxidation at ground level does not occur over the land but in the shallow layer over the sea, from industrial emissions transported there by the nocturnal land breeze. Indeed, many industrial CO sources are still active at night. This phenomenon appears to be reproducible for each land-sea breeze episode on the site. If we have a look at the bottom figures of the DEGRADVOC tracer maxima for CO, we can see that surprisingly, the largest fraction of CO emitted over the sea will not give rise to other VOC oxidation, maybe due to the fact that the

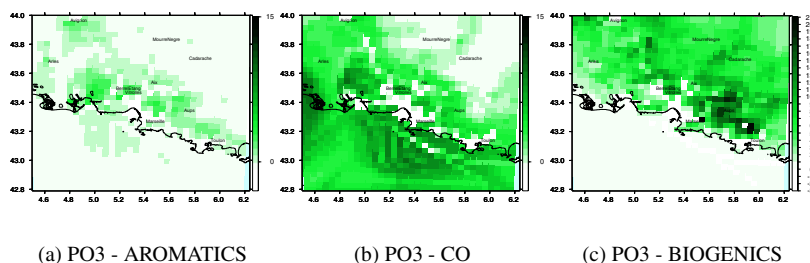


Figure 4: 2D visualisation of tracers of ozone production (ppbv/h) from CHIMERE simulations for aromatic compounds, carbon monoxide and biogenic species. A different color scale is used for biogenic compounds.

air mass is VOC-poor. The ozone plume over the sea on this day may be resulting only from CO industrial emitters. From this process, a large part of the emitted CO will not influence regional inland ozone production as the nocturnal sea plume never completely penetrates inland. After the morning sea breeze reverse, the second zone intensively impacted by current CO emissions is a large region along the coast and the East of the domain. The intensity of this impact is directly linked to that of CO emissions, and the thickness of the zone is due to the longer CO lifetime. The maximum degradation processes are observed at the East of the domain, due to the presence of synoptic winds blowing from the Northwest. As a consequence, only biogenic emissions impact the right upper corner of the domain on this day due to their presence on the whole inland region. This aspect needs to be tested on pure breeze days. Finally (Figure 4), it appears that all VOCs participate in ozone production mainly according to the intensity of their sources, with biogenic emissions that produce up to 20ppbv/h of ozone on a wide region, compared to less than 10ppbv/h for CO inland and a few ppbv/h for the other species. The rural areas appear thus sufficiently NO_x-rich to produce ozone very fast. Similar maximum values are observed for ethylene (not shown here) and aromatics.

3.3 Analysis of the temporal evolution of photochemistry from urban to rural areas

The observation of the coevolution of VOC degradation and their subsequent ozone production along an air mass trajectory may bring crucial information on the way the different primary species produce ozone: does ozone production happen at the same time for all VOCs? what is the participation of each species on the ozone peak build-up? what is the intensity of local ozone production? Figure 5 has been obtained by determining a plume trajectory made up of 14 points along which the quantity of ozone molecules issued from the decomposition of 8 highly reactive VOCs was plotted. The details of the modelled local ozone composition along the plume trajectory (from the central and coastal city of Marseilles to the

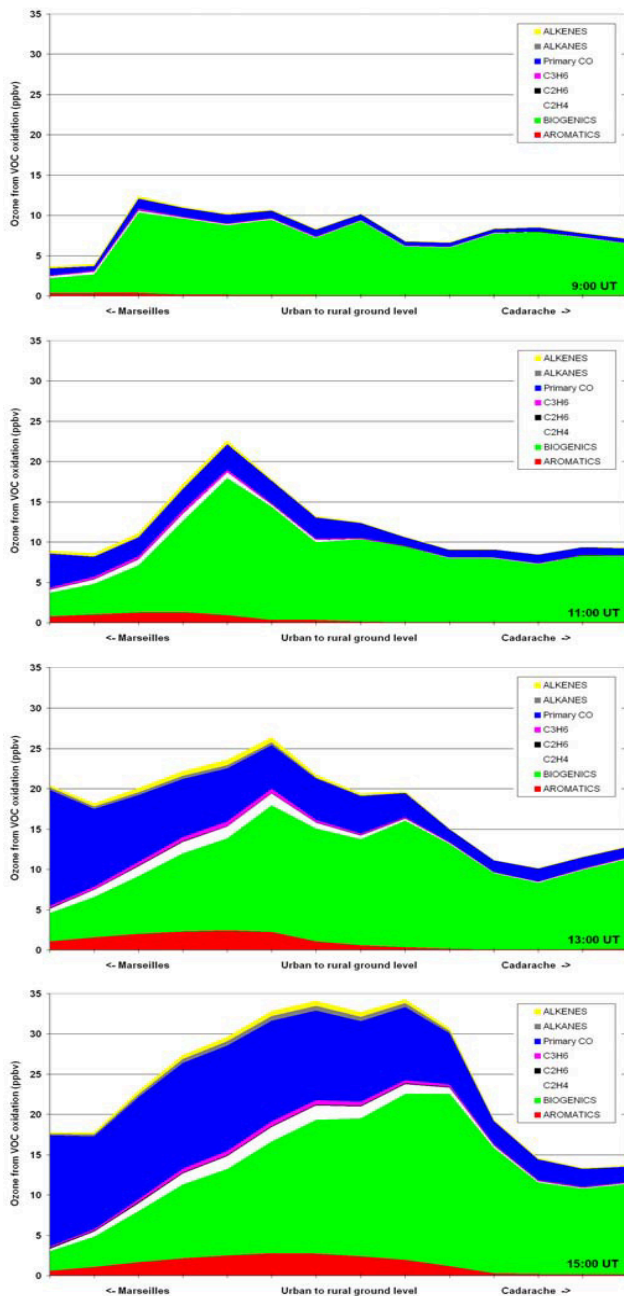


Figure 5: Evolution of the composition of locally produced ozone at ground level along the plume trajectory, from an urban to a rural place.



Northeastern part of the domain), is plotted for 4 hours of the day on 25 June 2001. On these figures, we will see the determining role of biogenic VOCs when located downwind anthropogenic sources, but the major role of primary CO will also be lightened.

At 9H UT on the trajectory, more than 10ppbv of ozone can be attributed to local production, out of the urban center (left point of the graph). The main species responsible for such production are biogenic VOCs which account for more than 80% of the formed molecules. Two hours later, the total quantity of locally produced ozone is more than 20ppbv, with still a large percentage of the local ozone coming from the oxidation of biogenic VOCs, but the part of ozone coming from CO and also from aromatic species has largely increased. From 11H TO 13H UT the plume extends towards the rural region and transports ozone from several origins. The participation of ethylene appears significant, albeit much lower than CO and biogenic VOCs. At 15H UT, the ozone peak is now far from the urban center, and the calculated part of local production reaches 35 ppbv. The contribution of primary carbon monoxide is nearly the same as that of biogenic species. Such a phenomenon is not local. The simulated composition of the 20 highest ozone maxima observed all over the domain at any time on 25 June 2001 has been plotted (not shown here). The composition is remarkably constant while the location and time of the simulated maxima differ.

4 Conclusion

The purpose of this work is to highlight how different VOC families and species play a role in regional ozone build-up, according to the characteristics of their emissions and their chemical particularities. 3D modelling studies with the CHIMERE model have been conducted on the Marseilles-Berre region, using inert tracers in the chemical mechanism to follow the evolution of each VOC from its initial oxidation to its ozone production. The situation encountered here accounts for the determining role of biogenic emission when located under the influence of large urban centers, but it overall underlines the extremely large effect of CO on local ozone production compared to very reactive species such as light alkenes. Anyway, the non negligible role of individual and combined primary anthropogenic VOCs in producing OH and other oxidized species needs to be investigated with further insights into the chemical mechanism: how important is the role of very reactive species in producing radicals for the further oxidation of other VOCs? In the frame of a wider project, the same simulations with tracers will be conducted on 2010 projected emission and evaluate from the inside of the ozone production mechanism the efficiency of the engaged regulation.

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